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**USE OF LITHIUM PEROXIDE
FOR ATMOSPHERE REGENERATION**

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FOREWORD

This study was initiated by the Biomedical Laboratory, Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. The research was conducted by the Electric Boat division of General Dynamics, Groton, Connecticut, under Contract F33615-67-C-1514.

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This technical report has been reviewed and is approved.

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ABSTRACT

The chemistry of lithium peroxide has been studied for use as a nonregenerative air revitalization material for oxygen supply and carbon dioxide removal. The use of catalysts to accelerate the decomposition of the hydrogen peroxide formed as an intermediate in the reaction of lithium peroxide with water vapor was investigated. Catalyst screening studies, kinetic studies of the reactions of several lithium peroxide formulations with water vapor and carbon dioxide, and complete chemical kinetic studies for the air revitalization reactions of a peroxide/silver metal powder formulation were performed. A commercially available lithium peroxide pellet formulation was evaluated for air regeneration purposes. The thermal stability characteristics of various lithium peroxide formulations were ascertained.

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SECTION I

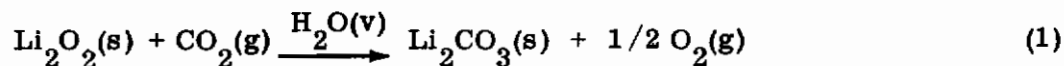
INTRODUCTION

GENERAL

As man extends himself deeper into outer space, new, reliable life support systems must be developed to meet the demands of space flights of long duration. In recent years, the development of air revitalization systems for space cabin use has centered on the development of regenerative-type systems. For long-term space flights, such emphasis is justified to overcome the weight and volume penalties associated with a nonregenerative air revitalization system. However, simple, nonregenerative systems will continue to play a major role in short-term space flights, such as scientific explorations, intercontinental space travel, shuttle trips to manned space stations or to the moon, excursion vehicles, oxygen storage on the moon, extra-vehicular space equipment, and emergency back-up systems to regenerative life support systems.

For these specific applications, "active chemicals" for nonregenerative air revitalization systems have been the subject of extensive basic research studies conducted both in the United States and the U. S. S. R. (Petrocelli, 1965b). Active chemicals are defined as multifunctional chemical compounds suitable for use as an oxygen source and capable of removing carbon dioxide from gaseous environments. Particular attention in this regard has been paid to alkali metal and alkaline earth peroxides, superoxides, and ozonides. A recent monograph (Vol'nov, 1966) presents a detailed description of the chemical and physical properties of these compounds. For air regeneration purposes, they react with water vapor to release oxygen and produce a base capable of absorbing carbon dioxide, thus forming metal carbonates and/or bicarbonates. The potential of alkali metal superoxides and ozonides as chemical air regeneration agents has been confirmed (Petrocelli et al, 1964, 1965, 1966).

Of the alkali or alkaline earth peroxides, lithium peroxide is most often considered as a potential air revitalization material. In the presence of moisture, it will react with carbon dioxide to form lithium carbonate with an accompanying release of oxygen according to the following overall stoichiometry:



The theoretical respiratory quotient for a system employing only lithium peroxide would be 2.0, indicating an under-production of oxygen compared to the respiratory balance required by man in a closed environment. The theoretical capacity of the lithium peroxide for carbon dioxide is approximately 4% greater than that of the corresponding hydroxide. Lithium peroxide would appear attractive, therefore, only in a mixed active chemical system wherein advantage could be taken of its greater

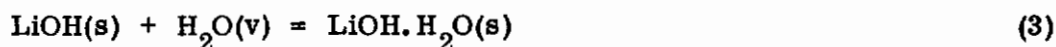
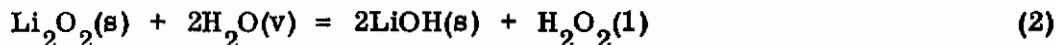
carbon dioxide absorption capacity while providing some additional oxygen supply. Such a system could employ lithium peroxide in proper combination with sodium or potassium superoxide.

PREVIOUS STUDIES

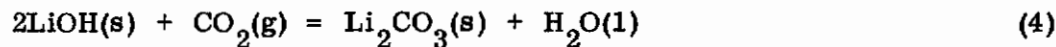
In recent years, laboratory research studies have been conducted on the synthesis of lithium peroxide (Markowitz, 1964) and the utilization of lithium chemicals for air regeneration (Markowitz, 1964, Bach, 1965).

The work of Bach et al, (1965) was principally concerned with the efficiency of lithium oxide as an absorber for carbon dioxide. This study showed that the retention of carbon dioxide by the oxide could be as high as 90% and that nearly complete conversion of the oxide to the carbonate could be attained.

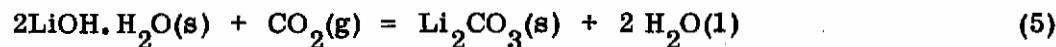
The results of the research conducted by Markowitz and Dezmelyk (1964) confirmed that oxygen evolution and carbon dioxide absorption by lithium peroxide in the presence of water vapor do occur. However, the oxygen evolution lagged behind the amount anticipated on the basis of reaction equation 1. To account for the observed lag in oxygen evolution with respect to carbon dioxide absorption, Markowitz (1964) postulated that these processes resulted from two different reaction mechanisms; the first involving the reaction of the lithium peroxide with water vapor to yield the active carbon dioxide absorbents, lithium hydroxide, hydrated lithium hydrogen peroxide:



Carbon dioxide would then be absorbed via the reactions:



and

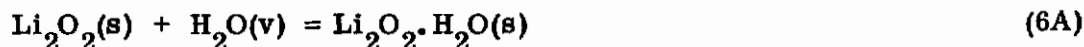


The oxygen lag then results from the slow decomposition of hydrogen peroxide:

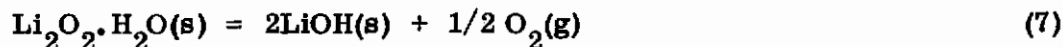


Markowitz (1964) also noted that hydrogen peroxide formed by the interaction of water with lithium peroxide could be stable in a lithium peroxide/hydrated hydroxide solid mixture. Such stability would contribute to the lag in oxygen evolution. When a peroxide sample was pelletized with 2% manganese dioxide, a somewhat greater yield of oxygen was observed by Markowitz (1964) and was attributed to the possible catalysis of the hydrogen peroxide decomposition by the presence of the manganese dioxide.

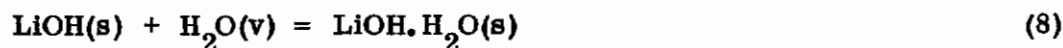
Selezneva (1960) has investigated the interaction of lithium peroxide with water vapor and carbon dioxide from ambient conditions to as high as 300 C. Up to 100 C, there was virtually no reaction between dry carbon dioxide and the peroxide. Reactions were observed under all other conditions in which moisture was present. Selezneva postulated that the first step in the reaction mechanism at 23 C was due to hydration with the resultant formation of lithium peroxide monohydrate:



Some lithium hydroxide monohydrate from:



and



was also considered present owing to the observed evolution of oxygen. Incomplete reactions and low oxygen yields were noted also by Selezneva (1960).

Therefore, to improve the oxygen yield from the pertinent air revitalization reactions of lithium peroxide, the decomposition of intermediate peroxide species must be accelerated. To this end, the subject research program was undertaken.

TECHNICAL APPROACH

The objective of this program was to develop lithium peroxide in an optimum chemical and physical form suitable for air revitalization. The research program was designed to continue the development of lithium peroxide as an active chemical and further the knowledge of its chemical and physical characteristics. An optimum chemical was desired that would react at practical rates with water vapor and gaseous carbon dioxide to release oxygen and absorb carbon dioxide in quantities approaching the stoichiometries of the pertinent air revitalization reactions. The reactions must proceed efficiently at a proper balance so as to maintain an adequate respiratory quotient. Major emphasis in this program was placed on the investigation of catalyst systems to promote and accelerate oxygen evolution from the reaction of lithium peroxide with water vapor. The introduction of catalysts would accelerate the decomposition of the intermediate hydrogen peroxide formed in the water vapor reaction.

To fulfill the objectives of the research program the following scope of work was pursued:

1. Evaluation of pure lithium peroxide samples, both powdered and pelletized (Foote Mineral Environmental Grade) materials. This evaluation was made by performing chemical kinetic studies of the reactions of the subject material with various concentration levels of water vapor and gaseous carbon dioxide.
2. Screening of several catalyst systems. The effect of a number of catalysts on the reaction of lithium peroxide with water vapor was determined by performing the appropriate chemical kinetic studies. This study was intended primarily as a screening process to select those catalyst systems requiring more detailed kinetic studies.
3. Kinetic studies of selected lithium peroxide/catalyst formulations. Those catalysts selected from the screening process were incorporated into powdered formulations with lithium peroxide. Chemical kinetic studies were performed for the reactions of water vapor and gaseous carbon dioxide with these formulations. The most promising catalyst/peroxide formulation was subjected to more detailed study. This task also included a dynamic kinetic study for Foote Mineral Environmental Grade pellets wherein the pellets were subjected to a constant inlet concentration of reactants and the outlet gas stream monitored for oxygen and carbon dioxide.
4. Thermal stability of lithium peroxide formulations. Gravimetric and volumetric techniques were employed to investigate the stability of lithium peroxide formulations at 50 C.

SECTION II

DISCUSSION OF EXPERIMENTAL STUDIES

MATERIALS

Lithium Peroxide

Powdered lithium peroxide material was obtained from the Foote Mineral Company and Lithium Corporation of America. In addition, Foote Mineral Environmental Grade pellets were obtained for evaluation as received.

All starting materials were assayed for peroxide, carbonate, and hydroxide content. The purity of the lithium peroxide samples was determined by titration with a standard potassium permanganate solution. The carbonate and hydroxide contents were determined by dissolving the peroxide sample in water and titrating with standard acid to the phenolphthalein and methyl orange endpoints. The hydroxide present in the initial sample was calculated as the difference between that found in the acid titration and that produced by the lithium peroxide-water reaction. Unaccountable material was attributed to inerts or hydrated water. The analytical results are presented in table I.

Catalyst Selection

As noted previously, the use of catalysts was proposed to promote and accelerate the evolution of oxygen from the reaction of lithium peroxide with water vapor. Since hydrogen peroxide was suspected to be an intermediate in this reaction, materials known to catalyze the decomposition of hydrogen peroxide were chosen for study. Table II lists the candidate catalyst materials which were mixed (10% w/w) with powdered lithium peroxide for the screening procedure described in subsequent sections.

Commercial copper oxychloride was obtained from the International Chemical Corporation. A laboratory sample was prepared by the addition of sodium hydroxide to a hydrochloric acid solution of cupric chloride. The prepared sample assayed as 59.4% copper and 21.2% chloride compared to a theoretical 53.6% copper and 36.9% chloride for the formula shown in table II.

Copper phthalocyanine was synthesized following two procedures. The Roman numeral (I) refers to the polymeric compound obtained by the reaction of cupric chloride with urea, pyromellitic anhydride, and phthalic anhydride. The second compound, referred to by Roman numeral (II), was obtained by reacting cupric chloride with pyromellitic anhydride and urea. Both reactions were carried out at 250 C.

TABLE I
ANALYTICAL RESULTS FOR LITHIUM PEROXIDE
STARTING MATERIALS

Sample	Assay (%)			Unaccountable
	Li ₂ O ₂	Li ₂ CO ₃	LiOH	
Foote Mineral Co. - Powder				
Lot 612-1				
-14 Mesh	95.45	5.63	0	--
Foote Mineral Co. - Pellets				
Environmental Grade				
Lot 704-2 (0.53 g/cc density)	92.19	5.08	2.93	--
Lot 505-10 (0.78 g/cc density)	93.05	5.78	2.95	--
Lithium Corporation of America - Powder	94.10	3.05	2.20	0.65

TABLE II
CANDIDATE MATERIALS FOR CATALYSTS
FOR THE LITHIUM PEROXIDE-WATER
VAPOR REACTION

Silver (powder)	Ag
Silver Oxide	Ag ₂ O
Pioneer Research Co.	Silver Catalyst (proprietary)
Raney Silver	Ag
Raney Nickel	Ni
Raney Cobalt	Co
Copper Oxide	Cu ₂ O
Copper Oxychloride	CuCl ₂ · 2CuO · 4H ₂ O (probably)
Copper Phthalocyanine (I)	Polymeric
Copper Phthalocyanine (II)	Polymeric
Paladium Oxide	PdO
Vanadium Oxide	V ₂ O ₃
Vanadium Oxide	V ₂ O ₅
Titanium Oxide	TiO ₂
Nickel Oxide	NiO
Cadmium Oxide	CdO
Manganese Dioxide	MnO ₂
Iron Oxide	Fe ₂ O ₃
Iron Oxide	Fe ₃ O ₄

WATER VAPOR REACTION STUDIES

Apparatus

The techniques employed in these laboratories for studying the reactions of alkali metal peroxides, superoxides, or ozonides with water vapor have been described elsewhere (Petrocelli et al, 1964). The apparatus consists essentially of a reaction chamber containing a stoppered vial and the sulfuric acid/water solution necessary to provide and maintain a given relative humidity. The stopper is controlled outside of the reaction chamber by a glass rod through a mercury seal. A glass sleeve connects the chamber to a gas burette for volumetric measurement of any evolved gas(es).

Procedure

The sample to be studied was loaded into the empty chamber in a dry box, and approximately 15 ml of the solution required to maintain the desired humidity was added. Distilled water was used to maintain the atmosphere at 100% relative humidity; a 43.1% aqueous solution of sulfuric acid was employed to produce an atmosphere of 50% relative humidity. The chamber was set in a thermostated bath (25 C) and the gas burette attached to the side arm. When equilibrium had been attained, the sample was exposed to the atmosphere of water vapor by raising the glass rod through the mercury seal. The rod was clamped in position with the stopper located well above the sample vial. The volume of oxygen evolved during the reactions of the lithium peroxide/catalyst formulations with water vapor was monitored with time.

Since this study was performed to screen candidate catalyst materials, the reaction was allowed to proceed not to completion, but until an adequate measurement of the rate of gas evolution was obtained. The apparatus was then dismantled and the sample removed for analysis of residual peroxide content (via permanganate titration). The indicated rates of reaction and yields of oxygen were compared to provide a basis for the selection of the more promising catalysts for subsequent kinetic studies.

KINETIC STUDIES

General

Kinetic studies of the pertinent air revitalization reactions of the lithium peroxide formulations being investigated were required to elucidate reaction mechanisms, to determine the extent of conversion to carbonate, to confirm oxygen yields, and to relate the observed respiratory quotient (ratio of moles of oxygen evolved to the moles of carbon dioxide absorbed) to that required for man in a closed environment. A closed test system with a circulating gas atmosphere (as opposed to a flow-through system) was chosen to simulate more closely the conditions of a close environment (such as a space cabin). The apparatus described below had been successfully employed previously for kinetic studies of the reactions of active chemicals with water vapor and gaseous carbon dioxide (Petrocelli et al, 1964).

Apparatus

The apparatus designed for kinetic studies of the reactions of air revitalization chemicals with water vapor and carbon dioxide is illustrated in figure 1. The measuring instruments were a Beckman Infrared CO₂ Analyzer and a Beckman Paramagnetic Oxygen Analyzer. These instruments were calibrated external to the system prior to each experiment. The calibrating gases, dry nitrogen, 5% CO₂ in dry nitrogen, and 5% in dry nitrogen were passed through the instruments at the flow rate to be observed during the actual experiment (236 cc/min). Ballast flasks were necessary to allow mixing of the reaction or product gases prior to introduction to the instruments or sample tube.

Procedure

To obtain reproducible initial equilibrium conditions and consistent, true baselines for the initial gaseous concentrations, the following procedure was observed. During calibration of the instruments, the sample tube was charged with the active chemical under nitrogen in a dry box and introduced into the apparatus under a cone of dry nitrogen. After calibration, the instruments, sample tube, and sulfuric acid solution were isolated from the system while the glassware between stopcocks A and D was evacuated to about 0.1 mm. The MacLeod gauge and the vacuum pump were isolated and the reaction gas mixture (e.g., 5% CO₂ in dry N₂) was introduced until the system had attained atmospheric pressure and was then circulated through the instruments. During each flushing operation, the gas over the sulfuric acid solution was separately evacuated and replaced with the reaction gas mixture which was not circulated. This operation was repeated 2-3 times to assure flushing of the system of extraneous gases. Having attained an indication that the extraneous gases had been satisfactorily flushed from the system, the reaction gas mixture was then allowed to pass through the humidity control solution of sulfuric acid. When an initial equilibrium condition and a starting concentration baseline was attained, the sample tube was introduced into the circulating gas stream. This time was recorded as "zero time" for the kinetic study. The O₂ and CO₂ concentrations were monitored with time until the reactions of the "active chemical" were completed as indicated by no change in the gas concentrations recorded by the instruments.

Early in the program a shift in the zero baseline for the oxygen meter was observed, thus necessitating a blank determination wherein all reaction conditions were repeated with no sample present. A blank determination was made whenever the humidity conditions were changed or at least after seven consecutive experimental studies.

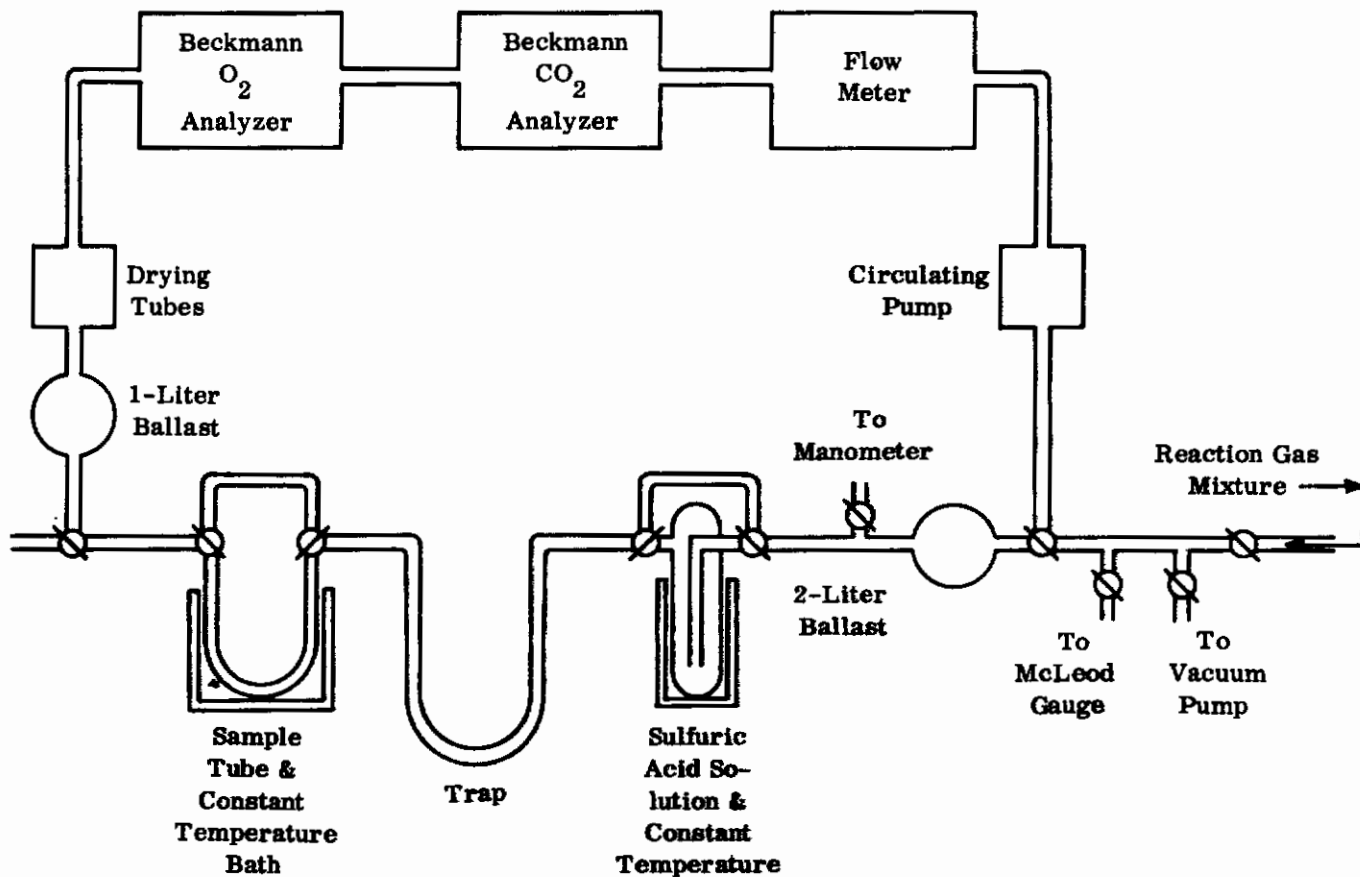


FIGURE 1. APPARATUS TO STUDY THE KINETICS OF THE REACTIONS OF AIR REVITALIZATION MATERIALS WITH CARBON DIOXIDE AND WATER VAPOR

ENGINEERING STUDY

Design Criteria

A dynamic kinetic study of the Foote Mineral Environmental Grade pellets was designed wherein the pellets were subjected to a constant inlet concentration of gaseous carbon dioxide and water vapor. The outlet gas stream was monitored for oxygen and carbon dioxide content. This engineering evaluation was designed to provide experimental data from which information pertaining to a full-sized air regeneration system could be obtained for a commercially available lithium peroxide formulation. Flow conditions necessary to allow such an extrapolation to an operational unit were observed in this test scheme. Gas absorption test equipment previously used (Thomson, 1967) to evaluate magnesium oxide as a carbon dioxide absorbent was available. The apparatus was modified to adapt to the design criteria noted in table III. A desirable study would produce an oxygen supply in accordance with the requirements of a metabolic respiratory quotient (0.8-0.9). Since the design criteria were based entirely on carbon dioxide removal performance of the pellet bed, the oxygen supply was not included as part of the design criteria.

The system configuration and bed size required to meet the conditions noted above were developed from the following relationships:

$$C_{eq} = \frac{I}{Rf} \quad (9)$$

where C_{eq} is the equilibrium concentration (grams of carbon dioxide/ cubic centimeter of air), I is the introduction rate (grams of carbon dioxide/minute), R is the processing rate (cubic centimeters of air/minute), and f is the processing efficiency-single pass;

$$R = 60 q_m \quad (10)$$

where q_m is the inlet gas flow rate (cc/sec); and

$$q_m = A_x v \quad (11)$$

where A_x is the cross-sectional area (cm²) of the pellet bed, and v is the superficial flow velocity (cm/min). By substituting equations (10) and (11) and the design criteria from table III into equation (9), the cross sectional area of 510 cm² which could be fulfilled with a 25.4 cm diameter tube was determined for the system configuration.

At a superficial air velocity of 10 cm/sec, the absorption rate of carbon dioxide required to remove 80% of the inlet carbon dioxide with the 38 cm long reactor tube remained to be confirmed. The design criteria should be fulfilled ideally over a time period sufficient to allow high utilization of the theoretical carbon dioxide capacity.

TABLE III

DESIGN CRITERIA FOR ENGINEERING
EVALUATION OF LITHIUM PEROXIDE
FORMULATIONS

Criterion	Level
Carbon Dioxide Removal Rate	45.4 grams/man-hour
Number of Men	3
Residual Carbon Dioxide	0.5% (v)
Single-pass Removal Efficiency	80% overall
Superficial Air Velocity	10 cm/sec
Nominal Air Temperature	21 C

The design criteria and system configuration for regenerating 4700-5650 cc/sec air for three men appeared entirely practical and suitable for aerospace applications. Any increase in requirements or change in the design criteria would require a proportional change in the flow rate of gas stream and the cross-sectional area of the bed without altering the flow velocity.

Test Apparatus

The pipe reactor of sufficient length to permit a realistic contact time between gas and solid designed to contain a bed of lithium peroxide pellets is shown in figure 2. The reactor consisted essentially of a stainless 304 pipe section, 38 cm long, threaded at both ends. A small piece of fiber glass filter was placed at each end of the bed and a 40-mesh stainless screen, which was sandwiched between two washers, was fitted and placed flush over each end of the pipe. The screens were held in place with threaded one inch standard brass caps with inlet and outlet tube fittings inserted into the ends of each cap. Small pressure taps were attached near each end of the pipe to allow for bed pressure drop measurements.

The reactor was designed to permit accurate weighing before and after a given study to avoid the necessity of removing and transferring of material. If desired, two reactors could be connected in series to provide a total flow path of as long as 76 cm.

The reactor was placed into an absorption system designed to control and measure various gas temperatures, pressures, humidities, and flow rates, and also to monitor the inlet and exit carbon dioxide and oxygen concentrations. The absorption system is illustrated in figure 3. Premixed, analyzed calibration gas (0.5% CO₂ in air) was used for the inlet gas atmosphere to avoid the complexity and inherent errors of separate inlet gas mixing and sampling subsystem. This system provided constant inlet oxygen and carbon dioxide concentrations.

The mercury manometer served primarily as a safety device to indicate system pressure and to allow for relief of any excessive pressure transient. The absolute humidity level was established by dew point control before the gas reached the mixing chamber so that the gas flow and temperature could be measured and adjusted before entering the reactor. The gas leaving the reactor was passed through a bed of anhydrous sodium sulfate to remove moisture before entering the gas analyzers, a Beckman Infrared carbon dioxide analyzer and a Beckman Paramagnetic oxygen analyzer. The gas flow stream was regulated to the desired analyzer flow rate which was measured using the small rotometer. A bypass was provided around the reactor so that system parameters could be adjusted before the run and the composition of both the inlet and exit gas could be measured. The tube heat exchangers were constructed from concentric copper tubing with water flowing through the inner tube and air in counter-current flow in the annular space.

- | | |
|-------------------------|-----------------------|
| ① Sample Chamber | ④ Screen Retainer (2) |
| ② Pressure Taps (2) | ⑤ Washers (4) |
| ③ Fiberglass Filter (2) | ⑥ Threaded Caps (2) |

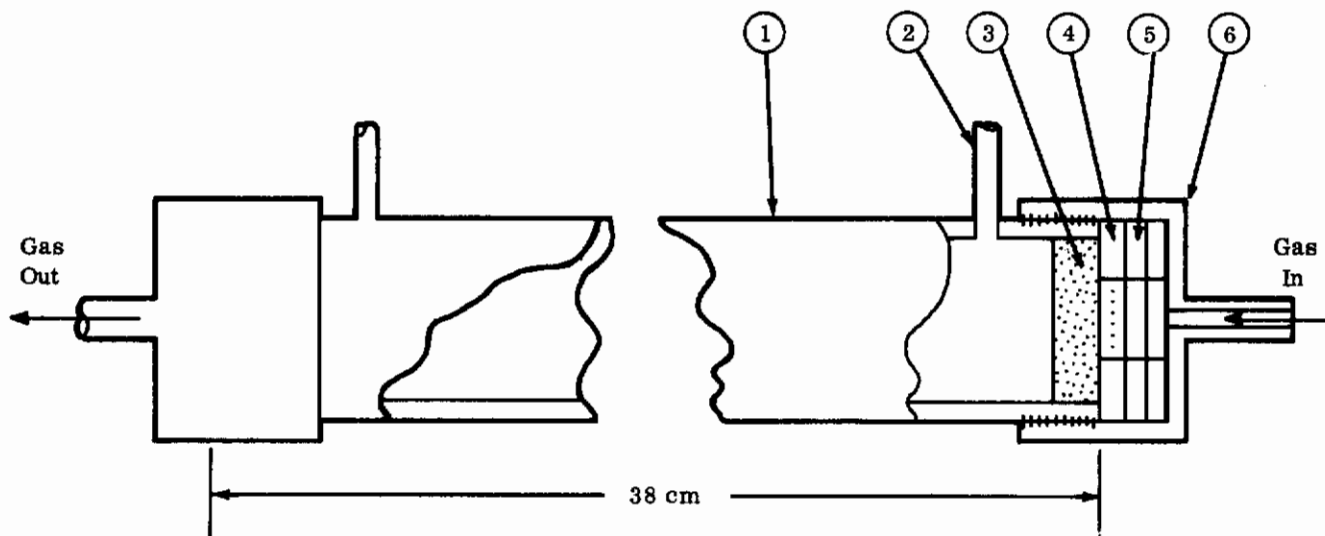


FIGURE 2. SCHEMATIC OF BED REACTOR FOR DYNAMIC KINETIC STUDIES OF THE REACTIONS OF LITHIUM PEROXIDE FORMULATIONS WITH WATER VAPOR AND GASEOUS CARBON DIOXIDE

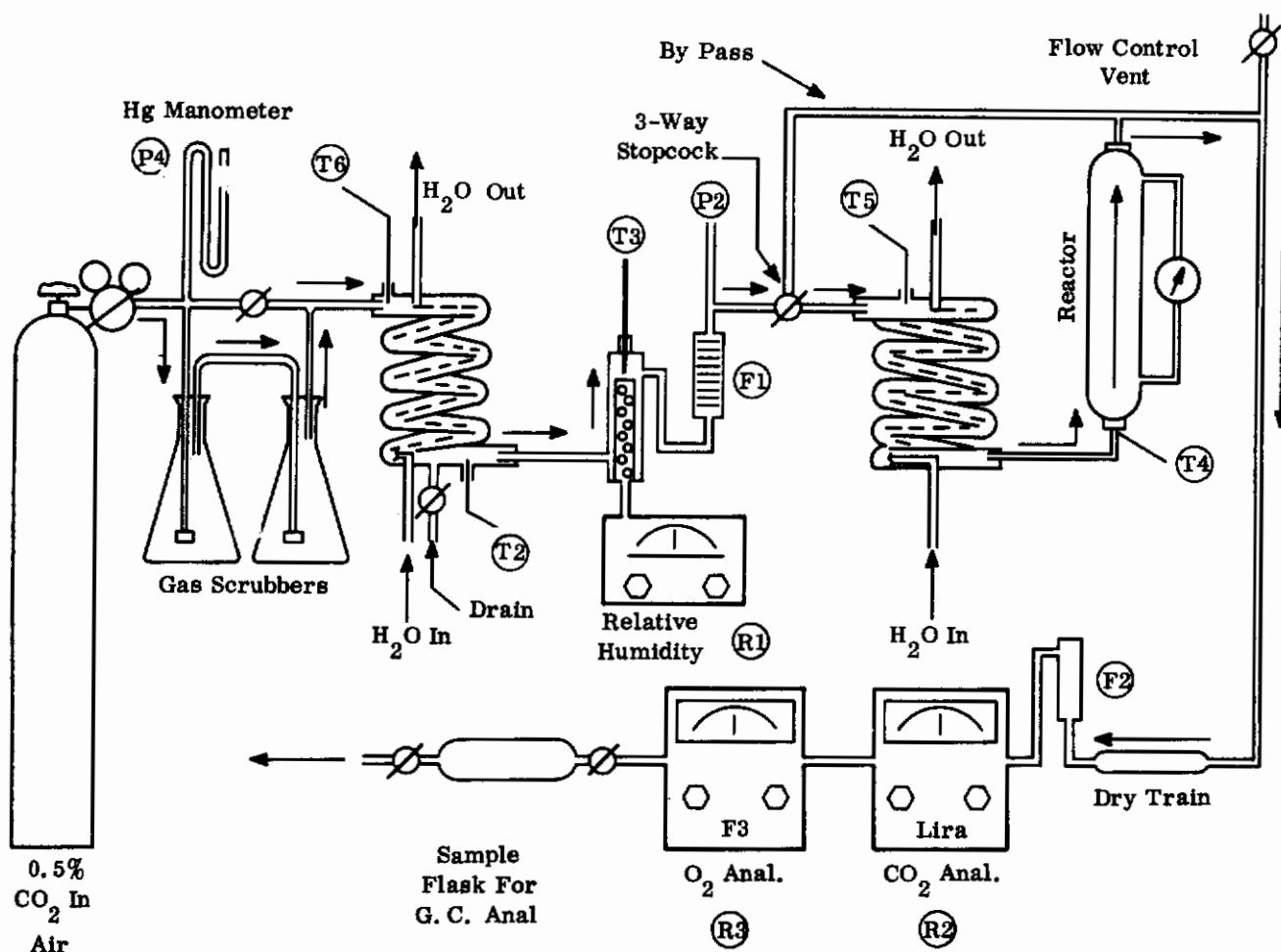


FIGURE 3. APPARATUS FOR DYNAMIC KINETIC STUDIES OF THE REACTIONS OF LITHIUM PEROXIDE FORMULATIONS WITH WATER VAPOR AND GASEOUS CARBON DIOXIDE

Procedure

Dynamic kinetic studies of the reactions of Foote Mineral Environmental Grade pellets were performed with the apparatus shown in figure 3 following the procedure described below. The tared reactor was loaded with the pellets in a dry box under nitrogen, sealed at the ends, reweighed, then stored in the dry box until required. The two gas analyzers were calibrated with the appropriate calibrating gases with the air flow on bypass. The desired air flow rate was established on the rotometer. The absolute humidity was then adjusted by controlling the cooling-water temperature in the condensing coil. Water is thus removed until the desired water vapor composition is attained as measured at the narrow range sensing element located downstream from the condensing coil. Humidification of the dry inlet air mixture was accomplished prior to introduction to the condensing coil by use of a series of gas bubblers charged with water. A partial air bypass control valve and a heat source were also available for additional humidification control when necessary.

A second cooling coil, placed between the flow meter and the reactor, allowed for adjustment of the air temperature prior to the reactor. When all operating conditions had attained equilibrium, the reactor was inserted into the system and placed on-stream at time zero. The oxygen and carbon dioxide concentrations in the inlet and exit gas streams were monitored with time. The desired operating conditions were also carefully monitored throughout the experiment and proper adjustments made to maintain constant conditions.

It was anticipated that the experiment would be terminated when the exit carbon dioxide concentration reached a level that resulted in an overall removal efficiency equal to the desired design level. Since 100% removal of the carbon dioxide was anticipated throughout the major portion of the experiment, the thermal efficiency was expected to be as low as 30-40% before the design value of 90% overall removal efficiency would be attained.

Two gas samples were taken during the run for gas chromatographic analysis of oxygen and carbon dioxide content. Upon completion of the experiment, the reactor was removed from the system under a cone of nitrogen sealed at the ends, and reweighed. The reaction products were removed from the reactor in a dry box, ground to insure a homogeneous sampling, and analyzed for peroxide, hydroxide, and carbonate content. Respiratory quotients were determined on the bases of data collected during the run, flow analysis, gas analyses, and weights and compositions of the starting material and product. Comparisons were made to ascertain the performance of the Environmental Grade pellets as an air regeneration material.

THERMAL STABILITY STUDIES

General

Any lithium peroxide formulation to be used for air regeneration must be thermally stable to provide an adequate shelf life. Dry storage conditions are understood since the material is hygroscopic and reactive to water vapor. The early phases of the program were concerned with thermal stability studies of the pure commercial lithium peroxide samples. Volumetric and simple gravimetric techniques were employed to allow long term storage of the test samples. The thermal characteristics of the selected catalyst-peroxide formulation was evaluated using thermogravimetric analysis techniques.

Volumetric Methods

Thermal stability studies were planned wherein commercial samples would be kept in a constant temperature bath (50 C) and monitored with time for gas evolution. Such evolution would indicate decomposition of the lithium peroxide to the oxide plus oxygen.

The apparatus employed in these studies consisted simply of sample tubes submerged in a thermostated oil bath. The sample tubes were connected to a gas burette for observation of any evolved gas(es). Sample vials containing the peroxide samples to be studied were loaded in a dry box and transferred to the sample tubes under a cone of nitrogen. The sample tubes were previously flushed with nitrogen to insure a dry atmosphere. Lithium peroxide samples for these studies included Foote Mineral Company powder and Environmental Grade pellets (Lot 505-10) and Lithium Corporation of America powder. Upon completion of the study, the samples were removed for analysis and the product composition compared to the starting analysis for verification of thermal decomposition or stability.

Gravimetric Methods

An alternate thermal stability study of pure lithium peroxide was also initiated to avoid dependence on gas volumetric measurements and any accompanying problems due to variations in ambient conditions over extended periods of time. Samples of the same three materials noted previously were weighed into vials and stored in a desiccator at room temperature. The vials were weighed weekly. One sample of each formulation was to be analyzed every three months for peroxide content. The assays and any observed weight changes over the study period were used to ascertain the thermal stability of the materials in question.

Thermogravimetric Methods

The thermal stability characteristics of lithium peroxide (powder) and a lithium peroxide/silver metal powdered formulation at 50 C was also investigated using thermogravimetric methods. The apparatus employed for this study was similar to that used previously for thermogravimetric analysis of other "active chemical" systems (Petrocelli et al, 1966). A chainomatic dampered balance was modified by removing one pan and substituting a rhodium-plated jewelers chain and sample holder. The sample holder was suspended by the chain below the balance in a Hoskins electric furnace which was placed in a completely enclosed chamber. A glass tube was used to line the inside of the furnace. The entire chamber and the tube in which the sample holder was suspended could be purged with nitrogen prior to and during operation. A thermocouple was placed midway in the oven and the oven temperature was maintained at a nearly constant temperature with a Leeds-Northrup Speedomax temperature programmer. The oven temperature was manually recorded periodically by means of a potentiometer.

After loading in a dry box, the weighed sample and sample holder were transferred under a cone of dry nitrogen to the chain and suspended in the heated oven. The sample holder was allowed to attain thermal equilibrium and reweighed in place. The sample weight and oven temperature were then monitored with time. Readings were made at least every two hours during the working day. Upon completion of a particular study, the sample tube was removed from the oven, allowed to cool, and reweighed on an analytical balance. The sample was analyzed for peroxide content using the permanganate titration and compared to the starting material analysis.

SECTION III

RESULTS OF EXPERIMENTAL STUDIES

WATER VAPOR REACTION STUDIES

The screening of candidate catalyst materials was accomplished by performing kinetic studies of the reactions of the prepared lithium peroxide powder formulations with water vapor according to the procedures discussed previously. The results of these studies, which included pure lithium peroxide samples as well as catalyst-containing samples are summarized in table IV for reactions at 100% relative humidity and table V for some corresponding studies at 50% relative humidity. These data include the catalyst concentration, total sample weight, elapsed time, and the observed volumes and rates of oxygen evolved on a normalized basis. The extent of reaction has been determined on the basis of the amount of oxygen evolved compared to theoretical, as well as by analysis of the product material for residual peroxide content at the completion of each run.

The results in tables IV and V illustrate that the presence of a catalyst has a definite effect on the rate of reaction of powdered lithium peroxide with water vapor. The samples with catalysts are noted in the apparent order of decreasing rate of oxygen evolution, i. e., decreasing catalytic activity. The effect of catalysts is also noted in the subsequent permanganate titration for residual peroxide content. Yields based on product analyses were high compared to the yield obtained on the basis of oxygen evolution indicating that the catalyst is probably decomposing the hydrogen peroxide in solution prior to and during the analytical titration.

Data for the pure materials, as well as those samples with poor catalytic activity, confirm the slow reaction between lithium peroxide and water vapor. It is important to note that these data were obtained from a static system and, hence, are difficult to compare to the results reported by Markowitz (1964) who employed a dynamic system. Another difference between the two studies lies in the fact that constant relative humidity levels were employed here versus a varying humidity level for the data reported by Markowitz (1964). In addition, these reactions have not been subjected to a complete study; rather the reaction was halted upon reaching an indication of the reaction rate for comparison purposes.

Although providing a measure of the catalytic ability of the selected materials, these studies were disappointing from the point of view of their intended use, i. e., screening of catalysts. These studies were unsuccessful in the sense that the length of time involved for each sample prevented a rapid evaluation for the screening process. As a result, a clear-cut selection of promising materials for the subsequent kinetic studies could not be made. Consequently, nearly all of the peroxide/catalyst formulations were subjected to at least limited kinetic studies of their reactions with both water vapor and gaseous carbon dioxide.

Contrails

TABLE IV

SUMMARY OF KINETIC DATA TO EVALUATE THE EFFECTS OF CATALYSTS ON THE REACTION OF LITHIUM PEROXIDE (POWDERED) WITH WATER VAPOR (100% RELATIVE HUMIDITY) AT 25 C.

Catalyst	Total Sample Weight (grams)	Elapsed Time (hrs)	Volume Evolved/ Gram of Li ₂ O ₂ (ml at S T P/g)	Rate ^(a) of Oxygen Evolution (ml/g/hr)	Percentage (%) Completion Based on	
					Volume ^(b)	Analysis ^(c)
None ^(d)	0.2414	96.5	56.0	0.58	-	-
		210.3	136.1	0.65	-	-
		350.0	181.5	0.50	-	-
		518.7	187.5	0.36	76.8	98.8
None ^(e)	0.2482	220.2	224.4	0.98	91.9	98.1
9.7% Cu ₂ O	0.2382	46.5	154.2	3.75	63.2	74.9
10.1% MnO ₂	0.2347	47.7	148.1	3.13	60.6	89.8
10.1% Copper Oxychloride (Lab Preparation)	0.3808	45.5	136.3	2.91	55.8	98.0
10.0% Cu -Phthalocyanine(II)	0.3969	26.5	61.5	2.30	25.2	91.0
9.9% Copper Oxychloride (commercial)	0.2901	53.0	131.8	1.85	53.9	99.7
9.9% Fe ₂ O ₃	0.1959	45.5	85.3	1.82	34.9	42.2
10.1% PdO	0.3091	44.7	59.7	1.67	24.5	47.0
9.9% TiO ₂	0.2348	44.0	59.9	1.60	24.6	22.7
10.3% Raney-Ni	0.2459	46.7	74.4	1.46	30.5	33.6
9.9% Cu-Phthalocyanine (I)	0.3092	26.0	40.0	1.41	16.4	40.2
10.0% Pioneer Ag Catalyst	0.3598	48.0	50.6	1.26	20.7	99.7
10.0% Raney-Co.	0.2957	47.0	60.0	1.1	24.6	99.6
9.6% CdO	0.3257	117.0	73.7	0.36	30.0	39.2

- a. From plot of volume evolved per gram versus time.
- b. Based on: $2 \text{ Li}_2\text{O}_2 + 2 \text{ H}_2\text{O} = 4 \text{ LiOH} + \text{ O}_2$
- c. Permanganate titration of residual peroxide.
- d. Foote Mineral Co. Environmental Grade pellets.
- e. Foote Mineral Co. lithium peroxide powder.

TABLE V

SUMMARY OF KINETIC DATA TO EVALUATE THE EFFECTS OF CATALYSIS ON THE REACTION OF LITHIUM PEROXIDE (POWDERED) WITH WATER VAPOR (50% RELATIVE HUMIDITY) at 25C.

Catalyst	Total Sample Weight (grams)	Elapsed Time (hrs)	Volume Evolved/ Gram of Li_2O_2 (ml at S T P/g)	Rate ^(a) of Oxygen Evolution (ml/g/hr)	Percentage (%) Completion Based on	
					Volume ^(b)	Analysis ^(c)
9.9% Copper Oxychloride (commercial)	0.2573	46.3	87.5	1.72	35.4	48.5
10.1% Copper Oxychloride (Lab pre- paration)	0.2280	45.8	83.3	1.58	34.1	51.1
9.9% Copper Oxychloride (commercial)	0.4234	45.5	60.0	0.98	24.6	41.2
9.9% Cu-Phthalo- cyanine (I)	0.2001	44.3	20.9	0.83	8.6	9.3
10.0% Cu-Phthalo- cyanine (II)	0.3576	46.0	23.7	0.83	9.7	23.4

- a. From plot of volume evolved per gram versus time.
 b. Based on: $2 \text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} = 4\text{LiOH} + \text{O}_2$
 c. Permanganate titration of residual peroxide.

KINETIC STUDIES

Blank Determinations

To characterize the zero baseline shift in the oxygen analyzer used in kinetic studies of this program, blank determinations were made on the kinetic apparatus described previously. All conditions and procedures were duplicated as with a typical kinetic run except that no sample was present in the sample take. The blanks were repeated on a regular basis and for each change in the humidity conditions. The zero baseline for the oxygen analyzer was seen to drift 0.0018% per minute. This value was readily duplicated; variations therefrom indicated a need for regreasing and tightening the stopcocks in the glass apparatus.

Commercial Lithium Peroxide

Kinetic studies of the reactions of commercially available lithium peroxide with water vapor and gaseous carbon dioxide were performed to obtain a basis for comparison for the catalyst containing formulations. The samples studied and their compositions as analyzed have been noted previously. The results of these studies are summarized in table VI.

The data for the Foote Mineral Company powder, though scattered, indicated an immediate take up of carbon dioxide. Except in one case, a lag in oxygen evolution was observed resulting in a high initial respiratory quotient. The data for that one case, shown in figure 4, illustrate high yields for both oxygen evolution and carbon dioxide absorption. Such high yields were not repeated in subsequent experiments. The initial respiratory quotient noted was recorded after the reaction had proceeded for thirty minutes. The respiratory quotient gradually decreased to approach the theoretical value of 2 near the end of the 5 hour run. The kinetic rate constants varied depending apparently on the size sample employed. This material was used throughout the program for the evaluation of catalyst-containing formulations.

The lithium peroxide sample from the Lithium Corporation of America showed no evidence of oxygen evolution in these studies and low values for carbon dioxide absorption. This material was not considered for further studies.

The Environmental Grade pellets from Foote Mineral Co. also exhibited divergent results from run to run. The rate of carbon dioxide absorption was definitely slower than that observed for the powdered samples. This slower absorption rate is illustrated in figure 5 for two experiments and led to respiratory quotients of 1.2 and 1.4 at completion of the 5 hour runs. The reaction yields were not reproducible, however, a fact which could perhaps be attributed to variations in the densities of supplied material.

Kinetic results for Environmental Grade pellets that had been pulverized are also summarized in table VI. The data exhibited only slight differences in the reaction yields, respiratory quotient range, and rates of reaction from those obtained on the initial powdered samples. The results strongly indicate that pelletizing the lithium peroxide material can effectively, though not in itself adequately, control the rate of carbon dioxide absorption and thus adjust, to some extent, the observed respiratory quotient.

TABLE VI

**SUMMARY OF DATA OBTAINED DURING KINETIC STUDY OF THE REACTIONS OF
COMMERCIAL LITHIUM PEROXIDE SAMPLES WITH WATER VAPOR AND CARBON DIOXIDE
(5% CO₂ in N₂, ROOM TEMPERATURE, AMBIENT PRESSURE, 236 cc/min)**

Sample	Relative Humidity (%)	Respiratory Quotient Range	Final Volume/Gram of Lithium Peroxide (ml at S T P/g)		First-Order Kinetic Rate Constant (min ⁻¹)		Percentage (%) Reaction based on		
			O ₂	CO ₂	O ₂	CO ₂	O ₂		
			Evolved ^(a)	Absorbed ^(b)	Evol'n	Abs'n	(c) Evol'n	(c) Abs'n	Product (d) Analysis
Footo Mineral Co. Powder									
	100	5.3-2.2	188.9	415.1	.0033	.0114	77.4	85.0	--
	100	8.9-2.4	149.8	355.5	.0116	.0189	61.4	72.7	--
	50	Oxygen analyzer suspect	345.1		--	--	--	70.6	--
	50	7.8-3.0	114.2	355.8	.0022	.0050	46.8	72.8	98.8
Lithium Corp. of America Powder									
	100	--	--	77.7	--	--	--	15.9	10.8
	100	--	--	105.7	--	--	--	21.6	--
	50	--	--	108.9	--	--	--	22.3	5.5
Footo Mineral Co. Environmental Grade Pellets (Lot 505-10)									
	100	5.8-1.2	209.7	241.3	.0011	.0021	85.9	49.4	--
	100	8.3-5.4	61.2	329.7	.0057	.0056	25.1	67.5	--
	100	6.3-3.2	66.6	216.1	.0050	.0086	27.3	44.3	36.1
	50	7.0-1.4	197.7	273.1	.0048	.0028	81.0	55.9	--
Footo Mineral Co. Environmental Grade Pellets Pulverized (Lot 505-10)									
	100	6.4-2.9	128.0	369.7	.0037	.0067	52.4	75.7	99.3
	100	8.0-3.9	100.8	391.9	.0063	.0067	41.3	80.3	62.7
	100	> 10	77.6	333.3	.0013	.0064	31.8	68.3	37.6
	50	9.4-3.3	96.9	318.1	.0044	.0064	39.7	65.2	34.7
	50	7.7-3.1	119.6	366.8	.0041	.0077	49.0	75.1	41.1

- a. Theoretical = 244.1 ml/g.
- b. Theoretical = 488.2 ml/g.
- c. Calculated from theoretical.
- d. Permanganate titration for residual peroxide content.

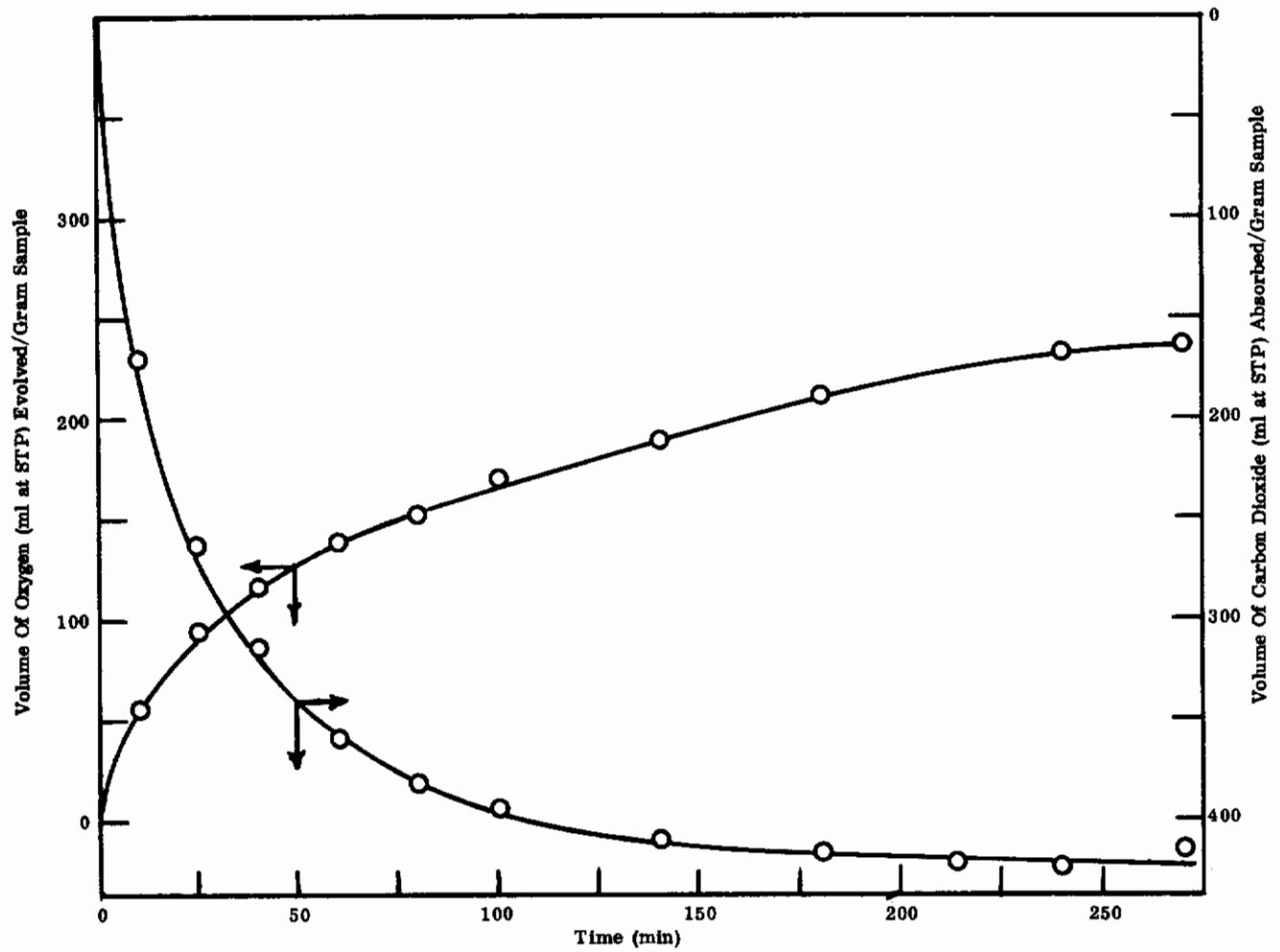


FIGURE 4. KINETIC DATA OF REACTIONS OF LITHIUM PEROXIDE (FOOTE MINERAL CO. - POWDER) WITH WATER VAPOR (100% RELATIVE HUMIDITY) AND CARBON DIOXIDE (5% in dry N₂, 236cc/min) AT AMBIENT TEMPERATURE AND PRESSURE

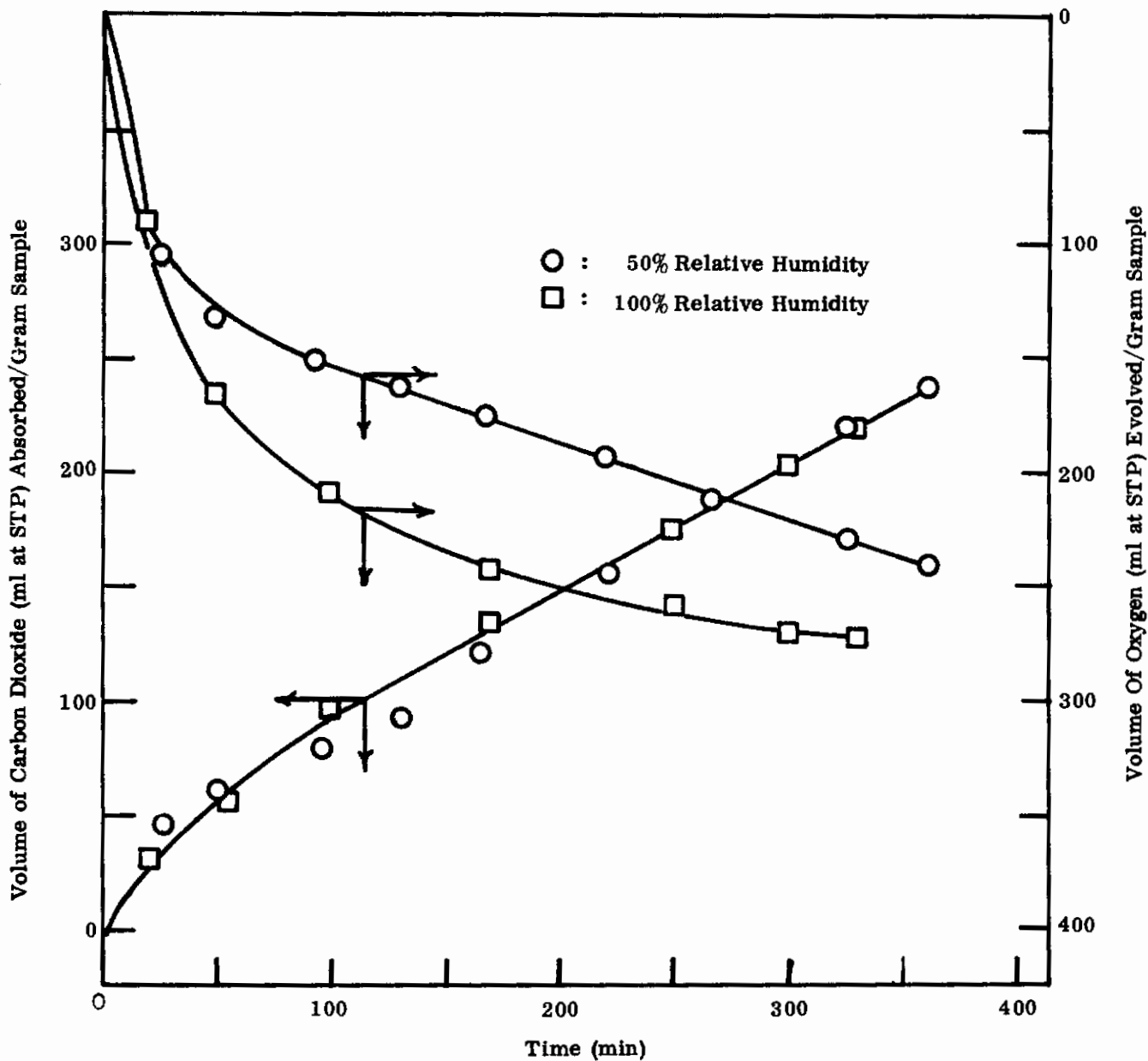


FIGURE 5. KINETIC DATA OF REACTIONS OF LITHIUM PEROXIDE (FOOTE MINERAL CO. - ENVIRONMENTAL GRADE PELLETS) WITH CARBON DIOXIDE (5% in dry N₂, 236cc/min) AND WATER VAPOR AT AMBIENT TEMPERATURE AND PRESSURE

Catalyst Formulations

Kinetic studies of the pertinent air revitalization reactions of lithium peroxide were performed with catalyst-containing formulations. Powdered lithium peroxide samples were prepared with the catalysts (10% by weight, primarily) noted previously. The standard gas atmosphere for these studies, except in a few cases, was 5% carbon dioxide in dry nitrogen. The gas flow was 236 cc/min (superficial velocity equal to 186 cm/min over the powdered sample).

The results of these studies are summarized in tables VII and VIII for all catalyst systems investigated except silver powder, which is discussed in the subsequent section. The reaction characteristics were very similar to those illustrated in figures 4 and 5 for pure samples, hence the results are presented in tabulated form. For the most part, a lag in oxygen evolution, or induction period, was noted resulting in very high respiratory quotients for the first 20-40 minutes of the 5 hour runs. Those respiratory quotients are not noted in the data tables. By the end of any given kinetic experiment, the absorption of carbon dioxide was completed, however, small amounts of oxygen continued to be evolved resulting in a slowly decreasing respiratory quotient.

Examination of the varying kinetic data in tables VII and VIII indicates that the silver, copper oxychloride, Raney-Ni, and Raney-Co catalysts have some effect on the yields of oxygen evolved and carbon dioxide absorbed. The kinetic rate constants (slopes of the straight lines obtained from the log concentration vs time plots) do not exhibit a consistent trend and this cannot be used to draw sound conclusions regarding rates of oxygen evolution and carbon dioxide absorption.

The data for the proprietary Pioneer silver catalyst indicate that varying the catalyst concentration from 10 to 5% at the 100% relative humidity concentration does not effect the reaction yields. Lowering the humidity level with the same catalyst system results in a higher and wider respiratory range (slower oxygen release) indicating the necessary role of water vapor in the reaction mechanism. Reducing the inlet carbon dioxide concentration by one-half for the Pioneer silver catalyst system did not appear to affect the reaction characteristics at the 100% relative humidity condition but did indicate a slight decrease in oxygen and carbon dioxide yields at the 50% relative humidity level.

Silver Powder Formulations

A clear-cut choice of the most promising catalyst for lithium peroxide air revitalization reactions could not be made based on the previously discussed kinetic studies because of the scattered non-reproducible data that was obtained. As a result, powdered silver metal was arbitrarily chosen as the catalyst for the more complete kinetic studies to be performed. The selection, however, was not completely without basis. Indications of activity of silver metal with peroxide systems were noted in the previous studies, for decomposition of dilute hydrogen peroxide solutions in a liquidus water/sodium superoxide-peroxide reactor (Bolles et al, 1964), and in an oxygen supply system based on concentrated hydrogen peroxide as the source of oxygen (Schmauch et al, 1966).

TABLE VII

SUMMARY OF DATA OBTAINED DURING KINETIC STUDY OF THE REACTIONS OF LITHIUM PEROXIDE/CATALYST FORMULATIONS WITH WATER VAPOR (100% RELATIVE HUMIDITY) AND CARBON DIOXIDE (N₂ ATMOSPHERE, ROOM TEMPERATURE, AMBIENT PRESSURE, 236 cc/min)

Catalyst	Catalyst Conc'n (%)	Carbon Dioxide Conc'n (%)	Respiratory Quotient Range	Final Volume/Gram of Lithium Peroxide (ml at S T P/g)		First Order Kinetic Rate Constant (min ⁻¹)		Percentage (%) Reaction Based on		Product Analysis(d)
				O ₂ Evolved ^(a)	Absorbed ^(b)	O ₂ Evol'n	CO ₂ Abs'n	O ₂ (c) Evol'n	CO ₂ (c) Abs'n	
Copper Oxychloride	9.9	5.0	5.4-2.7	127.9	349.8	.0075	.0175	52.4	71.7	--
Copper Oxychloride	9.9	5.0	8.5-3.8	94.7	356.4	.0114	.0114	38.8	73.0	--
Copper Oxychloride (Lab)	10.1	5.0	6.7-1.5	238.0	357.3	.0024	.0144	97.5	73.2	--
Cu-Phthalocyanine(I)	9.9	5.0	9.1-7.4	43.4	393.1	--	--	17.6	80.6	--
Cu-Phthalocyanine(I)	9.9	5.0	6.5-2.3	138.1	312.0	.0054	.0146	56.6	63.9	--
Cu-Phthalocyanine(II)	10.0	5.0	7.0-3.0	114.8	349.3	.0183	.0187	47.0	71.6	--
Raney-Ni	10.3	5.0	2.9-2.0	202.4	411.8	.0096	.0135	82.8	84.5	--
Raney-Co	10.0	5.0	5.7-2.7	150.3	401.6	.0060	.0110	61.6	82.3	--
MnO ₂	10.1	5.0	8.4-4.1	101.5	419.7	--	--	41.6	86.0	--
Fe ₂ O ₃	9.9	5.0	4.7-3.8	84.7	322.2	.0103	.0139	34.7	66.0	--
Al-oxinate	10.0	5.0	4.3-3.6	106.8	385.3	.0110	.0106	43.8	78.9	43.4
Ag ₂ O	9.9	5.0	6.3-4.6	97.9	447.0	.0077	.0076	40.1	91.6	32.7
Ag ₂ O	9.9	5.0	6.9-5.8	53.1	359.7	--	.0132	21.8	73.7	28.5
PdO	10.1	5.0	5.7-2.6	155.7	402.8	.0039	.0071	63.8	82.5	36.8
PdO	4.5	5.0	14.3-9.4	50.5	475.1	.0024	.0059	20.7	97.3	33.8
Pioneer-Ag	10.0	5.0	6.6-3.0	110.4	349.4	.0185	.0221	45.2	71.6	--
Pioneer-Ag	4.9	5.0	5.2-3.1	118.6	376.5	.0045	.0184	48.6	77.1	23.8
Pioneer-Ag	4.9	5.0	5.5-4.3	82.5	367.4	.0130	.0114	33.8	75.3	29.3
Pioneer-Ag	4.9	2.5	5.2-4.2	96.7	404.3	.0097	.0114	39.6	82.8	22.3

a. Theoretical = 244.1 ml/g.

b. Theoretical = 488.2 ml/g.

c. Calculated from theoretical.

d. Permanganate titration for residual peroxide content.

TABLE VIII

SUMMARY OF DATA OBTAINED DURING KINETIC STUDY OF THE REACTIONS OF LITHIUM PEROXIDE/CATALYST FORMULATIONS WITH WATER VAPOR (50% RELATIVE HUMIDITY) AND CARBON DIOXIDE (N₂ ATMOSPHERE, ROOM TEMPERATURE, AMBIENT PRESSURE, 236 cc/min)

Catalyst	Catalyst Conc'n (%)	Carbon Dioxide Conc'n (%)	Respiratory Quotient Range	Final Volume/Gram of Lithium Peroxide (ml at S T P g)		First Order Kinetic Rate Constant (min ⁻¹)		Percentage (%) Reaction Based on		Product Analysis(d)
				O ₂ Evolved ^(a)	Absorbed ^(b)	O ₂ Evol'n	CO ₂ Abs'n	O ₂ (c)	CO ₂ (c)	
Copper Oxy-chloride	9.9	5.0	5.4-3.8	99.3	383.8	.0031	.0067	40.7	78.6	--
Copper Oxy-chloride (Lab)	10.1	5.0	3.4-2.4	148.1	353.3	.0056	.0085	60.7	72.4	--
Cu-Phthalocyanine (I)	9.9	5.0	8-4.0	88.8	351.2	.0050	.0064	36.3	71.9	--
Cu-Phthalocyanine (II)	10.0	5.0	4.0-1.6	248.5	396.7	.0053	.0061	101.8	81.3	--
Raney-Ni	10.3	5.0	6.1-3.5	169.7	593.2	.0036	.0054	69.5	121.5	--
Raney-Co	10.0	5.0	5.6-2.6	155.4	402.5	.0032	.0061	63.7	82.5	--
Fe ₂ O ₃	9.9	5.0	5.1-3.7	98.7	366.0	.0043	.0052	40.4	75.1	65.3
Fe ₃ O ₄	10.0	5.0	6.8-5.2	55.8	353.8	.0094	.0141	22.9	72.5	--
Fe ₃ O ₄	10.0	5.0	8-5.0	76.1	380.5	.0054	.0072	31.2	77.9	84.6
Pioneer-Ag	10.0	5.0	7-2.5	139.6	343.5	.0037	.0053	57.2	70.4	96.6
Pioneer-Ag	4.9	5.0	6.5-4.6	93.7	445.5	.0048	.0065	38.4	91.3	29.8
Pioneer-Ag	4.9	2.5	5.9-4.8	78.7	375.4	.0065	.0086	32.2	76.9	26.3

a. Theoretical = 244.1 ml/g.

b. Theoretical = 488.2 ml/g.

c. Calculated from theoretical.

d. Permanganate titration for residual peroxide content.

More complete kinetic studies were performed therefore with lithium peroxide/powdered silver metal formulations. The results of these studies are summarized in tables IX and X. Formulation samples included simple mixed powders, powdered samples which were ground in a mortar and pestle to insure intimate contact of the catalyst with the peroxide material, and pelleted samples which were prepared in a Parr hand press from the pulverized samples.

Overall, high respiratory quotients were observed, indicating that the catalyst was not effective at all in the early reaction stages. In only one case, illustrated in figure 6, was a reasonably constant respiratory quotient observed during the course of the reaction, figure 7. The catalyst concentration, in this case, was 19.5%, certainly an unattractive level from the view-point of cost and weight considerations.

As noted previously, reaction yields and rate constants for a given formulation were varied and non-reproducible. This scattering of data cannot be traced to any variations in sample preparation, handling, or treatment, nor to any irregularities in operational procedures in performing the kinetic studies. Nonetheless, certain trends can be ascertained. Increasing the catalyst concentration level up to 10% did not appear to affect the reaction characteristics; only at the 19.5% concentration were significant differences noted. Grinding of the catalyst with the lithium peroxide starting material to provide better contact did improve the yield of oxygen somewhat for the previously cited example. Pelletizing the mixture lowered the rates of reaction for both oxygen evolution and carbon dioxide absorption thus excluding any improvement in the respiratory quotient.

ENGINEERING EVALUATION

A kinetic air regeneration study was performed to evaluate Foote Mineral Company Environmental Grade pellets under dynamic conditions employing the procedures and apparatus discussed previously. The test was carried out for 19.4 hours over a two day period before the first break-through of carbon dioxide was noted in the reactor exit. The inlet gas atmosphere flow rates, designed to represent full-scale conditions for a three-man unit, were 1.47 l/min for the first 11.3 hours and 2.90 l/min for the remaining 8.1 hours. The air inlet containing 0.53% carbon dioxide was maintained at about 26.7C and 50% relative humidity. System pressure drops were less than 0.2 in. of water per foot of bed at 518 cm/min flow velocity. The total gas-solid contact time was about four seconds.

The results of the single study that was performed are summarized in table XI. These data, treated according to four different analytical processes, include amounts of carbon dioxide absorbed and oxygen generated, the observed overall respiratory quotient, and the fraction of the theoretical carbon dioxide capacity that was achieved. Two observations are immediately evident. First, an overall respiratory quotient of about 2.9 was achieved for the 19 hour test compared to the theoretical value of 2.1 expected from the stoichiometric air regeneration reactions and sample composition. Secondly, less than one-quarter of the carbon dioxide capacity was attained when carbon dioxide

TABLE IX

SUMMARY OF DATA OBTAINED DURING KINETIC STUDY OF THE REACTIONS OF LITHIUM PEROXIDE/SILVER POWDER CATALYST FORMULATIONS WITH WATER VAPOR (100% RELATIVE HUMIDITY) AND CARBON DIOXIDE (N₂ ATMOSPHERE, ROOM TEMPERATURE, AMBIENT PRESSURE, 236 cc/min)

Catalyst Conc'n (%)	Carbon Dioxide Conc'n (%)	Respiratory Quoitent Range	Final Volume/Gram of Lithium Peroxide (ml at S T P/g)		First Order Kinetic Rate Constant (min ⁻¹)		Percentage (%) Reaction Based on		Product Analysis(d)
			O ₂ Evolved ^(a)	Absorbed ^(b)	O ₂ Evol'n	CO ₂ Abs'n	O ₂ (c) Evol'n	CO ₂ (c) Abs'n	
5.0	5.0	8.9-6.6	56.1	367.8	.0045	.0072	23.0	75.3	32.4
5.0	5.0	7.9-2.7	124.1	329.1	.0044	.0085	50.8	67.4	16.7
9.9	5.0	4.6-4.2	98.3	422.3	.0148	.0099	40.5	86.5	40.6
9.9	5.0	4.9-3.5	101.2	354.1	.0093	.0119	41.5	72.5	--
9.9	5.0	5.3-3.0	121.6	365.0	.0042	.0114	49.8	74.8	71.5
19.5 ^(e)	5.0	4.4-3.3	135.4	354.7	.0043	.0077	55.5	93.1	39.8
19.5 ^(e)	5.0	4.6-3.6	117.3	422.5	.0060	.0102	48.0	86.5	48.4
19.5	5.0	7.3-5.8	40.2	266.1	.0062	.0040	16.5	54.5	27.5

- a. Theoretical = 244.1 ml/g.
- b. Theoretical = 488.2 ml/g.
- c. Calculated from theoretical.
- d. Permanganate titration for residual peroxide content.
- e. Ground mixture.
- f. Pelletized ground mixture.

TABLE X

SUMMARY OF DATA OBTAINED DURING KINETIC STUDY OF THE REACTIONS OF LITHIUM PEROXIDE/SILVER POWDER CATALYST FORMULATIONS WITH WATER VAPOR (50% RELATIVE HUMIDITY) AND CARBON DIOXIDE (N₂ ATMOSPHERE, ROOM TEMPERATURE, AMBIENT PRESSURE, 236 cc/min)

Catalyst Conc'n (%)	Carbon Dioxide Conc'n (%)	Respiratory Quotient Range	Final Volume/Gram of Lithium Peroxide (ml at S T P/g)		First Order Kinetic Rate Constant (min ⁻¹)		Percentage (%) Reaction Based on		Product Analysis(d)
			O ₂ Evolved ^(a)	CO ₂ Absorbed ^(b)	O ₂ Evol'n	CO ₂ Abs'n	O ₂ (c)	CO ₂ (c)	
1.17	5.0	6.0-4.7	82.7	388.1	.0059	.0066	33.9	79.5	34.8
5.0	5.0	4.7-3.4	124.4	426.0	.0052	.0066	51.0	87.3	27.1
5.0	2.5	5.2-3.7	107.4	397.4	.0051	.0066	44.0	81.4	29.0
9.9	5.0	6.4-4.3	94.1	406.5	.0039	.0073	38.6	83.3	60.3
9.9	5.0	7.2-5.7	63.2	374.0	--	.0065	25.9	76.6	98.7
19.5	5.0	6.7-4.3	93.5	401.0	.0061	.0063	38.3	82.1	26.1
19.5	5.0	6.6-4.8	99.9	474.4	.0042	.0054	40.9	97.2	47.5
19.5	5.0	6.8-4.6	78.6	364.2	.0053	.0056	32.2	74.6	34.2
19.5 ^(e)	5.0	3.6-2.3	188.0	438.1	.0046	.0042	77.0	89.7	43.4
19.5 ^(e)	5.0	5.1-2.4	163.6	396.1	.0031	.0051	67.0	81.1	39.6
5.0 ^(f)	5.0	5.7-4.1	119.5	494.5	.0012	.0032	49.0	101.2	46.7
5.0 ^(f)	5.0	6.5-4.5	103.1	463.0	.0007	.0038	42.2	94.8	38.3
19.5 ^(f)	5.0	7.6-3.0	111.3	334.6	--	.0044	45.6	68.5	35.2

- a. Theoretical = 244.1 ml/g.
- b. Theoretical = 488.2 ml/g.
- c. Calculated from theoretical.
- d. Permanganate titration for residual peroxide content.
- e. Ground mixture.
- f. Pelletized ground mixture.

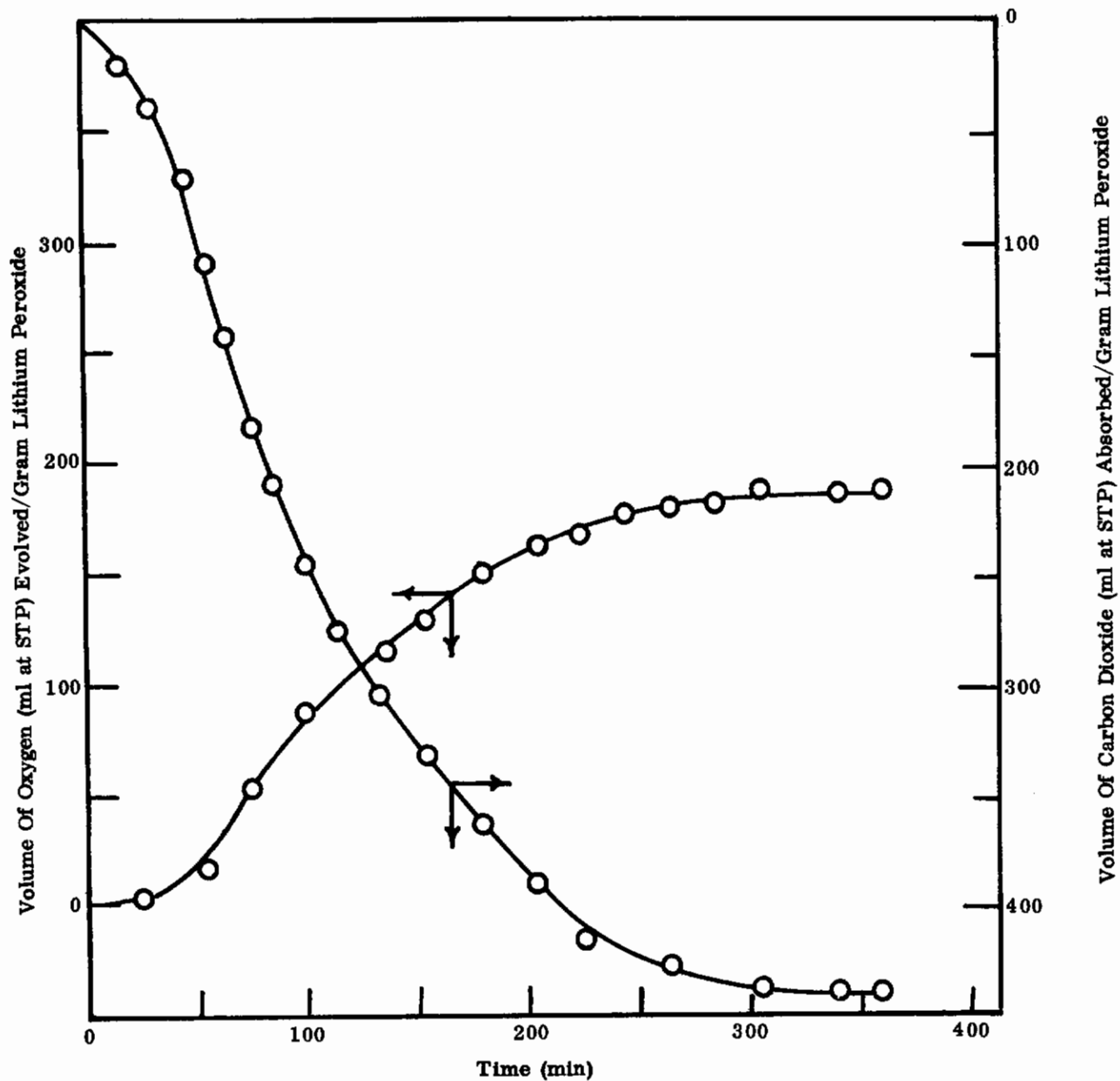


FIGURE 6. KINETIC DATA OF REACTIONS OF A LITHIUM PEROXIDE/19.5% SILVER POWDER GROUND MIXTURE WITH WATER VAPOR (50% RELATIVE HUMIDITY) AND CARBON DIOXIDE (5% in dry N₂, 236cc/min) AT AMBIENT TEMPERATURE AND PRESSURE

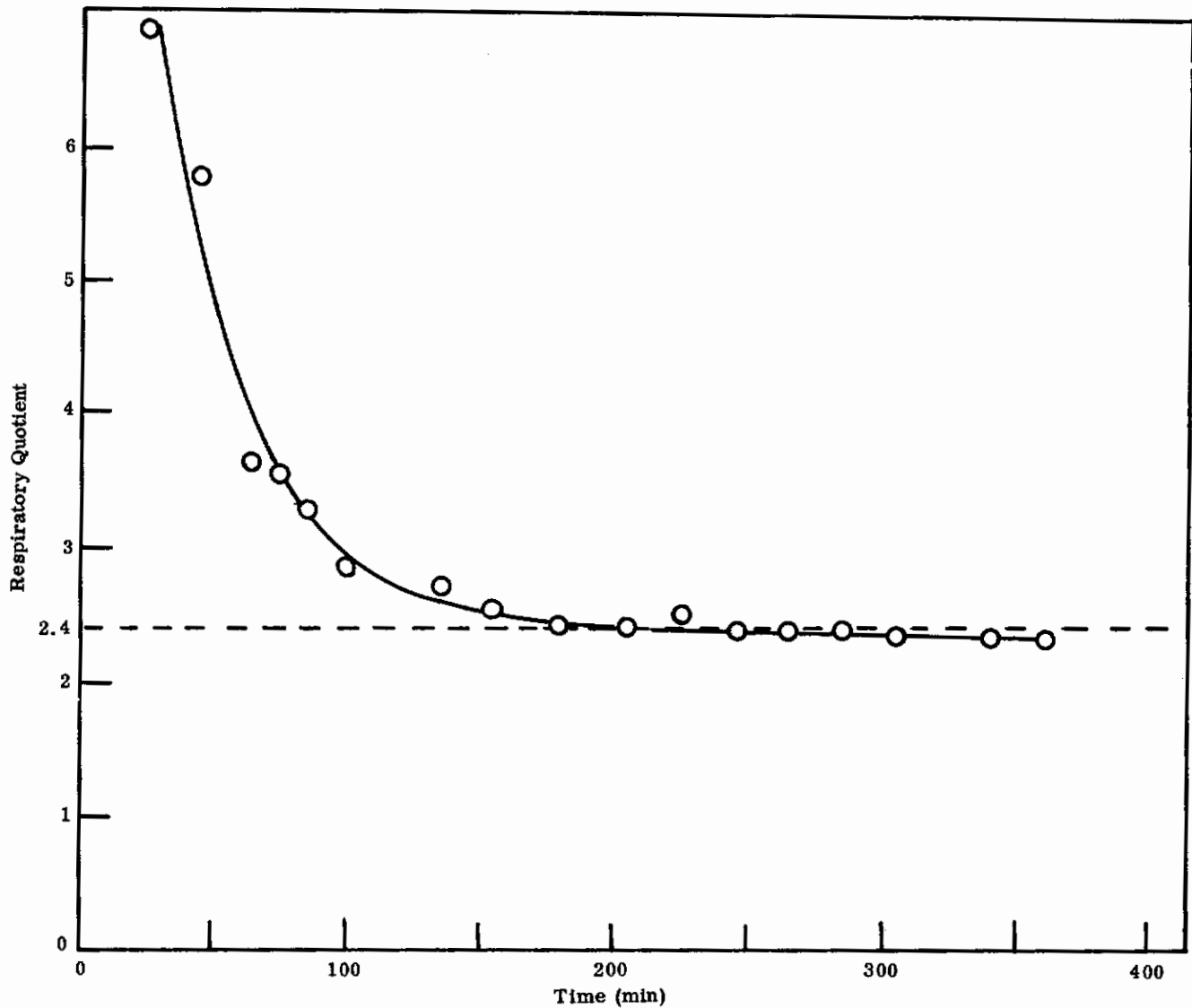


FIGURE 7. VARIATION IN RESPIRATORY QUOTIENT AS A FUNCTION OF TIME DURING KINETIC STUDY OF THE REACTIONS OF A LITHIUM PEROXIDE/19.5% SILVER POWDER GROUND MIXTURE WITH WATER VAPOR (50% RELATIVE HUMIDITY) AND CARBON DIOXIDE (5% in dry N_2 , 236cc/min) AT AMBIENT TEMPERATURE AND PRESSURE

TABLE XI

DATA OBTAINED FOR DYNAMIC KINETIC STUDY
OF THE REACTIONS OF FOOTE MINERAL ENVIRON-
MENTAL GRADE PELLETS WITH WATER VAPOR
AND GASEOUS CARBON DIOXIDE (0.5% in air) AT
25C.

Analytical Process	Analysis Method		Weight (g)		Overall Respiratory Quotient
	Oxygen	Carbon Dioxide	Oxygen	Carbon Dioxide	
Assay, Based on product distribution of Li+ from sample	Reaction of Li ₂ O ₂	Gain in Li ₂ CO ₃	6.0	19.6	2.4
Sample and product composition and weight	Difference in Li ₂ O ₂	Gain of Li ₂ CO ₃ in product	4.8	20.5	3.1
Flow Analysis	Paramagnetic detection of oxygen	Infrared detection of CO ₂ difference	5.4	22.5	3.0
Flow Analysis and wt. change	Sample wt. change	Infrared CO ₂ detection	5.2	22.5 (same as above)	3.1
Average value of above methods			5.4	21.3	2.9
Theoretical Values from sample composition			33.4	98.0	2.1
Capacity achieved in run (% of Theoretical)			16%	22%	—

break-through was observed in the exit stream. After 19.4 hours, the overall removal was about 97% of the carbon dioxide which entered the reactor, indicating that considerable absorption capacity remained to be utilized. No attempt was made to estimate the net carbon dioxide absorption capacity at the desired design point of 80% overall removal efficiency.

The analytical processes employing different methods of measurement for oxygen evolution and carbon dioxide removal provided the bases for calculation of the overall respiratory quotient. The accuracy of the carbon dioxide analyses appears to be well-founded on good instrumental and flow data. The measured increase in weight of lithium carbonate in the sample at the end of the run served as an adequate check of the amount of carbon dioxide absorbed. This weight change also indicated that water absorption was minimal.

The most questionable area rested with the measurement of the oxygen generated. A paramagnetic oxygen analyzer with a 0-25% range (0.5% increments) was employed even though the inlet gas was mostly air. Nevertheless, a definite increase of 0.1-0.2% oxygen content could be discerned between the inlet and outlet gas streams.

Two other methods were used to estimate the extent of oxygen evolution and to confirm the accuracy of the data. A comparison of the analyses of the starting sample and final product provided one measure of the extent of lithium peroxide reacted. A second check was based on the observed weight change in the sample after accounting for the carbon dioxide that had been absorbed.

Gas samples were also collected for gas chromatographic analysis for oxygen and carbon dioxide content at the 0.5 and 1.8 hour marks of the 19 hour study. These results, 21.65 and 22.05% vs 20.95% in the inlet stream, appeared to be unreasonably high and erratic and were not factored into the treatment of data for table XI. The gas chromatographic results did, however, confirm the complete absence of carbon dioxide in the exit stream at these early stages of the experiment.

THERMAL STABILITY STUDIES

Volumetric Methods

Thermal stability studies were performed for Foote Mineral Co. powdered and pelleted lithium peroxide samples maintained in a thermostated 50C oil bath. The closed, dry atmosphere was monitored for gas evolution by gas burette. The powdered sample appeared to remain inert at 50C after about 120 days as indicated by no significant change in the gas burette level. The data for the pellet sample indicated that some decomposition occurred - 12% by weight after about 90 days - as measured by the observed change in the burette level. Analyses of both samples upon termination of the study revealed that significant losses in peroxide content (greater than 30%) had occurred, thus indicating moisture leakage into the sample chamber. These data, therefore, can be considered neither reliable nor significant.

Gravimetric Methods

Samples of commercial lithium peroxide material were stored in a desiccator for an extended period of time with only slight weight changes being observed. The Foote Mineral Company powder and Environmental Grade pellets after nine months exhibited a weight gain of approximately 1.5% over the starting weight. The Lithium Corporation of America powder, over the same period of time, showed a weight loss of 0.9% from the starting weight.

Samples of each material were analyzed for peroxide content after four and nine months. The results of these analyses are summarized in table XII. The Foote Mineral Company powder and pellets, which had exhibited a weight gain over the nine month period, assayed to a slightly lower peroxide content over the same period. The peroxide assay of the Lithium Corporation of America powder revealed a decrease in concentration commensurate with the weight loss observed.

Thermogravimetric Methods

The results of the thermal stability studies at 50C following the thermal/gravimetric techniques described previously are summarized in table XIII. The samples studied included pure lithium peroxide powder and a peroxide/catalyst formulation containing approximately 20% by weight of silver powder. The data in table XIII indicate that these samples are indeed stable at the prescribed temperature when maintained in a dry atmosphere.

Thermal studies conducted previously (Petrocelli et al, 1966) in these laboratories should be noted. DTA (differential thermal analysis) thermograms were obtained using an R. L. Stone Model DTA-11M for pure lithium peroxide and for lithium peroxide samples containing approximately 10% by weight of manganese dioxide (MnO_2), vanadium oxide (V_2O_3) and polymeric copper phthalocyanine. All DTA thermograms yielded relatively simple curves which displayed a slight exotherm at ca. 260C. This exotherm has been attributed to a reversible polymorphous phase change by several authors (Petrocelli et al, 1966, Rode et al, 1955, Notz et al, 1962).

The endotherm corresponding to the thermal decomposition to the oxide did not begin until slightly above 300C. The samples were apparently thermal stable to temperatures up to 300C. Those studies concluded that the catalysts had little effect on the thermal decomposition of lithium peroxide.

As part of the same study, simultaneous DTA (differential thermal analysis), TGA, and DTG (differential thermogravimetric analysis) data were obtained from the Mettler Instrument Corp. for pure lithium peroxide and a lithium peroxide sample containing 1% by weight of copper oxide (Cu_2O).

TABLE XII

ANALYSIS OF LITHIUM PEROXIDE SAMPLES AFTER LONG-TERM STORAGE IN A DRY ATMOSPHERE AT ROOM TEMPERATURE

	Lithium Peroxide Content (%)		
	Original Analysis	Four-month Analysis	Nine-month Analysis
Foote Mineral Company - Powder	95.5	92.2	93.8
Foote Mineral Company- Environmental Grade Pellets (Lot 505-10)	93.1	92.2	91.4
Lithium Corporation of America - Powder	94.1	94.4	93.2

TABLE XIII

RESULTS OF THERMOGRAVIMETRIC
ANALYSIS OF SOME POWDERED LITHIUM
PEROXIDE FORMULATIONS at 50C.

Sample	Exposure Time (hrs.)	Weight Loss (mg)	Lithium Peroxide Content (%)		Percentage (%) Lost based on	
			Start	End	Weight Loss	Chemical Analysis
Li_2O_2	51	1.3	96.2	96.3	0.6	0
Li_2O_2	94	2.0	96.2	96.4	1.0	0
Li_2O_2 +19.5% Ag	96	2.0	77.4	77.9	0.9	0
Li_2O_2 +21.0% Ag	93	1.4	76.0	77.5	0.8	0

Contrails

The thermograms obtained were similar to those noted above with a single endotherm beginning near 300C for the decomposition to the lower oxide. A small exotherm occurring at 245C was again observed but with no accompanying weight loss. The source of the exotherm appeared to be an irreversible, physical transition. Markowitz has suggested that the peak may represent the crystallization of small amounts of amorphous lithium peroxide (Petrocelli et al, 1964), while others have suggested an irreversible crystallographic transition (Rode et al, 1955). Nevertheless, the data have shown that lithium peroxide samples, both pure and containing catalytic materials, if kept in a dry atmosphere, are thermally stable at temperatures at least near to 300C.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

In general, it must be concluded from the results observed in this research program that lithium peroxide is not an efficient air regeneration material. Although adequate for carbon dioxide removal, this material, in commercially available forms or in the various formulations with and without catalysts studied in this program, cannot be made to evolve oxygen via the water vapor reaction mode at a sufficiently rapid rate to achieve at least the respiratory quotient dictated by the pertinent air revitalization reactions.

Kinetic studies of the air revitalization reactions with several catalyst-containing lithium peroxide formulations indicated that silver metal, copper oxychloride, Raney-nickel, and Raney-cobalt did affect, to some extent, the rates and yields of the pertinent reactions. More complete kinetic studies with lithium peroxide formulations containing a silver metal catalyst failed to improve the efficiency of the air revitalization reactions nor did they provide the desired respiratory quotient balance. Significant effects on these reactions with the latter formulations were observed only at a catalyst concentration near 20% by weight. Severe weight and volume disadvantages are immediately obvious. Also, since the densities of the materials in this formulation are significantly different from one another, it would be very difficult to maintain a homogenous powdered mixture for extended periods of time. It is further concluded that intimate mixture of the catalysts with the lithium peroxide material to provide a driving force for completion of the oxygen evolution process was not attained.

The kinetic studies performed did not provide adequate information for ascertaining the mechanisms of the pertinent air revitalization reactions. It is certain, however, that hydrogen peroxide is formed as an intermediate. The complexities of the reactions involved and the lack of mechanistic information do not permit a choice between the mechanisms noted previously nor the proposal of any new or definitive reaction mechanisms.

The results of a single engineering evaluation of a commercially available lithium peroxide pellet formulation using a dynamic flow system to study the pertinent air regeneration reactions demonstrated that an overall respiratory quotient of about 3 could be attained while removing almost all of the carbon dioxide (0.5% level) from an inlet air atmosphere. In this aspect, then, the pellets studied are not competitive with superoxides for oxygen generation nor do they clearly demonstrate any superiority over lithium hydroxide for a carbon dioxide absorption.

The results of these research studies confirm the fact that lithium peroxide should be employed only as a supplementary source for oxygen supply or carbon dioxide removal in life support systems of limited duration. The use of lithium peroxide in mixed active chemical systems must necessarily be tempered by the observation that theoretical

yields of oxygen evolution and carbon dioxide absorption have not been attained even by the introduction of catalytic materials. Future research programs for continued development of lithium peroxide as an air regeneration material cannot be recommended unless directed towards engineering evaluations of the type noted in order to confirm the potential use of this material in emergency, back-up and/or supplementary systems.

Certain observations and recommendations should be made regarding the use of "active chemicals" for air regeneration. Studies conducted in these laboratories under NASA Contract NASw-559 (Petrocelli et al, 1966) concluded that

"the chemistry of sodium and potassium superoxides has been sufficiently developed to allow the application of these materials in air revitalization systems. The reactions of the compounds with water vapor and carbon dioxide have been extensively studied. In a semi-passive unit, designed for use in closed environments such as space cabins, the desired respiratory quotient may be readily maintained by proper control of flow rates and levels of humidity. The usefulness of these compounds, moreover, has been ably demonstrated: the microcontactor (using potassium superoxide) developed at General Dynamics, Electric Boat division, under the auspices of NASA (Bolles et al, 1964); the five-man test (employing sodium superoxide) successfully completed by the Boeing Aircraft Co. under the direction of NASA (Boeing, 1964, Del Duca et al, 1964); the atmosphere control unit (using potassium superoxide discs) designed and fabricated by the MSA Research Corporation in cooperation with the Aerospace Medical Division of Wright-Patterson Air Force Base (Manstellar et al, 1965, McGoff et al, 1966); the company-sponsored efforts of General Dynamics, Electric Boat division, in developing a 'Potassium Superoxide Air Revitalization System' for small submersibles (Presti, 1964); and the dramatic use of sodium or potassium superoxide in the Russian Vostok and Voshkod manned flights", (Seryapin, 1962, Volynkin et al, 1962, Petrocelli, 1965b).

In our NASA studies (Petrocelli et al, 1966) weight and volume characteristics were presented for an air revitalization system based on the reaction of sodium or potassium superoxide with water vapor and the data compared to other technically advanced, non-regenerative systems for a given mission length. In addition, several other advantages of superoxides were cited that would enter into consideration for a trade-off study. These advantages included

"control of cabin relative humidity, removal of air-borne bacteria and odoriferous human body waste products from the cabin atmosphere (thus offering possible reduction or elimination of auxiliary system for removal of toxic contaminants), and the simplicity and reliability of operation compared to other candidate air regeneration systems."

Contrails

A summary of active chemicals, their availability, adaptability to long or short duration space missions, and experience factors concerning their applicability as air revitalization materials was presented in tabular form (Petrocelli et al, 1966). In that report (Petrocelli et al, 1966) it was noted that the use of lithium peroxide for air revitalization purposes would necessitate long term (at least 2-3 years) studies, including engineering-type evaluations, in order to insure its reliability in space missions. Sodium and potassium superoxide were considered "ready for use pending design and test of an actual flight system" (Petrocelli et al, 1966).

We strongly recommend that future Air Force efforts in this area of life support be directed toward the design, evaluation, and test of a superoxide air revitalization system oriented toward a specific full-sized space mission. It is further recommended that this system be based on the reaction of sodium or potassium superoxide with water vapor.

REFERENCES

1. Bach, R. O., Boardman, W. W., Jr., and Robinson, J. W., Jr., 1965. Application of Lithium Chemicals for Air Regeneration of Manned Spacecraft, AMRL-TR-65-106, (AD619 497), Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio.
2. Boeing Company, Anonymous, 1964. Manned Environmental System Assessment, NASA Contractor Report CR-134, National Aeronautics and Space Administration, Washington, D.C.
3. Bolles, T. V., Speziali, V. A., and Thomson, G. W., 1964. Microcontactor Utilizing High Density Metallic Superoxides, Final Report General Dynamics/Electric Boat U413-64-164.
4. DelDuca, M. G., and Inglefinger, A. L., 1964. "Future Life Support Systems - A Prospectus," Paper delivered at the SAE National Meeting, Los Angeles, California.
5. Markowitz, M. M., and Dezmelyk, E. W., 1964. A study of the Application of Lithium Chemicals to Air Regeneration Techniques in Manned, Sealed Environments, AMRL-TDR-64-1,(AD435815), Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio.
6. Maustellar, J. W., McGoff, M. J., Keating, D. A., and Weiswurm, K., 1965. "Superoxide Atmosphere Control System for Manned Space Assemblies," Paper delivered at the 36th Annual Meeting of the Aerospace Medical Association, New York.
7. McGoff, M. J., and King, J. C., 1966. Superoxide Configurations for Atmosphere Control Systems, AMRL-TR-66-167, (AD647135), Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio.
8. Notz, K. S., Jr., and Bach, R. D., 1962. "Concerning an Allotrope of Lithium Peroxide," Paper presented at Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee.
9. Petrocelli, A. W., and Capotosto, A., Jr., 1964. The Synthesis and Utilization of Low Molecular Weight Ozonides for Air Revitalization Purposes, NASA Contractor Report CR-125, National Aeronautics and Space Administration, Washington, D.C.
10. Petrocelli, A. W., and Capotosto, A., Jr., 1965. The Synthesis and Utilization of Low Molecular Weight Ozonides for Air Revitalization Purposes, Interim Report General Dynamics/Electric Boat U413-65-204.
11. Petrocelli, A. W., 1965. "Survey of Soviet Activity in the Use of Active Chemicals for Space Cabin Air Revitalization," Aerospace Medicine, 36, 1187.

12. Petrocelli, A. W., Marriott, J. A., Uno, R. T., and Capotosto, A., Jr., 1966. The Synthesis and Utilization of Low Molecular Weight Ozonides for Air Revitalization Purposes, Supplement to Interim Report - General Dynamics/Electric Boat U413-66-081.
13. Presti, J. B., 1964. Semi-passive Potassium Superoxide Air Revitalization System, Final Report General Dynamics/Electric Boat U413-64-202.
14. Rode, T. V., Dobrynina, T. A., and Golder, G. A., 1955. "Physicochemical Study of Lithium Peroxide," Izv. Akad. Nauk, SSR, Otdel, Khim., 611.
15. Schmauch, G. E., and Bailey, B., 1966. Oxygen Supply System for Manned Space Enclosures, AMRL-TR-66-169, (AD652247), Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio.
16. Selezneva, K. I., 1960. "Interaction of Lithium Peroxide with Water Vapor and Carbon Dioxide," Russian J. Inorg. Chem., 5 (8), pp 820-823.
17. Seryapin, A. D., 1962. Problems in Space Biology, Vol. I, Moscow.
18. Thomson, G. W., 1967. Improved Habitability in Submarines and Other Sealed Systems. Task A, Final Report General Dynamics/Electric Boat U413-67-204.
19. Vol'nov, I. I., 1966. Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals, Plenum Press, New York.
20. Volynkin, Yu. M., and Yazlovskiy, V. I., 1962. "The First Manned Space Flights," Akad. Nauk, SSR, Otd. Biol. Nauk, Moscow.

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13. ABSTRACT The chemistry of lithium peroxide has been studied for use as a nonregenerative air revitalization material for oxygen supply and carbon dioxide removal. The use of catalysts to accelerate the decomposition of the hydrogen peroxide formed as an intermediate in the reaction of lithium peroxide with water vapor was investigated. Catalyst screening studies, kinetic studies of the reactions of several lithium peroxide formulations with water vapor and carbon dioxide, and complete chemical kinetic studies for the air revitalization reactions of a peroxide/silver metal powder formulation were performed. A commercially available lithium peroxide pellet formulation was evaluated for air regeneration purposes. The thermal stability characteristics of various lithium peroxide formulations were ascertained.			

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