

14

FDL-TDR-64-22 - Pt. 12  
PART II

20

465422

6

# INVESTIGATION OF CATALYTIC REACTIONS FOR CO<sub>2</sub> REDUCTION.

## PART II - EVALUATION OF BASE METAL OXIDE CATALYSTS

9 Interim rept. Nov 5 - 11 64,

10 by

EDWARD B. THOMPSON, JR.

TECHNICAL DOCUMENTARY REPORT. No. EDL-TDR-64-22, PART II.

11 APRIL 1965,  
12 2 1

AIR FORCE FLIGHT DYNAMICS LABORATORY  
RESEARCH AND TECHNOLOGY DIVISION  
~~AIR FORCE SYSTEMS COMMAND~~  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO.

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
Springfield, Va 22151

## NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified users may obtain copies of this report from the Defense Documentation Center.

The distribution of this report is limited not because it contains classified information according to the standards of AFR 205-1, but for the reason that immediate release to CFSTI would make the technical content available to unfriendly foreign governments in competition with U. S. Defense industries. It may be released in December 1968.

More than one hundred copies of this report will be distributed to recipients in Government, industry, and educational institutions. Copies will also be available to NASA and DOD agencies and contractors through the Defense Documentation Center. This will give U. S. defense agencies and industry time to assimilate and take advantage of the information contained in the report.

It is limited also because it contains technology identifiable with items on the strategic embargo lists excluded from export or re-export under U. S. Export Control Act of 1949 (63 STAT.7), as amended (50 U.S.C. App. 2020.2031), as implemented by AFR 400-10.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

FDL-TDR-64-22  
PART II

**INVESTIGATION OF CATALYTIC REACTIONS  
FOR CO<sub>2</sub> REDUCTION  
PART II — EVALUATION OF BASE METAL OXIDE CATALYSTS**

*EDWARD B. THOMPSON, JR.*

This document has been approved  
for public release and sale; its  
distribution is unlimited

*Details of illustrations in  
this document may be better  
studied on microfiche*

FDL-TDR-64-22  
Part II

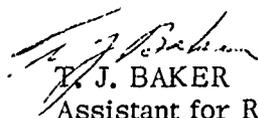
## FOREWORD

The work described herein was conducted as Part II of an in-house research effort concerning the investigation of catalysts for the reduction of carbon dioxide for space vehicle atmospheric control. This effort is being conducted by the Air Force Flight Dynamics Laboratory of the Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Project No. 6146, "Atmosphere and Thermal Control," Task No. 614612 "Oxygen Recovery from Carbon Dioxide." The chief investigator is Mr. E. B. Thompson, Jr. with assistance from Messrs. A. Civetz, K. Wess and J. Brennan Gisclard of the Air Force Flight Dynamics Laboratory, and Mr. E. Bryan of the Harshaw Chemical Company.

Manuscript released by author January 1965 for publication as an RTD Technical Documentary Report.

The second phase of this research was conducted during the period November 1963 to July 1964.

Publication of this technical report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



T. J. BAKER  
Assistant for Research & Technology  
Vehicle Equipment Division  
AF Flight Dynamics Laboratory

ABSTRACT

Several base metal and base metal oxide CO<sub>2</sub> reduction catalysts were selected for investigation as Part II of an in-house research program to determine catalytic effectiveness in promoting the reduction of carbon dioxide by hydrogen to methane and water. A catalytic reactor having a length to diameter ratio of five was designed and fabricated. Each catalyst was then evaluated individually in a series of continuous reaction runs; each run being of two hours duration. Each experimental series was conducted over the temperature range of 450°F to 800°F with the equivalent flow of 2.2 lbs CO<sub>2</sub> per day being processed through the reactor. The catalysts which were evaluated included cobalt-on-alumina, copper-on-alumina, thorium-on-alumina, and two types of molybdena-on-alumina catalysts. The cobalt catalyst proved to be the most effective for promoting the Sabatier or methanization reaction. A peak conversion efficiency of 64 percent at a temperature of 700°F at atmospheric pressure was obtained for this catalyst. The conversion efficiencies for the other catalysts ranged from essentially zero to 13 percent. The hydrogen to carbon dioxide flowrate ratio was maintained at 4.70 during all of the experimental runs. Each catalyst was periodically examined during the experimental program to determine and correlate changes in physical properties with catalytic effectiveness. In several instances, some reduction of the catalyst itself occurred although cobalt did not exhibit this effect. This report describes the experimental program and the resulting data in detail, and is concluded by recommendations for follow-on work in selecting catalysts for evaluation in reactors of varying configuration.

TABLE OF CONTENTS

SECTION	PAGE
1. INTRODUCTION . . . . .	1
1.1 Program Objectives . . . . .	1
2. ANALYTICAL PROGRAM . . . . .	1
2.1 Basis for Catalyst Selection . . . . .	1
2.2 Analysis of Selected Catalysts . . . . .	2
2.2.1 General Description . . . . .	2
2.2.2 Catalyst Properties . . . . .	3
2.2.2.1 Bulk, Particle, and Solid Densities . . . . .	3
2.2.2.2 Surface Area . . . . .	4
2.2.2.3 Effective Particle Size . . . . .	4
2.2.2.4 Effectiveness Factor . . . . .	5
3. EXPERIMENTAL PROGRAM . . . . .	5
3.1 General Plan . . . . .	5
3.2 Apparatus . . . . .	6
3.3 Experiments . . . . .	7
4. CONCLUSIONS AND RECOMMENDATIONS . . . . .	15
4.1 Conclusions . . . . .	15
4.2 Recommendations . . . . .	15
5. REFERENCES . . . . .	16

ILLUSTRATIONS

FIGURE	PAGE
1. Photograph of CO <sub>2</sub> Reduction System . . . . .	17
2. Schematic of CO <sub>2</sub> Reduction System . . . . .	18
3. Schematic of Catalytic Reactor . . . . .	19
4. Photograph of Catalytic Reactor . . . . .	20
5. Photograph of Cobalt Pellets . . . . .	21
6. Photograph of Copper Pellets . . . . .	22
7. Photograph of Thorium Pellets . . . . .	23
8. Photograph of Molybdena-on-Alumina (Type A) Pellets . . . . .	24
9. Photograph of Molybdena-on-Alumina (Type B) Pellets . . . . .	25
10. Graph Illustrating Water Yield vs. Temperature . . . . .	26
11. Graph Illustrating Percentage of Theoretical Yield vs. Temperature . .	27

## 1. INTRODUCTION

### 1.1 Program Objectives

This report summarizes the work conducted during the second phase of a continuing in-house research program concerning the Sabatier methanization reaction or the reduction of carbon dioxide to methane and water by hydrogen catalysis. The scope of this entire in-house program is planned to provide for accomplishing the two-fold objective of, first, determining a practical technique for an experimental evaluation of methanization reaction catalysts and, secondly, to determine the catalysts which are most effective in promoting this reaction to maximum water yield at minimum temperature conditions and atmospheric pressure. The general approach taken during the first phase of this program was to evaluate the effectiveness of a nickel-on-kieselguhr catalyst for promoting the methanization reaction. The results of this work were reported in FDL-TDR-64-22, Part I. The data obtained on the nickel-kieselguhr catalyst effectiveness is given in Part I and serves as reference criteria for selecting the base metal oxide catalysts for evaluation during the second phase of this program.

The particular catalysts which are experimentally evaluated during this program must satisfy the following general conditions to be considered favorable for promoting the methanization reaction:

- (1) The physicochemical properties of the catalyst must be identifiable for correlation with its effectiveness in promoting the reaction.
- (2) The catalyst must be capable of initiating and sustaining the reaction at a temperature range of 300°F to 600°F and a pressure of 1 atmosphere.
- (3) The catalyst must be capable of sustaining the reaction at maximum CO<sub>2</sub> conversion at the reaction conditions specified in (2) above.
- (4) The catalyst must be resistant to "poisoning" by sulfur compounds and halogen compounds, and so forth, or be easily regenerable by hydrogen purging or chemical scrubbing techniques.
- (5) The catalytic reactor containing the catalyst being evaluated must be designed with consideration to diffusion kinetics and flowrate of 2.20 pounds of CO<sub>2</sub> per day.

## 2. ANALYTICAL PROGRAM

### 2.1 Basis for Catalyst Selection

Nearly all of the experimental work conducted to date on the Sabatier or methanization reaction has centered on composition variations of nickel catalysts which would initiate the reaction at a low temperature while still effecting the maximum conversion of carbon dioxide. The performance of nickel catalysts, when well established and documented, serves as an excellent reference basis for evaluating the effectiveness of potentially new and more effective types of catalysts for this reaction. Furthermore, knowing the physicochemical properties of these catalysts makes it possible to correlate these properties with the yield obtained from the reaction occurring at a specific temperature with other variables being held constant.

## Part II

The "theory of catalysis" is discussed in some detail on pages 3, 4, and 5 of FDL-TDR-64-22, Part I. The following catalysts which chemical literature consider favorable for promoting the methanization reaction is listed on page 6 of the Part I report.

Cobalt  
 Iron  
 Iron with copper and cobalt  
 Nickel  
 Cobalt sulfate with cupric oxide and manganese oxide  
 Nickel on magnesium oxide granules  
 Nickel on porcelain  
 Nickel on porcelain with ceria  
 Nickel-on-kieselguhr  
 Nickel on pumice  
 Nickel plus promoters on pumice  
 Nickel with thoria and ceria on carbon  
 Ruthenium on asbestos  
 Ruthenium-thorium on asbestos

This list served as a partial guide to selecting catalysts for the second phase catalyst evaluation in comparison to nickel-kieselguhr. Literature reviewed since this list was prepared stated that thorium, molybdenum, and copper bearing catalysts may also be favorable for the reduction reactor.

Since it is the intention to explore the "precious" metal hydrogenation catalysts in the third phase of this program, ruthenium, rhodium, and iridium bearing catalysts were not considered for this second phase investigation. Accordingly, representative catalyst of the literature were screened in comparison to those materials available commercially. The following catalysts were used in the experimental program:

<u>Metal Type (on Alumina)</u>	<u>Harshaw Chemical Company Designation</u>
Cobalt	Co-0202 T 1/8"
Copper	Cu-0803 T 1/8"
Thorium	Th-0101 T 1/8"
Molybdenum (A)	Mo-1201 T 1/8"
Molybdenum (B)	Mo-1202 T 1/8"

## 2.2 Analysis of Selected Catalysts

2.2.1 General Description - The catalysts selected for this second phase of the experimental effort are described as follows:

**Cobalt** - A common catalyst for hydrogenation and Fischer-Tropsch syntheses. The catalyzing coating is composed of 32 percent cobalt in the form of cobalt oxide and 6 percent thorium oxide mounted on a kieselguhr carrier. The thorium oxide is present as a promoting agent. This catalyst is in the form of 1/8 in. cylindrical pellets.

**Copper** - This catalyst consists of 10 percent copper oxide mounted on high activity alumina and is normally used as an oxygen removal agent. This catalyst exists as 1/8 in. cylindrical pellets.

Part II

Thorium - A thoria catalyst normally used in Fisher-Tropsch syntheses. It contains 10 percent thorium oxide mounted on activated alumina and comes in the form of 1/8 in. cylindrical pellets.

Molybdena Alumina - This catalyst contains 11 percent molybdenum oxide mounted on tableted alumina. It is normally used in hydrogenation reactions in the form of 1/8 in. cylindrical pellets.

Molybdenum - This catalyst consists of 10 percent molybdenum oxide mounted on 1/8 in. cylindrical pellets. It is normally used in de-hydrogenation and hydroforming processes.

The catalysts listed above can be prepared by any of the following general techniques:

Decomposition of a thermally unstable chemical compound to give a finely divided compound such as a pure metal or metal oxide from a metal salt.

Impregnation of a carrier or support material with a solution of the catalyst salt followed by ignition of the mixture, leaving pure metals or metal oxides deposited on materials with high surface area to volume ratios.

Precipitation of a catalyst material from a solution with subsequent washing of extraneous ions, and final conversion usually by heating or drying.

Application of active metal catalysts to surfaces by actual evaporation of the metal with condensation on the support surface, under vacuum or the presence of very low pressure gases such as argon or nitrogen.

## 2.2.2 Catalyst(s) Properties

### 2.2.2.1 Bulk, Particle, and Solid Densities

In chemical reactions catalyzed by solid surfaces the reaction rate per unit mass of catalyst is influenced by the size and shape of the catalyst particle. Since hydrogenation catalysts are generally porous, the reaction occurs not only on the external available surface of the catalyst pellets but also on the interior surfaces. The external area is sometimes only a fraction of the total effective area. The availability of the interior of the catalysts pellets for catalysis depends on the size, shape, and permeability of the pore structure. Generally, it is required that the pores and capillaries be of large and uniform cross section and be interconnected with the external surface of the pellet.

In considering the properties of the catalyst bed the external void space must be distinguished from the internal void space within the particles. This distinction is marked from the experimental determination of three densities; bulk density,  $\rho_B$ , expressed as mass per unit volume of bed; particle density,  $\rho_P$ , mass per unit volume of particle; and solid density,  $\rho_C$ , mass per unit volume of solid free from all voids, external and internal. The measured values of these densities for all the catalysts considered were determined by liquid displacement techniques. The internal and external void fractions were calculated as follows:

FDL-TDR-64-22  
Part II

Catalyst	Bulk Density ( $P_B$ )	Particle Density ( $P$ )	Solid Density ( $C$ )	Void Fractions	
				Internal	External
Cobalt	1.07 gms/cc	1.43 gms/cc	3.17 gms/cc	0.550	0.251
Copper	0.85 gms/cc	1.25 gms/cc	2.78 gms/cc	0.550	0.320
Thorium	0.96 gms/cc	1.67 gms/cc	3.71 gms/cc	0.550	0.0575
Molybdena	0.91 gms/cc	1.43 gms/cc	3.17 gms/cc	0.550	0.364
Alumina (A)					
Molybdena	0.85 gms/cc	1.25 gms/cc	2.78 gms/cc	0.550	0.680
Alumina (B)					

The common value for internal void fraction indicates the use of alumina as the carrier for each catalyst. The internal and external void fractions were calculated from the following relationships:

$$F_e = 1 - \frac{B}{P}$$

$$F_i = 1 - \frac{P}{C}$$

### 2.2.2.2 Surface Area

The total surface area available from a given weight of a particular catalyst was calculated from the general relationships developed in FDL-TDR-64-22, Part I.

The total surface area available from the weight of each catalyst batch (specified in Section 3.0, Experimental Program) was calculated as follows:

Catalyst	Weight	Surface Area
Cobalt	797.5 grams	16,716 m <sup>2</sup>
Copper	820.0 grams	112,200 m <sup>2</sup>
Thorium	806.0 grams	59,000 m <sup>2</sup>
Molybdenum (A)	740.0 grams	103,600 m <sup>2</sup>
Molybdenum (B)	726.0 grams	116,160 m <sup>2</sup>

### 2.2.2.3 Effective Particle Size

The effective particle size for a catalyst was calculated from the relationships developed in FDL-TDR-64-22, Part I.

Using the form:

$$D_p' = \frac{6V_p}{A_p}$$

to solve for the effective particle size common to all catalysts investigated during this second phase:

$$D_p' = \frac{6V_p}{A_p} = \frac{6(0.026)}{(0.482)} = 0.324 \text{ centimeters}$$

#### 2.2.2.4 Effectiveness Factor

The first report gives in detail the work carried out under this investigation. It stressed that an effectiveness factor of 1.0 indicates that the reaction rate at all interior surfaces is the same as that at exterior surfaces. This is particularly true when (1) the particle size is small, (2) the pores are large and well interconnected, (3) the rate factor of the reaction is relatively low, and (4) the diffusion coefficients of reactants and products are high. It has been proven for reaction in which the rate is proportional to the first power of the concentration at the interface. The effectiveness factor is a function of a modulus which is defined as follows:

$$M = \frac{D_p'}{2} \sqrt{\frac{K}{cD_v}}$$

The modulus may also be expressed in the form:

$$M = \frac{D_p' a' \frac{b'}{T}}{F_i^{1/4}}$$

where  $a'$  and  $b'$  are empirical constants, characteristic of the reaction process and  $F_i$  is the internal void fraction.

By calculating the modulus for a number of temperature values it is possible to determine the effectiveness factor for the catalyst from standard reference graphs depicting effectiveness factor versus Thiele's Modulus.

The effectiveness factor for each catalyst investigated during this entire program will be determined and reported in FDL-TDR-64-22, Part III, Evaluation of Precious Metal Catalysts.

### 3. EXPERIMENTAL PROGRAM

#### 3.1 General Plan

The experimental program consisted of evaluating the effectiveness of several base metal oxide materials as catalysts for reducing  $\text{CO}_2$  to methane and water through hydrogen catalysis or the Sabatier methanization reaction. A laboratory scaled catalytic reactor, shown in Figures 3 and 4 having a length-to-diameter ratio of five was designed and fabricated. The reactor was fitted with a readily removable plug for rapid loading and unloading of catalyst batches. Five different catalysts were then selected for experimental evaluation in the following order:

Cobalt  
Copper  
Thorium  
Molybdenum (A)  
Molybdenum (B)

The procedure was to hold all conditions such as flowrates and the  $H_2/CO_2$  flowrate ratio and reactor pressure constant, and vary only the catalyst bed temperature. Eight experimental runs, each run of two hours duration for each catalyst, comprised an experimental series. The first run was conducted at a temperature of 450°F, with each succeeding run occurring at a 50°F higher increment temperature. The eighth and last run occurred at 800°F.

The data results from the evaluation of the nickel-kieselguhr catalyst in report, FDL-TDR-64-22, Part I, served as a guide in deciding what flowrates and flowrate ratios would be used, as well as the temperature range to be investigated.

### 3.2 Apparatus

The catalytic reduction system was arranged as shown in Figures 1 and 2. The major components of this system were the (1)  $H_2$  and  $CO_2$  gas sources comprised of two cylindrical tanks complete with gauges, regulators, and valves; (2) two dessicator columns containing calcium sulfate; (3) two rotameters for precise metering of the  $H_2$  and  $CO_2$  gas flowrates; (4) the reactor containing the catalyst; (5) a Weston potentiometer for thermocouple temperature recording, and (6) the condenser coil and graduated cylinder for water collection and measurement.

The catalytic reactor No. 2 designed specifically for this second phase of the experimental program is shown diagrammatically in Figure 3, and in photograph Figure 4. The reactor is a cylinder 30.5 centimeters long x 5.7 centimeters diameters, made of 304 stainless steel with a wall thickness of .32 centimeters. The incoming hydrogen and carbon dioxide gases mix in the copper coiled heat exchanger inlet tube (shown in Figure 3). The mixed gases in the ratio of 4.36 to 1, hydrogen to carbon dioxide, leave the tube at the rear end of the reactor, reverse direction, and flow back over the catalyst bed. Since five different catalysts were used in individual runs, the weight and description of each catalyst is given in other sections of this report.

The catalyst bed was heated through the outer cylindrical wall by a 12.7 cm long x 10.2 cm diameter ceramic enveloped nichrome wire electrical resistance heater. The nichrome wire coils were separated by approximately 1/16 inch from the wall. The nichrome wire resistance heater required 290 watts at 57.5 volts, 5.05 amps, to heat the catalyst bed in thirty minutes to a nominal temperature of 650°F which is the temperature shown later in this report to be ideal for this type of catalyst. The  $H_2$  and  $CO_2$  gases diffuse and react in the catalyst bed with the water vapor and methane products leaving through an exit port at the front end of the reactor.

The water condenser consisted of a cylindrically wound copper tubing coil (8 inches long x 6 inches diameter) and a graduated cylinder of 100 milliliter capacity. Water vapor leaving the reactor was condensed in the coil and collected in the graduated cylinder, thus providing direct measurement of yield. The products were not recycled through the reactor and therefore the apparatus did not include a recycling pump.

## Part II

Two Brooks - Perkins gas flow rotameters were used for metering of the  $H_2$  and  $CO_2$  gases to the reactor inlet manifold. The rotameter for hydrogen flow measurement (Brooks Model 1110) has a stainless steel ball float for metering hydrogen in a range of 200-2800 cc/min; specific gravity at 0.069, gas temperature and pressure at 70°F and 4 psig. The tolerance of accuracy is  $\pm 2$  percent of maximum flow. The rotameter for  $CO_2$  flow measurement (Brooks Model 1110) has a sapphire float for metering  $CO_2$  in a range of 50-500 cc/min, specific gravity at 1.529, gas temperature and pressure at 70°F and 4 psig. The tolerance of accuracy is also  $\pm 2$  percent of maximum flow.

The feed gases of  $H_2$  and  $CO_2$  were stored in two separate cylindrical tanks and metered individually through high pressure regulators to a lower pressure of 4 psig. The pressure level of 4 psig was maintained with precise accuracy since both rotameters were calibrated for this pressure and the flowrate is a direct indication of the  $CO_2$  reduction rate. The high pressure regulators were also equipped with feed throttle valves for manual adjustment of the feed flow rates to meet the  $H_2/CO_2$  flowrate ratio requirement set for any particular experiment. Two dessicator drying columns containing  $CaSO_4$  were installed in parallel in both outlet lines from the high pressure regulators to remove any residual water vapor in the gas feed lines.

Foxboro potentiometer, Model No. 8106, Serial No. D74155, was equipped with three iron-constantan thermocouples (installed at equal intervals along the longitudinal wall of the catalyst bed) for direct continuous readings of temperature in the catalyst bed.

The potentiometer has two scales; one scale for low temperature reading in the range of 0 - 1000°F, and the second for high temperature readings in the range of 1000°F - 2000°F. The tolerance of accuracy on the low and high ranges is 0.5 percent and 0.1 percent respectively. Since the catalyst bed temperatures encountered in this experimental program were on the order of 400°F - 700°F, a practical tolerance of 0.3 percent can be assumed. The iron-constantan thermocouple was used instead of copper-constantan because of its high reliability for readings in the medium temperature range.

It is worth noting that after thermocouples have been used for sometime at high temperatures, it is difficult if not impossible to determine how much the calibrations are in error except by removing them from an installation and testing in a laboratory furnace. The thermocouples are usually heterogeneous after such use and in such a condition that the EMF (Electromotive Force) developed by the couples deteriorate.

### 3.3 Experiments

Experimental reaction runs were conducted at eight different temperatures for two hours at each temperature for each of the six catalysts. These temperatures were in 50°F increments beginning at 450°F and ending at 800°F, making a total of eight runs for each catalyst. The same catalytic reactor, described in paragraph 3.2, was used throughout the investigation. Preliminary checkout runs had been previously made to insure that the system was leakproof and operable, and to gain familiarization with the assembled apparatus for data recording purposes. The preliminary runs revealed that varying weights of catalyst batches would be employed during the investigation because of different catalyst densities for the same internal reactor volume. An excess of catalyst was present,

FDL-TDR-64-22

## Part II

however, in each run to insure removal of gaseous impurities from the incoming hydrogen-carbon dioxide gas stream without impairing the efficiency of the catalyst bed. Since the cross-section of the bed nearest the gas inlet port is cooler than the remainder of the bed, this would assist in trapping the poisons. It was decided to place the catalyst(s) loosely in the reactor in random density without "packing." The preliminary runs seemed also to confirm the necessity of purging the reactor with hydrogen to remove residual poisons from the catalyst before initiating the reduction of carbon dioxide. The purging time was set at one hour.

### Results - Cobalt

Eight experimental runs were conducted with this catalyst. The weight of catalyst required for all the runs was 798 grams. The hydrogen/carbon dioxide flowrate ratio was held at 4.36 to 1 throughout the experiments as learned from the first phase evaluation of nickel-kieselguhr.

Each of the eight runs was made at a different temperature; the first at 450°F, then an additional seven at 50°F successive increments.

The carbon dioxide and hydrogen gases were metered from the storage at 4 psig and "dried" in  $\text{CaSO}_4$  dessicator columns prior to entering the reactor.

Hydrogen purging of the catalyst bed was accomplished at 450°F for 1 hour prior to conducting the experimental runs.

All three thermocouples indicated the same temperature throughout the experiment conducted at 450°F. There was a negligible water yield of three milliliters during this run. The succeeding runs at 500°F, 550°F, 600°F, 650°F, 700°F, 750°F and 800°F. Maximum water yield of forty milliliters occurred at 700°F, even though this yield had been closely approached at 600°F.

A slight fluctuation of approximately 5 percent for each of the two rotameter ball floats were noted at the initiation of reaction at each temperature. The floats readily stabilized.

The cobalt catalyst was inspected after each run. There was evidence of carbon deposition on the catalyst for the reaction occurring at 800°F.

### Results - Copper

Eight experimental runs at different temperatures were made for this catalyst. The first run was made at 450°F, and each succeeding run was conducted at 50°F higher increments. The weight of catalyst required to fill the reactor for all runs was 820 grams. The hydrogen/carbon dioxide flowrate ratio was kept at 4.36 to 1 throughout all experimental runs.

The catalyst bed was purged with hydrogen for one hour at a temperature of 450°F before conducting each run.

Since there was no evidence of a reaction water yield for any of the experimental runs, this catalyst was eliminated from any further consideration.

### Results - Thorium

Eight experimental runs were conducted with this catalyst. The temperatures of the runs ranged from 450°F to 800°F; each run conducted at 50°F higher increments. The weight of catalyst required to fill the reactor for all runs was 806 grams. The hydrogen/carbon dioxide flowrate ratio was maintained at 4.36 to 1 for all experimental runs.

The catalyst bed was purged with hydrogen for one hour at 450°F prior to conducting each experimental run.

There was evidence of a reduction reaction occurring at the higher temperatures of 750°F and 800°F. The water yield at 800°F was five milliliters but this was apparently due to reduction of the catalyst itself. The catalyst weight after completion of all runs was 776 grams.

Since this catalyst evidenced little effectiveness in promoting the carbon dioxide reduction reaction, it was eliminated from further consideration.

### Results- Molybdenum

Eight experimental runs were conducted at different temperatures with this catalyst. The first run was made at 450°F, and each succeeding run at a 50°F higher increment. The weight of catalyst required to fill the reactor was 726 grams. The hydrogen/carbon dioxide flowrate ratio was maintained at 4.36 to 1 throughout the experiments.

The carbon dioxide and hydrogen gases were "dried" in two  $\text{CaSO}_4$  desiccator columns prior to entering the reactor. Both gases were metered from storage at 4 psig.

Hydrogen purging of the catalyst bed at 450°F for one hour was accomplished prior to conducting each experimental run.

Since this catalyst evidenced no effectiveness in promoting the methanization reaction at any temperature, it was eliminated from further consideration.

### Results - Molybdena Alumina

The total of eight experimental runs were conducted with this catalyst; the first at a temperature of 450°F and each succeeding one at 50°F higher increments. The weight of catalyst required to fill the reactor bed was 740 grams.

The hydrogen/carbon dioxide flowrate ratio was kept at 4.36 to 1 for all experimental runs. Both gases were "dried" in two  $\text{CaSO}_4$  desiccator columns before entering the reactor.

Hydrogen purging of the catalyst bed was accomplished at 450°F for one hour prior to conducting each experimental run.

This catalyst failed to effect the reduction of carbon dioxide at any temperature, and it was eliminated from further consideration.

TABULATION OF EXPERIMENTS  
(COBALT)

Experiment	Reactor Temp(°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (Hr <sup>-1</sup> )	Water Yield (cc)	Remarks
1.	450	2000	425	4.7	166	26.0	Reaction started immediately. Moderate water yield
2.	500	2000	425	4.7	166	30.0	Yield slightly higher
3.	550	2000	425	4.7	166	33.0	Yield increased
4.	600	2000	425	4.7	166	37.5	Further increase in yield
5.	650	2000	425	4.7	166	37.0	Essentially same yield
6.	700	2000	425	4.7	166	40.0	Yield increased
7.	750	2000	425	4.7	166	40.0	Yield remained the same
8.	800	2000	425	4.7	166	40.0	Yield constant
9.	850	2000	425	4.7	166	39.5	Yield essentially the same
10.	900	2000	425	4.7	166	39.0	Yield essentially the same

TABULATION OF EXPERIMENTS  
(COPPER)

Experiment	Reactor Temp(°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (Hr <sup>-1</sup> )	Water Yield (cc)	Remarks
1.	450	2000	425	4.7	166	2.0	Water formation believed due to reduction of the catalyst material itself
2.	500	2000	425	4.7	166	2.5	
3.	550	2000	425	4.7	166	3.0	
4.	600	2000	425	4.7	166	4.5	
5.	650	2000	425	4.7	166	4.5	
6.	700	2000	425	4.7	166	6.0	
7.	750	2000	425	4.7	166	7.0	
8.	800	2000	425	4.7	166	8.5	
9.	850	2000	425	4.7	166	11.0	
10.	900	2000	425	4.7	166	11.0	

TABULATION OF EXPERIMENTS  
(THORIUM)

Experiment	Reactor Temp(°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (Hr <sup>-1</sup> )	Water Yield (cc)	Remarks
1.	450	2000	425	4.7	166	None	Water formation believed due to reduction of the catalyst material itself
2.	500	2000	425	4.7	166	None	
3.	550	2000	425	4.7	166	None	
4.	600	2000	425	4.7	166	None	
5.	650	2000	425	4.7	166	Condensate in gas outlet line	
6.	700	2000	425	4.7	166	Condensate in gas outlet line	
7.	750	2000	425	4.7	166	1.0	
8.	800	2000	425	4.7	166	5.0	
9.	850	2000	425	4.7	166	8.5	
10.	900	2000	425	4.7	166	11.0	

TABULATION OF EXPERIMENTS

MOLYBDENUM (A)

Experiment	Reactor Temp(°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (Hr <sup>-1</sup> )	Water Yield (cc)	Remarks
1.	450	2000	425	4.7	166	None	Water formation believed due to reduction of the catalyst material itself
2.	500	2000	425	4.7	166	None	
3.	550	2000	425	4.7	166	None	
4.	600	2000	425	4.7	166	None	
5.	650	2000	425	4.7	166	Condensate in gas outlet line	
6.	700	2000	425	4.7	166	3.0	
7.	750	2000	425	4.7	166	5.5	
8.	800	2000	425	4.7	166	6.5	
9.	850	2000	425	4.7	166	9.5	
10.	900	2000	425	4.7	166	12.0	

TABULATION OF EXPERIMENTS  
MOLYBDENUM (B)

Experiment	Reactor Temp(°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO Flowrate Ratio	Space Velocity (Hr <sup>-1</sup> )	Water Yield (cc)	Remarks
1.	450	2000	425	4.7	166	None	
2.	500	2000	425	4.7	166	None	
3.	550	2000	425	4.7	166	None	
4.	600	2000	425	4.7	166	None	
5.	650	2000	425	4.7	166	None	
6.	700	2000	425	4.7	166	None	
7.	750	2000	425	4.7	166	2.0	Water formation believed due to reduction of the catalyst material itself
8.	800	2000	425	4.7	166	6.0	
9.	850	2000	425	4.7	166	8.0	
10.	900	2000	425	4.7	166	10.0	

#### 4. CONCLUSIONS AND RECOMMENDATIONS

##### 4.1 Conclusions

The overall conclusion gained from the Phase 2 investigation of base metal oxide catalysts is that none of these materials effect the reduction of carbon dioxide as well as the nickel-kieselguhr catalyst evaluated during Phase 1. Pending the results of future investigations to be made in this program, nickel-kieselguhr would be the choice catalyst at this time for spacecraft application to oxygen recovery systems.

Supplementary conclusions reached from the Phase 2 investigation are as follows:

(a) Cobalt-on-alumina is the most effective base metal oxide catalyst investigated for promoting the methanization reaction.

(b) The conversion rate of 64 percent can be attained using the cobalt catalyst in a single pass reactor. An excess of catalyst must be used for a reactor space velocity of  $150 \text{ hr}^{-1}$  to  $175 \text{ hr}^{-1}$ .

(c) The cobalt catalyst requires hydrogen purging for at least one hour at a temperature of  $450^\circ\text{F}$  for removal of residual poisons such as hydrogen sulfide before initiating the reduction reaction.

(d) The oxides of copper, thorium, and molybdenum are virtually ineffective as carbon dioxide reduction catalysts. At temperatures above  $600^\circ\text{F}$  each of these catalysts was slightly reduced resulting in a loss in total weight.

(e) The electrical resistance heater of coiled nichrome wire is satisfactory for heating the catalyst bed to  $450^\circ\text{F}$  in 15 minutes. A conversion rate of 40 percent occurs at this temperature over the cobalt catalyst.

(f) All instrumentation including the rotameters, and the potentiometer functioned perfectly during the experimental program.

(g) The catalytic reactor designated as reactor No. 2 for this experimental program functioned perfectly. There were no problems with leakage or clogging of the inlet and exit ports.

##### 4.2 Recommendations

The following recommendations concern ideas to be implemented in future investigations for evaluating  $\text{CO}_2$  reduction catalysts:

(a) Harshaw cobalt catalyst, Co-0202 T 1/8 in. should be investigated for its' effectiveness in reactors of varying length/diameter ratios; consideration also given to varying the size and shape of the catalyst particles.

(b) The size and shape of the cobalt catalyst should be altered in future work to correlate this parameter with catalytic reduction effectiveness.

Part II

(c) Hydrogen purging of the catalyst beds was continued during this phase of the program to maintain experimental conditions consistent with Phase I data. It should be discontinued as soon as all potential catalysts have been evaluated.

(d) Gas chromatographic techniques would be helpful during future programs concerning strict quantitative analysis of the reactor exit gas composition

5. REFERENCES

1. Thompson, E. B. Jr., Investigation of Catalytic Reactions for CO<sub>2</sub> Reduction, Part I - Evaluation of a Nickel-Kieselguhr Catalyst, FDL-TDR-64-22, Part I, October 1964.
2. Dole, S. H. and R. A. Tamplin, The Salatier Reaction for Inorganic Recovery of Oxygen in Manned Space Capsules, Closed Circuit Respiratory Systems Symposium, WADC TR 60-574, August 1960.
3. Foster, J. F. and J. S. McNulty, Study of a Carbon Dioxide Reduction System, Aeronautical Systems Division, ASD TR 61-388, August 1961.
4. Babinsky, A. D., Reduction of CO<sub>2</sub> Using a Fluidized Catalyst Bed, Thompson-Ramo-Wooldridge Report TRW-ER 5159, 15 December 1962.

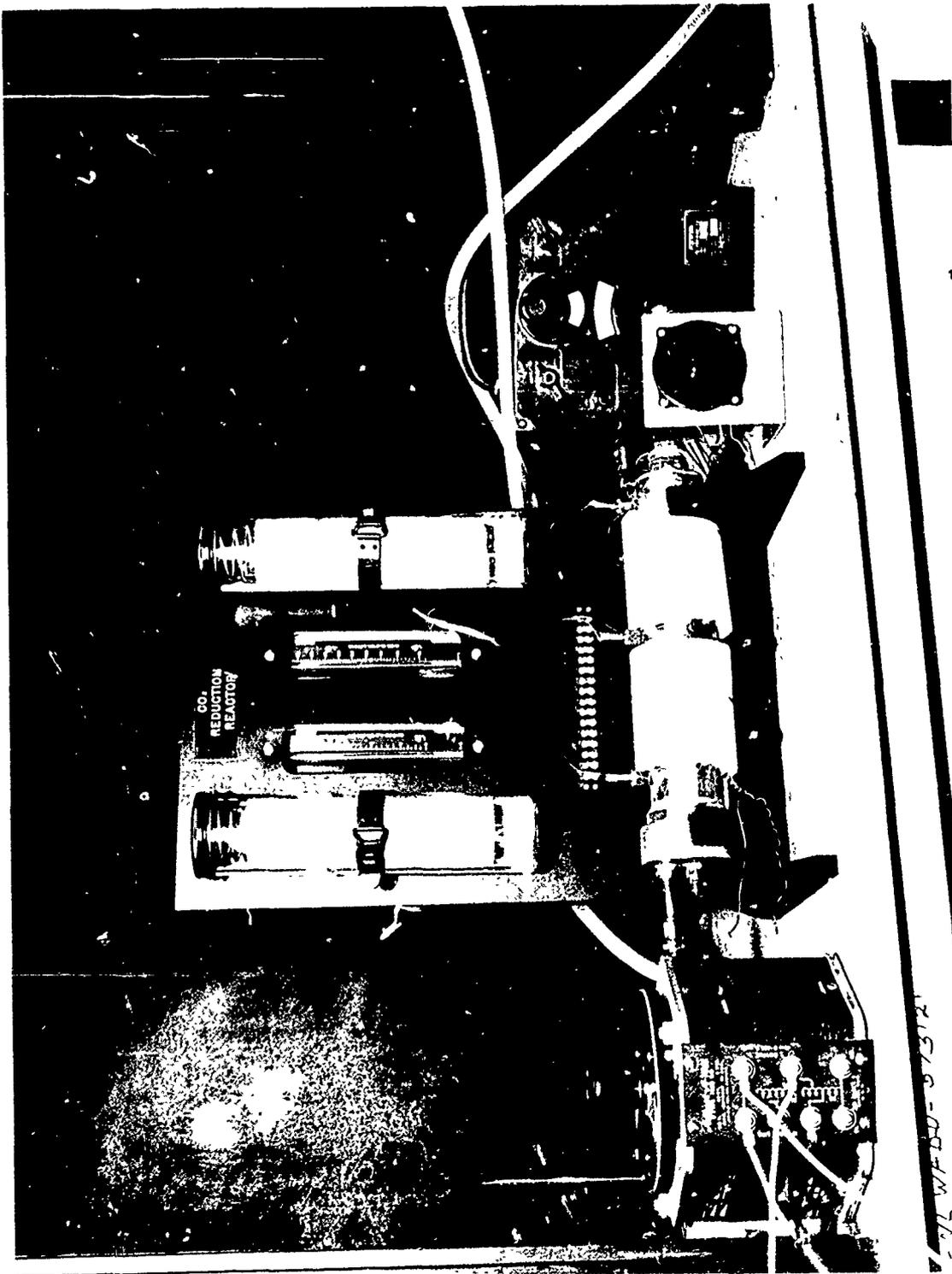


Figure 1. Photograph of CO<sub>2</sub> Reduction System

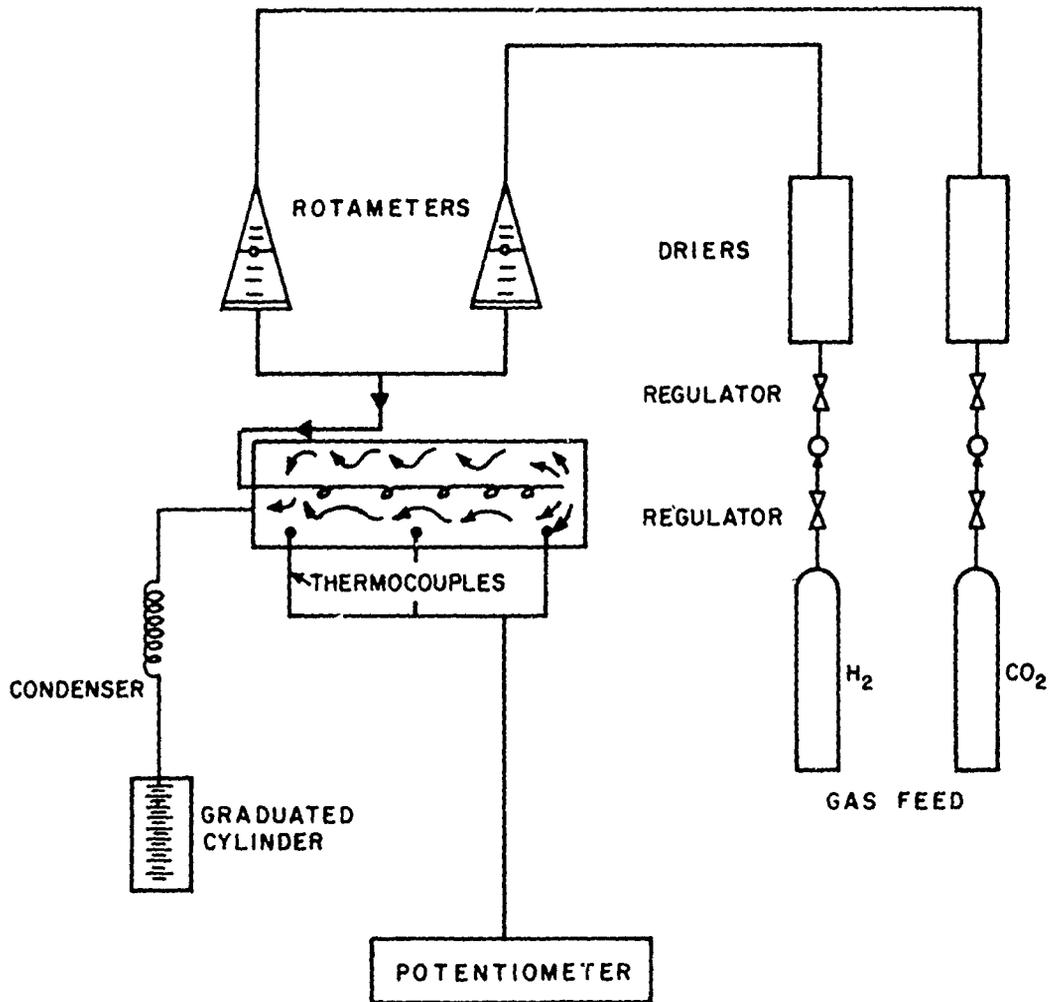


Figure 2. Schematic of CO<sub>2</sub> Reduction System

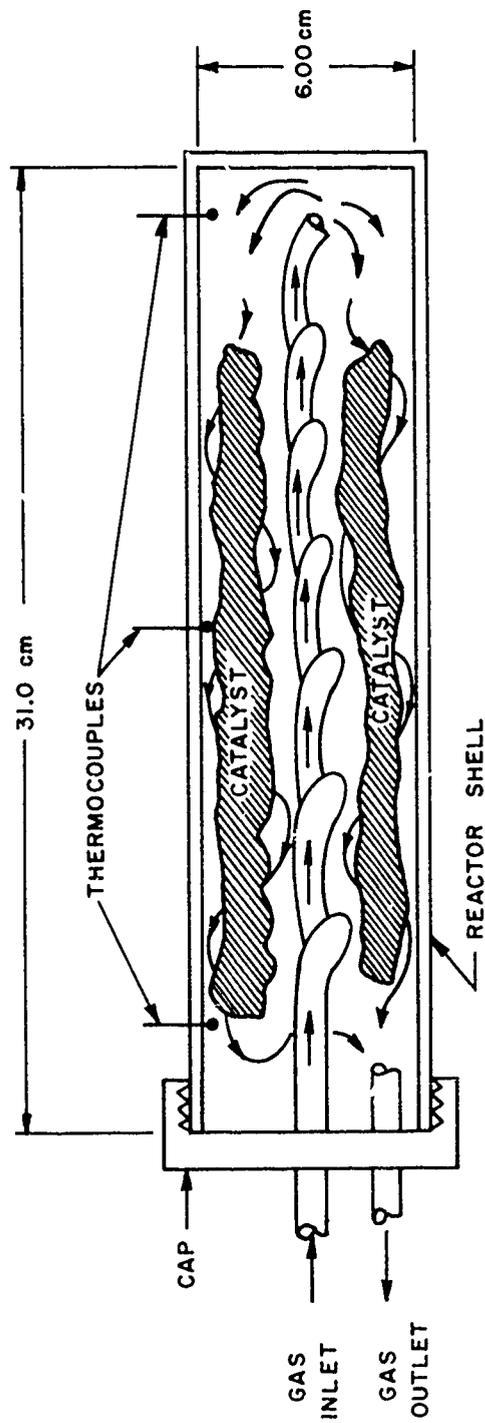


Figure 3. Schematic of Catalytic Reactor

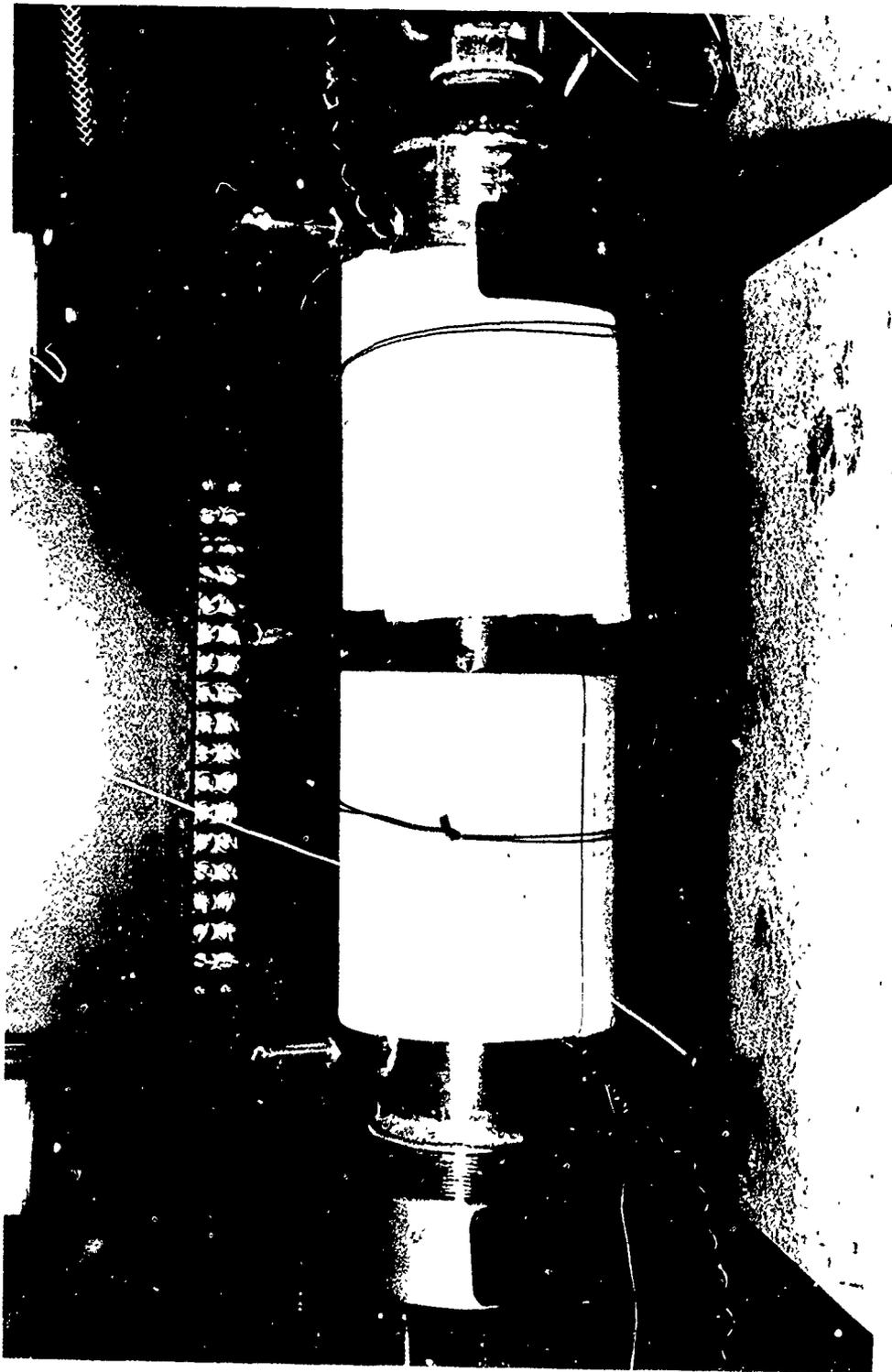


Figure 4. Photograph of Catalytic Reactor



Figure 5. Photograph of Cobalt Pellets



Figure 6. Photograph of Copper Pellets

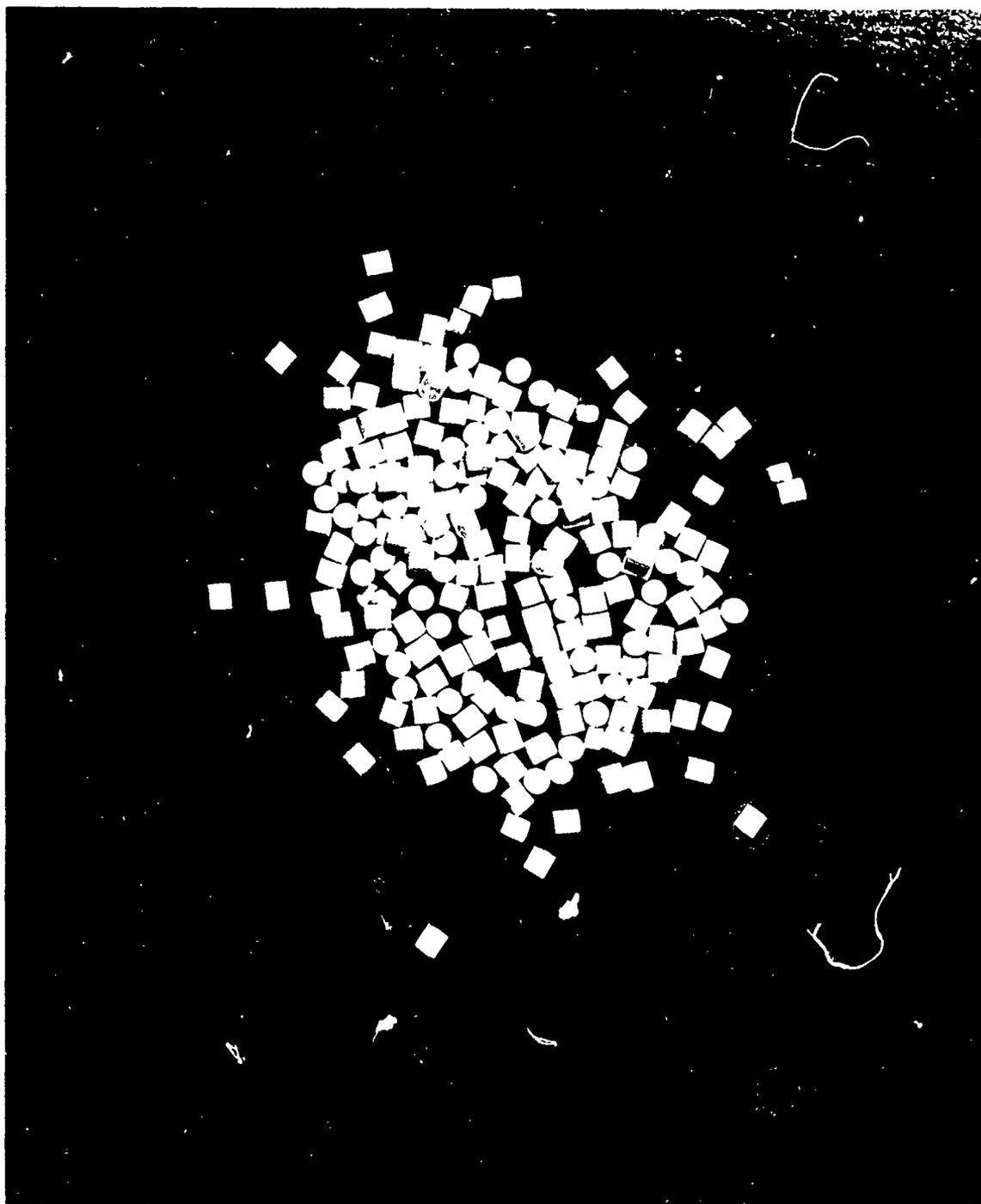


Figure 7. Photograph of Thorium Pellets



Figure 8. Photograph of Molybdena-on-Alumina (Type A) Pellets

Reproduced from  
best available copy.



Figure 9. Photograph of Molybdena-on-Alumina (Type B) Pellets

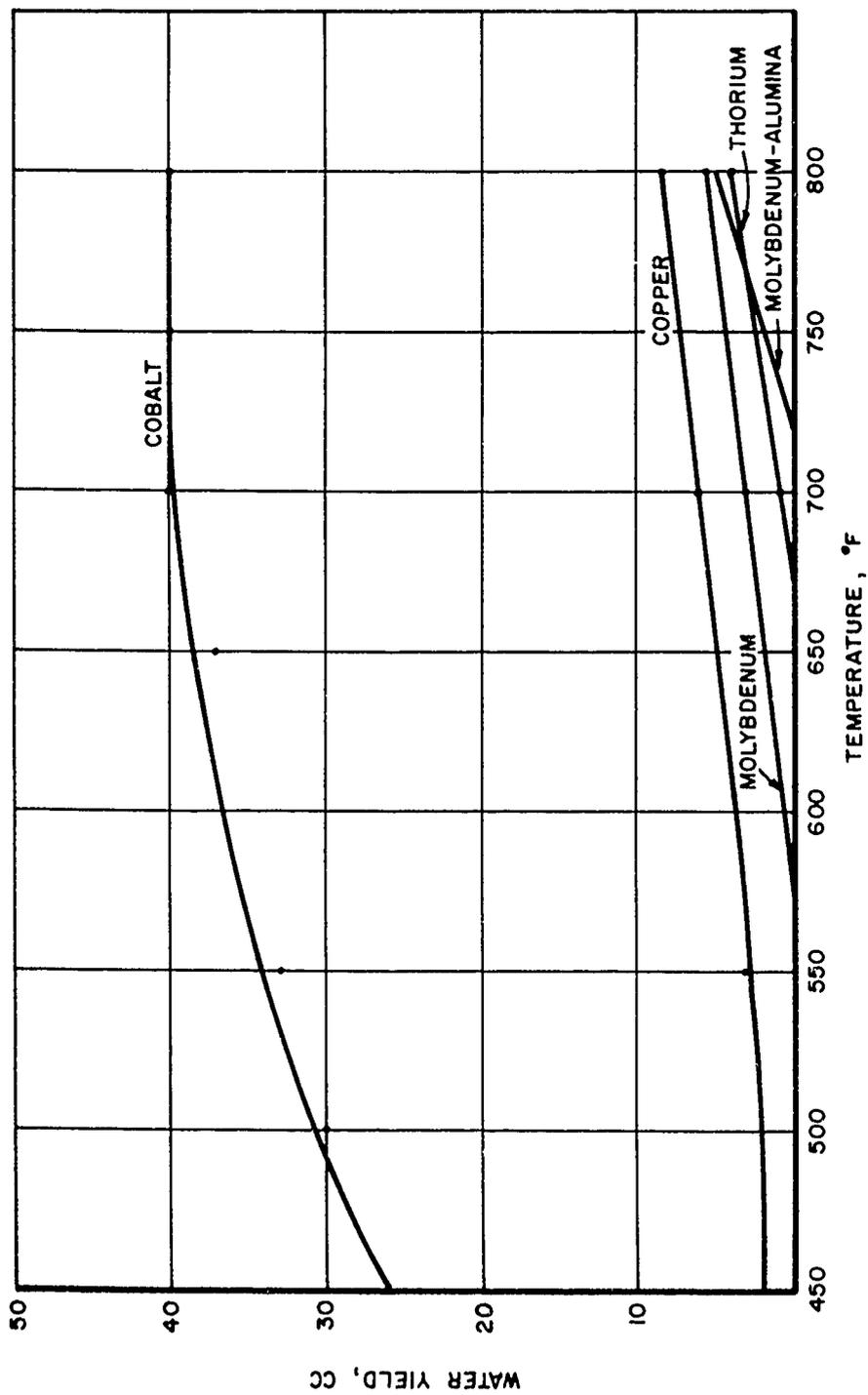


Figure 10. Graph Illustrating Water Yield vs. Temperature

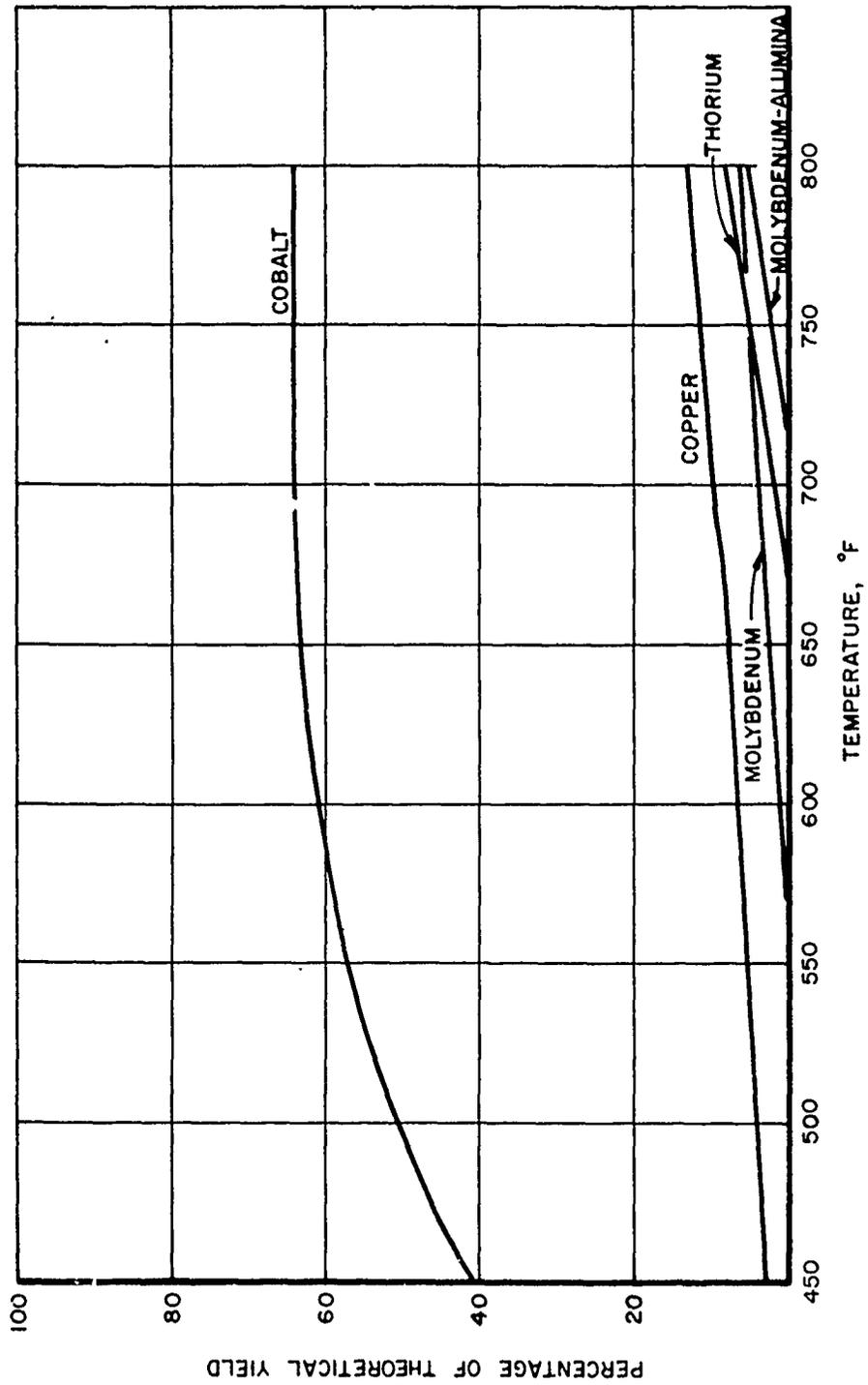


Figure 11. Graph Illustrating Percentage of Theoretical Yield vs. Temperature

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Flight Dynamics Laboratory Research & Technology Division		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Investigation of Catalytic Reactions for CO <sub>2</sub> Reduction, (Part II - Evaluation of Base Metal Oxide Catalysts).			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Interim Report			
5. AUTHOR(S) (Last name, first name, initial)  Thompson, Edward B., Jr.			
6. REPORT DATE January 1965		7a. TOTAL NO. OF PAGES Twenty-seven	7b. NO. OF REFS Four
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) FDL TR 614-22, Part II	
b. PROJECT NO. 6146			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. AVAILABILITY/LIMITATION NOTICES  Release to OTS will be withheld until November 1968.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY  Same as Block #1	
13. ABSTRACT Several base metal and base metal oxide CO <sub>2</sub> reduction catalysts were selected for investigation as Part II of an in-house research program to determine catalytic effectiveness in promoting the reduction of carbon dioxide by hydrogen to methane and water. A catalytic reactor having a length to diameter ratio of five was designed and fabricated. Each catalyst was then evaluated individually in a series of continuous reaction runs, each run being of two hours duration. Each experimental series was conducted over the temperature range of 450°F to 800°F with the equivalent flow of 2.2 lbs CO <sub>2</sub> per day being processed through the reactor. The catalysts which were evaluated included cobalt-on-alumina, copper-on-alumina, thorium-on-alumina, and two types of molybdena-on-alumina catalysts. The cobalt catalyst proved to be the most effective for promoting the Sabatier or methanization reaction. A peak conversion efficiency of 61% at a temperature of 700°F at atmospheric pressure was obtained for this catalyst. The conversion efficiencies for the other catalysts ranged from essentially zero to 13%. The hydrogen to carbon dioxide flowrate ratio was maintained at 4.36 during all of the experimental runs. Each catalyst was periodically examined during the experimental program to determine and correlate changes in physical properties with catalytic effectiveness. In several instances, some reduction of the catalyst itself occurred although cobalt did not exhibit this effect. This report describes the experimental program and the resulting data in detail, and is concluded by recommendations for follow-on work in selecting catalysts for evaluation in reactors of varying configuration.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
catalytic reduction of carbon dioxide						
oxygen recovery from carbon dioxide						
Sabatier reaction						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U)

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.