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A 99% PURITY MOLECULAR SIEVE OXYGEN GENERATOR

G. W. Miller
Crew Technology Division
Armstrong Laboratory
Brooks AFB, San Antonio, Texas 78235-5301

ABSTRACT

Molecular Sieve Oxygen Generating Systems (MSOGS) have become the accepted method for the production of breathable oxygen on military aircraft. These systems separate oxygen from aircraft engine bleed air by application of pressure swing adsorption (PSA) technology. Oxygen is concentrated by preferential adsorption of nitrogen in a zeolite molecular sieve. However, the inability of current zeolite molecular sieves to discriminate between oxygen and argon results in an oxygen purity limitation of 93-95% (both oxygen and argon concentrate). The goal of this effort was to develop a new PSA process capable of exceeding the present oxygen purity limitations. A novel molecular sieve oxygen concentrator was developed which is capable of generating oxygen concentrations of up to 99.7% directly from air (U.S. Patent No. 4,880,443). The process is comprised of four adsorbent beds, two containing a zeolite molecular sieve and two containing a carbon molecular sieve. This new process may find use in aircraft and medical breathing systems, and industrial air separation systems. The commercial potential of the process is currently being evaluated.

INTRODUCTION

Molecular sieve oxygen generating systems are replacing liquid oxygen systems as the principal method for the production of breathable oxygen on-board military aircraft. The oxygen-rich product gas is breathed by the aircrew for the prevention of hypoxia at high altitudes. When compared to conventional liquid oxygen (LOX) systems, MSOGS systems offer many benefits, such as, reduced life cycle cost, reduced logistic support, increased aircraft versatility, and improved safety. Presently, the U.S. Air Force has several MSOGS-equipped aircraft, the F-15E "Strike Eagle," and the B1-B and B-2 strategic bombers.[1] Also, the U.S. Navy has several MSOGS-equipped aircraft, such as, the AV-8B. In the future nearly all U.S. military aircraft will be equipped with an MSOGS breathing system.

MSOGS breathing systems are comprised primarily of a molecular sieve oxygen concentrator (or generator) and associated equipment for distribution and delivery of the product gas, such as, breathing regulators. The critical component of the system is the oxygen concentrator which separates oxygen from the aircraft engine bleed air (compressed air) by pressure swing adsorption technology. Using this technology, nitrogen is preferentially adsorbed in the molecular sieve at moderate pressures, thereby, concentrating oxygen. Subsequently, the nitrogen is released to the ambient atmosphere as a waste gas and the oxygen is breathed by the aircrew. Control of the oxygen concentration is accomplished by either diluting the product gas with cabin air or by varying one of the concentrator operating parameters, such as, cycle time. The concentrator need only be supplied engine bleed air and a small amount of electrical power to produce a continuous stream of concentrated oxygen.

An oxygen generator based on the current technology is comprised of two zeolite molecular sieve adsorbent beds, several valves, a purge orifice, and an electronic timer (Figure 1). The electronic timer controls the opening and closing of the valves. Bleed air pressure is typically in the range of 137.9 to 344.8 KPa (20 to 50 psig) (referenced to the ambient atmospheric pressure). The pressure swing adsorption technique is achieved by alternating the pressurization of the two adsorbent beds. While one bed is pressurized, the opposite bed is depressurized and exhausts previously adsorbed gases to the surrounding atmosphere. In an aircraft this exhaust gas is vented overboard. In Figure 1, the cycle begins by the simultaneous opening of valves V1, V4, and V6. In this step of the cycle bed A is pressurized and nitrogen in the feed air is adsorbed in the molecular sieve. Hence, oxygen is concentrated and withdrawn through V1.

Simultaneously, bed B is vented to the surrounding atmospheric pressure through valve V6 and purged by a countercurrent flow of product gas entering through the purge orifice. In the second half-cycle valves V2, V3, and V5 are opened and valves V1, V4, and V6 are closed. The beds simply reverse roles, whereby, bed B produces the product gas and bed A is vented. A typical concentrator has a cycle time (duration of pressurization and depressurization) of 10 seconds. By alternating the opening and closing of the two sets of valves, a continuous stream of concentrated oxygen is produced.
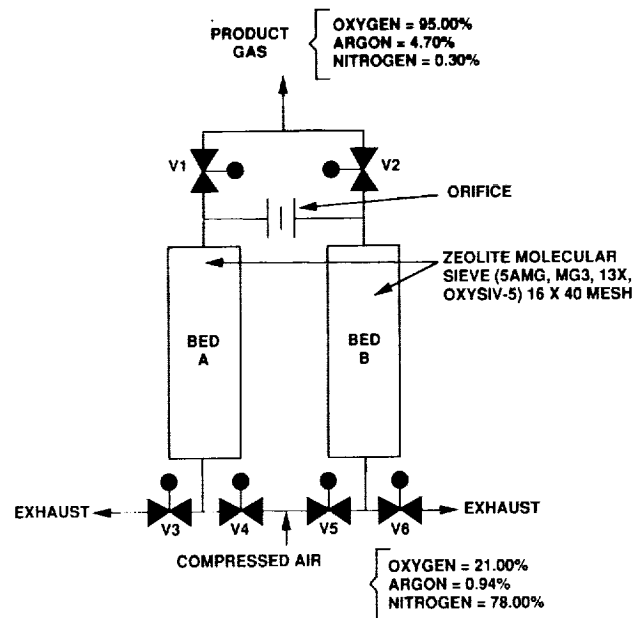

Figure 1. A Standard Two-bed Molecular Sieve Oxygen Generator.

Current molecular sieve oxygen concentrators use adsorbent beds containing exclusively zeolite molecular sieves. Several varieties (5AMG, MG3, 13X, and OXYSIV-5) are commercially available, however, most oxygen concentrator manufacturers presently use either 5AMG or OXYSIV-5 (products of UOP, Des Plaines, IL). Zeolite molecular sieves are synthetic alkali metal aluminosilicates which have as their basic building blocks SiO_4 and AlO_4 tetrahedra with exchangeable cations. The type of crystal framework and exchangeable cation will determine the dimension of the crystal pores. 5AMG molecular sieve has Type 5A zeolite crystallites with uniform pore openings of 4.2 Angstroms. MG3, 13X, and OXYSIV-5 have 13X zeolite crystallites with pore openings of 7.4 Angstroms. These materials are generally stable at high temperature but slowly deactivate in the presence of water due to the water molecule's small kinetic diameter and high polarity. Because nitrogen, oxygen, and argon have molecular kinetic diameters of 3.64, 3.46, and 3.40 Angstroms, respectively, these gases readily enter the 5A and 13X crystallites.[2] Separation of oxygen and nitrogen is possible because of a difference in equilibrium adsorption capacity (Figure 2). Molecular sieves adsorb greater quantities of nitrogen than oxygen due to the nitrogen molecule's slight polarity. Oxygen and argon concentrate because zeolite molecular sieves are unable to discriminate between these molecules. This characteristic is verified by the nearly identical oxygen and argon equilibrium adsorption isotherms in Figure 2. Both oxygen and argon are nonpolar and have nearly identical kinetic diameters. Hence, the maximum oxygen concentration from current oxygen concentrators is constrained at 95% (the remainder is mostly argon with less than 1% nitrogen). Further, an oxygen concentration of 95% is only produced under the most ideal

conditions. In general, the most probable concentration limit is 93% oxygen (the remainder is mostly argon with 1-3% nitrogen).

The 95% oxygen concentration constraint is one limitation of the present oxygen concentrator technology. Conventional liquid oxygen systems have routinely supplied oxygen at a concentration of 99.5%. Although these higher concentrations may not always be required, situations do occur while
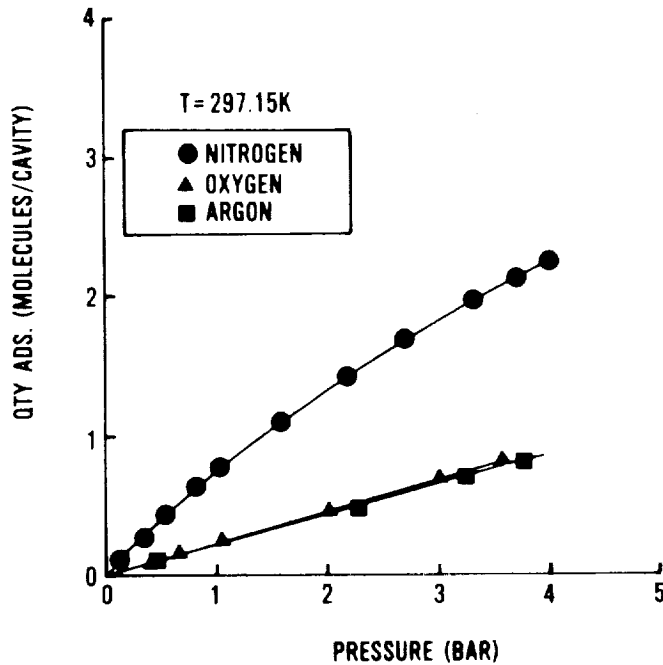

Figure 2. Equilibrium Adsorption Curves for 13X Molecular Sieve.

flying where breathing very high purity oxygen ($\geq$99%) would be desirable. Current MSOG systems generally require a bottled backup oxygen system pressurized with 99.5% oxygen. Although MSOGS technology offers many advantages over conventional liquid oxygen systems, this technology is presently unable to produce the oxygen purity which has been routinely available from the conventional liquid oxygen systems. Hence, the goal of this work was to develop a process based on PSA technology which is capable of exceeding the 93-95% oxygen concentration constraint of current technology.

ADSORPTION BREAKTHROUGH STUDIES

In 1986 an effort was initiated with the goal of identifying an adsorbent capable of discriminating between oxygen and argon. Because of the very slight differences in adsorption characteristics between oxygen and argon molecules, the probability of finding an adsorbent with the proper characteristics was considered low. Several commercially available adsorbents (zeolite molecular sieves, such as, 3A, 4A, 5AMG, 13X, and MG3, and carbon molecular sieves) were evaluated by analysis of adsorption breakthrough curves. It was hypothesized this ability to discriminate between oxygen and argon would manifest itself as a shift in the oxygen and argon concentration wavefronts at the outlet of a single adsorbent bed. Further, it seemed logical that the oxygen wavefront must
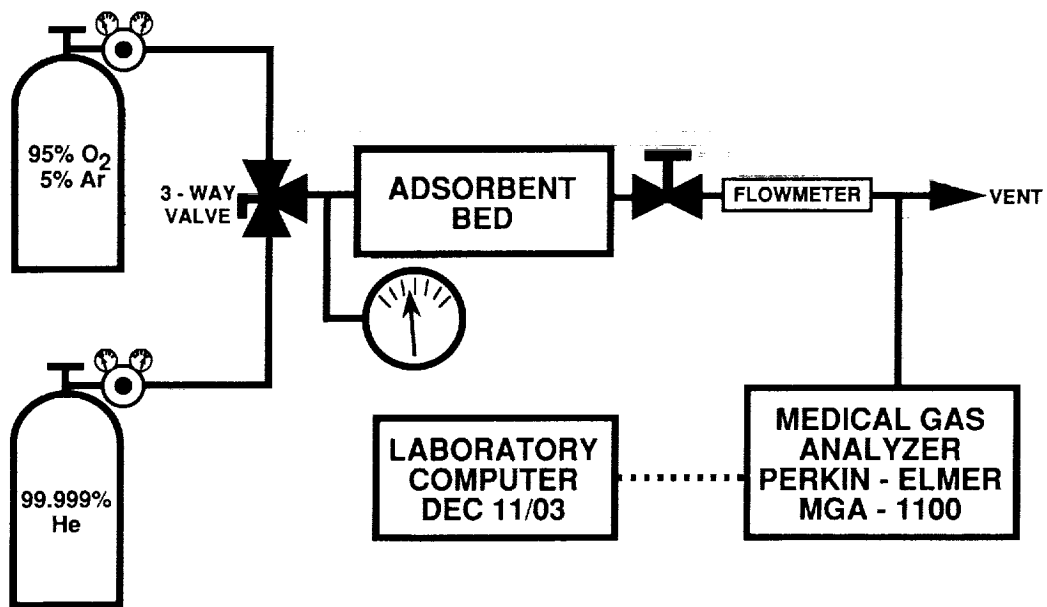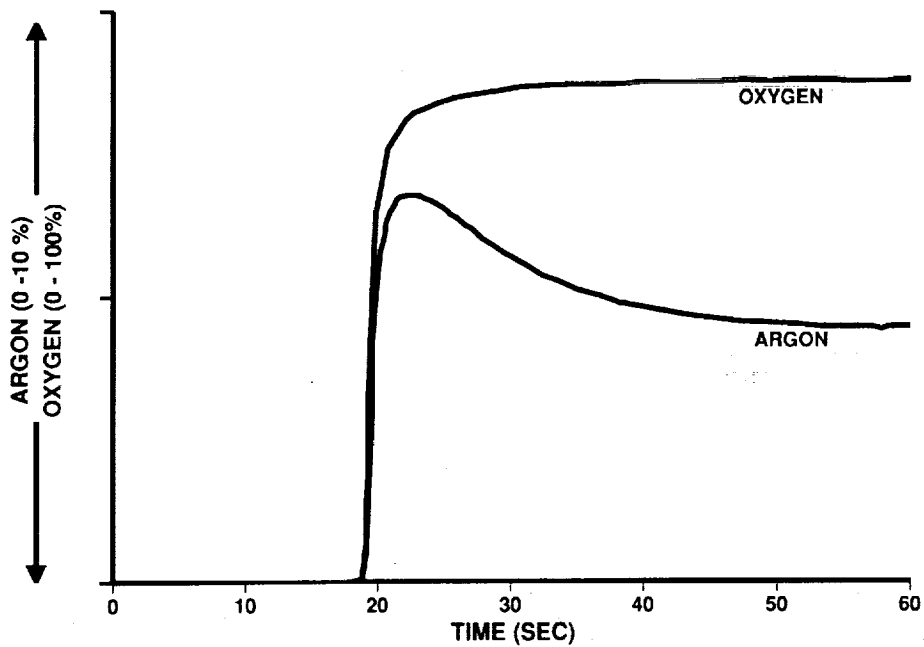
Figure 3. Adsorption Breakthrough Apparatus.

Figure 4. Adsorption Breakthrough Curves for 13X Molecular Sieve.

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lead the argon wavefront, if oxygen is to be extracted as the final product from an operating oxygen concentrator.

In these experiments a single bed or column was filled with the candidate adsorbent and flushed with helium (Figure 3). Helium is used as the purge gas because it adsorbs in negligible quantities. A gas mixture with a concentration of 95% oxygen and 5% argon was then allowed to flow through the bed. This gas mixture was selected because it was assumed the product from a conventional oxygen concentrator would become the feed gas to a final oxygen purifier. The wavefronts exiting the bed were monitored by a mass spectrometer (Perkin-Elmer Medical Gas Analyzer, Model No. MGA-1100). If the oxygen and argon wavefronts overlapped upon exiting the bed, the adsorbent was considered unable to discriminate between oxygen and argon (Figure 4). However, if a noticeable shift in the wavefronts occurred, it was assumed the adsorbent could discriminate between oxygen and argon. Based on a qualitative analysis of the data, only a carbon molecular sieve caused a shift in the oxygen and argon wavefronts (Figure 5). The next step was to configure a PSA apparatus with carbon molecular sieve beds, such that, this shift in wavefronts could be effectively applied for the further purification of oxygen from a conventional oxygen concentrator.
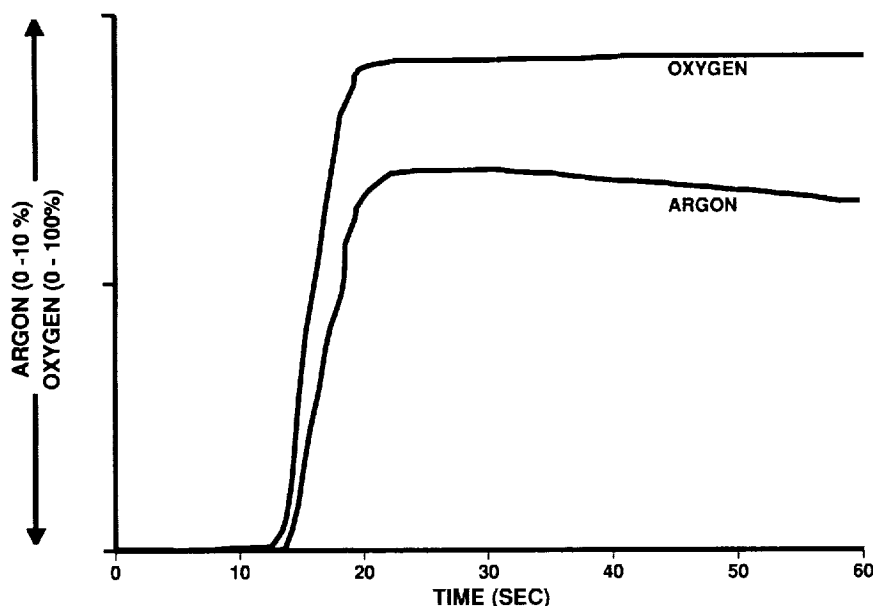

Figure 5. Adsorption Breakthrough Curves for Carbon Molecular Sieve.

SECONDARY OXYGEN PURIFIER

In 1987 a small-scale device, referred to as the "secondary oxygen purifier," demonstrated that further purification of the product gas from a standard oxygen concentrator was possible (Figure 6).[3,4] The device was comprised of two carbon molecular sieve adsorbent beds, several valves, and an electronic timer. Operation of the valves was identical to that of a standard oxygen concentrator. However, the device did not possess a purge orifice (Figure 1). The elimination of the purge orifice improved the performance of the unit and reduced the inlet gas consumption. The apparatus was fed a bottled gas with a composition of 94.73% oxygen, 5.00% argon, and 0.27% nitrogen which simulated a standard oxygen concentrator product gas. During the pressurization step argon preferentially adsorbs on the carbon molecular sieve, thereby, increasing the purity of the oxygen in
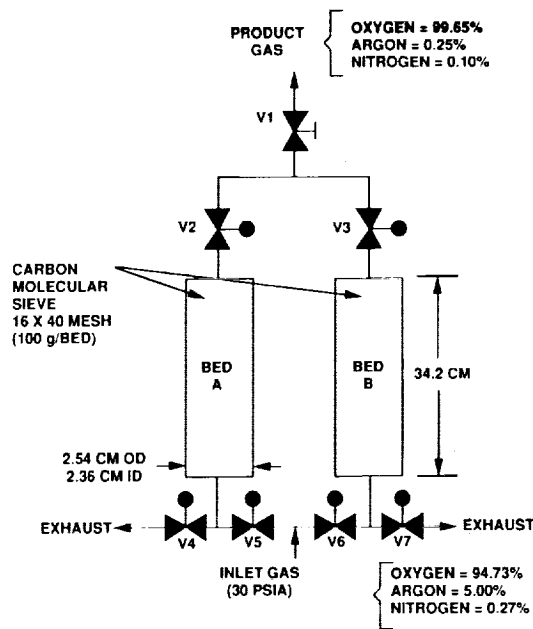
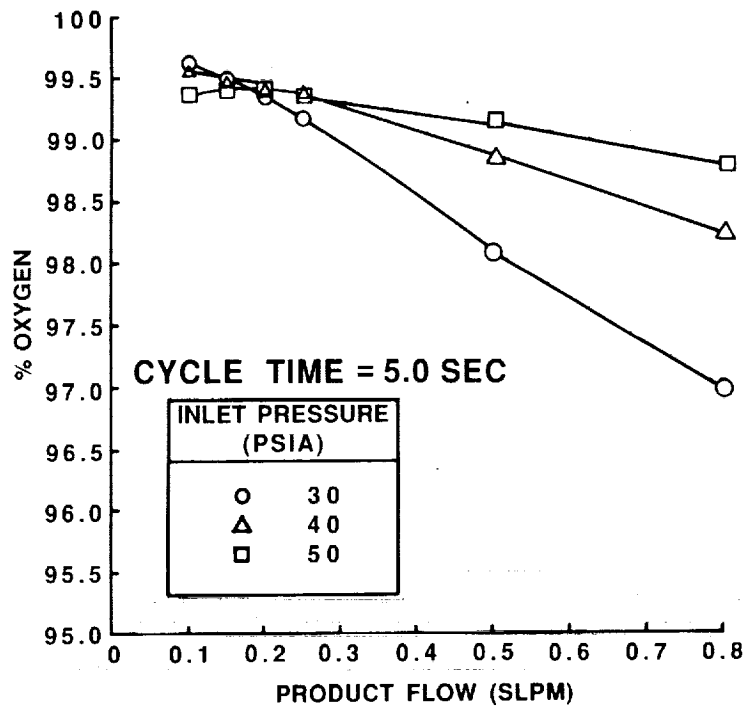Figure 6. A Small-scale Secondary Oxygen Purifier.

Figure 7. Performance Curves for the Small-scale Secondary Oxygen Purifier.

the gas phase. During depressurization the argon is exhausted to the surrounding atmosphere. The device produced a product gas with a concentration of 99.65% oxygen, 0.25% argon, and 0.10% nitrogen. Also, the apparatus produced nearly the same concentrations when operated at simulated altitudes (reduced exhaust pressures). Performance curves for the device while operating at atmospheric pressure are shown in Figure 7.

Information about carbon molecular sieves is scarce due to the proprietary status of the current manufacturing processes.[5,6,7] Carbon molecular sieves have demonstrated stability at high temperature and in acidic media, and a low affinity for water. They are produced by pyrolysis of many thermosetting polymers, such as, polyvinylidene chloride (PVDC), polyfurfuryl alcohol, cellulose triacetate, and saran copolymer. In contrast to zeolite molecular sieves which have a uniform pore size, carbon molecular sieves
have a narrow pore size distribution. Further, this size distribution may be adjusted by changing the conditions of the manufacturing process.

In this work a carbon molecular sieve referred to as Takeda 3A was determined the most effective at separating oxygen and argon. This material is manufactured by Takeda Chemical Industries, Ltd., 12-10, Nihonbashi 2-chome, Chuo-ku, Tokyo 103, Japan. The material was provided to our laboratory by the U.S. representative for Takeda Chemical; TIGG Corporation, Box 11661, Pittsburgh, Pennsylvania. Although during this work the Takeda 3A carbon molecular sieve could only be obtained in limited quantities, this material is currently available in bulk quantities. The material was received as ~1/8 inch pellets (a typical pellet had a diameter of 2.36 mm and a length of 5.18 mm). These pellets were reduced in size in our laboratory by a Model No. 3383-L10 Wiley mill with a 10 mesh delivery unit. A mechanical sieving procedure was used to separate the mesh size desired. In general, mesh sizes of 10X40 and 16X40 were used in this work. Residual dust was removed by blowing compressed air through sieving screens containing the material. Size reduction was the only pretreatment performed before loading the material into the experimental apparatus. Size reduction was conducted to improve the mass transfer characteristics of the adsorbent. Experiments with different mesh sizes clearly indicated that the smaller mesh sizes are more effective at separating oxygen and argon.

Although the secondary oxygen purifier was capable of generating 99% purity oxygen, one disadvantage is the requirement for a feed gas with a concentration of approximately 95% oxygen and 5% argon. The next goal of this effort was to construct a new oxygen concentrator capable of generating 99% purity oxygen directly from compressed air. The approach was to devise a method for integrating the secondary oxygen purifier into a standard oxygen concentrator. The new device would have the capability of separating nitrogen and argon from compressed air.

99% PURITY MOLECULAR SIEVE OXYGEN GENERATOR

In 1989 a small-scale adsorption apparatus consisting of four interconnected adsorption beds, several valves, and an electronic timer demonstrated that oxygen concentrations of 99% could be achieved directly from compressed air using a PSA technique (Figure 8).[8,9] In Figure 8 adsorption beds A and B contained 585g of 16X40 mesh 5AMG zeolite molecular sieve and beds C and D contained 394g of 10X40 mesh carbon molecular sieve. The carbon molecular sieve was reduced in particle size from pellets having a diameter of ~2.36 mm to 10X40 mesh by the mechanical grinding procedure described previously. Adsorbent containment was achieved by four assemblies, each consisting of a metal screen, a foam pad, and a coil spring. Two assemblies were located at the inlets to beds A and B and two were at the outlets of beds C and D. The zeolite and carbon molecular sieve beds were connected in series. Hence, the gas flow passed sequentially from the zeolite molecular sieve bed to the carbon molecular sieve bed. The adsorption beds were constructed from 5.08 cm (2.00 in) OD stainless steel tubing. Beds A and B had a length of 43.1 cm and beds C and D had a length of 36.8 cm. The zeolite molecular sieve beds (A and B) were connected near their outlets by a 0.71 mm ID purge orifice. Valves V2-V7 were air operated valves

manufactured by the Whitey Company (Part No. SS-92MA-NC). An electronic valve timer permitted adjustment of the cycle time of the apparatus. The device was fed dry compressed air with a concentration of 20.97% oxygen, 0.96% argon, and 78.07% nitrogen, as measured by a Perkin-Elmer medical gas analyzer (Model No. MGA-1100). The accuracy of the gas analyzer was ±0.1%.

During operation the apparatus was alternately cycled through steps of pressurization and depressurization in a manner similar to a standard oxygen concentrator. In the first half-cycle valves V2, V5, and V7 are activated open, while valves V3, V4, and V6 remain closed. Inlet air pressurizes beds A and C, and establishes a product flow at the outlet port of bed C. As the air passes through the adsorbent beds, nitrogen is preferentially adsorbed in bed A and argon is preferentially adsorbed in bed C. Hence, oxygen is concentrated and withdrawn as a product gas through valves V2 and V1. Simultaneously, bed B is regenerated by depressurization to the surrounding ambient pressure, countercurrent purging by a portion of the product flow from bed A, and countercurrent purging by a flow resulting from the partial depressurization of bed D. This depressurization exhausts the previously adsorbed nitrogen and argon to the ambient surroundings. During the second half-cycle valves V3, V4, and V6 are opened, while valves V2, V5, and V7 are closed. During this phase of the cycle beds B and D are pressurized and product gas is withdrawn through V3 and V1. Hence, in the second half-cycle beds B and D simply exchange roles with beds A and C. By repeating steps of adsorption and desorption, a continuous stream of very high purity oxygen is produced. Additionally, it should be noted that the apparatus does not require a purge flow for regeneration of the secondary or carbon molecular sieve adsorbent beds during the depressurization cycle. This feature improves the efficiency of the apparatus by reducing the feed air consumption.
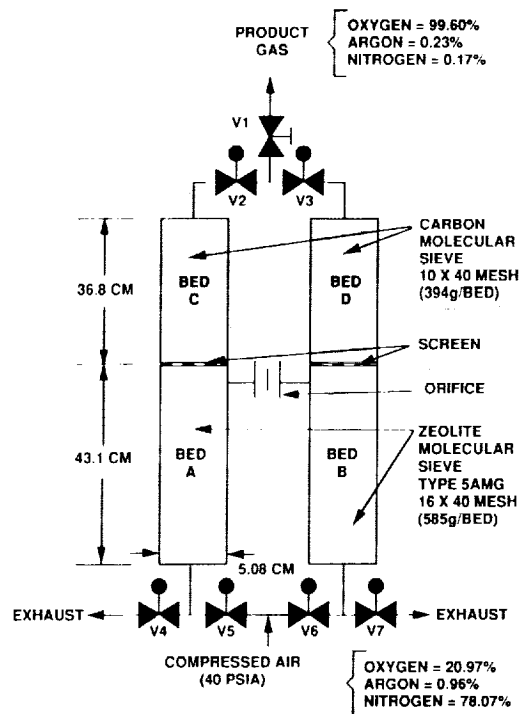

Figure 8. A Small-scale 99% Purity Molecular Sieve Oxygen Generator.

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The effects of inlet air pressure on the oxygen purity produced by the small-scale 99% purity oxygen generator are given in Figure 9 and Table 1. The corresponding argon and nitrogen concentrations are shown in Figures 10 and 11. Clearly, the device is capable of producing 99% purity oxygen directly from compressed air. The maximum observed oxygen purity of 99.6% occurred at an inlet pressure of 275.8 KPa (40 psia). (The maximum oxygen purity has recently been increased to 99.7%.) At 241.3 KPa (35 psia) the oxygen purities at low product flows were high but decreased significantly as the product flow increased. At 344.8 KPa (50 psia) the device did not quite achieve 99% purity even at low product flows. Argon concentrations in the product gas decreased as the inlet pressure increased (Figure 10). Inlet air flows at pressures of 241.3 (35), 275.8 (40), 310.3 (45), and 344.8 KPa (50 psia) were 52, 61, 71, and 80 SLPM, respectively. Inlet air flow remained nearly constant with changes in product flow. This characteristic is also observed for standard oxygen generators.

Table 1. Oxygen Concentrations for the Small-Scale 99% Purity Oxygen Generator at a Cycle Time of 15 Seconds and Bed Temperature of 297K.

Oxygen Concentration (%)

Product Flow (SLPM)	Inlet Pressure, KPa (psia)			
	241.3 (35)	275.8 (40)	310.3 (45)	344.8 (50)
0.1	99.50	99.60	99.44	98.77
0.2	99.50	99.50	99.48	98.85
0.3	99.37	99.44	99.27	98.58
0.4	99.00	99.17	99.15	98.37
0.5	98.79	98.94	98.85	98.12
0.6	97.92	98.58	98.50	97.67
0.7	97.08	98.10	98.33	97.25
0.8	96.08	97.38	97.58	96.63
0.9	94.35	96.65	96.88	95.63
1.0	91.10	95.21	95.65	95.00

Oxygen recoveries were calculated based on Eqn. 1 and are given in Table 2 for purities of 99% and 95%. Recovery is a measure of how effectively oxygen is separated from the inlet air flow. Generally, oxygen recoveries are lower for small-scale oxygen concentrators when compared with full scale concentrators. The recoveries at 95% purity are similar to those obtained for other small-scale standard oxygen concentrators.[10]

$$\text{Oxygen Recovery (\%)} = \frac{m_p \, y_o}{m_i \, (0.21)} (100) \qquad (1)$$

Table 2. Oxygen Recovery at 99% and 95% Purity for the Small-scale 99% Purity Oxygen Generator.

Oxygen Recovery (%)

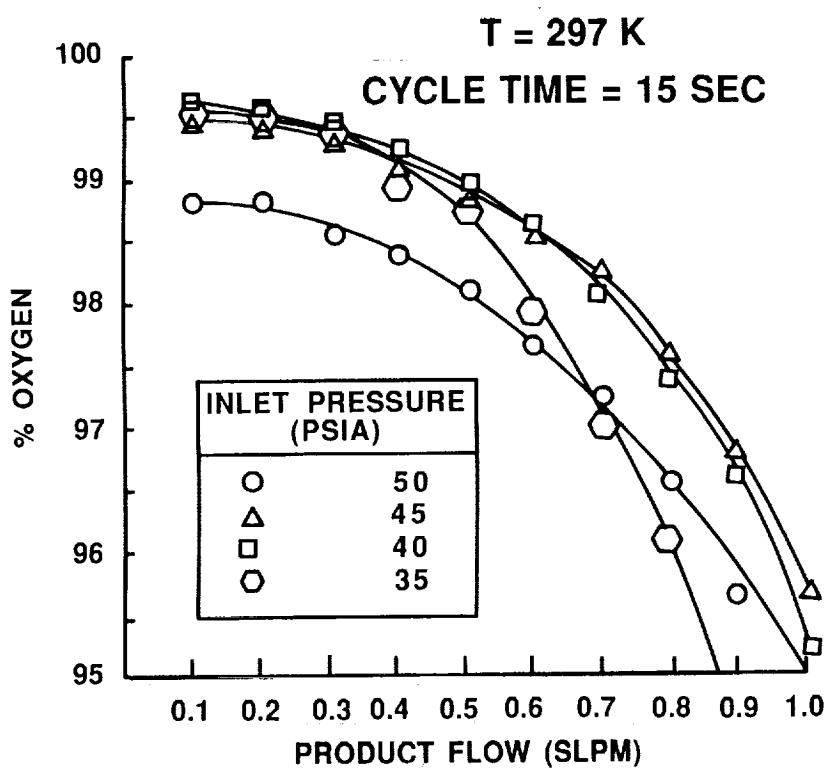|	Inlet Pressure, KPa (psia)			
	241.3 (35)	275.8 (40)	310.3 (45)	344.8 (50)
99% Purity	4.17	3.81	3.15	--
95% Purity	7.73	7.45	6.67	5.59

Figure 9. Oxygen Concentrations for the Small-Scale 99% Purity Oxygen Generator at Several Inlet Air Pressures.
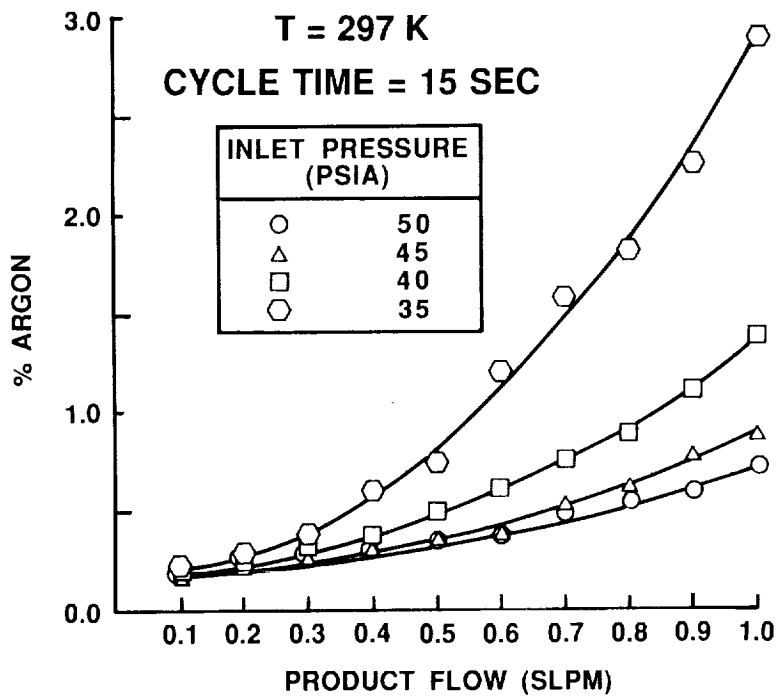
Figure 10. Argon Concentrations for the Small-Scale 99% Purity Oxygen Generator at Several Inlet Air Pressures.
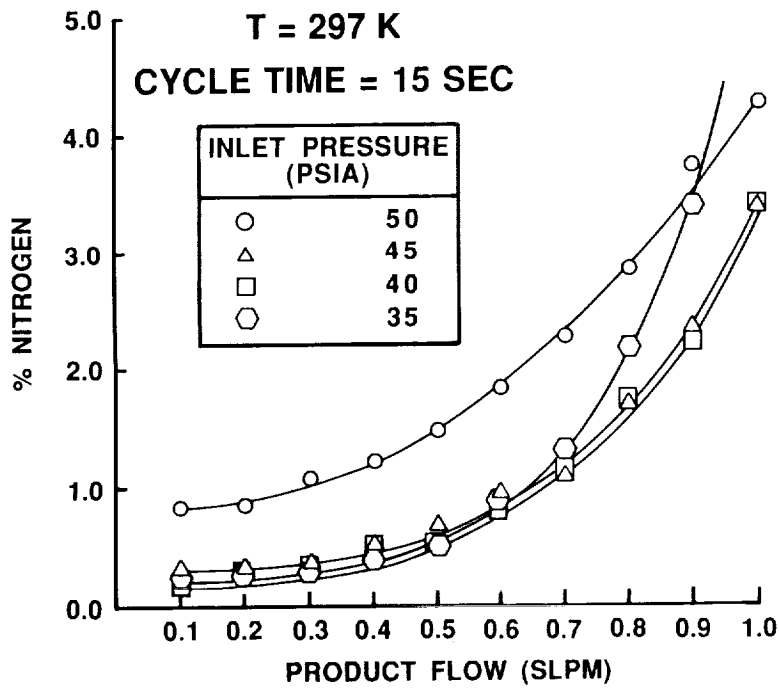

Figure 11. Nitrogen Concentrations for the Small-Scale 99% Purity Oxygen Generator at Several Inlet Air Pressures.

Operation of the oxygen concentrator at higher adsorbent bed temperatures causes a decrease in performance which is similar to that observed for standard oxygen generators.[11] This performance reduction occurs because molecular sieve adsorption capacity is reduced at higher temperatures. However, decreasing the cycle time of the concentrator will generally compensate for this reduced capacity.

Optimization studies of the 99% purity oxygen generator indicate a carbon to zeolite molecular sieve bed length ratio of 3/4 appears to maximize performance, assuming the diameter of the beds is equal.[12] Comparison of performance curves for 5AMG and OXYSIV-5 zeolite molecular sieves show increased performance with OXYSIV-5. The current highest oxygen productivity observed for the 99% molecular sieve oxygen generator is 0.33 (SLPM of 99% oxygen)/(Kg of total adsorbent).

TECHNOLOGY TRANSFER

The invention may be useful in any application where 99% purity oxygen is required or desired. Possible applications include filling of oxygen storage vessels or gas bottles, welding, glassblowing, industrial air separation processes, medical breathing systems, aircraft breathing systems, and space breathing systems. The invention would appear to be ideally suited to remote locations requiring 99% oxygen.

Further development of the technology is needed before the invention can be applied commercially. Presently, only small-scale laboratory devices have been constructed using this process. The next logical step in the development of the technology would be to construct a larger device with the capability of generating greater quantities of 99% oxygen. Armstrong Laboratory is considering two approaches toward commercialization. The first approach would be outright licensing of the invention. The second approach would involve a Cooperative Research and Development Agreement (CRDA) and licensing with a commercial firm. Any interested parties should contact Mr Douglas Blair, Armstrong Laboratory, Office of Research and Technology Applications (AL/XPPO), Brooks AFB, Texas (512-536-2838).

CONCLUSIONS

A new molecular sieve oxygen generator capable of generating oxygen purities of up to 99.7% directly from compressed air has been invented. The apparatus appears to have characteristics similar to standard oxygen generators but produces higher oxygen purities. The device may find use in aircraft and medical breathing systems, and industrial air separation systems.

NOMENCLATURE

m	=	mass flow rate
psia	=	pounds/square inch absolute
psig	=	pounds/square inch gauge
SLPM	=	standard liters/minute (referenced to 273K and 1 atm)
y	=	mole fraction in the gas phase

Subscripts

i	=	inlet
o	=	oxygen
p	=	product

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