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The purpose of this work was to determine the ability of high performance molecular sieve oxygen concentrator (MSOC) to remove methane while operating at high oxygen purity levels. This work was accomplished using a laboratory scale, four-bed, high performance MSOC (U. S. patent #4,880,443) which consisted of two primary beds containing OXYSIV-5 zeolite molecular sieve and two secondary beds containing Takeda 3A carbon molecular sieve. The concentrator operated at an inlet air pressure of 45 psia, a cycle time of 14 seconds, and a product flow rate of one standard liter per minute. Methane was injected into the MSOC inlet gas stream at levels up to approximately 5000 parts per million by volume (ppmv). Contaminant levels were allowed to reach steady-state and measured in the MSOC inlet, product, and exhaust gases with a Beckman, model 402 hydrocarbon analyzer. The experimental results indicate the contaminant introduced into the MSOC inlet gas was separated and carried out with the exhaust gas. The injected methane was not detected in the product gas. The results indicate the high performance MSOC may be more capable of removing contaminants from the inlet gas stream than standard MSOCs, i.e., those containing only zeolite molecular sieve. Further experimental work with other contaminants is planned.

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Methane Challenge of a High Performance Molecular Sieve Oxygen Concentrator

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ABSTRACT *The purpose of this work was to determine the ability of a high performance molecular sieve oxygen concentrator (MSOC) to remove methane while operating at high oxygen purity levels. This work was accomplished using a laboratory scale,, four-bed, high performance MSOC (U.S. patent #4,880,443) which consisted of two primary beds containing OXYSIV-5 zeolite molecular sieve and two secondary beds containing Takeda 3A carbon molecular sieve. The concentrator operated at an inlet air pressure of 45 psia, a cycle time of 14 seconds, and a product flow rate of one standard liter per minute. Methane was injected into the MSOC inlet gas stream at levels up to approximately 5000 parts per million by volume (PPMV). Contaminant levels were allowed to reach steady-state and measured in the MSOC inlet, product, and exhaust gases with a Beckman, model 402 hydrocarbon analyzer. The experimental results indicate the contaminant introduced into the MSOC inlet gas was separated and carried out with the exhaust gas. The injected methane was not detected in the product gas. The results indicate the high performance MSOC may be more capable of removing contaminants from the inlet gas stream than standard MSOCs, i.e., those containing only zeolite molecular sieve. Further experimental work with other contaminants is planned.*

INTRODUCTION Molecular sieve oxygen concentrator (MSOC) technology is gradually replacing liquid oxygen (LOX) converters as a means to provide high purity oxygen to air crew members for hypoxia protection. This novel technology reduces cost and logistics demands, and increases aircraft safety and versatility. Current MSOCs use pressure-swing adsorption (PSA) and a single adsorbent, zeolite molecular sieve (ZMS), to separate oxygen from air. However, even when operating at optimum conditions these units produce oxygen that is 93 to 95 per cent pure (the balance is mostly argon). The argon component remains because the ZMS is unable to separate argon.

The development of high performance MSOC technology marks the next step in the advancement of pressure-swing adsorption technology. With this method, the previous limitation of 95 per cent oxygen has been surpassed, and oxygen concentrations in excess of 99 per cent can be achieved.[1,2] The primary differences between a high performance MSOC and current MSOCs are the addition of two carbon molecular sieve (CMS) adsorbent beds and a modified process configuration. The carbon molecular sieve allows the high performance MSOC to separate the argon component from air

A laboratory-scale, four-bed, high performance MSOC is shown in Figure 1. It consists of four adsorbent beds (two primary and two secondary), flow control valves, and a purge orifice. In Figure 1, the beds labeled ZMS are the primary beds which contain zeolite molecular sieve. The beds labeled CMS are the secondary beds which contain carbon molecular sieve. In the first half cycle of operation, valves V2, V5, and V7 open, allowing compressed air, typically at a pressure of 45 pounds per square inch absolute (PSIA), to enter the beds labeled A. The compressed air diffuses into the porous cavities of the zeolite molecular sieve adsorbent where nitrogen is preferentially adsorbed. An oxygen and argon gas mixture then enters the secondary bed. In the secondary bed argon is adsorbed and removed, thus producing very pure oxygen which exits through valves V2 and V1. Simultaneously, the beds labeled B are vented to ambient pressure to desorb and eliminate the gases previously adsorbed at a higher pressure. A small portion of the gas produced by ZMS BED A flows through a purge orifice and exits through ZMS BED B. This purge flow enhances the desorption of the nitrogen which entered during the previous pressurization cycle

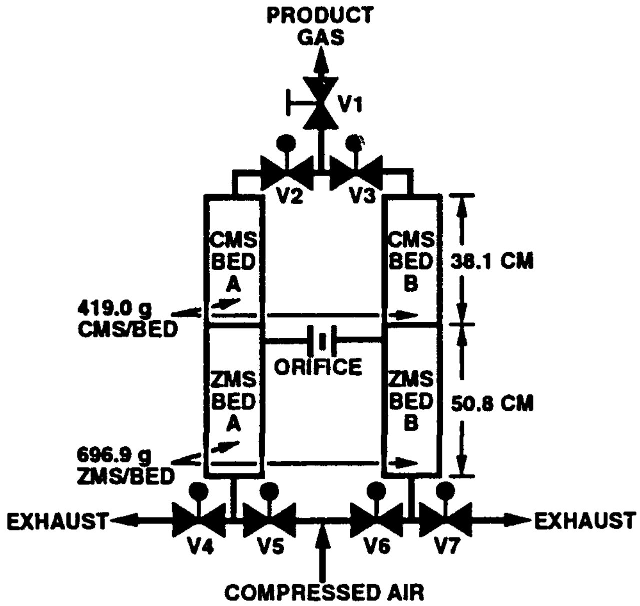

Figure 1. A Four-bed, Laboratory-scale, High Performance Molecular Sieve Oxygen Concentrator.

In the second half cycle, valves V2, V5, and V7 close and valves V3, V4, and V6 open, which essentially reverses the roles of beds A and B. The beds which previously adsorbed nitrogen and argon are vented to a lower ambient pressure and purged of adsorbed gases The previously vented beds now begin adsorbing nitrogen and argon. An electronic timer is used to control the cyclic operation of the valves.

When MSOC technology is used on-board aircraft, engine bleed air is supplied to the MSOC. Further, the engine bleed air could potentially contain contaminants which could enter the MSOC adsorbent beds. A serious concern is the degree the contaminants penetrate the MSOC beds and whether they enter the product gas. The ability of an MSOC to remove contaminants from its inlet air stream depends largely on the aperture or pore size of the adsorbent, and the kinetic diameter and polarity of the contaminant species.[3] Generally, contaminant molecules with a kinetic diameter smaller than the adsorbent pore size are able to diffuse into the crystalline framework and adsorb. During the desorption phase of the cycle the contaminant is purged from the MSOC. Hence, this process prevents the contaminant from entering the product gas. Methane possesses a kinetic diameter of 3.8 Å and does not exhibit polarity.[4] Hence, methane should diffuse into the zeolite molecular sieve.

Previous investigation has shown the ability of current MSOC technology to remove contaminants from the inlet air.[3] The goal of this work was to examine the ability of a high performance MSOC to remove contaminants from the inlet air stream. Methane was chosen as an experimental contaminant because it has been shown that standard MSOCs have difficulty removing methane.[3]

EXPERIMENTAL The concentrator used in this study is shown in Figure 1. The primary beds were cylindrical tubes which measured 50.8 cm (20 in) in length with an outer diameter (OD) of 5.08 cm (2 in) and an inner diameter (ID) of 4.70 cm (1.84 in). The secondary beds were 38.1 cm (15 in) long and had the same OD and ID as the primary beds. A 15.2 cm (6 in) length of Microbore tubing with an ID of 0.071 cm (0.028 in) served as the purge orifice. Air flow through the concentrator was controlled by six Whitey, normally closed, air-actuated valves, part no. SS-92M4-C (V2 through V7). A Numatics MK-7 solenoid actuator, controlled by a computer, directed the flow of compressed air to open or close the valves. During this study, the concentrator adsorbent beds operated at a temperature of 298 °K.

The primary beds contained OXYSIV-5 zeolite molecular sieve manufactured by UOP, Des Plaines, Illinois. This material is a synthetic, alkali-metal, alumno-silicate possessing 13X type crystal structure with uniform pore openings of 7.4 Angstroms. Each primary bed contained 696.9 g of OXYSIV-5. The adsorbent in the secondary beds was Takeda 3A CMS produced by Takeda Chemical Industries, Ltd., Tokyo, Japan. Information about the structure and properties of this particular sieve is limited, but it is reportedly produced by pyrolysis of several thermosetting polymers, such as polyvinylidene chloride (PVDC), polyfurfuryl alcohol, cellulose triacetate, and saran copolymer.[5] The pores in the CMS are not uniform, in contrast to the OXYSIV-5 pores, but possess a narrow pore size distribution. Each secondary bed in the high performance MSOC contained 419.0 g of CMS.

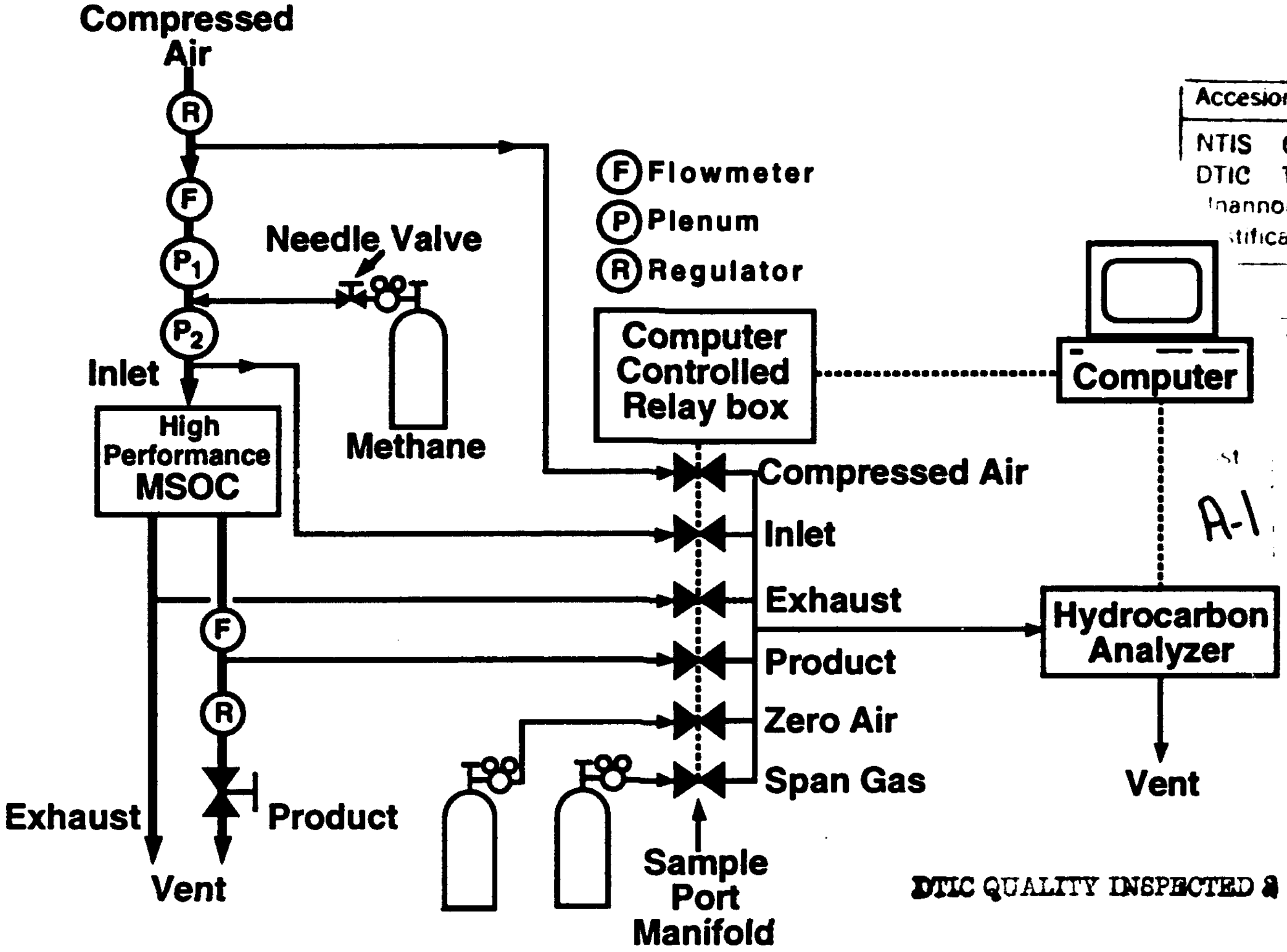

Figure 2. Diagram of Experimental Apparatus for Testing the High Performance MSOC.

The experimental apparatus, shown in Figure 2, was comprised of a high performance MSOC, an inlet and product flow meter, a hydrocarbon analyzer, and a computer which sent signals to a relay box controlling a sample manifold. MSOC inlet and product flow were measured by a Tylan FM 362 mass flow meter and a Tylan FM360V mass flow meter, respectively. The inlet flow meter had a range of 0 to 300 standard liters per minute (SLPM), and the product flow meter had a range of 0 to 5 SLPM. Both flow meters produced a 0-5 volt DC signal. Analysis of methane was performed by a Beckman, model 402 hydrocarbon analyzer. The analyzer, which produced a 0-1 volt DC signal proportional to the amount of methane detected, gave consistent and linear results at an analysis temperature of 398 °K and a sample flow of 1.0 SLPM. Span gases containing known amounts of methane were prepared in the laboratory and were used to calibrate the full range setting of the analyzer. Zero air (air containing no hydrocarbons) was used to calibrate the zero baseline of the analyzer. A Macintosh Quadra 950, equipped with a National Instruments NB-MIO-16-25L multipurpose analog to digital conversion board, executed a LabVIEW data acquisition and control program for experimental control of the MSOC and the chemical analysis. The program controlled the valves in the sample port manifold which were sequentially sampled.

Laboratory compressed air fed into the high performance MSOC was supplied by an Atlas-Copco oilless compressor and conditioned by a Hankison pressure-swing adsorption air dryer. The air then passed through a one micron particulate filter, a coalescing oil removal filter, and an activated carbon filter. The temperature of the supply air was 298 °K. The hydrocarbon content of the supply air was approximately 1-3 parts per million by volume (PPMV).

The methane injected into the high performance MSOC inlet air was supplied by a high pressure bottle of commercially available, ultra-high-purity methane (99.97 %; the sum of N_2, O_2, CO_2, C_2H_4, and H_2O less then 300 PPMV). The amount of methane injected into the inlet air stream was controlled by a Whitey SS-22R24 needle valve. A two-stage regulator on the methane cylinder was set approximately 30 PSIA above the pressure of the MSOC inlet air. This higher pressure permitted the injection of the methane into the supply air.

The supply air was regulated at 45 PSIA by a Norgren R12-400-RGLA pressure regulator and monitored with a Wallace and Tiernan absolute pressure gauge. Because fluctuations in MSOC inlet pressure affected the amount of methane entering the system, the methane injection port was placed between two plenums, shown in Figure 2 as P1 and P2. This configuration attenuated the pressure fluctuations and minimized changes in the methane flow rate. The plenum downstream of the methane injection port also functioned as a mixing chamber allowing the injected methane to mix thoroughly with the inlet compressed air. The internal volume of P1 and P2 was 8.19 l (500 in^3) and 34.41 l (2100 in^3), respectively. During all experiments, the high performance MSOC was operated at a cycle time of 14 seconds. Product flow was controlled by a Whitey SS-1KS4 manual valve set at 1 SLPM. The product gas pressure was regulated to 25 PSIA by a Norgren R07-100-RGKA pressure regulator.

A data run began by opening the needle valve on the high pressure bottle of methane while the control program cycled the high performance MSOC and monitored the inlet and product flow. The needle valve was adjusted until the desired concentration of methane in the MSOC inlet air was achieved. The control program then sequenced through the valves in the sample port manifold to analyze gases in sequential order: 1) MSOC inlet air, 2) MSOC exhaust, 3) span gas, 4) zero air, and 5) MSOC product. The three MSOC gases were each sampled for a period of five minutes, and samples of the zero air and span gas were collected for a period of two minutes each. Sampling of the zero air and span gas permitted convenient verification of the hydrocarbon analyzer calibration. As each gas was sampled, the control program generated real-time plots showing the methane concentration. The gases were sampled until steady-state operation was achieved. At the end of each data run a data file was generated which contained the methane concentrations of the sampled gases. The oxygen concentration of the MSOC product gas was determined by a Perkin-Elmer, Model 1100, medical gas analyzer.

RESULTS Data were collected while the MSOC inlet air contained concentrations of 100, 500, 1000, and 5000 PPMV methane. A total of eight data runs, two at each concentration of methane, were performed. The results are summarized in Table 1. A plot showing methane concentrations in the MSOC exhaust, inlet, and product gases, span gas, and zero air for a typical data set is shown in Figure 3. For this data set the full scale range of the hydrocarbon analyzer was set at 6000 PPMV and was calibrated with zero air and a 3000 PPMV methane span gas. During the run, the MSOC inlet air contained 5000 PPMV methane. The MSOC exhaust gas methane concentration was slightly higher because the injected methane was removed and carried out in the exhaust gas. The level of methane in the product gas was near the baseline of the plot. After the methane flow into the MSOC inlet air was turned off the concentrations of methane in the inlet and exhaust gases returned to near baseline levels within ten minutes.

Table 1. Experimental Data from the Methane Challenge of the High Performance MSOC.

Run Number	Inlet CH_4 (ppmv)	Exhaust CH_4 (ppmv)	Product CH_4 (ppmv)
1	100	101	0.95
2	107	109	0.89
3	515	525	1.03
4	501	512	0.81
5	1015	1040	0.94
6	1036	1070	0.88
7	5024	5197	0.83
8	4996	5150	0.90

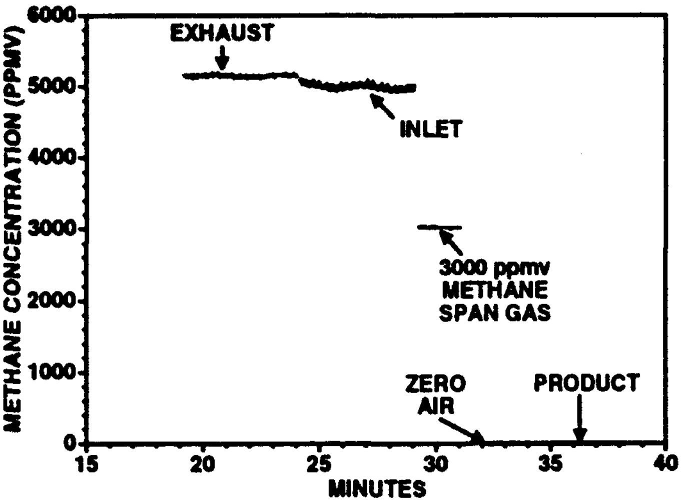

Figure 3. Experimental Data at an Inlet Methane Concentration of 5000 PPMV and an Analyzer Full Scale Setting of 6000 PPMV.

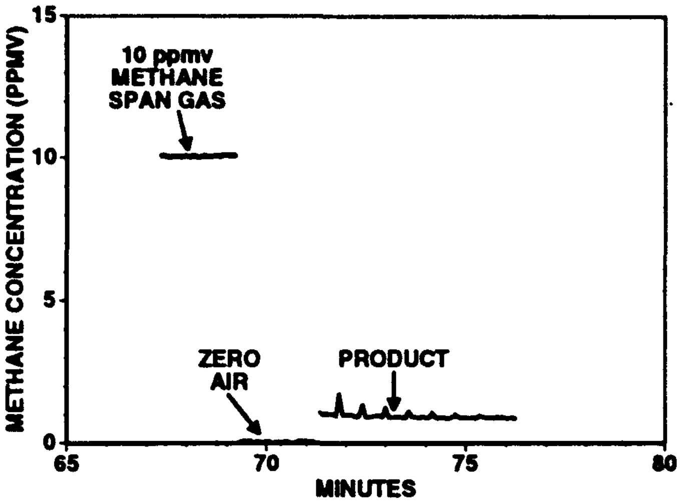

Figure 4. Experimental Data at an Inlet Methane Concentration of 5000 PPMV and an Analyzer Full Scale Setting of 15 PPMV.

To obtain a more accurate reading of the MSOC product methane concentration, the full scale range of the hydrocarbon analyzer was reduced to a more sensitive range during the data run and recalibrated. Figure 4 shows the span gas, zero air, and MSOC product gas readings for the same data run with the analyzer adjusted to a full scale range of 15 PPMV. The exhaust and inlet gas readings were off-scale during this phase of the data run. The MSOC product gas methane concentration was approximately 1 PPMV.

Background concentrations were measured without injecting methane to determine the background hydrocarbon content in the inlet air supply. Figure 5 shows background signals in the MSOC exhaust, inlet, and product gases. The background concentrations of the inlet air and product gas were approximately 2 PPMV and 1 PPMV, respectively. For this data set, the hydrocarbon analyzer was calibrated with 10 PPMV methane span gas and zero air. It is interesting to note that the product gas reading is slightly lower than the exhaust and inlet gas readings indicating the high performance MSOC was capable of reducing the background hydrocarbon level.

Figure 6 shows MSOC inlet methane concentrations and MSOC product methane concentrations for this study. Product methane levels were about 1 PPMV for all conditions tested. These product gas concentrations are identical to the background signal, hence the injected methane did not penetrate into the product gas.

The oxygen concentration of the product gas remained constant at approximately 98 per cent throughout the study. Hence, the methane had no effect on the oxygen concentrating ability of the high performance MSOC. Although the maximum oxygen concentration produced by the high performance MSOC is 99.7 per cent, the operating parameters used in this study produce an oxygen concentration slightly below the maximum. MSOC inlet flow during this work averaged approximately 75 SLPM. Mass balance closure, shown in Table 2, was calculated for each data set and was within three per cent.

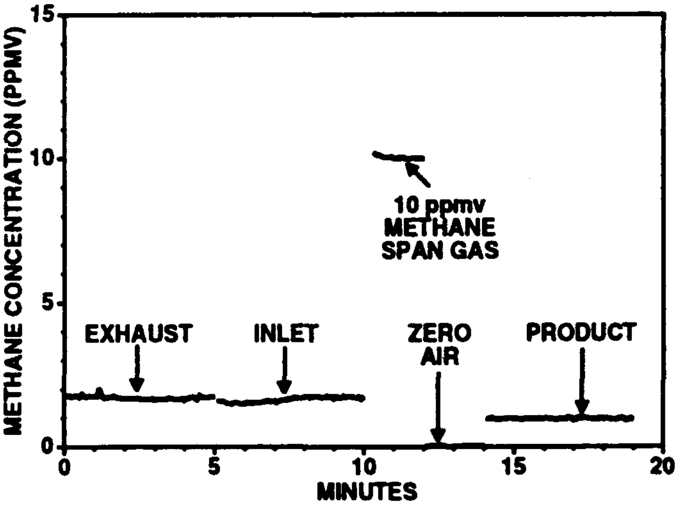

Figure 5. Background Hydrocarbon Concentrations for the MSOC Exhaust, Inlet, and Product Gases.

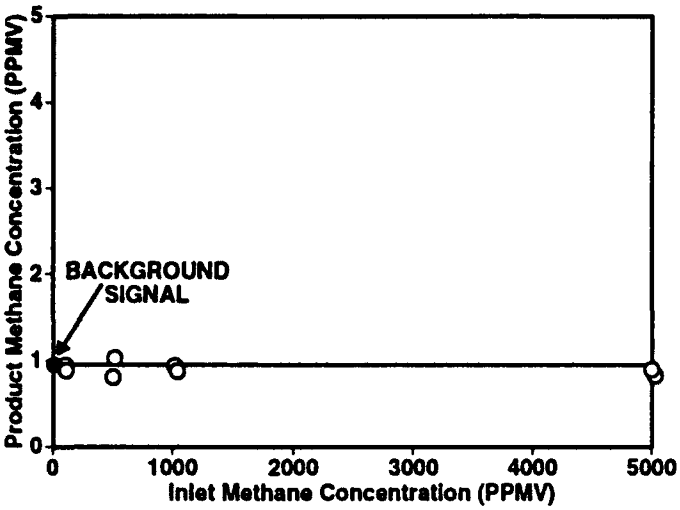

Figure 6. Experimental Data from the Methane Challenge of the Laboratory-Scale, High Performance MSOC.

CONCLUSIONS

The experimental results indicate the methane injected into the high performance MSOC inlet air stream, at levels ranging from 100 to 5000 PPMV, did not penetrate into the product gas of the MSOC. This finding suggests that the high performance MSOC is extremely efficient at removing methane and may be more effective at removing contaminants than current MSOCs. Future investigation with contaminants possessing a range of kinetic diameters and polarities is planned.

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Table 2. Experimental Data Mass Balance.

Run Number	Inlet CH4 Mass (g/min)	Exhaust CH4 Mass (g/min)	Product CH4 Mass (g/min)	Mass Balance Closure (%) Inlet-(Exhaust+Product)
1	1.6487E-2	1.6529E-2	2.0824E-6	-0.27
2	1.7515E-2	1.7685E-2	1.9509E-6	-0.98
3	8.4827E-2	8.5413E-2	2.2577E-6	-0.69
4	8.3072E-2	8.3856E-2	1.7755E-6	-0.94
5	1.7122E-1	1.7317E-1	2.0605E-6	-1.14
6	1.6969E-1	1.7289E-1	1.9289E-6	-1.89
7	8.1732E-1	8.3404E-1	1.8193E-6	-2.05
8	8.2838E-1	8.4272E-1	1.9728E-6	-1.73

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BIOGRAPHIES

Aaron M. Shakocius is a research chemist for KRUG Life Sciences, San Antonio Texas. He received his bachelor's degree in Computer Science (minor in Chemistry) from Angelo State University, San Angelo, Texas. His primary field of research is molecular sieve oxygen generating systems.

George W. Miller is a Research Engineer for KRUG Life Sciences, San Antonio Texas. He has authored and co-authored several technical papers on adsorption and aircraft molecular sieve oxygen generating systems (MSOGS), and has been awarded six US patents. He has been involved in the development and flight qualification of the B-2, YA-7F, F-15E, and F-22 MSOGS systems. Mr. Miller holds a BS in Chemical Engineering from Auburn University, Auburn, Alabama and an MS in Chemical Engineering from Ohio State University, Columbus, Ohio.