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BREATHING OXYGEN: PURITY OF OXYGEN GENERATED BY A FLUOMINE-BASED SYSTEM

September 1976

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USAF SCHOOL OF AEROSPACE MEDICINE
Aerospace Medical Division (AFSC)
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This technical report has been reviewed and is approved for publication.

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Oxygen from a fluomine-based open-loop oxygen-generating system (OLOGS) was analyzed for purity. Major contaminants observed in the product oxygen were H_2O, CO_2, and CO. The accumulated CO (20-50 ppm) is not considered harmful, nor is CO_2 (150-300 ppm) harmful. H_2O accumulation was strongly affected by its concentration in supply air and varied between 100 ppm and 5%; oxygen life-support hardware requires its removal. Normal operation of a fluomine-based OLOGS should produce oxygen remarkably free of contamination due to chemical off-gassing.

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SUMMARY

Oxygen systems currently used on high-performance military aircraft provide aircrew breathing oxygen from stored supplies and are thus constrained in mission duration and deployment capability because of ground logistic requirements. To overcome the logistics problem, the Air Force is developing self-contained aircraft oxygen systems, one of which uses a complex chemical chelating agent (fluomine) that is potentially toxic. The purpose of this study was to examine the physiologic consequences of the fluomine-based advanced oxygen system with reference to trace gas contaminants that might be produced in the normal mode of operation as well as under various overload conditions. Since fluomine is a complex chemical chelate that degrades in performance as a function of use, degradation data is automatically generated during the oxygen purity studies. This effort was done for the B-1 Systems Program Office (SPO) at the request of the 412A Life Support SPO, letter dated 10 February 1972, Oxygen Generating System Contaminant Investigation, and in response to ASD TN 71-50.

Oxygen produced by a model B-1 open-loop oxygen-generating system (OLOGS) was analyzed for purity. Ten samples obtained from three separate and independently prepared batches of fluomine chemical were used in the study. All three batches performed similarly in respect to oxygen purity. Off-gassing of fluomine was confined to water, carbon dioxide, carbon monoxide, acetaldehyde, and acetone, with no significant amounts of other volatile inorganic or organic compounds.

Neither carbon monoxide nor carbon dioxide concentrations in the accumulated oxygen product were considered harmful. Water concentrations in the oxygen product were strongly affected by supply-air flow rate and water concentration; no effect on oxygen production was noted. Product-oxygen water concentrations varied between 100 ppm and 5%, with oxygen life-support hardware requiring its removal.

The observed acetaldehyde and acetone probably arose from chemical contamination rather than degradation and should be avoidable with proper manufacturing quality control procedures.

Normal operation of a fluomine OLOGS should produce oxygen remarkably free of contaminants due to chemical off-gassing.

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BREATHING OXYGEN: PURITY OF OXYGEN GENERATED BY A FLUOMINE-BASED SYSTEM

INTRODUCTION

This report is concerned with the purity of oxygen produced by onboard-aircraft oxygen-generating systems; specifically, those systems designed around the use of fluomine [bis (3-fluorosalicylaldehyde) ethylenediimine cobalt (II)]. Fluomine is a crystalline chemical chelate with the ability to reversibly sorb and desorb oxygen. The molecular structure of fluomine is given in Figure 1.

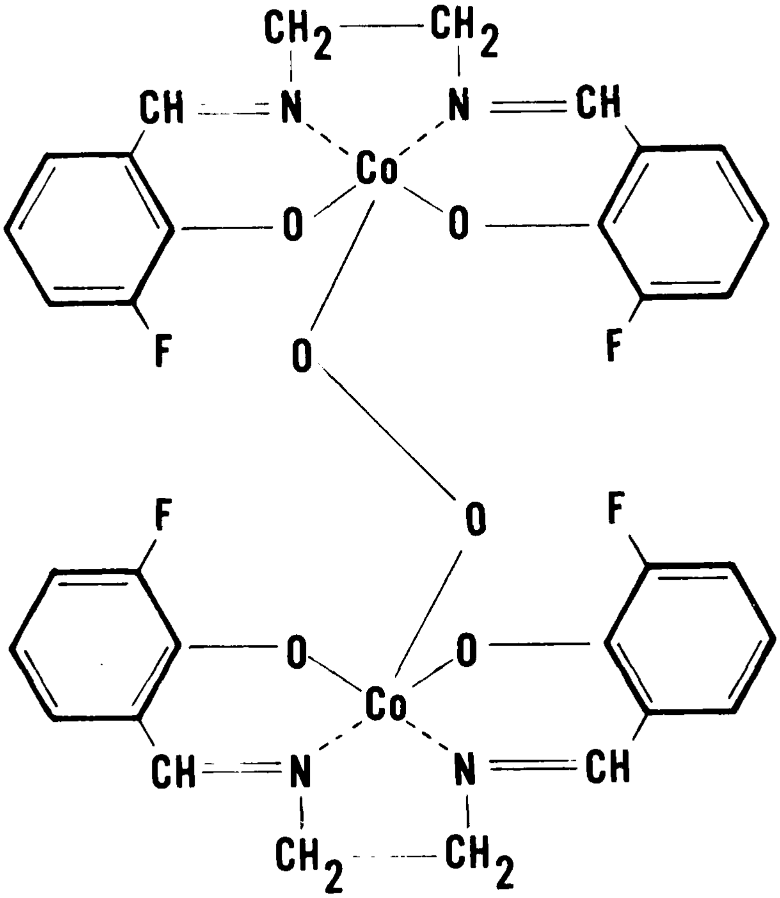

Figure 1. Stoichiometric representation of the fluomine-oxygen complex.

The chemical reaction is described in the following equation which can be used to follow the sequence of operation of the open-loop oxygen-generating system (OLOGS). (OLOGS is the acronym given to the specific system which is under development for use on the B-1.)

$$(1) \qquad 2\,\mathrm{FLUOMINE} + O_2 \underset{P_2T_2}{\overset{P_1T_1}{\rightleftharpoons}} \mathrm{FLUOMINE}_2 \bullet O_2$$

Breathing oxygen is generated by introducing aircraft bleed air into a bed containing pelletized fluomine. Oxygen is removed from the air and concentrated as a fluomine-oxygen complex at low temperature ($T_1 \approx 38^\circ C$)/modest pressure ($P_1 \approx 40$ psig). In the reverse reaction, oxygen is released by the fluomine complex for aircrew use by increasing the bed temperature ($T_2 \approx 104^\circ C$) and lowering the bed pressure ($P_2 \approx 3$ psia). Using equal times to perform the sorption and desorption half cycles, two alternately operated beds provide a continuous supply of oxygen.

A previous report, USAFSAM-TR-73-37[1], describes our preliminary efforts to identify and measure contaminants off-gassed from fluomine during limited studies of a manually operated model test bed. General objective of this followup study is to more fully and extensively characterize the off-gassing behavior of fluomine, using more representative chemical samples than were earlier available, and to investigate fluomine performance over a wider range of anticipated operating conditions.

To replace the earlier manually operated system, two automated model test-bed systems were built and used to investigate the effects of fluomine quality, operating conditions, and input-air composition on both the purity of the oxygen product and the rate of fluomine degradation. Effects of input-air contamination are treated in more detail in a separate report to follow. USAFSAM-TR-73-37 and a recent comprehensive publication by J. Sieckhaus of Olin Corporation[2] include the background material and references necessary for those desiring a history of the fluomine program, and a more complete description of using fluomine in oxygen-generating systems.

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[1] Luskus, L. J., et al. Breathing oxygen systems: Contaminants in oxygen desorbed from fluomine. SAM-TR-73-37, Nov 1973.

[2] Sieckhaus, J. F. Definition and optimization of fluomine. Final report prepared for Airesearch Manufacturing Co., Torrance, Calif., by Olin Corp., Chemicals Group, New Haven, Conn., July 1974.

EXPERIMENTAL

Sample History

Fluomine was obtained from the preparers in a pelletized and active oxygenated form--ready for use in the model test beds. Upon receipt, the chemical was divided into accurately weighed 5-, 10-, or 50-g samples, depending on available amounts of the chemical, and stored over anhydrous calcium sulfate in a desiccator until needed. The fluomine samples were transferred directly from the desiccator to the beds without treatment or taking any special precautions.

The batches of fluomine tested were designated A, B, and C. Batch A is a mixture of SPORG 3 (80%) and SPORG 4 (20%), prepared and activated by Airesearch Manufacturing Co. at their Torrance, California plant. Batches B and C correspond to Olin's batches 8 and 23, respectively, prepared and activated by Olin Corporation of New Haven, Connecticut. Studies and tests performed on a given sample are identified by a "run" number and letter. For example, run 2B corresponds to all tests carried out using sample 2 of batch B (Olin's batch 8).

Description of Test Apparatus

The experimental setup used for this study is shown schematically in Figure 2. The fluomine test bed was configured as a double-pipe heat exchanger, with the chemical pellets contained in the inner core and heating/cooling liquids flowing through the outer core. Typically, a lightly hand-packed 50-g fluomine sample, held in place with glass wool plugs, occupied up to 75 cm of the inner tube which was a 92.5-cm length of 1.27-cm-O.D. x 0.07-cm-wall stainless steel. The outer jacket was a 74-cm length of 1.90-cm-O.D. by 0.09-cm-wall stainless steel tube. The inner and outer tubes were connected at both ends by heat exchange tees (Swagelok P/N 1210-3-8Bt-8-316). To accommodate smaller fluomine samples while simultaneously minimizing system dead space, both tubes were replaced as needed by tubes of shorter length.

The fluomine beds were heated and cooled by circulating liquid baths containing a mixture of 90% ethylene glycol and 10% water. The coolant reservoirs were 25-liter capacity constant-temperature circulators (Sargent model S-84890), and the heating baths were 2-liter-capacity constant-temperature circulators (Haake model FJ).

Supply air used to provide oxygen was from (a) high-pressure cylinders of zero-grade air (Matheson, THC < 0.2 ppm, variable amounts of water, CO, and CO_2), and (b) high-pressure cylinders of scientific-grade air (Linde, THC < 0.1 ppm, CO_2 < 2 ppm, H_2O < 9 ppm; dewpoint -32.2^{o}C). Desired amounts of moisture were added to the supply air by bubbling the air through water thermostated at the appropriate temperature.

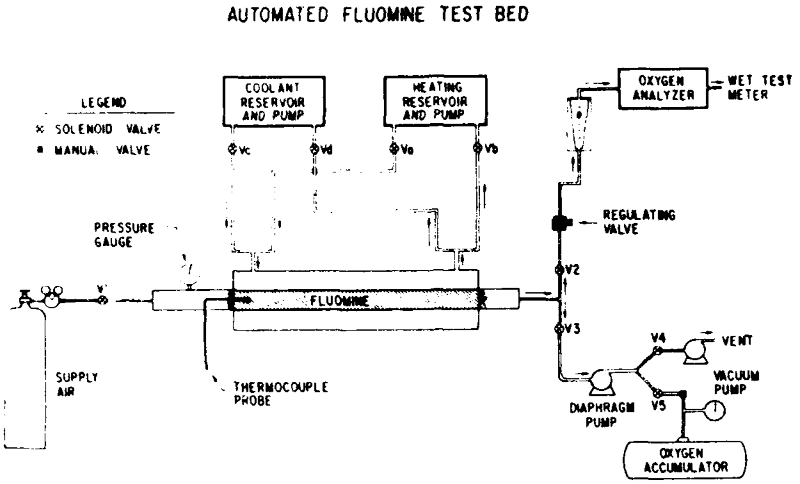

Figure 2. Schematic diagram of laboratory apparatus for study of fluomine off-gassing.

All supply and supply-adulterated air was completely analyzed in the laboratory prior to its use in a study. Supply air was metered through a standard 2-stage regulator and solenoid valve to the inlet of the core tube. Bed pressure was measured at the tube inlet by means of a dual-range pressure gauge (30-0 in Hg vacuum and 0-60 psig). The outlet of the core tube was teed to two solenoid shutoff valves. During the sorption half-cycle, effluent air was passed through a metering valve to an oxygen analyzer (Beckman model F3) and then exhausted through a wet-test meter. The metering valve was set to control the supply-air flow rate (between 35 and 125 ml/min per gram of fluomine as monitored by the wet-test meter) while maintaining the fluomine bed pressure (approximately 40 psia). The oxygen analyzer served to monitor the speed and completeness of loading.

Two pumps were used during test bed operation: (a) an oil vacuum pump (Duo Seal model 1402 to remove residual air prior to the desorption cycle to prevent contamination of the product oxygen with nitrogen, and (b) a diaphragm pump (Airshields model 12A) to displace the product oxygen from the bed to the accumulator tank.

A General Time Corp. timer motor (1/15 rpm), with a multiple-switch assembly and cams notched to give the cycling sequences detailed in Figure 2, was assembled and enclosed in a metal box. Panel lights and manual controls were provided to monitor the progress of the cycling apparatus and to allow for interruptions and holding at any point in the cycling sequence.

The temperature of the bed was measured by an iron-constantan thermocouple extending into the bed at the inlet end. Temperature was continuously recorded (Mosely model 681M).

Oxygen accumulators were standard Air Force gaseous oxygen cylinders, type D2 (capacity ~ 7 liters) and G1 (capacity ≈ 30 liters) fitted with shutoff valves and pressure gauges. Prior to installation on the test apparatus, accumulator tanks were evacuated to 0.1 mm Hg for 12 hours. A 1- or 9-liter Collins spirometer was used to measure the amount of oxygen generated during test bed operation.

Cycling Procedures

In tests, fluomine was automatically cycled to accumulate sufficient oxygen for contaminant analyses. In our studies, the smallest oxygen sample size useful for adequately sensitive IR analysis at a required 30-psia cell pressure was on the order of 7 liters. Obtaining 7 liters of oxygen from either the small 5-g or larger 50-g fluomine test samples required collecting composite oxygen samples; that is, oxygen accumulated over a number of sorption-desorption cycles. For example, a 5-g fluomine charge degraded to 50% of its theoretical oxygen-generating capacity would have to be cycled about 96 times (approximately 24 hrs) to produce an analyzable amount of oxygen. In general, oxygen samples were collected over 24-hr periods because of these sample-size requirements and work-scheduling convenience.

One complete sorption-desorption cycle required 15 minutes and was composed of the operations and sequences outlined in Table 1.

TABLE 1. FLUOMINE CYCLING SEQUENCES

Time Interval (min)[a]		Operation
Sequence 1	Sequence 2	
3	3.5	Sorption
1	1	Remove residual air
10.5	9	Desorption
0.5	1.5	Precool
15	15	Total

[a] Sequence 1 was used during Series A and B runs; sequence 2 during Series C runs.

The actual operating conditions (such as temperatures and pressures) during cycling are specified elsewhere (See Tables 2-4 in the Results and Discussions section). Typically, a sample of fluomine was lightly packed in the process tube of the test apparatus and held in place by glass wool plugs at both ends. After the bed had cooled below 30°C, a sorption half-cycle was initiated by actuating the supply-air "in" (V_1) and "out" (V_2) valves. Bed pressure was maintained at 40 psig with an appropriate supply gas flow rate. Using sequence 2 timing as an example, the sorption half-cycle continued for 3.5 minutes, during which time effluent-gas flow rate and oxygen content were monitored. At t=3.5 minutes, valves V_1 and V_2 were closed while V_3 and V_4 were opened; the pump-out of interstitial air through the vacuum pump was complete within 1 minute. At t=4.5 minutes, the desorption half-cycle was initiated by closing V_4, opening the accumulator valve (V_5), and starting the heat cycle. The heating half-cycle continued for 8.5 minutes with the bed pressure maintained between 28 and 20 in Hg vacuum by the diaphragm pump (which was also used to pressurize the product oxygen in the collecting cylinder). At t=13.5 minutes, all valves were closed except for those in the coolant supply circuit; this allowed 1.5 minutes of precooling prior to repeating the sorption-desorption cycle.

The following is a typical routine procedure during repeated cycling of the model OLOGS.

A spirometer for measuring the volume of oxygen generated was attached to the test apparatus in place of the accumulator tank.

Cycle 1 - The O_2 output was measured using a normal cycling operation.

Cycle 2 - The O_2 output was measured during an interrupted cycling operation: i.e., 3 minutes were added to the sorption half-cycle to insure complete oxygen saturation of the chelate, and 0-60 minutes were added to the desorption half-cycle to insure removal of all actively complexed oxygen.

Upon completion of cycle 2, the spirometer was removed and an accumulator tank hard plumbed in its place.

Cycles 3 through 96 - The oxygen product (a 94-cycle composite) was collected in the accumulator tank.

The accumulator, at this point removed for analysis of its oxygen contents, was replaced by the spirometer; and the procedures for cycles 1 through 96 were repeated until completion of the test run. The "normal" spirometer reading (cycle 1, 97, etc.) and the appropriate accumulator tank pressures were used to measure O_2 produced per cycle during normal system operation. Spirometer readings taken during prolonged cycling times (cycles 2, 98, etc.) were used as a measure of absolute fluomine O_2 capacity. Absolute O_2 capacity measurements were used to follow fluomine degradation--compared with "normal" measurements, they provided continuous indications of system efficiency.

Analytical Procedures

The accumulated oxygen samples were analyzed for constituents by gas chromatography (GC), infrared spectroscopy (IR), and combined gas chromatography/mass spectroscopy (GC/MS).

A dual-column instrument (Tracor model MT-150G) equipped with dual ultrasonic detectors was used for GC analyses. A molecular sieve column was used to quantify oxygen, nitrogen, and CO, and a "Porapak Q" column to quantify CO_2 and water. GC was used to verify analyses by IR and to monitor the nitrogen content of the product oxygen. Nitrogen levels were monitored to insure contaminants detected and measured arose from within the fluomine system rather than from outside air leakage or inadequate removal of residual supply air.

IR absorption spectra of the product oxygen were obtained using a high-resolution IR spectrophotometer (Beckman model IR-9) fitted with a variable 10-m gas cell. Sample-gas cell pressure, during measurement of major contaminants, was maintained at either 30 or 60 psia, depending on the accumulated oxygen sample size. The wavelength range of 4000-400 cm^{-1} (2.5-25 micrometers) was scanned and CO was quantified at 2160 cm^{-1}; CO_2, 719 cm^{-1}; H_2O, 1540 cm^{-1}; and acetaldehyde, 2730 cm^{-1}. In those instances where absorption was too intense for measurement, the sample mix was serially diluted with dry helium as many times as necessary to result in optimum analysis. Calibration curves were obtained for CO, CO_2, and trace contaminants such as acetaldehyde via standardized gases made up using common gas-dilution techniques; and for water, via dilution of room air whose water content was established using dry/wet bulb measurements. Accuracy of the water standardization method was investigated and compared favorably (±10%) with measurements made using an electrolytic hygrometer (The Hygromite; Beckman Instruments, Inc.).

Trace impurities in the product oxygen were detected and measured where possible using IR and a sample pressure of 150 psia. When such measurement was prohibitively limited by oxygen sample size or strong interference by water absorption, a GC/MS system was used (Varian model 1400 gas chromatograph coupled with a Dupont model 21-491B mass spectrometer and a Dupont model 21-094 data acquisition system). In general, using the GC/MS system necessitated concentrating the off-gassed contaminants by a factor of about 200 before analysis. Concentration was done cryogenically by passing the product oxygen through a 10 cm x 0.32-cm-OD stainless steel sample loop immersed in a liquid nitrogen bath.

RESULTS AND DISCUSSIONS

From the time a given test sequence (hereafter designated a run), was initiated, the model OLOGS apparatus was operated (cycled) continuously--24 hours a day, 7 days a week. In general, a test run was not terminated or interrupted until the fluomine was chemically or mechanically degraded beyond the point of providing expedient and usable information. Chemical problems were evident in a decrease in the chelate's ability to sorb and desorb oxygen; and mechanical problems, such as powdering of the fluomine pellets with an attendant pressure drop, made it impossible to operate the system under reasonable test conditions. Any deviation from continuous cycling is noted in our discussion of the specific test run in which it occurred.

Test parameters investigated during our studies are listed in Tables 2, 3 and 4--series A, B, and C runs respectively. All three tables will be continually referred to as we describe and discuss the tests individually and relative to each other. Parameters omitted from these tables will be noted in discussions of the specific runs involved. Runs 1A, 1B, and 1C are baseline studies and are to be used as major points of reference.

TABLE 2. SERIES A TEST SYSTEM CONDITIONS

				Supply Air					
		Temperature ($^{\circ}C$)[a]		Pressure[b]	Flow Rate	Minor Constituents (ppm)			
Run	Cycle	Sorb	Desorb	(psig)	(1/min)	H_2O	CO	CO_2	HC[c]
1A[d]	1-802	24	100	40	1.6	150	<2.0	218	<0.5
	804-1531	24	100	40	1.6	210	<2.0	242	<0.5
	1533-1887	24	100	40	1.6	240	<2.0	216	<0.5
2A	1-624	24	100	40	1.6	1500	<1.0	<225	<1.0
	626-894	24	100	40	2.5	1500	<1.0	<225	<1.0
	896-1073	24	100	40	2.5	8000	<1.0	<225	<1.0
3A	1-825	24	100	38	1.6	8000	<1.0	<250	<0.5
4A	1-815	24	100	40	1.6	1100	1000	240	<0.5
5A	1-810	24	100	40	1.6	100	<2.0	230	<1.5
	813-1270	24	116	40	1.6	100	<2.0	230	<1.5

a. Temperature attained at center core of bed.

b. Pressure at reactor bed inlet.

c. Total hydrocarbon (methane equivalents).

d. A refers to fluomine chemical designated by Garrett Manufacturing Co. as a mixture of SPORG 3 (80%) and SPORG 5 (20%); 50-g samples were used in all Series A runs.

TABLE 3. SERIES B TEST SYSTEM CONDITIONS

		Temperature (°C)[a]		Supply Air					
				Pressure[b] (psig)	Flow Rate (1/min)	Minor Constituents (ppm)			
Run	Cycle	Sorb	Desorb			H_2O	CO	CO_2	HC[c]
1B[d]	1-272	18-24	104	36	1.7	975	<1.0	245	<1.5
	274-363	18-24	104	36	1.7	4750	<1.0	65	<1.5
	365-1291	18-24	104	36	1.7	4	0	<2	0
1B Extended	1294-2588[e]	18-24	104	38	1.7	<100	0	10	<0.5
	2590-2955	18-24	104	38	1.7	4	0	<2	0
	2958-3524[e]	18-24	104	38	1.7	3000	<1.0	10	<0.5
	3526-4747	18-24	104	38	1.7	4	0	<2	0
2B[f]	1-1117	24	100	38	0.9	<100	0	5.5	<0.5

a. Temperature attained at center core of bed.

b. Pressure at reactor bed inlet.

c. Total hydrocarbon (methane equivalents).

d. B refers to fluomine chemical designated batch 8 by Olin Corp.

e. Nitrogen used in place of supply air.

f. Aviator's breathing oxygen used in place of normal supply air.

TABLE 4. SERIES C TEST SYSTEM CONDITIONS

		Temperature (°C)[a]		Supply Air					
				Pressure[b]	Flow Rate	Minor Constituents (ppm)			
Run	Cycle	Sorb	Desorb	(psig)	(l/min)	H_2O	CO	CO_2	HC[c]
1C[d]	1-2140	24	104	40	1.2	<100	<1.0	150	<0.5
2C	1-1524	24	104	40	1.2	150	<1.0	175	<1.5
	1526-2091[e]	24	104	40	1.2	100	0	8	<0.5
	2093-2529	24	104	40	1.2	150	<1.0	175	<1.5
3C	1-2206	24	104	10	0.65	150	<1.0	185	<1.5

a. Temperature attained at center core of bed.

b. Pressure at reactor bed inlet.

c. Total hydrocarbon (methane equivalents).

d. C refers to fluomine chemical designated batch 23 by Olin Corp.: 10-g sample size except for run 3C (5 g).

e. Aviator's breathing oxygen used in place of normal supply air.

Series A

Run 1A--Baseline study

Baseline run 1A test conditions are listed in Table 2, and results are condensed and illustrated in Figure 3. Figure 3a shows the extent of major contamination of the oxygen product, caused by off-gassing due to coadsorption and/or degradation of the working chemical (fluomine) as a function of time of OLOGS operation. Figure 3b illustrates chemical degradation as a function of use in the model OLOG system. To explain why particular data were used and how they were obtained, run 1A is more extensively discussed than the following runs.

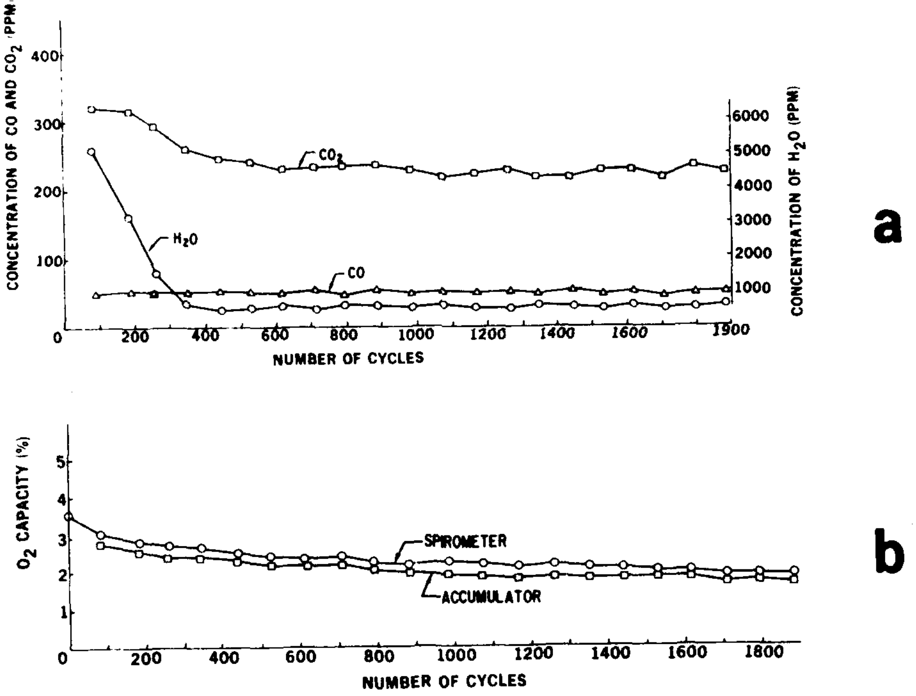

Figure 3. Run 1A: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine as a function of use.

Contaminant Study--CO, CO_2, and H_2O were the three major and persistent contaminants found in oxygen generated during test runs of all three series. Figure 3a illustrates baseline as well as general behavior of these contaminants during normal and other operating conditions. Other contaminants detected, such as acetaldehyde and acetone, were not specific to all batches of fluomine and decreased to undetectable levels within a few hundred hours of system operation. These oxygenated hydrocarbons and other contaminants found at very low concentration levels are treated in more detail later. In Figure 3a, the points which establish the contaminant profiles are based on average contaminant concentrations obtained from analysis of composite samples; e.g., the CO_2 measurement shown as a data point at cycle 91 was made on the total oxygen accumulated during uninterrupted cycling over the range of 3 to 91 cycles.

Degradation Study--Fluomine, as with organic compounds in general, will deteriorate with time when used in a repetitive reversible-reaction sequence. In our case, this unavoidable deterioration/degradation, while undesirable, does not detract from the usefulness of the chemical as long as the degradation (a) does not take place at an unreasonably rapid rate, and (b) does not produce harmful by-products that cannot be removed from the oxygen product. The degradation we are concerned with is chemical in nature and could include both molecular/atomic bonding changes and physical changes in orientation of the crystal lattice. Regardless of the cause, degradation is demonstrated by a decrease in oxygen production--a loss of oxygen capacity. Oxygen capacity is used in this report as the percent, by weight, of oxygen that fluomine is capable of complexing; theoretically, maximum oxygen capacity is 4.43% (4.43 g of oxygen produced for each 100 g of fluomine-oxygen complex used).

The upper curve in Figure 3b is a profile of the absolute degradation of sample 1A fluomine during optimum cycling conditions. Oxygen-production measurements used to determine this change in fluomine capacity were made using a spirometer. Sorption and desorption half-cycle times were lengthened by manually overriding the time sequencer to insure complete oxygen sorption and desorption. The lower curve in Figure 3b was derived by measuring accumulator tank pressure at the end of a collection period, prior to analyzing the tank's oxygen content. The curves, taken together, provide a measure of the completeness of the fluomine sorption-desorption process during system operation. As demonstrated for run 1A, all Series A series runs showed 85%-95% efficiency of possible oxygen production. All degradation curves reported in these studies are characterized by the same shape--a fast initial rate of degradation followed by a slower, more gradual, almost linear rate.

Run 2A--Effects of Water in Supply Air

One of the first system operation variables to be investigated was the effect of supply-air H_2O concentration on fluomine performance and contaminant production. Comparison of Figure 4 (wet supply-air tests) with Figure 3 (baseline performance) indicates two major differences. Figure 4 shows, first, a small increase in rate of degradation; and second, water reversibly concentrated by the fluomine chemical. The effects of humidity on rate of degradation have been cataloged by Jack Sieckhaus[3] and will not be discussed here in detail. Oxygen purity is our main concern, and while it can be seen that supply-air humidity has little if any effect on CO and CO_2 off-gassing, water levels are strongly affected. No contaminants were detected which were not present in baseline run 1A.

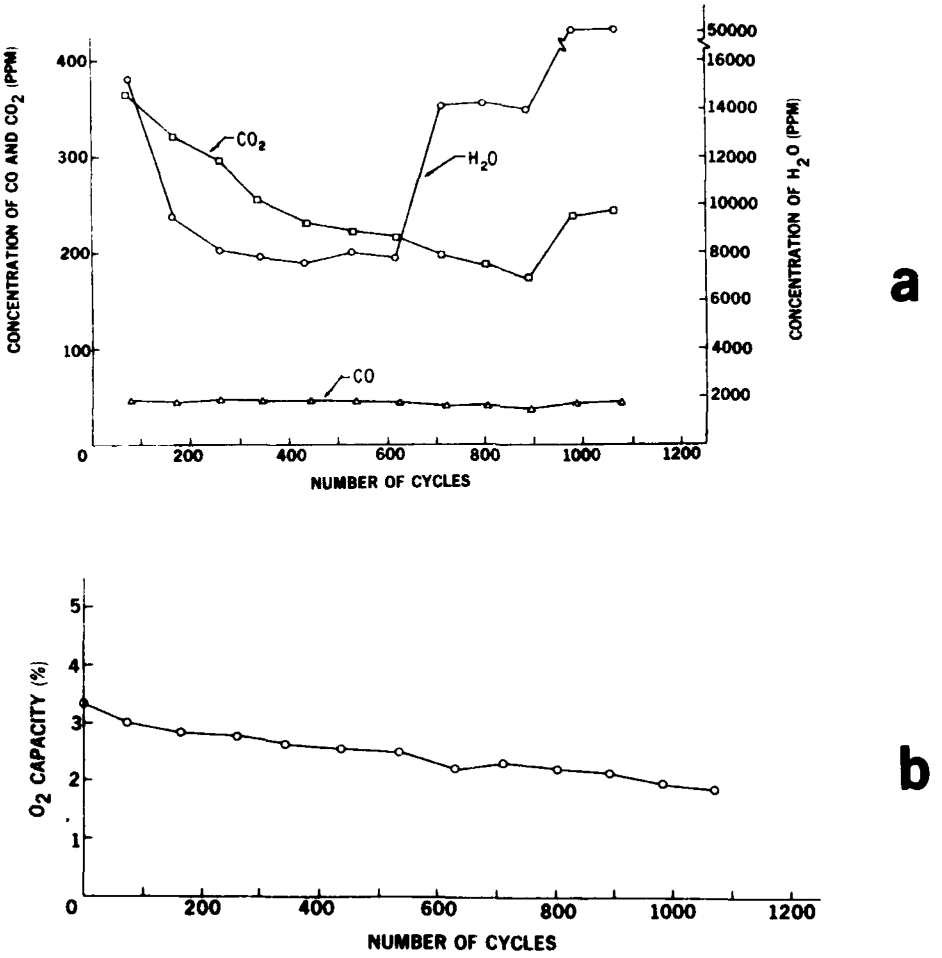

Figure 4. Run 2A: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine with use.

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[3] Ibid.

Concentration of water in the product oxygen is a function of the mass of water fluomine sees. This concentration effect is demonstrated in Figure 4a by the jump in product-oxygen water content caused by increasing supply-air flow rate at cycle 626 and the yet larger jump caused by increasing supply-air water-concentration levels at cycle 896. No interference was found in the oxygen sorption-desorption process. No attempt was made to set an absolute value on the concentration levels of water that could result from this cosorption phenomenon, although it does appear that the 5% (50,000 ppm) level reached and illustrated in Figure 4a is near maximum.

Run 3A--Effects of Supply Air Saturated with Water

Run 3A was made with supply air humidified to 8000 ppm (0.8%) of water. This was considered a worst-case condition. Concentration of water in the product oxygen was observed (Fig. 5a), with measured values averaging about 4.5% by volume--CO_2 and CO concentration levels were somewhat but not significantly less than those measured in baseline run 1A studies.

The rate of degradation appears to increase slightly (Fig. 5b), which is consistent with all of our and Olin Corporation's[4] studies.

Run 4A--Effects of Carbon Monoxide in Supply Air

Carbon monoxide at 1000-ppm level in the supply air produced no significant alterations in baseline behavior. Product-oxygen water levels were in the range expected for the supply air, which contained 1100 ppm water. CO concentrations were elevated over previous and subsequent runs; however, except for initial levels at 100 ppm or more (Fig. 6a), the higher levels are largely explained by dilution of the product oxygen with residual supply air containing CO. Some residual supply air is unavoidably added to the product oxygen because of the finite pressures used in purging the system before starting the accumulation cycle. GC analysis (O_2/N_2 concentration ratios) indicated that run 4A dilution by residual air was between 2% and 3%, which could account for as much as 30 ppm of the CO in the final oxygen product. Subtracting dilution effects from the curve of Figure 6a produces a new curve approximating baseline conditions. No explanation is offered for the observed larger initial concentrations. The CO_2 profile approximates baseline results except for the initial elevated level and gradual fall to a constant output, as experienced with CO.

Run 5A--Effects of Varying Desorb Temperature

At the time of this study a final decision had not been made as to the desorb temperature to be used in the OLOGS. Run 5A (Fig. 7) examines the effects of using a proposed higher temperature (116°C) on contaminant

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[4] Ibid.

levels in the product oxygen. A comparison of Figure 7 data with baseline results (Fig. 3) reveals no discernible effects on off-gassed contaminants or degradation rates.

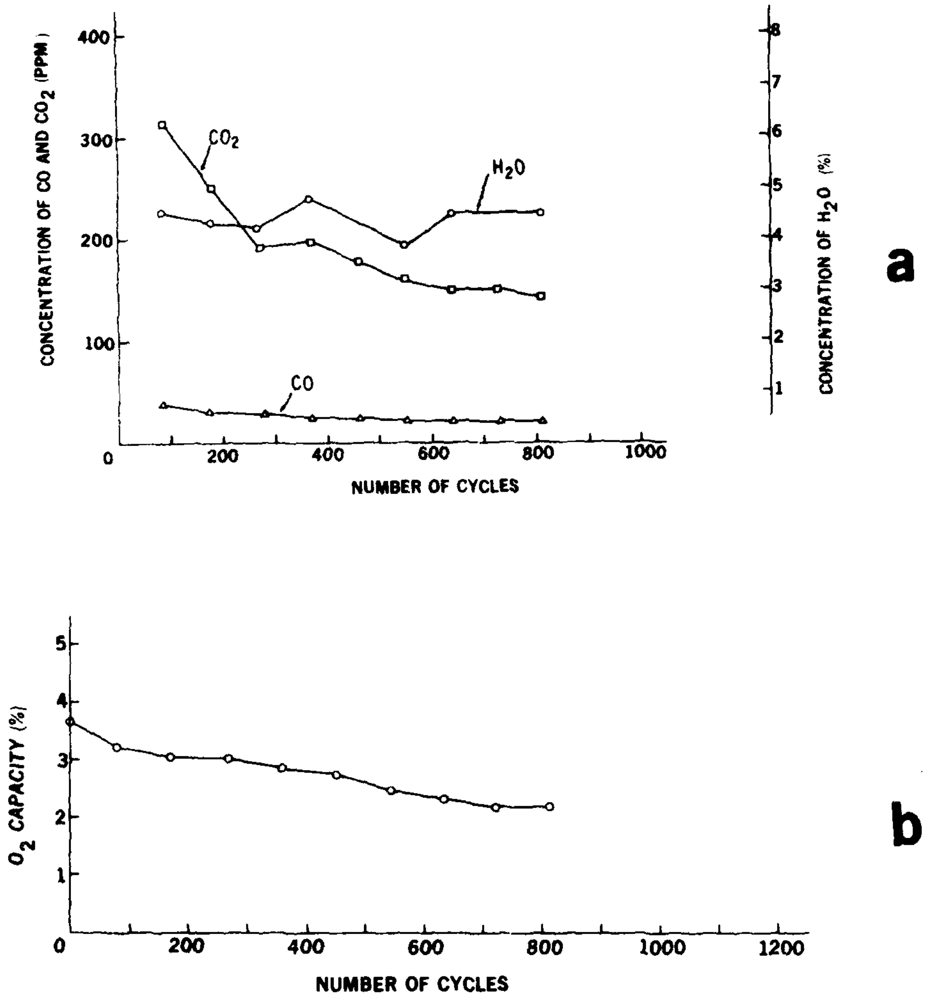

Figure 5. Run 3A: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine with use.

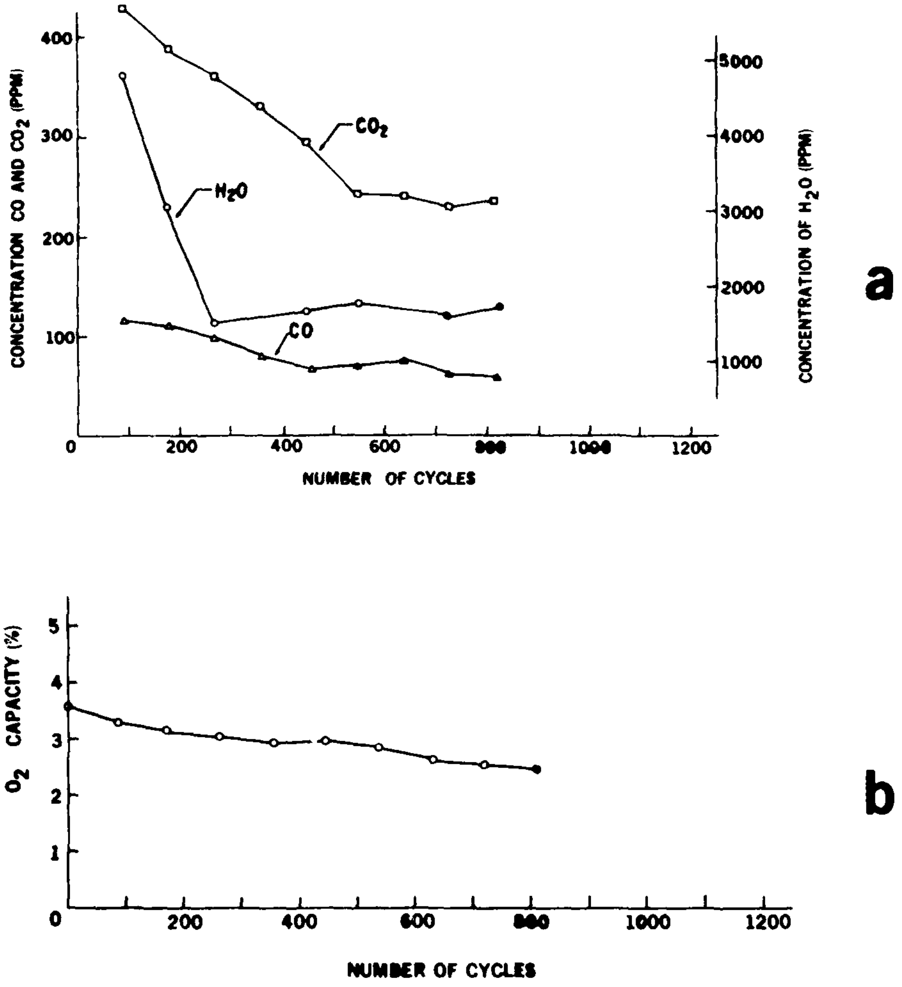

Figure 6. Run 4A--Effects of supply air containing 1000 ppm CO and O_2 purity: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine with use.

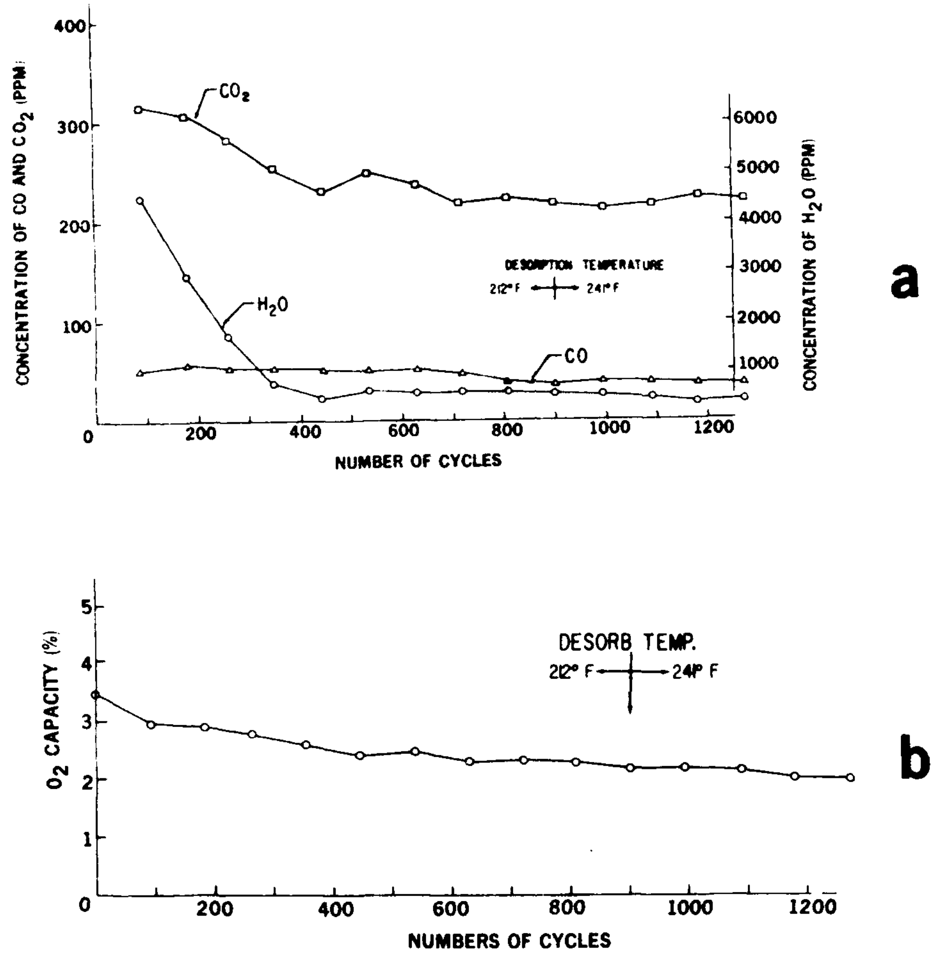

Figure 7. Run 5A--Effect of desorption temperature on O_2 purity: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine with use.

General Discussion (Runs 1A-5A)

Product-oxygen CO concentration varied from 117 ppm in run 4A to 15 ppm in run 3A (Fig. 8). Only oxygen from run 4A exceeded 50-ppm levels in CO content, and these higher levels could be largely attributed to incomplete removal of the 1000-ppm-CO residual supply air specific to this run. Since the working OLOGS should have a smaller residual volume with respect to oxygen output, and since bleed air CO levels as high as 1000 ppm are unlikely to be encountered, the 50-ppm maximum consistently observed is a firm value. The baseline CO profile (run 1A) was omitted from Figure 8 to avoid clutter but can be approximated for comparison purposes by the run 5A curve, which is for all purposes a duplicate.

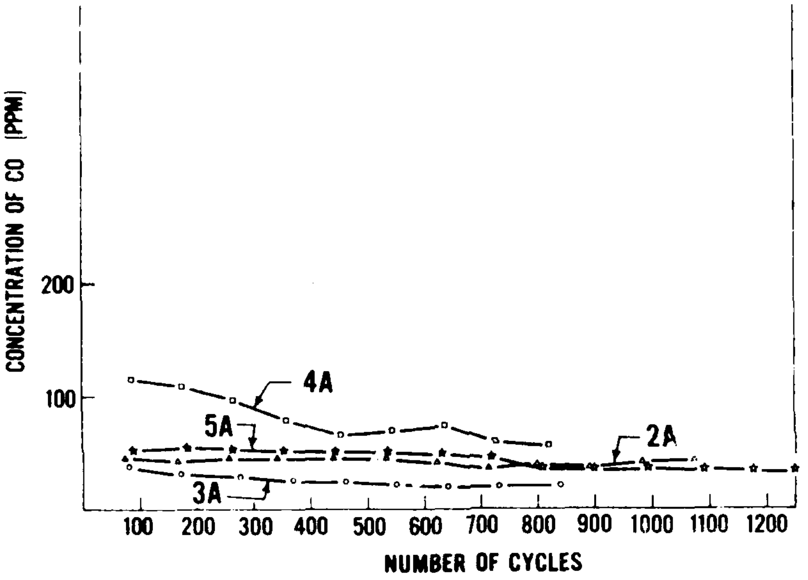

Figure 8. Carbon monoxide concentrations [illegible] oxygen generated during Series A runs.

Carbon dioxide concentration levels (Fig. 9) characteristically drop from an initially high level (420-320 ppm) to a moderate constant output of 250-150 ppm. The contaminant production curves, to a limited extent, parallel the shape of the degradation curves presented earlier. Higher CO_2 output during early stages of system operations could thus reflect an initial high rate of oxidative degradation. Deviations from baseline results (run 1A) are demonstrated by runs 3A and 4A. In both cases deviations are small and more informative than easily explainable. The run 1A CO_2 profile, as in the case for CO, duplicates run 5A contaminant production and is not included in Figure 9 to avoid clutter. CO_2 concentration varied little from ambient air concentration and would be of no concern to oxygen users.

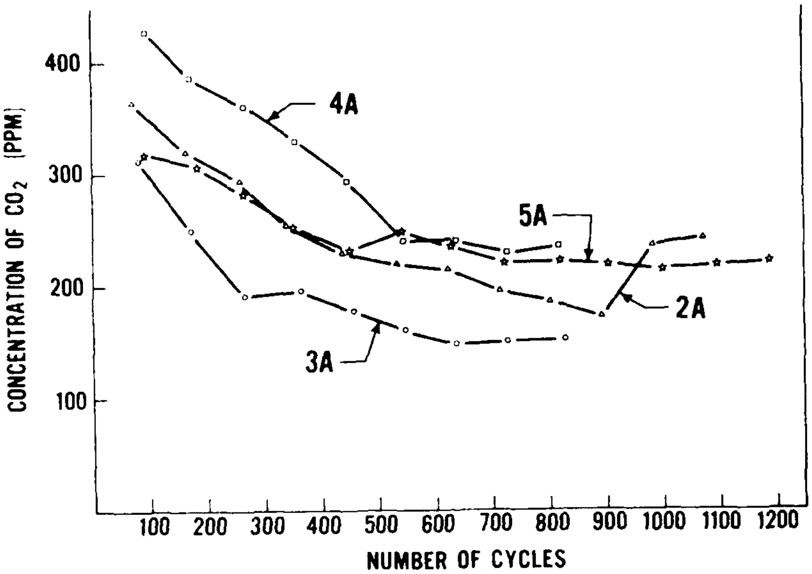

Figure 9. Carbon dioxide concentrations in oxygen generated during Series A runs.

Typical effects of water in supply air on the product-oxygen water levels are illustrated in Figure 10. Baseline run 1A uses a relatively dry supply air (≈ 200 ppm) which results in a steady state concentration of about 500 ppm in the accumulated oxygen. Run 2A illustrates what happens when baseline conditions are changed by adding more water to the supply air. The first part of curve 2A levels out at a constant output of 8000 ppm H_2O which is increased stepwise, first by increasing the supply-air flow rate and then by increasing supply-air humidity. There is no doubt that water is cosorbed and desorbed with oxygen to levels exceeding 5% under worst-condition testing.

Series B

Run 1B--Baseline Study

Run 1B was a baseline study using "batch 8" fluomine. Batch 8 chemical was a "best" performer in extensive degradation testing by Olin and Airesearch[5], and its behavior could be considered a major part of

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[5] Ibid.

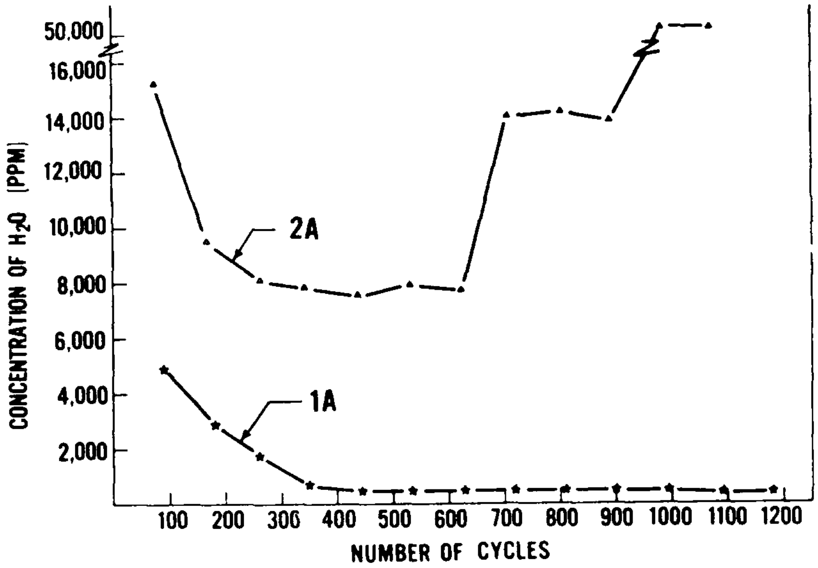
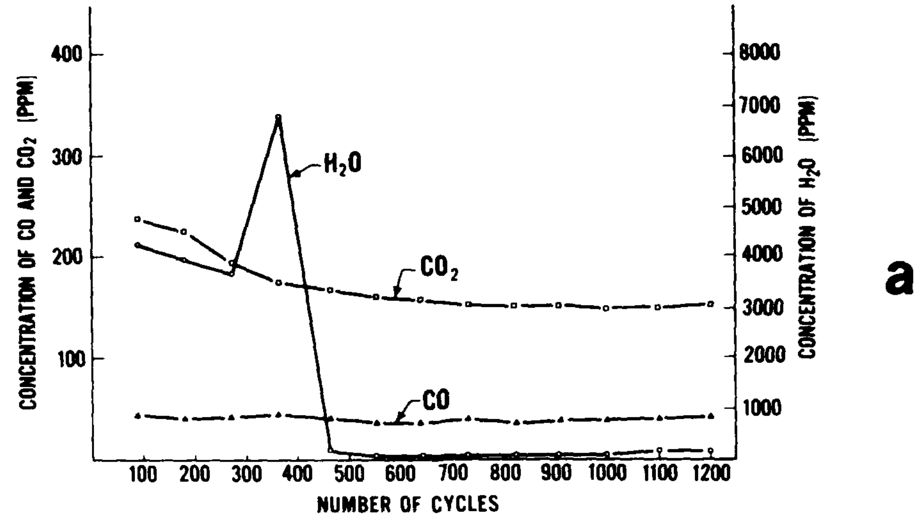


Figure 10. Water concentrations in oxygen generated during Series A runs.

the standards on which to base procurement and use specifications. Our results (Fig. 11) indicated no remarkable difference in performance between this fluomine and the SPORG samples used in Series A tests. Contaminant studies showed only the presence of CO, CO_2, and H_2O in an odorless product oxygen. No appreciable levels (> 0.5 ppm) of other volatile contaminants were detected, by IR and GC/MS analysis, which proved batch 8 to be the "cleanest" fluomine studied. The contaminant curves in Figure 11a indicate that CO and CO_2 levels are lower (about 20%) than those observed in Series A studies and are thus consistent with the small improvement shown by a decreased rate of degradation (Fig. 11b) and with preparer's claims. Water levels in the product oxygen are in line with results expected after completing Series A studies. The sharp jump in water output at cycle 363, which appears to be an anomaly, is in reality an error resulting from an inadvertent change to a supply-gas cylinder containing wet air. Water content in the product oxygen was immediately lowered when the cylinder was replaced at the start of the following collection sequence. Actually, the sharp change dramatically illustrates how efficient fluomine is as a reversible water concentrator. The spirometer versus accumulator curves of Figure 11b portray an oxygen-concentrating efficiency of 90% of theoretical.



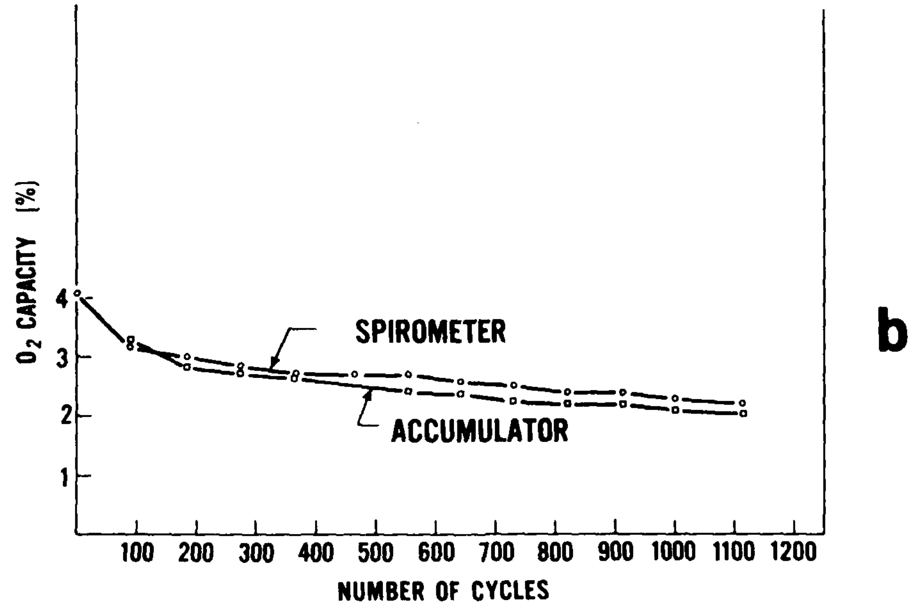


Figure 11. Run 1B: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine with use.

Run 1B Extended--Thermal and Water Effects Independent of Oxygen Generation

Run 1B was continued after a 30-day interruption, during which time the partially used 1B fluomine was stored in the reactor tube under ambient conditions. The continued tests examined the effects on fluomine degradation and off-gassing of test-bed operation independent of the effects of oxygen sorption-desorption and/or presence of oxygen itself. This was accomplished by using "dry" and "wet" nitrogen supply gases in place of air during normal operation of the test bed. The small amount of gas accumulated was mainly residual nitrogen but did provide an idea of fluomine off-gassing during operation with the nitrogen supply gases.

Figure 12 illustrates degradation with pertinent experimental conditions. Detailed test conditions are described in Table 3. Testing started on cycle 1294, with an O_2 capacity measurement showing that no fluomine degradation had occurred during the 30-day storage. Dry nitrogen (≈ 10 ppm H_2O) was used as a supply gas for about 1300 cycles of operation. At cycle 2590, an O_2 capacity measurement revealed that no degradation had occurred during operation with the dry nitrogen, and system operation was resumed using dry air (350 ppm H_2O) as a supply gas; degradation proceeded at a "normal" rate. A change at cycle 2958 to wet-nitrogen supply gas resulted in a 650-cycle test with no observable chemical degradation. Final testing used supply air and produced degradation at the same rate observed throughout most of the 1B study when supply air was used.

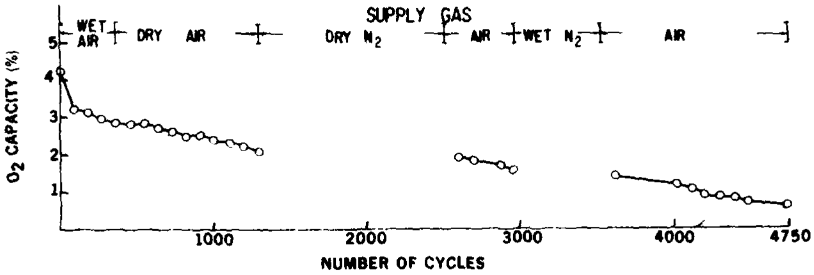


Figure 12. Thermal and supply-gas water concentration effects on fluomine performance independent of the presence of oxygen.

When nitrogen replaced air as the supply gas, fluomine off-gassing decreased to very low levels (CO, < 2 ppm; CO_2, < 10 ppm; H_2O, < 100 ppm). A return to the use of air resulted in an increase of the three off-gases to normal concentration levels.

These results indicate that (a) fluomine degradation takes place during the actual oxygen sorption-desorption process, (b) cosorption-desorption of water has no effect on degradation when oxygen is not present, and (c) no thermal degradation of the chemical occurs during normal system operation.

Run 2B--Use of 99.5% Oxygen as Supply Gas

Aviator's breathing oxygen (> 99.5% purity) was used as the supply gas for run 2B in an attempt to speed up and study oxidative fluomine degradation. The results are illustrated in Figure 13. Degradation was extremely rapid in the initial stages of system operation, with fluomine O_2 capacity dropping from 4.25% to 1.63% by cycle 104. This fast initial degradation was not accompanied by an expected large increase in contaminant off-gassing (compare Figs. 13a and 11a--the baseline run), which suggests that oxygen contributes strongly to (a) a physical degradation mechanism resulting in a change in crystal structure, or (b) a strictly chemical mechanism, such as oxidation of cobalt (II) to cobalt (III), with no molecular breakdown to and output of volatile contaminants. The physical pathway is most probable in light of earlier observations by Olin[6] which show limited cobalt (II) to cobalt (III) oxidation during air degradation studies using fluomine.

The degradation profile (Fig. 13b) indicates that the purely physical mechanism is complete by cycle 104, with degradation beyond that point very slow and related only to the off-gassing of the chemical oxidation products CO, CO_2, and H_2O. Observed CO and CO_2 concentrations are slightly higher than those in the baseline run and suggest somewhat accelerated oxidation because of the higher concentrations of oxygen seen by the test bed. Inaccuracy of H_2O measurements did not permit their use in analyzing these data except in a qualitative way.

Series C

Run 1C--Baseline Study

Run 1C was a baseline study using Olin-prepared batch 23 fluomine, considered of inferior quality when compared with batch 8 (Series B chemical). Major differences observed in 1C fluomine performance included a higher initial rate of CO_2 off-gassing (Fig. 14a), the appearance of acetone and acetaldehyde as trace contaminants, and accelerated degradation during the first 150 cycles (Fig. 14b). The rates of CO_2 and H_2O off-gassing are similar to Series A rates and might be useful as an index of fluomine quality. Acetone and acetaldehyde appeared at concentrations of 13 and 18 ppm, respectively, in the first oxygen collected. Undetectable levels were reached within 500 cycles of system operations. Both compounds were found in similar concentrations and behaved similarly in Series A tests. Neither compound was found during

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[6] Ibid.

Series B tests. Both compounds are believed to result from contamination during fluomine preparation and handling rather than from degradation of the chemical.

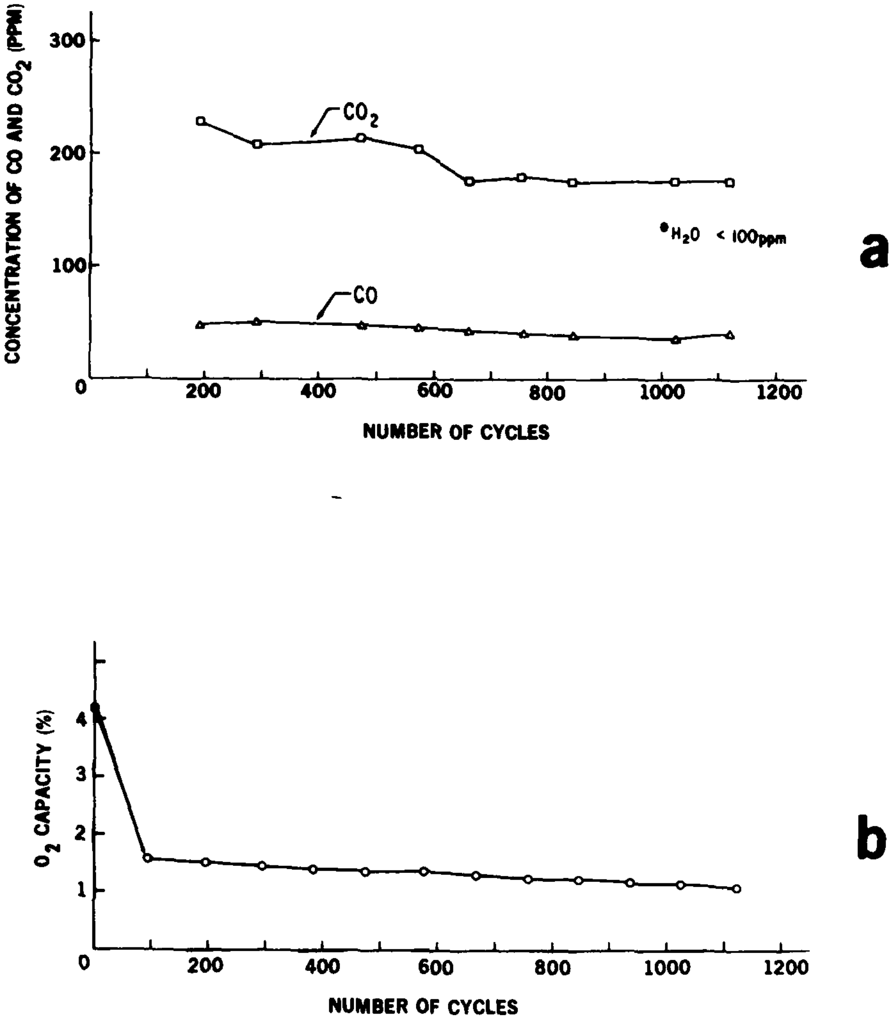

Figure 13. Run 2B--Effects of using pure oxygen supply gas on (a) fluomine off-gassing and (b) fluomine degradation.

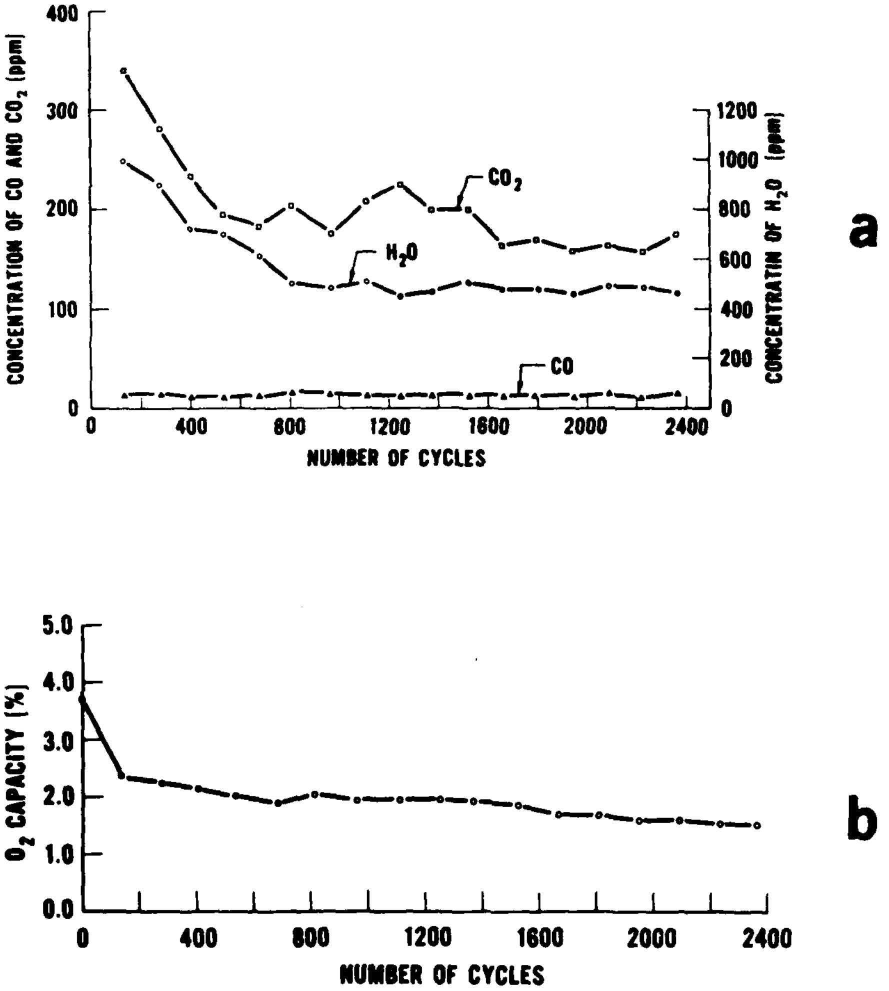

Figure 14. Run 1C: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine with use.

Run 2C--Effects of 99.5% Oxygen on Partially Deactivated Fluomine

Except for an interruption when pure oxygen was used as a supply gas, run 2C was a duplicate of baseline run 1C. (See Fig. 15 and Table 4 for test conditions and results.) In run 2B, aviator's oxygen caused initially fast and extensive degradation, leveling-off to a constant slower rate (Fig. 13). By comparison, no accelerated degradation was noted in run 2C. Using pure oxygen apparently has little effect on fluomine capacity once the fluomine chemical has been degraded to some as yet undetermined level of performance.

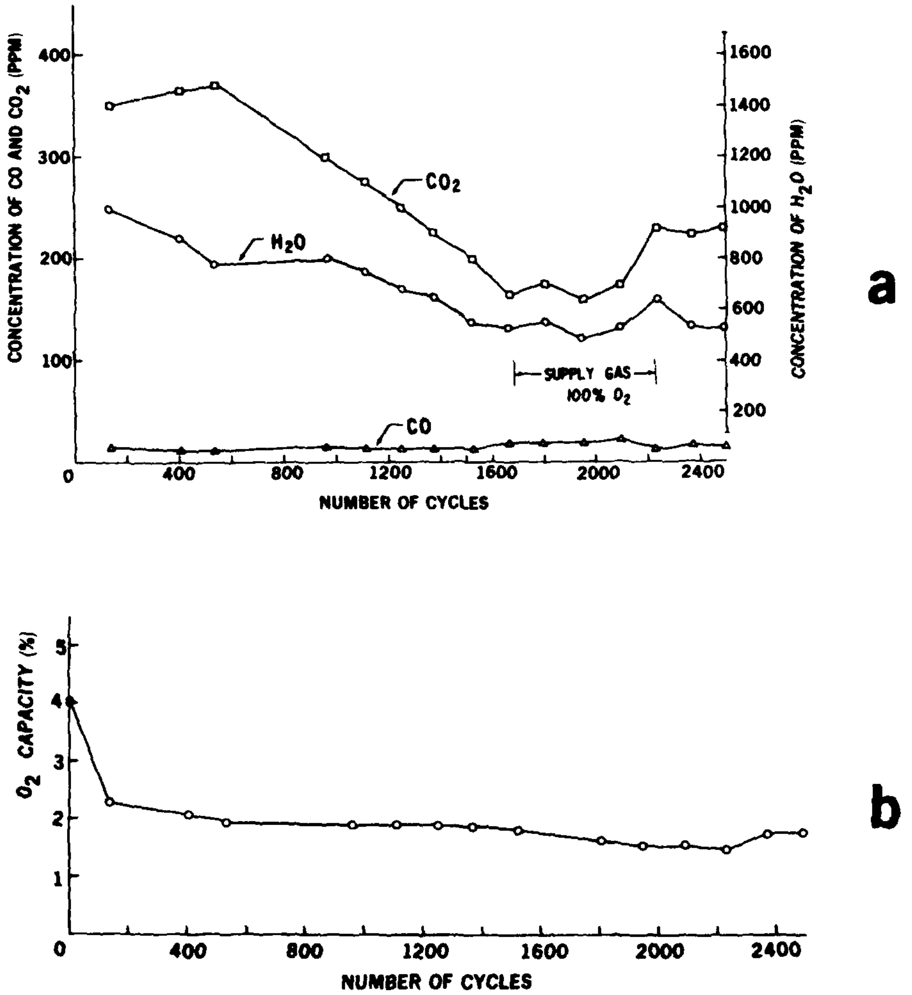

Figure 15. Run 2C: (a) Major contaminants in fluomine product oxygen; (b) Degradation of fluomine with use.

Reestablishment of supply air produced an increase in O_2 capacity (Fig. 15b). Similar unexplainable and inconsistent increases in O_2 capacity were observed by Olin[7] during their degradation studies. Overall, run 2C duplicated run 1C baseline performance.

Run 3C--Effects of Inefficient Oxygen Sorption/Desorption

Run 3C test conditions differed from those of 1C and 2C only in the use of lower supply-gas pressure (10 vs 40 psig) and flow rate (0.65 vs 1.2 liters per min). No oxygen-product contamination data were recorded because of sampling problems. What appears to be enhanced performance (Fig. 16) is more apparent than real since an accounting for partial loading of the chemical results in duplication of previous results; i.e., plot oxygen capacity versus weight of oxygen generated rather than cycle number. This would indicate that the percentage of loading is not a major factor in determining fluomine deactivation.

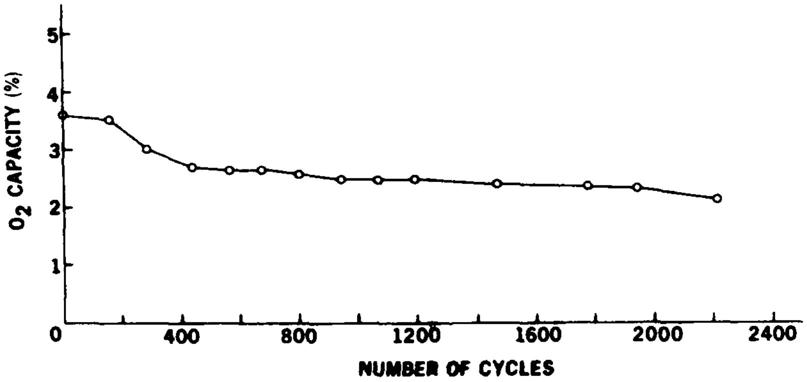

Figure 16. Run 3C: Degradation of fluomine with use.

CONCLUSIONS

The performance of a fluomine-based laboratory oxygen system was investigated to identify and quantify contaminants produced during cyclic operation. Oxygen generated by a model open-loop oxygen-generating system was analyzed for purity. Ten fluomine samples were investigated from three independently prepared batches of chemical, and all three batches produced oxygen of similar purity. Major contaminants observed in the product oxygen were water, carbon dioxide, and carbon monoxide. Some acetaldehyde and acetone (up to 20 ppm in the oxygen product) were found during the first few hundred cycles of system operation for two

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[7] Ibid.

of the three fluomine batches. No significant amount of any other trace volatile organic or inorganic contamination was evident. The oxygen product was odorless except for one test sequence where highly contaminated supply air was used.

Carbon monoxide accumulated as a fluomine degradation product in the generated oxygen at concentrations between 20 and 50 ppm. These concentrations in 100% oxygen are not considered harmful[8]. Carbon monoxide to 1000 ppm in the supply air did not concentrate to any appreciable extent in the oxygen product.

Carbon dioxide concentrations in the accumulated oxygen product were consistently between 150 and 300 ppm. Carbon dioxide is not harmful to either aircrew or oxygen life-support hardware and need not be removed.

Water concentrations in the oxygen product were strongly affected by supply-air flow rate and water concentration, indicating cosorption-desorption with oxygen. The lowest water concentrations recorded were about 100 ppm; the highest about 5%. Hardware requirements presently demand a maximum of 3 grains of water per pound of aviator's breathing oxygen.

Acetaldehyde was a contaminant found in oxygen produced by two of three batches of analyzed fluomine. One of the acetaldehyde-contaminated batches also produced acetone. Concentrations of both organic compounds in the oxygen product, initially between 10 and 20 ppm, decreased to undetectable levels within 500 cycles of system operation. Both contaminants are probably introduced during chemical preparation or handling and need control procedures to insure their removal.

Observed differences in fluomine degradation rates between different batches of chemical and with changing conditions of OLOGS operation had little effect on the kinds or concentration levels of contaminants in the oxygen product. These results are explainable in terms of two degradation mechanisms: (a) a chemical oxidation that produces the contaminants and is relatively unaffected by system operating conditions, and (b) a physical crystal lattice change that produces no contaminants but does deactivate the fluomine. Further work is necessary to completely define and identify the number and subtlety of factors affecting the extent and rate of fluomine degradation. Further work is not necessary, however, to conclude that oxygen can be obtained from a fluomine-based OLOGS with a minimum of contamination due to chemical off-gassing during normal modes of operation.

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[8] Back, K. C. Open-loop oxygen-generating-system contaminants. Letter report from AMRL/THT to ASD/SML, 10 Dec 1974.

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