INVESTIGATION OF AN INTEGRATED CARBON DIOXIDE-REDUCTION AND WATER-ELECTROLYSIS SYSTEM

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FOREWORD

This report was prepared by the Columbus Laboratories of Battelle Memorial Institute on Contract No. AF 33(615)-2288 under Project No. 6373, "Equipment for Life Support in Aerospace" and Task No. 637302, "Respiratory Support Equipment". The work was performed under the direction of the Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio, and was administered by Richard E. Bennett, Biotechnology Branch, Life Support Division, Biomedical Laboratory. The work reported here was done between 1 January, 1965, and 30 June, 1966.

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ABSTRACT

A new integrated system for oxygen recovery from carbon dioxide was investigated. Experimental studies indicated that it was feasible to integrate water electrolysis with carbon dioxide hydrogenation in an electrolysis cell using Pd-25Ag hydrogen-diffusion cathodes containing Sabatier catalyst. A closed system producing carbon appeared feasible from experiments on catalytic methane cracking followed by hydrogen separation from unreacted methane in an electrolytic hydrogen-concentration cell using Pd-25Ag electrodes. A small experimental breadboard system was designed and constructed.

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SECTION I

INTRODUCTION

Recovery of oxygen from CO_2 and water vapor given off by man in the sealed environment of space operation will be required for advanced missions. Three of the CO_2-reduction methods under consideration can be described briefly as follow (all systems use electrolysis of water for production of oxygen):

(1) The Bosch System ($CO_2 + 2H_2 \rightarrow C + 2H_2O$) is a single-step catalytic hydrogenation reaction with an iron catalyst that operates at about 700 C, and is considered the most developed at the present state of the art.

(2) The Open Sabatier System ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) is a single-step catalytic hydrogenation reaction with various catalysts (Ni/NiO, Ru, etc.), that operates at 180 to 250 C (methane is discarded).

(3) The Closed Sabatier System ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ and $CH_4 \rightarrow C + 2H_2$) is a two-step system that is comparable to the Bosch in overall production of carbon, but that has not been studied as extensively because of the problems associated with the second step of thermal methane cracking at about 1200 C to close the system.

The present feasibility study relates to a variation of the Closed Sabatier System and is based on utilization of the palladium-silver alloy hydrogen-diffusion electrode, which is an outgrowth of prior studies(1,2). Use of this electrode as a cathode in a water-electrolysis cell is being studied concurrently at Battelle under the other Air Force contracts for application in matrix-type cells and free-electrolyte cells. In particular, the present feasibility study is concerned with advantages of system integration as opposed to the usual concept of separate interconnected subsystems of water-electrolysis cell, Sabatier reactor, and methane cracker. Specifically, the exploratory research to determine the feasibility of the new integrated system was divided into four parts:

Part 1 (Section III)	Study of the methanation process was concerned with integration of the Sabatier reaction with a water-electrolysis cell using a palladium-silver alloy cathode for operation at about 200 C.

Part 2 (Section IV)	Study of the carbonization process involved exploratory research on two components: (1) the "methane cracker" for partial catalytic decomposition of methane to hydrogen at about 700 C, and (2) the "hydrogen stripper", an electrolysis unit operating as a hydrogen-concentration cell at about 200 C, with both anode and cathode of palladium-silver alloy for separation of hydrogen from unreacted methane.
Part 3 (Section V)	Preliminary design of an experimental system involved paper study of the complete system and engineering estimates for comparison with the Bosch system.
Part 4 (Section VI)	Investigation of the experimental system involved design, construction, and checkout of a complete, small-scale, breadboard system.

SECTION II

SUMMARY OF EXPERIMENTAL RESULTS

The feasibility of the important steps of a new integrated system for oxygen recovery from CO_2 was demonstrated on a small scale with the experimental setup shown schematically in Figure 1. The feasibility of integration of the Sabatier reaction with water electrolysis was demonstrated in an extended operational run of over 800 hr. A Pd-25Ag hydrogen-diffusion cathode tube (6.35-mm OD by 0.13-mm wall) of about 8-cm effective length with one end closed was filled with conventional nickel Sabatier catalyst and operated in a free electrolyte of 65 wt percent NaOH at about 200 C. Satisfactory hydrogen transmission (practically 100 percent) was maintained at a practical design current density of about 30 ma/cm^2. With a CO_2 feed adjusted to maintain a H_2/CO_2 ratio of about 4.2, over 99 percent conversion to methane was still obtained after 800 hr prior to termination of the run. The performance of the Sabatier reaction was relatively good for a nickel catalyst, considering the low temperature and small excess of hydrogen above the stoichiometric ratio.

The results of experiments on methane cracking with various catalysts are summarized in Figure 2. The best results were obtained with a catalyst of 5 percent palladium on carbon for a temperature of 700 C (corresponding to comparative Bosch reaction temperature) using a space velocity of 36 hr^{-1} in a run of about 50 hr. Limited experiments on the use of microwave energy for noncatalytic conversion of methane to acetylene (rather than carbon) indicated an alternative method for study.

The initial study of the hydrogen stripper (Figure 1) did not indicate any problem of poisoning of the Pd-25Ag tube operating anodically for 120 hr on methane-cracking product gases and 360 hr on Sabatier product gases. At an electrolyte temperature of 200 C, practically complete removal of hydrogen from the gas mixtures was obtained at 1 to 5 ma/cm^2 and a cell voltage of about 0.2 volt. Further improvement in operating current density useful for hydrogen-stripper-cell design was shown in subsequent experiments with special treatment of the gas-phase side of the Pd-25Ag tube anode. Rhodium black electrolytically deposited on the gas-phase side of the anode (with and without a subsequent heat treatment in an oxidizing atmosphere) plus ruthenium on asbestos packed in the tube permitted anodic operation on hydrogen (1-atm pressure) for over 100 hr at current densities of 30 to 40 ma/cm^2 at electrolyte temperatures from 88 C to 230 C and with cell voltages of 0.6 to 0.15 volt, respectively.

Preliminary comparative estimates of size, weight, and power for the new integrated system were about the same as for an integrated Bosch system.

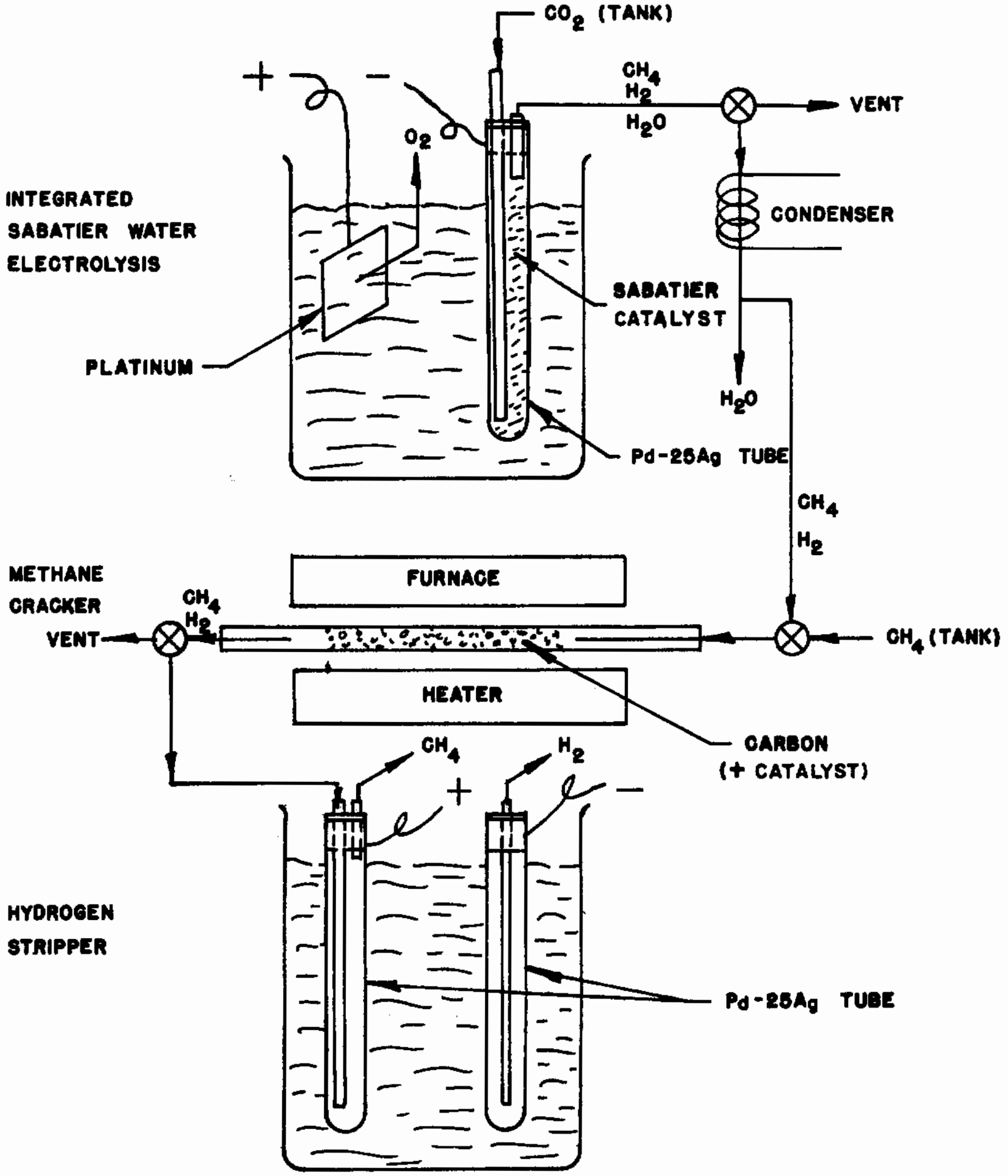

FIGURE 1. SCHEMATIC OF APPARATUS USED FOR EXPERIMENTAL STUDY (SINGLY OR IN COMBINATION) OF IMPORTANT SUBSYSTEM FOR AN INTEGRATED OXYGEN-RECOVERY SYSTEM

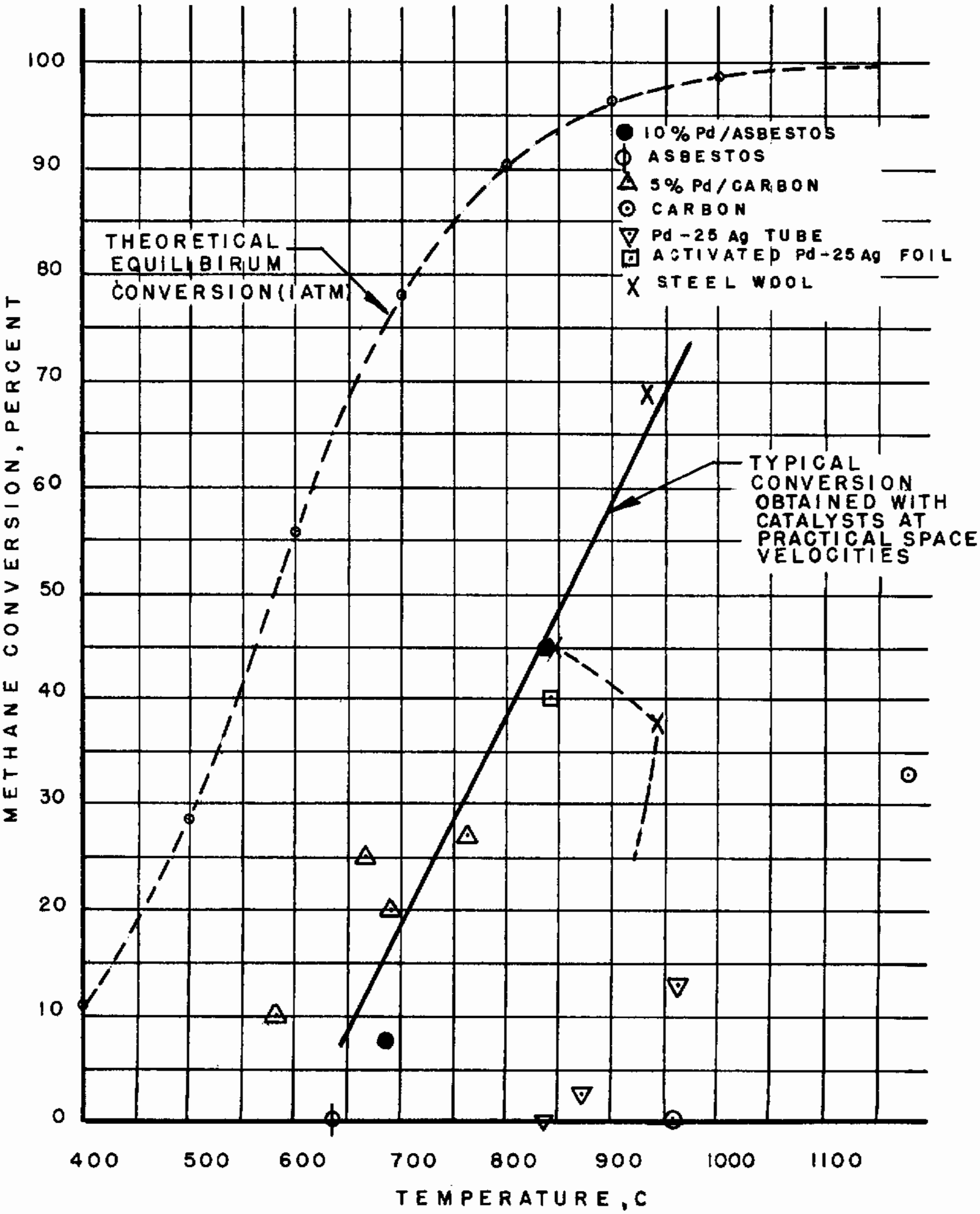

FIGURE 2. SUMMARY OF METHANE-CRACKING EXPERIMENTS WITH VARIOUS CATALYSTS

A breadboard model of the new system was designed and fabricated for experimental evaluation as an integrated system at up to 0.2-man capacity. The matrix-type water-electrolysis cell with Pd-25Ag cathode in the integrated breadboard system was operated at 200 C for the first time without evidence of cathode poisoning during 100 hr. However, intermittent satisfactory hydrogen transmission required modification of the water-vapor-feed design. Sealing problems in the water-electrolysis-cell design did not permit a complete checkout of all components of the breadboard model.

SECTION III

METHANATION OF CARBON DIOXIDE

Introduction

Objective

This part of the study investigates the feasibility of integrating the Sabatier reaction with the water-electrolysis cell using Pd-25Ag hydrogen-diffusion cathodes. The initial experiments were directed toward the feasibility of methanation of CO_2 on the gas-phase side of untreated Pd-25Ag tube cathodes transmitting hydrogen at practically 100 percent efficiency. In subsequent experiments, the cathode tube was filled with catalysts known to promote the Sabatier reaction at practical rates. Finally, an extended operational test was performed to determine the capability of the Pd-25Ag cathode to maintain 100 percent hydrogen transmission with a Sabatier reaction on the gas-phase side.

Experimental Apparatus

Figure 3 is a schematic of the experimental electrolysis apparatus used for study of methanation of CO_2. The experimental free-electrolyte cell was constructed of Teflon, with only platinum and Pd-25Ag in contact with the electrolyte to avoid electrolyte contamination and poisoning of the Pd-25Ag cathodes for hydrogen transmission. The NaOH electrolyte was prepared from cp NaOH pellets and distilled water and preelectrolyzed with auxiliary platinum electrodes at the operating temperature until no visible deposit accumulated on the platinum electrodes for 1 to 5 hr.

Activation of Pd-25Ag Electrodes

Except where specifically noted otherwise in this report, all Pd-25Ag electrodes were activated by the following procedure (after closing one end by welding):

(1) Clean the as-received tubes, outside and inside, with concentrated 37 wt percent HCl.

(2) Rinse well with distilled water and dry the inside of the tube with pipe cleaners

(3) Cathodically charge tube (with hydrogen) at 60 ma/cm^2 in electrolyte at operating temperature. If hydrogen

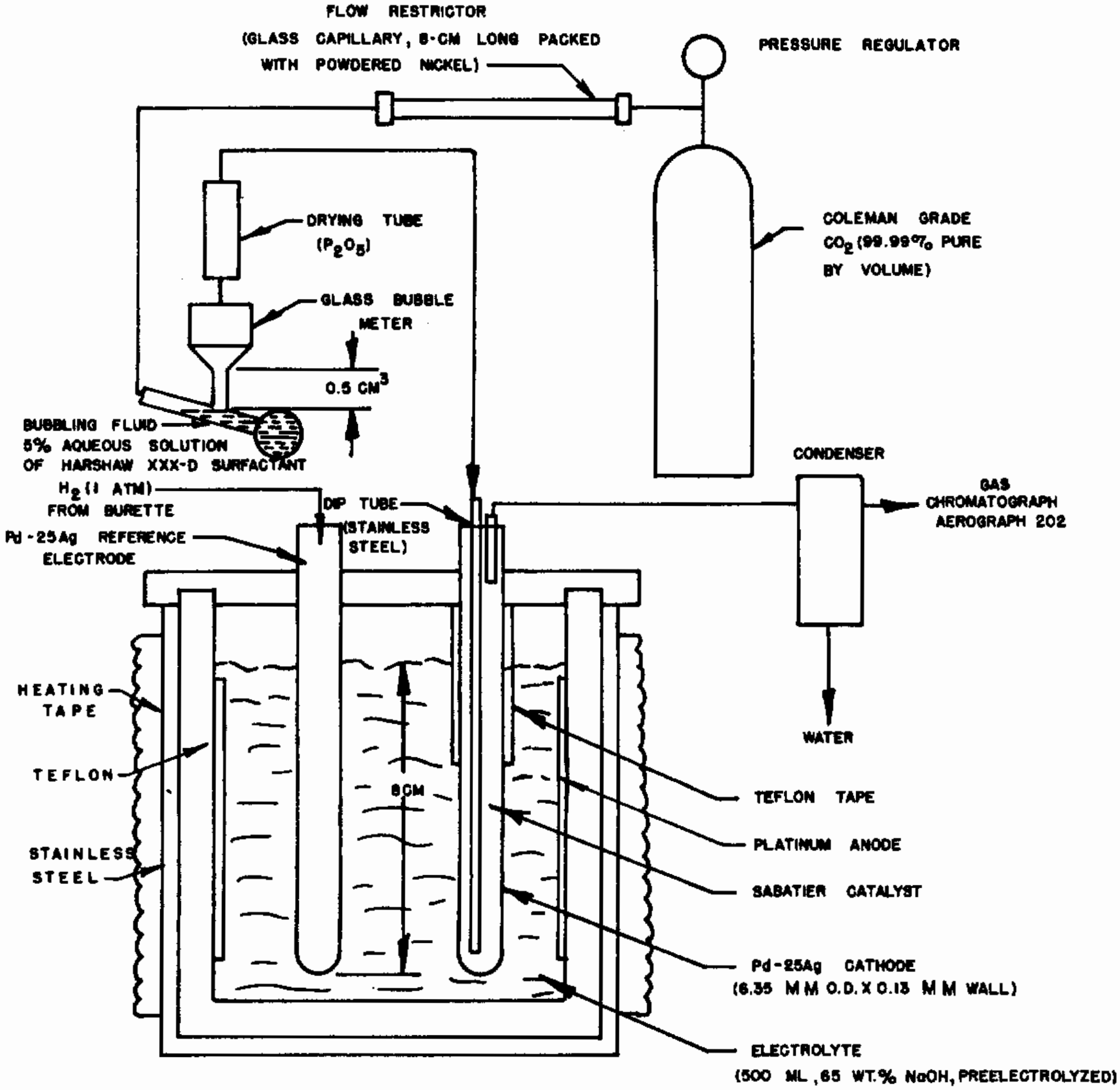

FIGURE 3. SCHEMATIC OF EXPERIMENTAL ELECTROLYSIS CELL AND APPARATUS FOR STUDY OF METHANATION OF CARBON DIOXIDE

bubbles are observed on cathode, continue for 2 to 3 min; if tube appears to be transmitting hydrogen, continue for 5 min.

(4) Remove tube from electrolyte and rinse off electrolyte with distilled water and then place tube in flame of bunsen burner with wing tip and bring tube to cherry-red color.

(5) If tube bubbled hydrogen in Step (3), it may be necessary to repeat Steps (3) and (4).

(6) For tubes activated in the above manner, practically 100 percent hydrogen transmission can be obtained when operated as cathodes. (The maximum efficient cathodic current density to be expected as a function of electrolyte temperature is shown later in this report in Figure 11 for "untreated tubes".)

Gas Analysis

Gas-chromatographic analysis in this study was performed with an Aerograph-202 gas chromatograph. A silica-gel column was used primarily for analysis. A molecular-sieve column was used for measurement of carbon monoxide, and special columns were used for detection of formaldehyde, formic acid, methanol, etc.

Exploratory Experiments

Pd-25Ag Cathode

Carbon dioxide was fed to the inside of the untreated Pd-25Ag cathode, which was transmitting hydrogen at 95 to 100 percent efficiency. The superficial space velocity was varied from 138 hr^{-1} to 24 hr^{-1}* and the temperature was varied from 100 C to 200 C, with a molar ratio of hydrogen to CO_2 of 1 to 4.2. The product gases from the cathode were passed directly into the sampling loop of the gas chromatograph. No methane was observed in the product gases with a chromatograph sensitivity that would have detected methane at concentrations as low as 100 ppm.

The final effort to reduce CO_2 inside an untreated Pd-25Ag tube was conducted at 300 C in a nonelectrolytic experiment. A small oven was constructed from a Pyrex tube sealed at one end to the Pd-25Ag tube by a Teflon plug and containing at the other end a stopcock through which gases

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*Space velocity in reciprocal hours (STP) = $\frac{cm^3 H_2/hr + cm^3 CO_2/hr}{\text{active vol of tube in } cm^3}$.

could be admitted or drawn off. The Pyrex tube was heated by means of an electrical heating tape. The inside of the Pd-25Ag tube was connected to a reservoir of CO_2 in a burette sealed with mercury. The hydrogen diffused in through the wall of the Pd-25Ag tube from the Pyrex oven, which was filled with hydrogen.

The tube was held at 300 C for 5 hr. During this time no noticeable change in the mercury level in the reservoir was observed; nor was there any indication of the formation of water vapor. The tube was removed from the oven, and samples of the contents were run through the gas chromatograph. No methane or CO was detected. The contents of the Pd-25Ag tube were also analyzed chromatographically for liquids such as methanol, formaldehyde, and formic acid. These liquids would presumably be intermediates formed by the reduction of CO_2 with hydrogen. The analysis showed a small unidentified peak that could have been formaldehyde. Also, water vapor was present in the sample.

In a subsequent experiment similar to the aforementioned one, the Pd-25Ag tube contained 4.4 grams of nickel catalyst. The oven was heated to 260 C and flushed with hydrogen for 3 hr before the CO_2 flow was started. Carbon dioxide was introduced into the bottom end of the Pd-25Ag tube by means of a capillary inlet tube at a rate of 3/4 cm^3/min. Hydrogen was passed into the tube at the rate of about 6 cm^3/min. Under these conditions, the chromatographic analyses showed a steady increase in methane concentration in the product gases. The methane concentration rose only to about 2 percent, indicating that a steady state had not been reached. The experiment was sufficient to demonstrate that methane formation occurred and was not continued to a steady state.

The above experiments disclosed that an untreated Pd-25Ag tube (without added catalyst) did not have sufficient catalytic activity on the gas-phase side to accomplish reduction of CO_2 to methane at practical rates. Consideration was given to various treatments of the gas-phase side to increase catalytic activity, but experimentation along this line was not pursued. Analysis of the integrated system indicated that the added weight of catalyst to completely fill the Pd-25Ag tube was relatively minor. Thus, subsequent studies were directed to the use of commercially available catalysts known to be effective for the Sabatier reaction.

Ruthenium Catalyst

Of the several methanation catalysts that have been studied(3), nickel and ruthenium were obvious choices. Ruthenium metal had been determined to be the optimum catalyst for the Sabatier reaction.(3) Of particular interest for integration with the water-electrolysis cell was the lower temperature of 180 C for ruthenium compared to about 200 C for a nickel catalyst.

When ruthenium catalyst was first investigated on this project, the information in Reference (3) was not available to guide in the selection of catalyst or in activation procedures. Thus, the results obtained are not considered optimum for ruthenium catalyst.

One gram of powdered ruthenium* finer than 325 mesh and of 99.99 percent purity was mechanically mixed with purified asbestos fibers and packed into a Pd-25Ag tube. The tube was lowered into the free-electrolyte cell of Figure 3, and CO_2 was introduced into the tube through a stainless steel capillary running to the bottom. The CO_2 flow rate was set at 0.91 cm^3/min (STP)**. The hydrogen flow rate was set by the electrolysis current to give a H_2/CO_2 ratio of 4.33. The temperature of the electrolyte was 207 C. These conditions correspond to a superficial space velocity of 111 hr^{-1} and a CO_2 flow rate of 0.11 g/hr per gram of catalyst. Under these conditions, the conversion to methane was 8.9 percent.

Since such a small amount of ruthenium was used in the Pd-25Ag tube, the space velocity was reduced to increase the conversion. At 200 C, when the CO_2 flow rate was reduced to 0.143 cm^3/min with a H_2/CO_2 ratio of 4.38, the conversion to methane increased only to 37 percent. These operating conditions correspond to a superficial space velocity of 18 hr^{-1} and a CO_2 flow rate of 0.018 g/hr per gram of catalyst. At this low space velocity, even with the small amount of catalyst present in the Pd-25Ag tube, almost complete conversion to methane should have occurred, according to results published in the literature. Apparently, the catalyst was not in its active state.

An additional 4 grams of ruthenium catalyst were obtained from the same vendor for further studies. Four grams of the catalyst were activated by the procedure described in Reference (3). This procedure involves treatment with 5N HNO_3 at 100 C for 5 min. The ruthenium was then washed and dried and baked in an oven at 400 C for 1 hr. Since the catalyst powder was very fine – less than 325 mesh – difficulty was encountered in the washing. Since the 3 grams of ruthenium remaining at the end of the activation procedure were not enough to fill the Pd-25Ag tube, the bottom portion of the tube (1.4 cm^3) was stuffed with purified asbestos fibers, and the ruthenium metal (0.6 cm^3) was packed into the upper portion of the tube with additional asbestos fibers (0.6 cm^3) to the electrolyte level. The CO_2 flow rate was 0.348 cm^3/min, and the H_2/CO_2 ratio was 4.56. These conditions correspond to a space velocity of 310 hr^{-1}. Since better than 99 percent conversion to methane had been reported [Reference (3)] at 180 C at a space velocity of 310 hr^{-1}, at least an equivalent conversion was expected for this experiment with an electrolyte temperature of 200 C. After running for 2 hr, however, the conversion had reached only to 24 percent. Apparently, the catalyst had not been activated properly.

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*Electronic Space Products, Incorporated, K4607A.

**Carbon dioxide flow rates were measured with a bubble meter, and are reported as dry gas at standard temperature and pressure.

Nickel Catalyst

The nickel catalyst used in these methanation studies was a commercially available catalyst of Ni-NiO on kieselguhr in the form of cylindrical pellets.* Since these tablets were too large to pack into the Pd-25Ag tube, they were ground in a mortar under an atmosphere of helium and screened. The fraction having mesh sizes between 20 and 35 mesh were used to pack the tube (the openings in 20- and 35-mesh screens are 0.841 and 0.420 mm, respectively).

For the first experiment, the Pd-25Ag tube was packed with 4.4 grams of catalyst, which filled about 14 cm of the tube. When the tube was immersed in the electrolyte to a depth of 8.3 cm, about 2.6 grams of catalyst were below the electrolyte level, and 1.8 grams of catalyst were above the electrolyte level. The volume of 2.61 cm^3 below the electrolyte level was considered the effective heated-reactor volume. Since the space above the electrolyte was somewhat cooler than the electrolyte, it is doubtful that all of the 1.8 grams of catalyst above the liquid level were effective. With the electrolyte at 200 C (measured by a thermocouple inside a Pd-25Ag dip-tube), the CO_2 was introduced into the bottom of the Pd-25Ag cathode at a flow rate of 0.118 cm^3/min. With excess hydrogen supplied by electrolysis (H_2/CO_2 ratio = 11.8), the CO_2 was completely reacted. The CO_2 flow rate was increased to 0.244 cm^3 (H_2/CO_2 ratio = 5.7) and the methane concentration increased, but no CO_2 appeared in the effluent. The CO_2 flow rate was increased to 0.615 cm^3/min (H_2/CO_2 ratio = 2.250), and in the effluent gas methane increased, hydrogen decreased, and CO_2 appeared; no CO was detected. With the CO_2 flow rate at 0.580 cm^3/min, the hydrogen was increased to 2.32 cm^3/min (0.333 ampere) to provide the stoichiometric ratio for the Sabatier reaction (H_2/CO_2 ratio = 4.0). The electrolyte temperature had increased to 232 C and after 40 min of operation, the CO_2 conversion had reached 87 percent at a superficial space velocity of 75 hr^{-1}. The experiment was ended when the percent hydrogen transmission decreased, as evidenced by bubbling of hydrogen on the electrolyte side of the Pd-25Ag cathode.

For the second experiment, the Pd-25Ag cathode tube was the same one used previously for the experiment with ruthenium. The ruthenium and asbestos were removed, and the tube was activated by the procedure on page 7, with Step 3 omitted. The tube was filled with 3.043 grams of nickel catalyst (fraction having mesh sizes between 25 and 30 mesh). The catalyst occupied 3.0 cm^3 (bulk density of 1.0 g/cm^3), with 2.6 cm^3 of tube volume below the electrolyte level. Thus, the catalyst filled the tube to

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*Harshaw nickel catalyst, Ni-0104, T 1/8, 474-022-44, Lot 178.

about 1.4 cm above the electrolyte level. The CO_2 flow rate was set at 0.347 cm^3/min, with a H_2/CO_2 ratio of 4.56. These conditions correspond to a superficial space velocity of 44 hr^{-1}, and a CO_2 flow rate of 0.013 g/hr per gram of catalyst. Under these conditions, the conversion to methane reached 99.9 percent in 5 hr at 200 C. After running overnight, the conversion was still 99.5 percent the next morning at a temperature of 205 C. The cathode current density was 14 ma/cm^2.

Since the optimum current density for electrolysis cell design is about 30 ma/cm^2, the current density was raised by increasing the CO_2 and hydrogen-flow rates. The CO_2 flow rate was increased to 0.9 cm^3/min with a H_2/CO_2 ratio of 4.4. The temperature was 202 C. Under these conditions the superficial space velocity was 96 hr^{-1}, and the CO_2 flow rate was 0.035 g/hr per gram of catalyst. The cathode current density was 35 ma/cm^2, based on the tube area below the electrolyte level. At the same time that the flow rates were increased, the upper portion of the Pd-25Ag tube was wrapped with Teflon tape to make only the lower 3.2 cm of the cathode tube effective for electrolysis. Thus, the true cathode current density was 92 ma/cm^2. This change was made to ensure the best use of hydrogen in the reaction. All of the hydrogen passed through some portion of the heated catalyst bed, and the possibility of bypassing of the hydrogen at the top of the bed was eliminated. After an operating time of 80 min under these conditions, the conversion reached 99 percent.

Since there was a good deal of excess hydrogen present in the product gases, the hydrogen flow rate was reduced to give a H_2/CO_2 ratio of 4.1. Since the product stream from the methanation electrode was to be passed directly to a cracking reactor, it was advantageous to keep the hydrogen concentration as low as possible. Under these new conditions, the conversion to methane was 99.3 percent after about 3 hr of running. The total operating time was about 24 hr during the initial period of adjustment. Since the system was performing satisfactorily, an extended operational test was begun.

Extended Operational Test of Integrated Sabatier/Water Electrolysis

The experimental integrated Sabatier/water-electrolysis system was operated satisfactorily for a total of 840 hr. During part of this test period, the Sabatier products were used as feed to the methane-cracker and/or the hydrogen-stripper cell. At the beginning of the extended test, the CO_2-feed rate was 0.900 cm^3/min, and the water-electrolysis-cell current was 0.530 ampere (3.69 cm^3/min), for a H_2/CO_2 ratio of 4.10. At an electrolyte temperature of 205 C, the conversion of CO_2 to methane was 99.3 percent. The actual cathode current density was 86 ma/cm^2, based on the exposed portion of the cathode (33 ma/cm^2, based on the portion of tube below the electrolyte level, and 29 ma/cm^2, based on the length of tube containing catalyst). After 600 hr of operation, some of the Teflon tape was removed from the cathode to expose more electrolysis area (actual cathode current density decreased to 53 ma/cm^2). This change had no noticeable effect on the operation of the Pd-25Ag cathode or the Sabatier reaction during the subsequent 240 hr of operation (CO_2 conversion above 99 percent). At the time, this extended test represented the longest operating time that had been demonstrated for a Pd-25Ag cathode operating with practically 100 percent hydrogen transmission. During the extended test, the cell voltage was about 1.60 ±0.05 volts. The latter voltage reflects primarily the oxygen overvoltage of the bright-platinum-foil anode at about 9 ma/cm^2. The potential of the cathode versus a Pd-25Ag/H_2 reference electrode was less than 0.05 volt, and the cell voltage drop due to ohmic resistance of the electrolyte was estimated to be about 0.05 volt.

During the extended operational test of the experimental integrated Sabatier water-electrolysis system, relatively little attention by the operator was required. A constant CO_2 flow rate was obtained by setting the upstream pressure regulator and was maintained constant by the flow restrictor (Figure 3), independent of downstream pressure. The water-electrolysis-cell current was 0.53 ±0.01 ampere throughout the test period, which corresponds to H_2/CO_2 ratios in the range of 4.02 to 4.18, assuming 100 percent hydrogen transmission through the Pd-25Ag cathode. High hydrogen-transmission efficiency can be inferred from the low H_2/CO_2 ratios and the high conversion of CO_2. Chromatographic analysis of product gas at intervals during the test indicated greater than 99 percent conversion of CO_2 to methane. After about 700 hr of operation, the temperature of the water-electrolysis-cell electrolyte was intentionally decreased to 180 C, and the CO_2 conversion decreased to about 70 percent, but recovered when the temperature was returned to above 200 C. An analysis made after 800 hr of operation indicated 99.8 percent conversion of CO_2 at 210 C, with a H_2/CO_2 ratio of 4.10.

SECTION IV

CARBONIZATION OF METHANE

Introduction

This part of the program consisted of an investigation of an electrochemical process wherein methane is converted to carbon and hydrogen utilizing a Pd-25Ag hydrogen diffusion electrode for recovery of hydrogen. Carbon-handling methods were not to be considered during this feasibility study, except to the extent that carbon removal affected the proper operation of the process. The experimental study was concerned with the integration of two processes:

Methane cracking	$CH_4 \rightarrow 2H_2 + C$
Anodic hydrogen recovery	$2H_2 \rightarrow 4H^+ + 4e$

(The complementary cathodic reaction for utilization of recovered hydrogen for the Sabatier reaction in Pd-25Ag tube cathodes was studied in Section III; the similarity of the cathodic reaction for use in two different parts of the system can be seen in the schematic flow diagram of the complete system in Figure 12.)

Four concepts for recovery of hydrogen from methane were investigated in exploratory experiments that are discussed in detail in the sections that follow. Figure 4 illustrates schematically the important principle in each of the four concepts, and the apparent advantages or disadvantages for an integrated system are summarized below with reference to Figure 4:

(A) Low temperature; integral methane cracker

Methane cracking at 200 C appears to provide an integration advantage (200 C preferred for Sabatier reaction and electrochemical-cell construction using Teflon).

(B) High temperature; integral methane cracker

Methane cracking rates are favored by higher temperature (500 to 1000 C), but a separate Sabatier reactor would be required.

(C) Noncyclic; separate methane cracker

A separate methane cracker at 500 to 1000 C appears more amenable to carbon removal; also, transfer of only

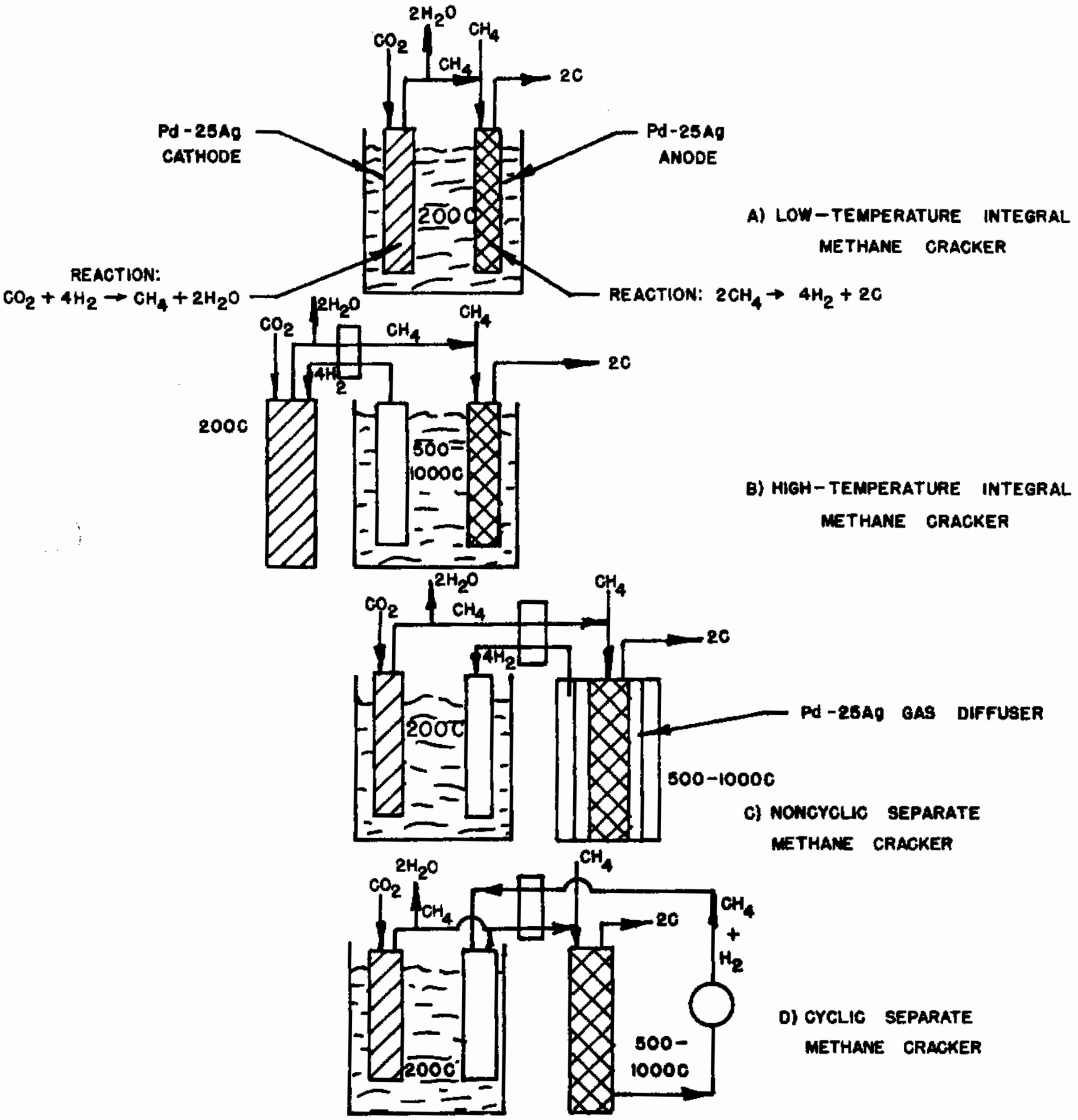

FIGURE 4. CONCEPTUAL INTEGRATED SYSTEMS USING Pd-25Ag ELECTRODES FOR RECOVERY OF HYDROGEN FROM METHANE FOR REUSE IN SABATIER REACTION

hydrogen from high to low temperature avoids recycle of unreacted methane.

(D) Cyclic; separate methane cracker

A more conventional methane cracker with partial decomposition per pass requires a recycle pump compared to (C) above, but eliminates gas-phase hydrogen permeation and associated hydrogen partial-pressure differential (i.e., higher hydrogen partial pressure supplied to anode and thus lower anode potential for the same methane-cracking results).

System (D) was studied in greater detail with respect to the catalytic methane-cracking reaction and the hydrogen stripper (anodic removal of hydrogen from methane-cracker products and also Sabatier products). In contrast to the aforementioned single-pass experiments, the experimental breadboard system discussed in Section VI was constructed for study of gas-product recycle.

Exploratory Experiments

Integral Methane Cracker

Low-Temperature Experiments. A series of anodic polarization experiments was conducted to determine the feasibility of conceptual System A of Figure 4. The experiments were designed to determine whether methane decomposition at 200 C temperature inside a Pd-25Ag tube anode would proceed at a practical rate (i.e., production of hydrogen at a rate equivalent to an anode current density of at least 1 ma/cm^2 and, preferably, above 30 ma/cm^2).

In the exploratory studies, five experiments, designated A to E, were performed with the experimental setup of Figure 5. One Pd-25Ag tube served as a reference electrode (Pd-25Ag/H_2, 1 atm) to measure the change in anodic potential of the working electrode into which hydrogen (generated electrolytically) and methane (tank) gases were fed. The recorded anode potentials versus the reference electrode were not corrected for voltage drop from ohmic resistance of electrolyte. However, at the current density used, the correction was estimated to be less than 5 mv.

The experimental procedure employed for obtaining the anodic-polarization data was as follows:

(1) The Pd-25Ag anode tube was activated by procedures described previously on page 7, and checked for

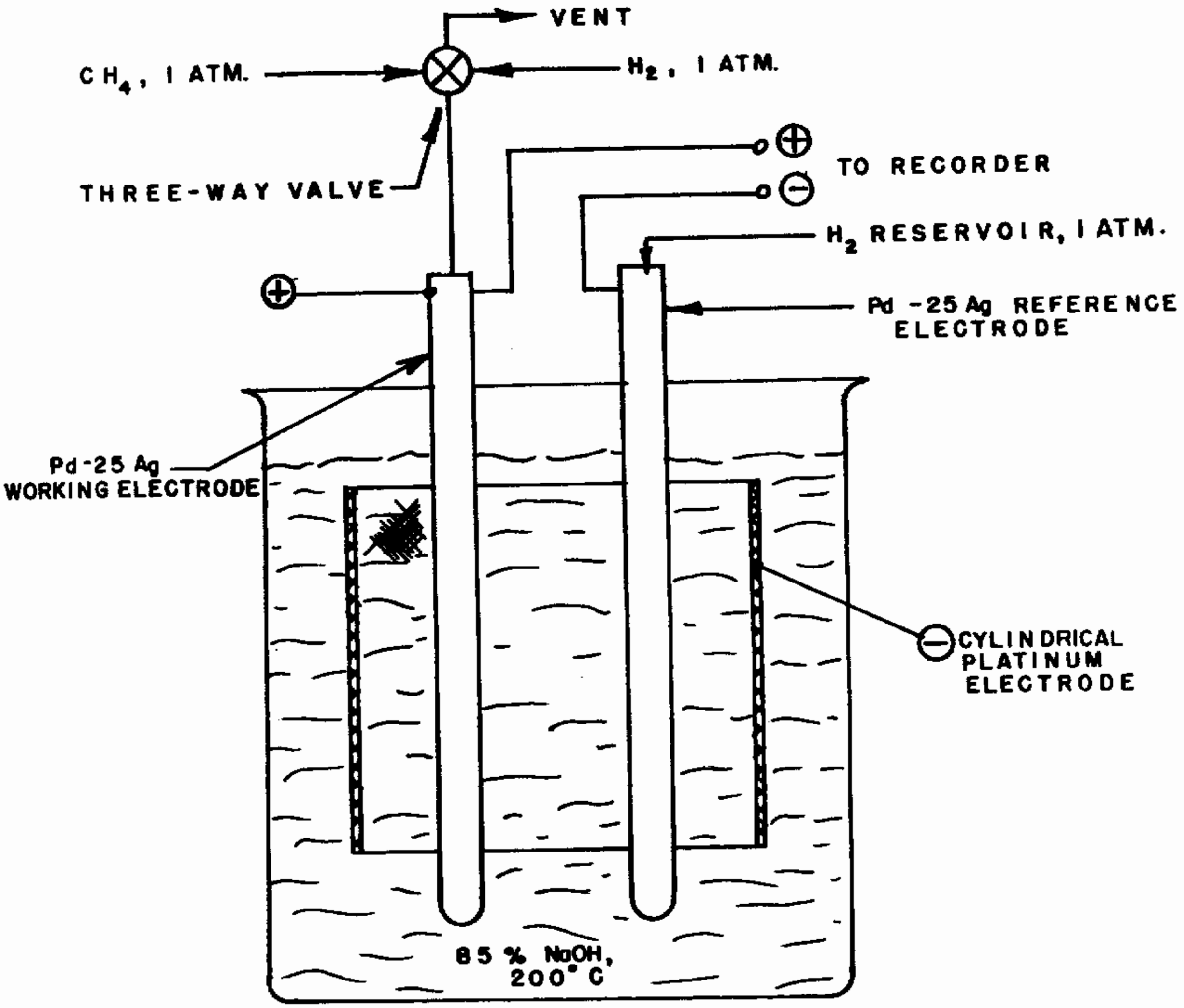

FIGURE 5. SCHEMATIC OF EXPERIMENTAL SETUP FOR OBTAINING ANODIC POLARIZATION DATA

essentially 100 percent cathodic hydrogen transmission at 37 ma/cm^2.

(2) After the tube was purged with hydrogen, the vent valve was closed.

(3) The working electrode containing hydrogen was then made anodic at 200-mv constant voltage until the current density decreased to 5 ma/cm^2.

(4) When the current density had decreased to 5 ma/cm^2, the current was held constant, and the change in anode potential versus the reference electrode was recorded.

(5) When the anode potential had increased to 300 mv, the valve was opened, admitting either hydrogen or methane gas to the working electrode.

(6) If the anode potential at the constant 5 ma/cm^2 current drain increased to 800 mv, the experiment was ended. Otherwise, the experiment was continued for a 20-min period.

Figure 6 summarizes the essential results of the five experimental runs (performed in alphabetical order). The as-received Pd-25Ag tube, activated but otherwise untreated (Experiment A), did not continue to polarize after hydrogen was introduced, whereas the same tube anodically polarized to 800 mv when either dry or moist methane (saturated with water vapor at room temperature) was introduced (Experiments B and C). Similar results were obtained when the inside (gas-phase side) of the Pd-25Ag anode contained a palladized coating (Experiments D and E).

The results with hydrogen clearly indicated that the gas-phase side of the tube was sufficiently active to support an anodic current density of at least 5 ma/cm^2 at anodic potentials of less than 50 mv versus the reference electrode. The results with methane indicated that there was an insufficient rate of methane decomposition to hydrogen at 200 C to support an anodic drain of 5 ma/cm^2 (nor even 1 ma/cm^2 according to additional data not shown on Figure 6).

High-Temperature Experiments. These experiments were performed to determine whether methane decomposition at practical rates could be accomplished within a Pd-25Ag tube anode at temperatures higher than 200 C but lower than the temperature of about 1200 C normally considered for thermal cracking. The experiments were directed toward determining the feasibility of conceptual System B of Figure 4. As shown in Figure 4, a separate Sabatier reactor would be required that operated at about 200 C and

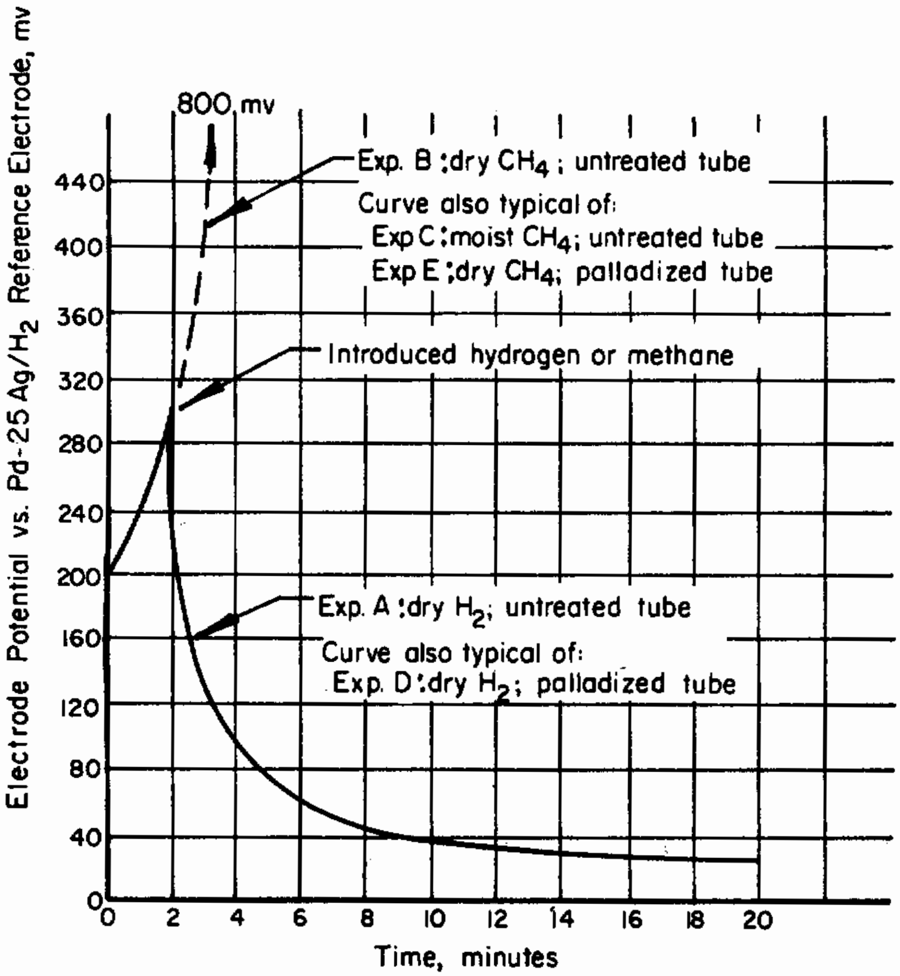

FIGURE 6. ANODIC POLARIZATION CURVES AT 5 MA/CM^2 AND 200 C FOR Pd-25Ag WITH HYDROGEN AND METHANE FEED

supplied with pure hydrogen recovered in the electrolysis cell at higher temperatures. One can conceive of an electrolysis cell with Pd-25Ag electrodes (hydrogen-concentration cell) operating at temperatures above 250 C with a caustic electrolyte, provided a suitable cell-construction material can be found to replace Teflon.

The experimental apparatus was similar to that shown in Figure 5, except that inside the Pd-25Ag tube (working electrode) there was a platinum resistance wire heater for locally heating the methane to the desired temperature. A separate d-c electrical circuit was provided to heat the platinum wire. Platinum-wire temperature was estimated from the electrical resistance (calculated from voltage and current used to heat the wire) and was compared to handbook data on specific resistance of platinum versus temperature.

Figure 7 shows the results obtained in two experiments. In the first experiment (Experiment A), with platinum wire but no asbestos, there was insufficient methane cracking even at 1000 C to provide hydrogen to support a current drain of 1 ma/cm^2 without the anode polarizing. In the second experiment (Experiment B), with asbestos packed around the platinum wire, the results were improved. A current drain of 1 ma/cm^2 (it possibly could have been higher) was supported with decreasing polarization at an estimated temperature of 650 C. During the 3-hr run, the average methane-consumption rate was within 10 percent of the theoretical rate to provide hydrogen for the 20-ma drain. After ending the run, an inspection of the tube contents showed evidence of carbon deposition on the asbestos and wire.

Because of the relatively large wattage (or heat) supplied to the wire, the Pd-25Ag tube anode was probably at much higher temperature than the bulk electrolyte temperature of 175 to 200 C. Thus, the low anode polarization in these experiments probably reflects the increased temperature of the anode. The steady-state concentration of hydrogen produced by methane cracking at these temperatures may not have been more than 1 percent. Subsequent experiments on catalytic cracking of methane with asbestos, reported later, showed essentially no methane decomposition at 640 C. Although the experimental data presented in Figure 7 show that the addition of asbestos had a beneficial effect, the exact mechanisms of the action are not clear.

From the limited experiments performed, there was evidence that an integral cracker with a "hot wire" might be feasible at temperatures below 700 C. However, this approach was not pursued, because the initial results did not appear sufficiently impressive in comparison to the anticipated problems of electrolysis-cell design and carbon removal from the inside of Pd-25Ag tubes.

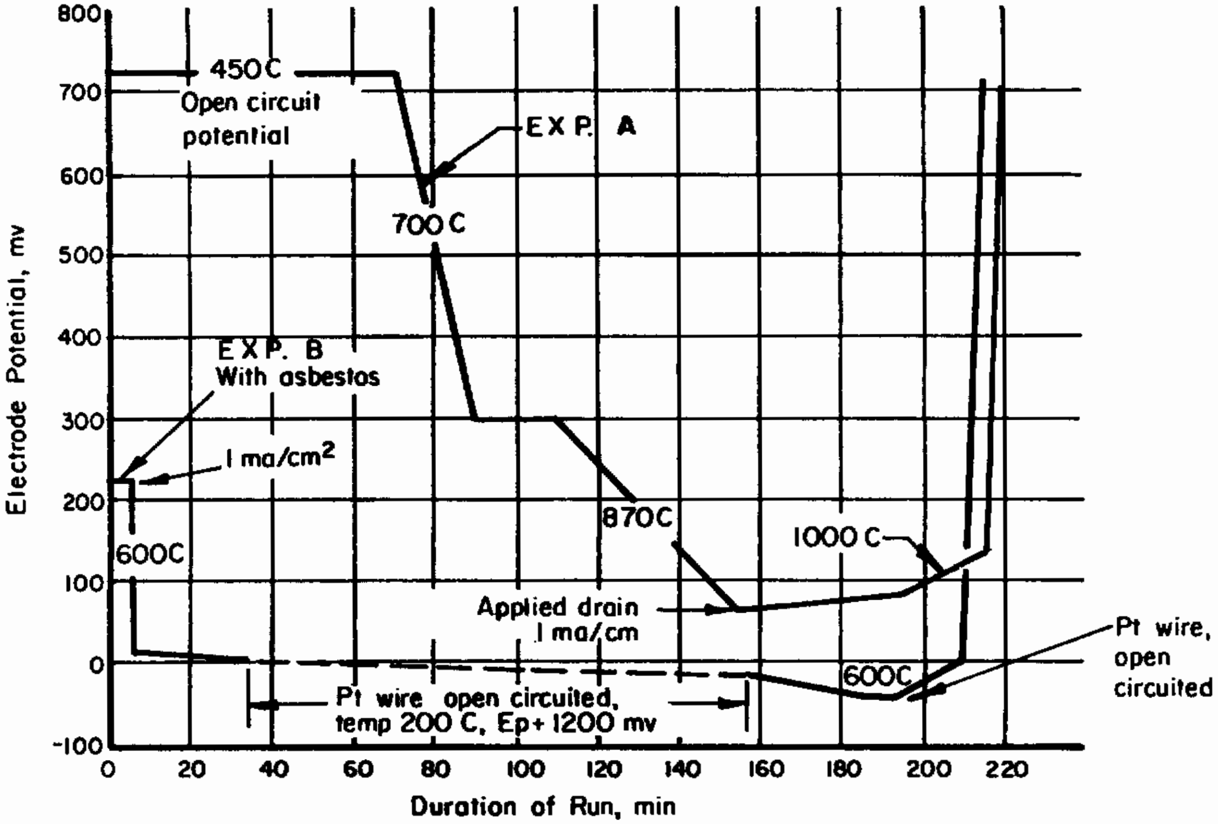

FIGURE 7. DECOMPOSITION OF METHANE INSIDE A Pd-25Ag ANODE AT ELEVATED TEMPERATURES

Separate Methane Cracker

Noncyclic System. These experiments were performed to determine whether conceptual System C shown in Figure 4 was feasible. The concept involved methane cracking at elevated temperatures (500 to 1000 C), separation of hydrogen from unreacted methane by gas-phase diffusion through Pd-25Ag membrane at the cracker operating temperature, and cooling the pure hydrogen to 200 C for feed to an anodic Pd-25Ag tube in the electrolysis cell. The experimental work was directed to a determination of the combination of hydrogen-partial-pressure difference and temperature required for permeation of hydrogen at the desired rate, and whether the low downstream hydrogen partial-pressure requirements could be maintained by Pd-25Ag tube made anodic in electrolyte at 200 C.

Figure 8 illustrates the experimental setup. In the first experiment, the Pd-25Ag tube, labeled the working electrode, was made cathodic to generate pure hydrogen for permeation of the Pd-25Ag diffuser tube in the cracker, which was maintained at 500 C. The hydrogen effluent from the diffuser tube was collected at atmospheric pressure. No significant gas-phase diffusion was noted until the differential pressure was about 0.07 atm. At 0.2 atm differential pressure, the hydrogen-permeation rate corresponded to about 32 ma/cm^2, based on the Pd-25Ag diffuser-tube area.

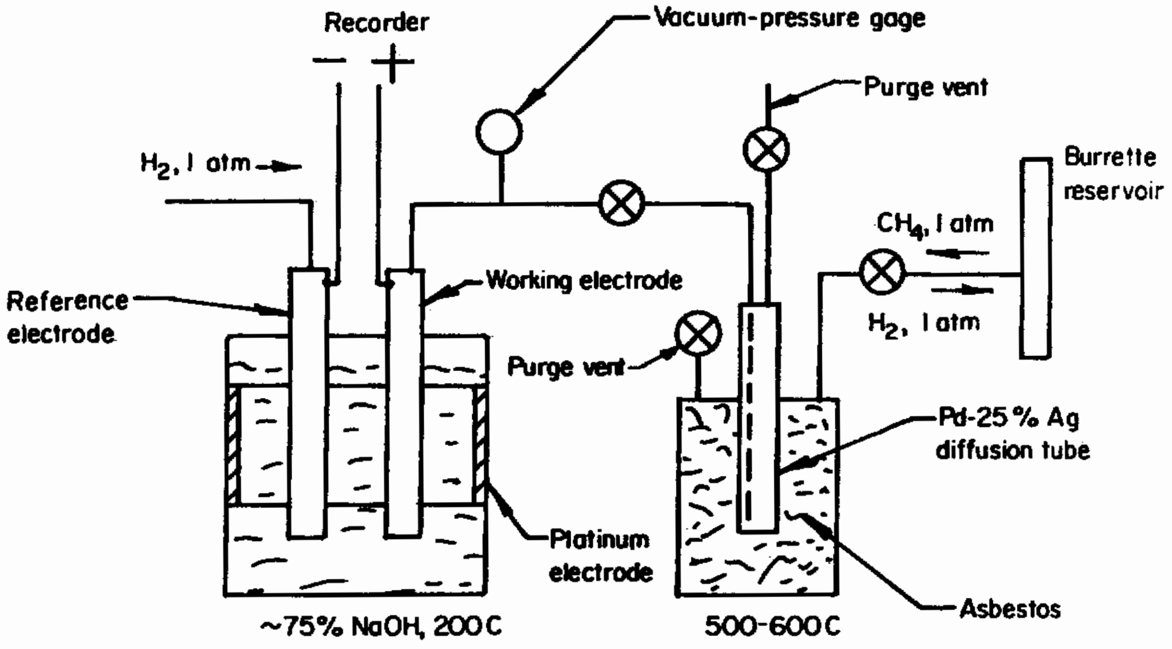

FIGURE 8. SCHEMATIC OF EXPERIMENTAL APPARATUS FOR STUDY OF A NONCYCLIC METHANE-CRACKING SYSTEM

In the second experiment, the Pd-25Ag tube in the electrolysis cell at 200 C was cathodically charged and purged with hydrogen for 2 hr. The vent valve was closed and the tube was drained anodically at 32 ma/cm^2 while the vacuum-pressure gage and the anodic potential versus the reference electrode was observed:

Anode Potential Versus Reference, volt	H_2 Pressure, atm
+0.07	1
+0.2	0.75
+0.8 (no O_2 evolution)	0.5
0.8 (O_2 evolution for 5 min)	0.47

In the third experiment, the above two systems were combined. Asbestos was used as a possible catalyst in the methane cracker. After purging the cracker unit with methane (upstream side) and hydrogen (downstream side), a run was made with a temperature of 600 C at the cracker and 200 C in the electrolysis cell. A 1-atm total pressure on the upstream side was maintained with the methane feed. A cell voltage of 1.2 volts was maintained between the Pd-25Ag tube anode and the platinum cathode.

At the start of the run, a large drain current was obtained from residual hydrogen left in the system and the anode tube. Within a few minutes, the downstream hydrogen pressure decreased to a steady-state value of 0.5 atm., which was maintained for the next 30 min. During the run, no methane consumption was indicated by any significant change in the burette volume. The reaction rate for the cracking reaction was considered too slow at these temperatures with asbestos as the catalyst. Later results (discussed in another section) showed that asbestos was a poor catalyst compared to others investigated, and that little or no cracking of methane could be expected at 600 C.

After the 30-min period, an attempt was made to increase the reaction rate by increasing the cracker temperature. However, the heaters burned out and the run was subsequently ended.

The third experiment was indefinitive in demonstrating the feasibility of the system, because the methane-cracking reaction was inadequate with just asbestos at 600 C. Subsequent experiments were directed toward finding suitable catalysts for methane cracking. The results reported in a later section and summarized in Figure 2 show that a catalyst such as 10 percent Pd on asbestos or steel wool would have provided about 45 percent conversion of methane to hydrogen at 840 C. The 45 percent conversion would correspond to a hydrogen partial pressure of 0.62 atm, as shown in Figure 9. At 840 C, the partial pressure required for gas-phase permeation of hydrogen equivalent to 32 ma/cm^2 would be less than the 0.2 atm differential pressure previously shown to be sufficient at 500 C. It seems probable then that the system would operate with an anodic potential of less than 0.5 volt versus the reference electrode (or below the oxygen-evolution potential). Further study of this concept was not pursued until additional data were obtained on the alternate cyclic system (discussed next) for comparison.

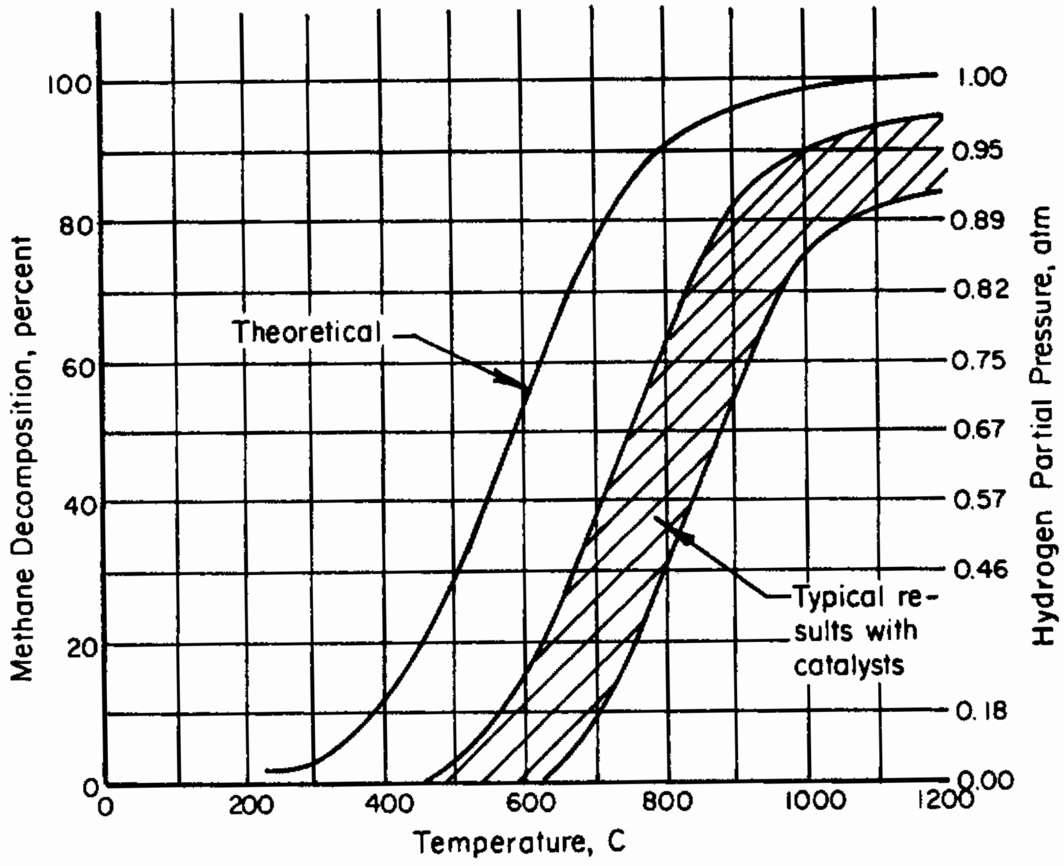

FIGURE 9. HYDROGEN PARTIAL PRESSURE FOR CATALYTIC DECOMPOSITION OF METHANE AT 1-ATMOSPHERE PRESSURE

Cyclic System. Concept D shown in Figure 4 was studied extensively. The experiments relating to a separate methane cracker are discussed later in the section on "Catalytic Methane Cracking". The experiments relating to removal of hydrogen from methane-cracking products and applicable to a recycle of unreacted methane are discussed in the section on "Hydrogen Stripper". One advantage of the cyclic concept that prompted further study was the possibility that with about 75 percent decomposition of methane, the unreacted methane could be discarded after separation of hydrogen and recycle could be eliminated. The advantages of a one-pass oxygen-recovery system with no gas recycle over the Bosch system would have to be weighed against the added energy requirements for operation of the methane cracker (above 700 C but possibly below about 1000 C).

Within the same concept, a cyclic system can be considered in which the thermal or catalytic cracking of methane to carbon is replaced by another methane-dissociation method, such as the use of a microwave plasma.

Use of a Microwave Plasma for Decomposition of Methane

An alternative to the thermal decomposition of methane to carbon and hydrogen for the purpose of hydrogen recovery would be to convert the methane to hydrogen and a hydrocarbon. If this hydrocarbon had a H/C ratio of unity or less, as acetylene (C_2H_2) does, it could provide alternative routes for the removal (or utilization) of carbon. One alternative would be to discard the acetylene gas, since it is a compound of carbon that is easily handled. This amount of hydrogen loss may not hamper the hydrogen balance necessary for the oxygen-recovery process*. The other alternative would be to recover the remaining hydrogen by the decomposition of acetylene in another section of the methane loop. This could be done easily, since the decomposition of acetylene is exothermic. The formation of acetylene from methane might also be compatible with future mission systems in which food regeneration will be necessary, since acetylene is an intermediate in many organic syntheses.

When microwave-coupled plasmas were used in the past to dissociate methane, acetylene was the principal gaseous product. However, the results of these experiments were ambiguous, especially with respect to side-product formation. The present experimental work was performed to determine the behavior of a methane plasma in a dynamic system and to determine whether acetylene alone can be formed from a microwave-coupled plasma of methane.

The microwave equipment used in these experiments consisted of a microwave power source and a magnetron capable of generating frequencies from 2350 to 3575 Mc/sec. All the present experiments were performed at 2450 Mc/sec. The output of the magnetron ranges from 50 to 1000 watts. The experimental cavity consisted of a section of S-band rectangular waveguide through which a fused-quartz tube could be oriented in the E-plane by means of a hole through the widest face. The fused-quartz reactor tube was part of an all-glass vacuum- and gas-handling system. The methane (Matheson cp grade) was metered into the system directly from the tank by means of a ratiometer and suitable valving. The pressure in the reactor tube was 10 to 20 mm Hg. The volatile products were condensed at -196 C and then transferred to sample balls for analysis (i.e., all gases except hydrogen). The product gases from the plasma were analyzed in an Aerograph Model 202 gas chromatograph, using a silica-gel column heated to 150 C.

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*As shown in Figure 12, which appears later in the report, an integrated system based on 1 mol O_2 can discard 0.6 mol C + 0.2 mol CH_4, which is equivalent to 0.4 mol C_2H_2.

At a preselected methane flow rate, the microwave power was increased until the plasma was initiated. The plasma was initiated by sparking the gas with a Telso coil.

The results of three experiments are summarized in Table I. Under three sets of conditions, three types of plasma behavior were observed. The intensity of the plasma varied with the power, ranging from a barely discernable lavender plasma at 250 watts to a very intense blue plasma at 570 watts. The nature of the products also appeared to depend upon the incident microwave power. When just-sufficient power to sustain the plasma was used (250 watts), only gaseous products were formed. No polymeric residues formed on the walls of the reactor, which remained cool to the touch. The product gas consisted mostly of methane, but some acetylene and ethane formed. In the same geometry, but using 430-watts incident power, amber-colored polymeric residues formed on the hot walls of the silica tube on the downstream side of the plasma and condensed in the cold traps. The polymeric residue has been reported to have a H/C ratio of 1.5. The volatile component from Experiment II was mostly acetylene.

In a small-diameter tube (Experiment III) with a power input of 570 watts, considerable decomposition to carbon occurred. The carbon deposit coupled to the microwave field and was heated to incandescence. The gaseous products were not anlyzed in this case. The hot carbon effectively quenched a major portion of the plasma.

The preceding exploratory experiments indicated that, under suitable conditions, methane can be converted principally to acetylene in a microwave-coupled plasma. This can be done at power levels just great enough to sustain the plasma. Greater power will increase the amount of acetylene formation, but it will also cause the formation of polymeric hydrocarbons. If the wall temperature is too high, carbon formation will occur. With the proper selection of power level, linear gas velocity, gas pressure, and wall temperature, along with the use of resonant cavities for efficient power coupling, high conversions of methane to acetylene appear possible. The effect of the microwave frequency on the decomposition of methane in a plasma would require further study.

Catalytic Methane Cracking

Figure 2 summarized the results of methane-cracking experiments with various catalysts at several temperatures in terms of percent methane conversion.

TABLE I. THE DISSOCIATION OF METHANE IN A MICROWAVE PLASMA

Experiment	Tube ID, mm	Input Power, watt	Time, min	CH_4 Flow, g/min(a)	Gaseous Product(b) and Its Concentration, vol percent	Remarks
I	25	250	30	11×10^{-2}	C_2H_2, 9.2 C_2H_6, 10	Wall temperature = ~35 C; no polymeric residue; no carbon formation; no liquid products
II	25	430	15	11×10^{-2}	C_2H_2, 78 C_2H_6, 12 CH_4, 10	Wall temperature >50 C; polymeric deposit downstream from plasma; no carbon formation; liquid products formed
III	7	570	20	7.3×10^{-2}	No analysis	Polymeric deposit formed and then turned to carbon; carbon heated to incandescence; temperature about 850-950 C; plasma only above hot carbon

(a) A methane flow of 25×10^{-2} g/min would correspond to a 1-man system.

(b) Collected by condensation at -196 C; does not include hydrogen formed.

Experimental Apparatus

In most of the cracking experiments, methane was passed through a heated quartz tube. The tube was approximately 3.5-mm ID and 5.5-mm OD. A portion of the tube was heated by means of a ceramic cylindrical heating element through which the tube was passed. The heated portion of the tube was approximately 8-cm long. Temperature measurements were made with a thermocouple attached to the outside of the quartz tube at approximately the center of the heated zone. In experiments in which the tube was packed with various catalysts, the catalysts usually did not fill all of this heated zone. In several of the experiments, research-grade methane was fed to the cracking unit; in the remainder of them, the product stream from the methanation unit was fed directly to the cracker. The products were analyzed with a gas chromatograph. In experiments in which the products were fed to the hydrogen stripper, the hydrogen removal (indicated by electrolysis current) provided an indication of methane conversion. Figure 1 was a schematic of the experimental apparatus.

Asbestos Catalyst

Purified asbestos fibers were packed into a section of the quartz tube. The asbestos occupied a volume of approximately 0.4 cm^3. The research-grade methane flow rate was 0.75 cm^3/min, corresponding to a superficial space velocity of 112 hr^{-1}. At a temperature of 640 C, there was no evidence of cracking of the methane.

Five Percent Palladium-on-Carbon Catalyst

Approximately 0.4 cm^3 of 5 percent palladium-on-carbon catalyst was packed into a section of the quartz tube. Research-grade methane was passed into the tube at a flow rate of 0.75 cm^3/min or a space velocity of 112 hr^{-1}. At a temperature of 665 C, about 25 percent of the methane was decomposed to hydrogen and carbon. Also present in the product stream were a small amount of CO_2 (less than 1 percent) and CO (approximately 3 percent). The CO is assumed to have come from the steam-reforming reaction: $CH_4 + H_2O \rightarrow CO + 3H_2$. Although the research-grade methane was free of water vapor, it undoubtedly picked up moisture by desorption from the walls of the connecting tubes. A water-sealed burette and leveling bulb for measuring the methane flow rate was provided between the methane cylinder and the cracker. Water vapor could diffuse from this reservoir into the stream of flowing methane. Several glass connectors, which could have desorbed water were also incorporated. The CO_2 present in the product stream could either have come from desorption from the glass surfaces or from decomposition of the CO in the cracker.

When the temperature was lowered to 455 C, there was no evidence of cracking of the methane. However, CO and hydrogen were still present in the exit gases, the hydrogen corresponding roughly to the amount that would have been expected from the reforming reaction.

Another experiment with the same catalyst was conducted later in the experimental program. A larger quartz tube (5-mm ID, 7-mm OD) was used, and a small amount of 5 percent palladium-on-carbon catalyst was sprinkled along the bottom of the tube for an 8-cm length, which corresponded to the heating zone. Based on a 0.9-cm^3/min flow of Sabatier product gases to the cracker, the space velocity was 36 hr^{-1}. The following results were obtained:

Cracker Temperature, C	Operational Time, hr	Methane Decomposition, percent
580	18	10
692	7	20
760	24	22

Steel-Wool Catalyst

Because iron is reported to be a good catalyst for the Bosch reaction, its catalytic activity for direct methane cracking was investigated. For this experiment, 0.2 gram of steel wool was packed into a 3.5-cm-long section of the quartz tube. The internal volume occupied by the steel wool was 0.34 cm^3. At temperatures up to 800 C, no cracking of the methane was evident. The presence of hydrogen in the product stream was detected at about 500 C, indicating the start of the reforming reaction. Carbon monoxide appeared in the product stream at a temperature of about 600 C. The presence of hydrogen from the reforming reactions made it difficult to determine the exact temperature at which the cracking reactions became significant. As the temperature was raised, the concentration of hydrogen rose rather slowly, as did the CO concentration. At 866 C, the superficial space velocity of 392 hr^{-1}, the hydrogen concentration in the product stream was approximately 10 percent.

Between 860 and 930 C, the hydrogen concentration in the products stream jumped sharply. At 941 C and at a superficial space velocity of 286 hr^{-1}, the amount of methane decomposed was 38 percent. The product analysis (in percent) was as follows:

Methane	37.6
Nitrogen	1.3
Oxygen	0.25
Carbon monoxide	1.5
Hydrogen	59.4

The sample was not analyzed for ethane or ethylene.

The total running time for this experiment was 13.5 hr during approximately 7 hr of which temperatures were sufficiently high for cracking to occur. At the end of the experiment, the pressure drop through the steel wool was rising, indicating that the interstices of the packing were being filled with carbon. Whereas at the start of the experiment approximately 0.5 cm of water pressure was sufficient to give a methane flow rate of about 1.8 cm^3/min, at the end of the run a pressure of about 7 to 8 cm of water was required for the same flow rate.

Note that near the end of the experiment, cracking of methane occurred at lower temperatures than at the start of the experiment. As the steel wool was being heated at the beginning of the experiment, the first indications of cracking of the methane appeared at about 900 C, and a conversion of 38 percent methane was achieved at 941 C. Near the end of the experiment, however, approximately 45 percent conversion was taking place at a temperature of 840 C, and at 941 C the conversion reached 69 percent. Therefore, the carbon that is deposited during the cracking reaction appears to promote the reaction. Possibly, iron carbide is formed on the surface of the packing, which is a more effective catalyst than the iron itself; this has been found to be so for the use of iron catalyst in the Bosch reaction.

When the packing was removed from the quartz tube and examined, the deposited material appeared to be granular in texture, but not powdery.

Carbon Catalyst

Since the 5 percent palladium-on-carbon catalyst had exhibited catalytic activity in methane cracking, it seemed advisable to investigate the effect of carbon alone to determine whether palladium was a necessary ingredient in the catalyst. Even if carbon were not a catalyst for the cracking reaction, a mathematical analysis of the heat effects in the proposed system indicated the posibility of operating the cracker at temperatures as high as 1000 C while retaining advantages over the Bosch system.

A small amount of activated-carbon powder (the kind used for decolorizing solutions) was placed inside the quartz tube. The carbon powder did not fill the tube but lay along the bottom of the inside of the tube. Only about 10 percent of the inner surface of the quartz tube was covered with the carbon powder.

While this experiment was being conducted, the continuous-methanation experiment with nickel catalyst inside a Pd-25Ag cathode tube was underway, so that the products of the Sabatier reaction (after the water condenser) could be fed directly into the quartz tube for cracking. Thus, the feed to the cracker had the following approximate composition: CO_2, less than 1 percent; water vapor, approximately 3 percent (saturated at room temperature); hydrogen, approximately 15 percent; ethane, a trace (estimated at 50 ppm); methane, 82 percent. This mixture was fed into the cracker at approximately 1.1 cm^3/min. Based on a 6-cm effective length of heated section of the quartz tube, this corresponds to a superficial space velocity of 110 hr^{-1}. The tube was heated gradually up to a maximum temperature of 1184 C.

As the temperature was raised to 754 C, the concentration of hydrogen in the effluent increased slightly. Also, a small amount of CO appeared in the outlet. As the temperature was increased to 851 C, the concentrations of both hydrogen and CO increased slightly, but the CO concentration remained below 1 percent. A trace of ethylene was also detected in the effluent. As the temperature was raised to 964 C, the hydrogen concentration continued to increase, along with the concentration of CO. The CO_2 concentration decreased sharply. The indication is that the increase in hydrogen concentration can be accounted for on the basis of the steam-reforming reaction of methane ($CH_4 + H_2O \rightarrow CO + 3H_2$).

The run was continued during the night, and the effluent from the cracker (at 971 C) showed the following concentration (in percent) the next morning:

Methane	69.5
Carbon dioxide	0.58
Carbon monoxide	4.78
Ethylene	0.082
Hydrogen	25 (estimated)

Also detected in the gas stream were a trace of nitrogen and a trace of oxygen.

Over a period of about 6 hr, the temperature was raised stepwise to 1184 C. At this temperature, the nichrome heating wire started to fail and burned out in a short time. As the temperature was raised, the CO_2 concentration fell to a trace, and the ethylene concentration continued to rise, up to about 1 percent. Hydrogen concentration also rose with temperature, indicating that cracking of the methane was taking place. Just before the heater burned out at 1184 C, the conversion of methane to carbon and hydrogen was estimated to be 34 percent.

Disassembly of the cracker disclosed that the carbon powder initially placed into the quartz tube had sintered into a rigid piece of carbon. Also, the surface of the quartz was covered by a thin layer of carbon, which appeared shiny through the quartz tube. This rigid carbon was removed from the quartz tube quite easily in one piece in the form of a cylindrical shell. Shiny carbon was formed over 6 cm of the tube. Approximately 1 cm on each side of this region, presumably where the temperature was lower, the deposited carbon had a sooty appearance.

Ten Percent Palladium-on-Asbestos Catalyst

In this experiment, a 2-cm length of 10 percent palladium-on-asbestos catalyst was packed inside a 3.5-mm ID quartz tube. The internal volume occupied by the catalyst was about 0.2 cm^3, so that with a gas flow of about 0.9 cm^3/min of Sabatier-reaction products, the superficial space velocity was about 270 hr^{-1}. The duration of the run was about 28 hr, during which time the temperature of the cracker was varied from 680 to 840 C. The run was ended when buildup of carbon in the cracker restricted the gas flow.

The percent methane decomposition obtained during the run at the temperatures investigated were:

Cracker Temperature, C	Operational Time, hr	Methane Decomposition, percent
680-700	24.5	7-8
840	2.5	45

Examination of the catalyst after the run showed that the carbon was intimately associated with the catalyst, and no powdered carbon could be detected when the catalyst was vigorously shaken in a glass vial.

Pd-25Ag-Foil Catalyst

In this investigation, a piece of Pd-25Ag foil 2-cm long, 0.6-cm wide, 0.0025-cm thick, and folded to reduce the width, was used as the cracking catalyst. Prior to installation in the cracker, the foil was activated by charging with hydrogen for 3 min at 500 ma/cm^2 in the caustic electrolyte, then discharged by heating to cherry red in a Bunsen-burner flame, and then charged with hydrogen again under the same conditions. The internal volume of the quartz tube occupied by the catalyst was about 0.2 cm^3, which corresponds to a space velocity of about 290 hr^{-1} with a 0.9-cm^3/min gas flow.

In testing, the cracker was operated at 845 C for a 25-hr period. The test was ended after this time due to gas restriction caused by carbon buildup in the quartz tube. During this period, about 40 percent of the methane in the Sabatier products entering the cracker was being decomposed to carbon and hydrogen.

Removal of the packing disclosed that the carbon had formed around the foil in hard chunks. Also, the foil was etched and appeared as if it were being consumed.

Pd-25Ag-Tube Catalyst

In this experiment, the cracker was modified to take a 6.4-cm-ID quartz tube, and a 5-cm length of 6.3-cm-OD Pd-25Ag tubing was installed inside to serve as the cracking catalyst. The tube was not activated as was the foil in the previous experiment. However, the tube was cleaned by soaking in the caustic electrolyte at 200 C for 24 hr.

One purpose of the experiment was to construct a cracker having a larger capacity for carbon and lower space velocity. With a gas flow of 0.9 cm^3/min to the cracker, the superficial space velocity was about 34 hr^{-1}. The test lasted 43 hr, during which time the cracker temperature was varied from 840 to 940 C. A summary of the results obtained are as follows:

Cracker Temperature, C	Operational Time, hr	Methane Decomposition, percent
840-845	20.5	None detected
875	2.5	2
935-940	20	12-14

In contrast to the above results, the Pd-25Ag foil, which was activated prior to use, showed about 40 percent decomposition at 845 C and a much higher space velocity. Apparently, the better cracking results obtained with the foil can be attributed to surface activation.

Hydrogen-Stripper-Cell Studies

Feasibility of Using Pd-25Ag Anodes

The studies of the hydrogen stripper were primarily concerned with performance of the Pd-25Ag anode operating on a low partial pressure of hydrogen contained in recycle gas to the methane cracker. Previous experiments on the noncyclic concept had shown that small anodic-current drains (1 to 5 ma/cm^3 at 200 C) could be supported with pure hydrogen at low partial pressure. Subsequent experiments were directed toward establishing the feasibility of stripping hydrogen from gas mixtures containing methane, CO_2, CO, and any other components that might be present.

Figure 10 shows the experimental system used in the preliminary experiments. A suitable constant-voltage source stable in the range of 0 to 500 mv was not available for the preliminary experiments, and manual adjustments of voltage were made to achieve the desired steady-state current corresponding to the hydrogen supplied by the gas stream. (Misleading transient currents are possible because of accumulation or depletion of hydrogen in the metal electrode.) During steady-state operation, the current drain was an accurate measure of hydrogen removed from the gas-feed stream (6.97 cm^3/min of H_2 (STP) per ampere).

Operation on Methane-Cracker Products. The first evaluation of the experimental hydrogen-stripper cell on methane-cracking products was made during an experimental run with steel-wool catalyst using a bottled methane-gas feed to the cracker of 1.25 cm^3/min. About 45 percent conversion of the methane was obtained in the cracker at 840 C, and the feed to the Pd-25Ag anode contained 62 percent hydrogen (plus 0.7 percent air and 0.7 percent CO). The cell voltage was maintained at 0.2 volt versus a platinum cathode (0.050 volt versus a Pd-25Ag/H_2 reference electrode), and the current was 157 ±3 ma (about 10 ma/cm^2 anodic current density). The exit gas from the stripper of 0.8 cm^3/min contained about 10 percent hydrogen (estimated from chromatographic analysis). The current corresponded to a removal of 1.09 cm^3/min of hydrogen in the stripper and provided a more accurate indication of percent cracking than could be obtained from chromatographic analysis of hydrogen after cracking.

At a higher cracker temperature of 941 C, there was 69 percent conversion of methane and a feed to the anode containing 81 percent hydrogen, which was stripped to about 10 percent hydrogen with a current drain of 250 ma (15 ma/cm^2) at a cell voltage of 0.2 volt versus a platinum cathode (0.030 volt versus a Pd-25Ag/H_2 reference electrode).

Subsequently, the same Pd-25Ag anode in the experimental hydrogen-stripper cell was used for a total of 120 operational hr on methane-cracking products. The latter period covered evaluation of the following catalysts for methane cracking: 10 percent palladium on asbestos, Pd-25Ag (activated strip), Pd-25Ag (tube), and 5 percent palladium on carbon. The feed to the methane cracker for the latter experiments was the products of the Sabatier/water-electrolysis unit after room-temperature condensation of water. (The integrated experimental system was shown schematically in Figure 1.) Thus, in containing a variety of gases, the gas mixture fed to the Pd-25Ag anode could be considered representative of methane-cracking products for an integrated system.

During the operational period of 120 hr, there was no evidence of poisoning of the gas-phase side of the Pd-25Ag anode. The hydrogen content of the feed gas ranged from about 15 percent (no methane cracking; excess hydrogen from Sabatier) to 60 percent (45 percent methane cracking). The anodic current density ranged from about 2 to 7 ma/cm^2, based on total area of the anode immersed in the electrolyte. The current density was limited primarily by the available hydrogen in the gas (i.e., for a feed of 1 cm^3/min of methane to the cracker, the maximum average anode current density possible with 100 percent conversion to hydrogen was 18 ma/cm^2). In general, if the anode potential was maintained at about 100 mv versus the Pd-25Ag/H_2 reference for a feed of 15 percent hydrogen, the

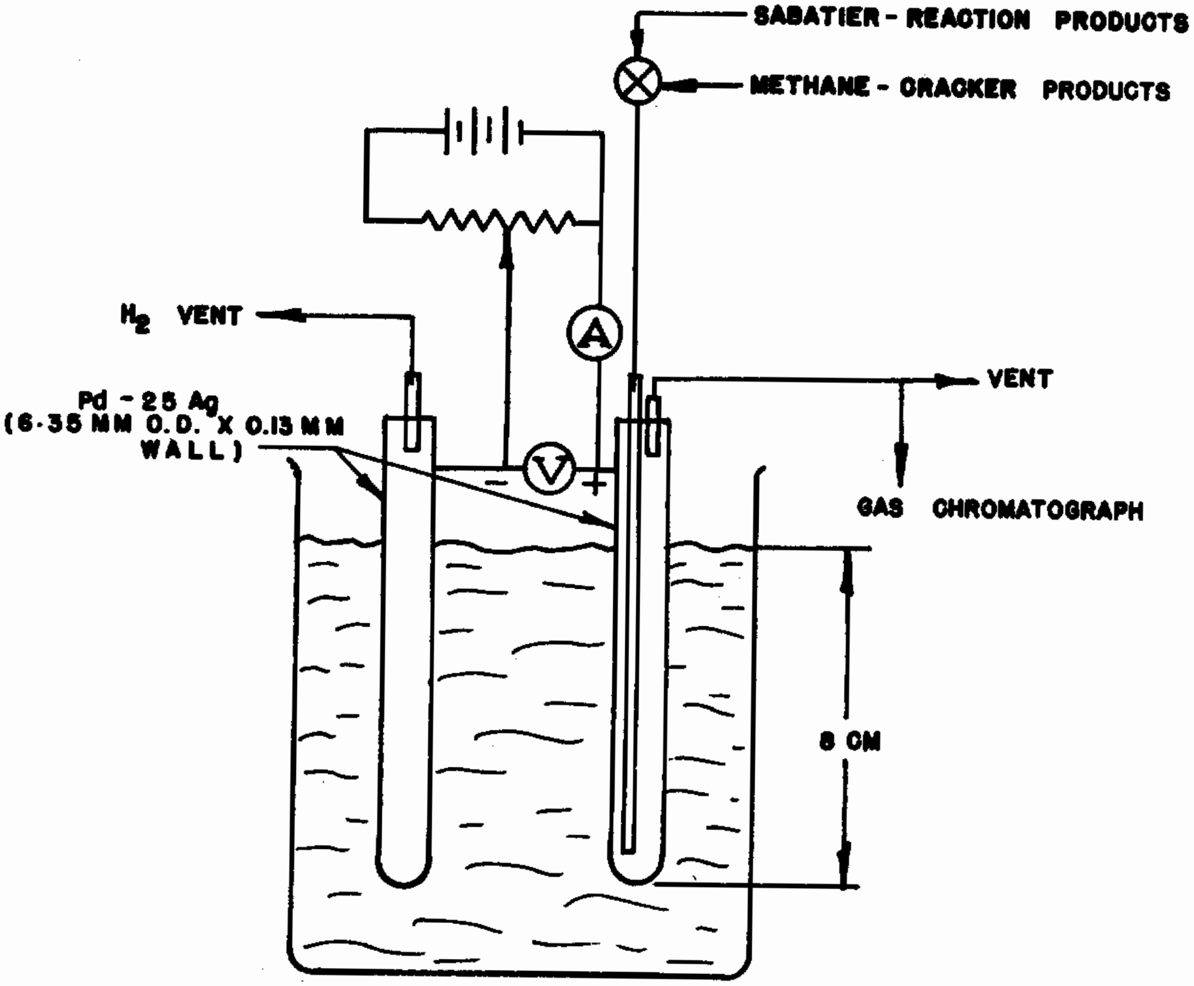

FIGURE 10. SCHEMATIC OF EXPERIMENTAL HYDROGEN-STRIPPER CELL

the exit gas from the stripper contained less than 1 percent hydrogen. At lower anode potential and higher concentration of hydrogen in the inlet gas, there was hydrogen in the stripper exit gas (i.e., 28 percent H_2 at 40 mv and 40 percent H_2 at 15 mv, for 6.3 ma/cm^2 drain). Higher anodic stripper current density might have been demonstrated with an increase in hydrogen supply (i.e., higher methane feed rate to cracker) or decrease in anode area. Fairly complete removal of hydrogen from the gas stream would be expected for anode potentials of 200 to 500 mv versus the Pd-25Ag/H_2 reference.

Operation on Sabatier Products. The experimental hydrogen-stripper cell was subsequently operated continuously for 360 hr on the products of the Sabatier/water-electrolysis unit after condensation of water at room temperature (methane-cracking unit bypassed). During this period there was no evidence of the Pd-25Ag anodes being poisoned by Sabatier products.

A typical composition of Sabatier products leaving the water condenser and fed to the Pd-25Ag anode of the experimental hydrogen-stripper cell is shown below for a representative operation of the integrated Sabatier/water-electrolysis cell at 200 to 210 C:

CO_2 feed (F)	0.90 cm^3/min (STP, dry)
H_2 supply (I_w)	0.535 ampere [3.725 cm^3/min (STP) for 100% H_2 transmission]
H_2/CO_2 ratio (R)	4.15
CO_2 conversion (E)	0.99

Products after water condenser:

CO_2	0.009	(0.8 percent)
H_2	0.175	(15.8 percent)
CH_4	0.888	(80.5 percent)
H_2O	0.032	(2.9 percent)
	1.104 cm^3/min (STP)	

In this product gas, the 15.8 percent hydrogen could be reduced to less than 1 percent by passage through the Pd-25Ag anode at a current of 0.024 ampere (1.5 ma/cm^2), which corresponds to hydrogen removal of 0.166 cm^3/min (STP). The latter current could be obtained at a cell voltage of less than 70 mv versus a Pd-25Ag cathode at the same current density. The average hydrogen partial pressure in the anode (entry to exit) was about 0.08 atm.

The experimental hydrogen stripper was found to be a useful analytical tool for measuring hydrogen in the gas stream. Gas-chromatographic analysis for hydrogen using a helium carrier gas was difficult and not very accurate at concentrations above about 5 percent. However, small concentrations of 1 percent or less could be determined to verify the efficiency of the hydrogen-stripper cell. As shown later in Figure 12, the integrated system includes a hydrogen-stripper cell for removal of excess hydrogen ahead of the methane cracker. One purpose is to increase the efficiency of the methane cracker by reducing the partial pressure of hydrogen at the inlet and allowing greater methane conversion to hydrogen per pass. However, a more important function of the hydrogen stripper operating on Sabatier products might be as an analytical device to provide a simple means means of continuous monitoring of the Sabatier/water-electrolysis unit.

Analytical Applications. The analytical applications of the hydrogen-stripper cell can be illustrated by the following equations, assuming the hydrogen leaving the hydrogen stripper is very small (less than 1 percent):

$$R = \frac{6.97\, I_w}{F} \tag{1}$$

$$I_s = I_w - \frac{4\, FE}{6.97} \tag{2}$$

$$F = \frac{6.97\, (I_w - I_s)}{4E} \tag{3}$$

$$E = \frac{6.97\, (I_w - I_s)}{4F} \tag{4}$$

$$R = \frac{4EI_w}{I_w - I_s} \tag{5}$$

where

I_w = current to water electrolysis cell (corresponds to hydrogen feed to Sabatier reactor for 100 percent cathodic hydrogen transmission), amperes

F = CO_2 feed rate cm^3/min (STP)

R = actual H_2/CO_2 ratio of feed to Sabatier reactor ($R = 4.00$ stoichiometric)

I_s = current in hydrogen-stripper cell, amperes

E = fraction of CO_2 converted to methane

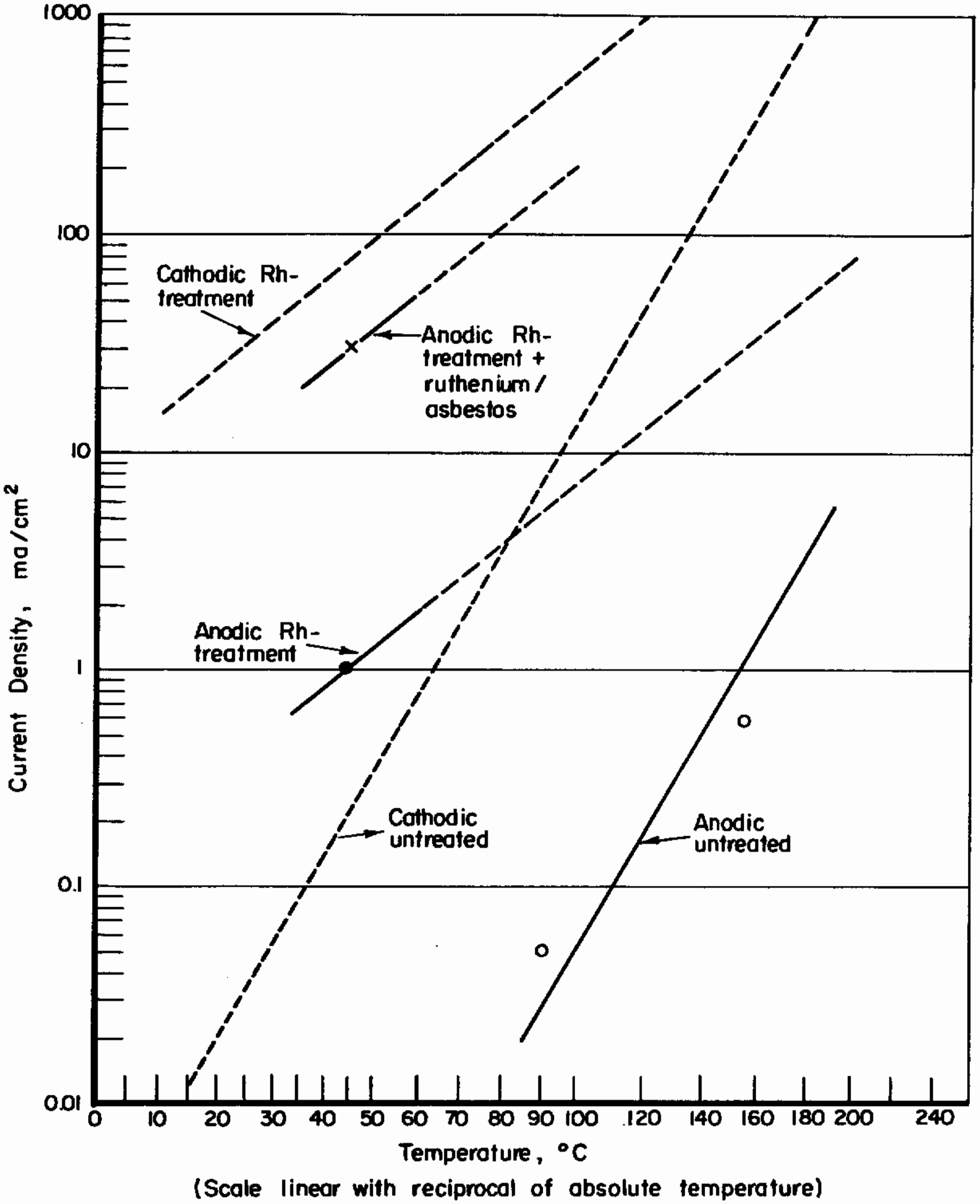

FIGURE 11. LIMITING CURRENT DENSITY AS A FUNCTION OF TEMPERATURE FOR ANODIC AND CATHODIC OPERATION OF Pd-25Ag ELECTRODES SHOWING THE EFFECT OF SURFACE TREATMENT

Equation (1) gives the H_2/CO_2 ratio (R) from the water-electrolysis-cell current (I_w) when the CO_2 feed rate is known accurately. For experimental studies using a gas chromatograph, the CO_2 conversion fraction (E) can be determined accurately by analysis of the product gas for CO_2 and $CH_4 \left(E = \frac{\text{mol } CO_2}{\text{mol } CH_4 + \text{mol } CO_2}\right)$. Thus, Equation (5) can be used to determine the H_2/CO_2 ratio (R) from the knowledge of CO_2 conversion (E) and the readings of electrolysis-cell current (I_w) and stripper-cell current (I_s). Also, the CO_2-feed rate (F) can be determined from Equation (3).

Perhaps the most practical use of the hydrogen-stripper cell for analysis is represented by Equation (4) because a means is provided of monitoring the Sabatier reaction without complex gas-analysis equipment. A CO_2-flow-measuring device with a remote-reading meter plus the two ammeters for I_w and I_s provide the necessary information for determining CO_2 conversion (E) from Equation (4) and H_2/CO_2 ratio from Equation (1). By suitable electrical circuitry, one could provide a single meter reading of CO_2 conversion and a single meter reading of H_2/CO_2 ratio.

Improvement of Anodic Performance of Pd-25Ag

Limiting Current Density for Untreated Pd-25Ag. A practical hydrogen-stripper-cell design for operation on products of the methane cracker requires a reasonably high electrode current density (at least 30 ma/cm^2) to provide optimum size and weight.

As shown in Figure 11, adequate cathodic current density [with 100 percent hydrogen transmission] can be obtained at 200 C using Pd-25Ag tubes activated by the procedure described on page 7. For similar activation, the limiting steady-state anode current density was expected to be too low even for hydrogen feed at 1 atm. For the same anode potential and temperature, the limiting anodic current density would be lower for hydrogen partial pressures below the 1 atm expected for the products from the methane-cracking step.

Figure 5 shows an experimental set-up similar to that used to study the anodic performance of Pd-25Ag anodes. The hydrogen gas supplied to the anode was pure (generated by diffusion through Pd-25Ag cathodes, collected and stored in burettes over dibutyl phthalate of low vapor pressure).

Preliminary experiments verified that untreated Pd-25Ag anodes would not support a high current density using hydrogen at 1-atm pressure and anode potentials of 0.5 mv versus a Pd-25Ag/H_2 (1 atm) reference electrode. The results of two experiments at 90 C and 155 C are indicated in Figure 11. The Pd-25Ag anode used in the latter experiments might not have been activated as well as possible. Straight-line extrapolation of the two data points to 200 C indicates a current density of about 2 ma/cm^2, which is a little lower than expected on the basis of prior data obtained with another Pd-25Ag anode that was used extensively in the experimental hydrogen-stripper cell at 200 C on methane-cracker and Sabatier products. (The mixed gases might improve anodic performance for the same hydrogen pressure.)

Rhodium Treatment. Much better anodic performance of Pd-25Ag appeared possible by special treatment of the gas-phase side based on studies of Pd-25Ag as a fuel-cell electrode. In this report, the term "treatment" is used to cover additions of some metal or oxide to either the gas-phase side or electrolyte side of the Pd-25Ag electrode. This "treatment" of the electrode is distinguished from "activation" of the electrode, which is primarily a surface-cleaning procedure and which might also involve forming a catalytic surface of palladium oxide.

Various surface treatments involving a variety of metals are known to influence the anodic performance of Pd-25Ag. Some treatments are proprietary and others have resulted from Government-sponsored research on fuel-cell applications. According to Reference 4, the use of 1 mg/cm^2 rhodium-black electrodeposited on both sides of Pd-25Ag foil (0.025-mm thick) supported an anodic current density of 250 ma/cm^2 for 336 hr at 55 C with pure hydrogen at 1 atm and an anode potential of 0.5 volt versus a hydrogen electrode in 5M KOH electrolyte. The latter current density was nearly five orders of magnitude higher than that observed with untreated tubes at 55 C in preliminary studies at Battelle.

For experiments at Battelle, Pd-25Ag tubes (6.3-mm (1/4-inch) OD x 0.13-mm wall) were prepared using the preferred procedure reported for rhodium treatment, which gave the above results (Reference 4):

(1) Anneal in argon in a sealed Vycor tube at 850 C for 2 hr

(2) Electrodeposit rhodium-black from an aqueous plating solution containing 0.01M $RhCl_3$ and adjusted to pH 1 with HCl

(3) Heat treat in air at 850 C for 2 hr and then at 700 C for 2 hr.

Three tubes that received a deposit of rhodium-black of 1 mg/cm^2 on the gas-phase side (inside) and a fourth tube that was plated on both sides were subsequently found to have cracked after heat treatment (a fine, hairline crack 3- to 6-mm long extending through the 0.13-mm wall of the tube at about 2 to 3 cm from the closed end). An embrittlement caused by diffusion of rhodium into the palladium-silver alloy during heat treatment is suspected. During electrolysis experiments at temperatures up to 150 C, electrolyte leaked into the tubes so that the poor results obtained in terms of anodic current density are indefinitive. In addition, the tube that had a rhodium-treatment on the electrolyte side appeared to have caused electrolyte contamination and poisoning of an untreated and previously active Pd-25Ag cathode in the same electrolyte.

One tube that received a rhodium-black deposit of 1 mg/cm^2 on the gas-phase side, but which was not subsequently heat treated did not exhibit cracks. Two tubes that received a rhodium-black deposit of only 0.1 to 0.2 mg/cm^2 did not crack after heat treatment and were used in experiments described below to determine anodic performance.

The first experiment with the rhodium-treated anode tube was performed at 135 to 140 C with an untreated Pd-25Ag tube as cathode. Both electrodes had a hydrogen supply interconnected to a burette reservoir to maintain atmospheric pressure. There was some evidence that the rhodium treatment improved anodic performance initially, but the effect could not be maintained. Anodic current densities as high as 125 ma/cm^2 at 0.1 volt were measured for the rhodium-treated tube, but polarization occurred and an anodic current density of 0.6 ma/cm^2 could not be maintained for more than 3 hr at 0.4 volt versus a reference electrode. The latter anodic performance was not as good as previously obtained with untreated tubes.

The second experiment with another rhodium-treated tube (0.1 to 0.2 mg/cm^2) was conducted at 44 C in an electrolyte of 40-wt-percent NaOH. The tube was used previously as a cathode for over 100 hr with improved cathodic performance attributable to the rhodium treatment (i.e., a maximum cathode current density of 80 ma/cm^2 for 100 percent hydrogen transmission, compared to an estimated 0.2 ma/cm^2 for an untreated cathode at the same temperature of 44 C). For this experiment, excess hydrogen generated by a Pd-25Ag cathode in another electrolysis cell was continually supplied to the anode, and the amount not consumed was collected in a burette for rate measurements.

Immediately prior to the experiment, the rhodium-treated tube was shown to be active for satisfactory hydrogen transmission at a cathodic current density of at least 37 ma/cm^2 at 44 C. The initial anodic current density of 33 ma/cm^2 at a cell voltage of 0.6 volt (versus a platinum cathode evolving hydrogen at nearly the same current density) could not be maintained, and over a weekend the anode polarized to oxygen evolution at the constant current density of 33 ma/cm^2. The current density was gradually reduced to 3 ma/cm^2 at a cell voltage 0.05 volt while recording the cell voltage. A sharp change in slope of the current-voltage curve at 22 ma/cm^2 suggested that a steady-state drain might be established. At a constant voltage of about 0.7 volt, the anodic current density was initially 22 ma/cm ma/cm^2, but polarized to 8 ma/cm^2 over the next 4 hr. About 40 hr later, a steady-state drain appeared to be established at an anodic current density of about 1 ma/cm^2 for a cell voltage of 0.69 volt at 44 C. Thus, the rhodium treatment appeared to offer an improvement in anodic performance (extrapolation indicated that 80 ma/cm^2 might be obtained at 200 C). However, the results were about two orders of magnitude lower than expected from reports in the literature(4) Possibly, the use of about one-tenth the weight of rhodium-black plus a 5-times-thicker Pd-25Ag were significant factors.

Rhodium Plus Ruthenium. Following the above experiment, the Pd-25Ag tube containing 0.1 to 0.2 mg/cm^2 of oxidized rhodium-black was packed with a mixture of 6-wt-percent ruthenium (325 mesh) on asbestos. The anodic performance began to improve with continuation of the experiment. The current density increased from 1 ma/cm^2 to 10 ma/cm^2, while the cell voltage decreased from 0.63 to 0.39 volt at 44 C. After 24 hr of operation, the current density was increased to 23 ma/cm^2 for 6 hr of satisfactory operation at a cell voltage of 0.58 volt and 46 C. For the next 100 hr, the anodic drain was maintained at 30 ma/cm^2, with a cell voltage of about 0.8 volt at temperatures from 46 C to 56 C.

The experiment was continued for 140 hr while the electrolyte temperature was increased toward 200 C to verify satisfactory anodic operation at temperatures required for the hydrogen-stripper unit in the integrated system. As the temperature was increased, the cell voltage decreased: 0.58 volt for 29 ma/cm^2 at 88 C and 0.14 volt for 39 ma/cm^2 at 180 C. While the temperature was being increased gradually, the NaOH concentration of the electrolyte was increased from 40 percent to about 75 percent (to reduce the vapor pressure). Most of the NaOH additions were made as an aqueous solution of 40 percent NaOH that had been preelectrolyzed and purified. However, the final addition to the electrolyte to increase the concentration to 85 percent NaOH was made as solid cp NaOH pellets, which caused electrolyte contamination and poisoning of the Pd-25Ag anode (the current density decreased to 0.5 ma/cm^2 at 0.5 volt and 181 C). Attempts to reactivate the tube were unsuccessful. While 95 to 100 percent hydrogen transmission could be obtained cathodically at 65 ma/cm^2, the tube polarized when made anodic.

A second Pd-25Ag tube which had been heat treated before and after receiving a rhodium-black deposit of 1 mg/cm^2, was filled with ruthenium on asbestos as in the previous test. During electrolysis at 180 C, this tube was found to be cracked as had been previous tubes which received the heavier rhodium-black deposit followed by heat treatment.

A third Pd-25Ag tube, which was annealed at 850 C in argon for 2 hr and had received a rhodium-black deposit of 1 mg/cm^2 on the gas-phase side but no subsequent heat treatment did not crack. The latter tube was filled with ruthenium on asbestos, as before. The mixture was prepared by adding 1 gram of asbestos (purified, acid-washed, medium fiber) and 0.071 gram of ruthenium metal powder (325 mesh) to a vial and hand shaking for 5 to 10 min. About 0.6 gram of the mixture containing 6.6-wt-percent ruthenium was packed loosely in the tube around the centrally located hydrogen-entry tube for a depth of about 8 cm. The anodic performance was satisfactory at 40 ma/cm^2 for 4 hr, and as the temperature was increased from 180 to 230 C, the cell voltage decreased from 0.21 to 0.16 volt. Problems with temperature control caused failure of the electrolyte container, and the run was terminated.

The preceding results indicated that adequate anodic performance could be obtained for operation of a hydrogen-stripper cell at 200 C and less than 0.2 volt for the desired design current density of at least 37 ma/cm^2. The experimental results indicated that the ruthenium-on-asbestos mixture was needed to obtain the desired anodic performance. Elimination of the subsequent heat treatment in the last experiment proved that oxidation of the rhodium-black and/or Pd-25Ag alloy tube was unnecessary. Possibly, the rhodium-black deposit is not required.

SECTION V

PRELIMINARY DESIGN ESTIMATES FOR INTEGRATED SYSTEM

Schematic Flow Diagram

Figure 12 is a flow diagram of a new integrated atmosphere-control system. The basis used for numerical simplicity in Figure 12 is 1 gram-mol of oxygen.* A metabolic ratio of 0.8 was assumed (varies with diet), so that 80 percent of the oxygen consumed appears as exhaled carbon dioxide and the other 20 percent as exhaled water vapor. This water vapor could be recovered from the cabin air and electrolyzed (in a water-vapor-electrolysis cell using phosphoric acid electrolyte as suggested in A in Figure 12) to make up the system oxygen deficit resulting from the metabolic ratio of 0.8 assumed. Carbon dioxide is removed from the air and concentrated at B. The remainder of Figure 12 relates to the integrated CO_2-reduction system.

The carbon dioxide feed is divided at C to provide the practical H_2/CO_2 ratio required for the Sabatier reaction in Pd-25Ag cathodes E and L. For example, the hydrogen feed from water electrolysis D is 1.6 mols H_2, and 0.4 mol of CO_2 fed to reactor E would provide the theoretical stoichiometric ratio of 4:1 for the Sabatier reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad .$$

In practice, an excess of hydrogen above the stoichiometric ratio is required to approach 100 percent conversion of CO_2 to methane. A ratio of 4.1:1 was assumed for Figure 12. Other ratios are possible by adjusting the CO_2 flow at C as shown below:

Division of CO_2 Flow at C, CO_2 to L/CO_2 to E	H_2/CO_2 Ratio for Sabatier Reaction in E	Excess H_2 to be Stripped at G
4.0/4.0	4.0/1	0
4.1/3.9	4.10/1	0.04
4.2/3.8	4.21/1	0.08
4.3/3.7	4.33/1	0.12
4.4/3.6	4.45/1	0.16

After condensation of product water at F and water separation from the gas stream (not shown in Figure 12), the gas stream from E passes to G, where the excess hydrogen for use in L is anodically stripped so that the gas stream leaving G is predominantly methane. Note that the sum of the

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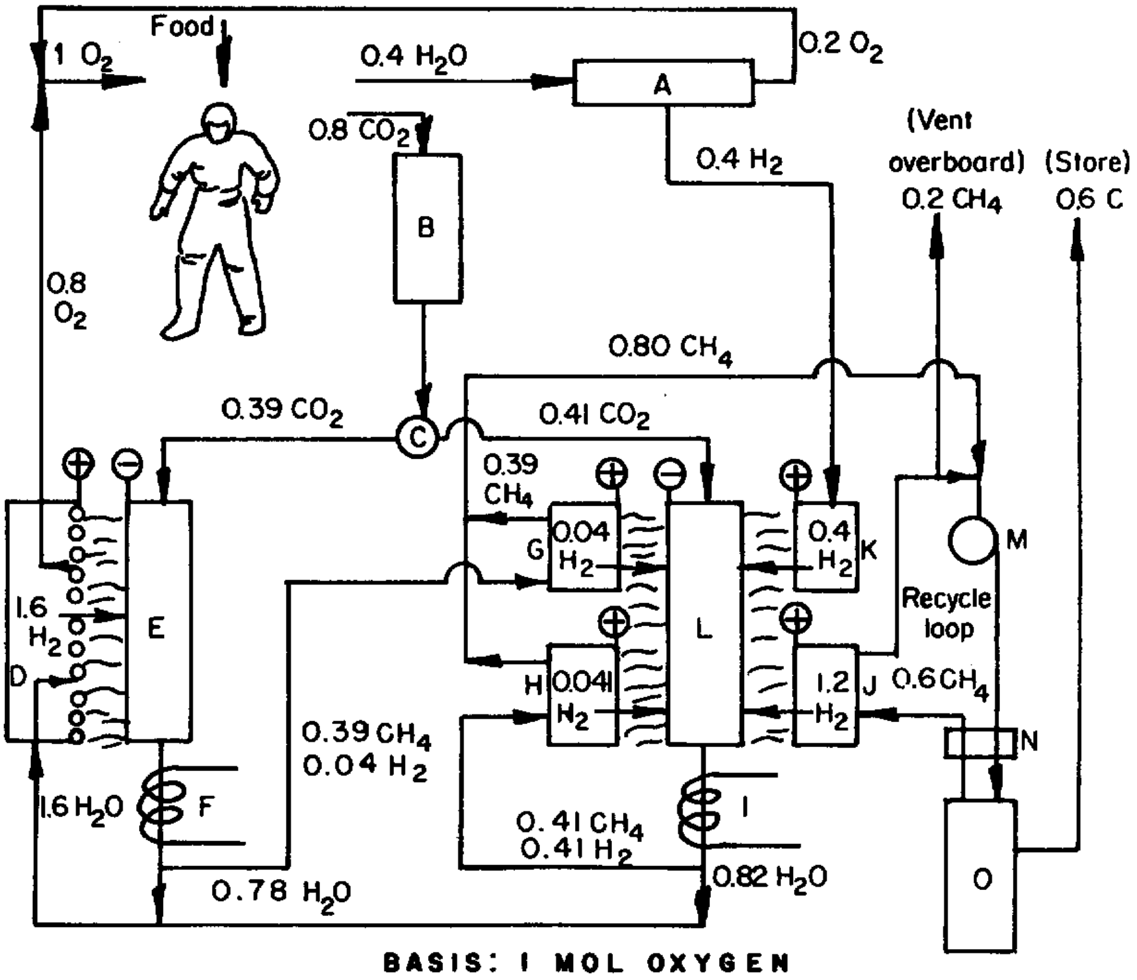
*Oxygen consumption per man is 28.4 gram-mol/day (2 lb/day).



A) Water-vapor electrolysis cell (cabin-air dehumidifier)
B) Carbon dioxide concentrator
C) Gas ratio control
D) Anodic water vapor electrolysis electrode
E, L) Pd-25Ag cathode/Sabatier reactor
G, H, J, K) Pd-25Ag anode hydrogen stripper
F, I) Water condenser
M) Recycle pump
N) Heat exchanger
O) Methane cracker

FIGURE 12. SCHEMATIC FLOW DIAGRAM OF NEW INTEGRATED SYSTEM FOR OXYGEN RECOVERY USING Pd-25Ag HYDROGEN-DIFFUSION ELECTRODES

hydrogen from anodic strippers J, K, and G ($1.2 + 0.4 + 0.04 = 1.64\ H_2$) provides the stoichiometric amount of hydrogen for the CO_2 fed to reactor L. The practical excess hydrogen for the Sabatier reaction in L is provided by anodic stripper H, which recycles the excess hydrogen from the product stream after condensation of water at I. For initial startup, the excess hydrogen above the stoichiometric amount required for the Sabatier reaction in L can be provided by anodic stripper J until the desired excess is being recycled by anodic stripper H.

Most of the hydrogen supplied to reactor L is obtained from methane cracking at 0 and anodic stripping of hydrogen at J. A recycle pump at M and heat exchanger at N are shown for the assumption of only partial decomposition of methane each pass. If 75 percent decomposition of methane ($0.8\ CH_4$ from G and H) per pass were obtained, there would be no need for recycle through the cracker, since the 25 percent unreacted methane ($0.2\ CH_4$) would be dumped after leaving anodic stripper J. Complete recovery of hydrogen from methane is not necessary when the deficit can be made up from another source, such as from Unit A in Figure 12.

For simplicity in Figure 12, 100 percent conversion of CO_2 was assumed. Practically, a conversion of 99 percent might be expected, and the unreacted hydrogen would be treated in the manner described previously for the excess hydrogen provided for practical H_2/CO_2 ratios. The untreated CO_2 and water left from incomplete condensation would be carried on to the cracker with the methane, where reactions might produce CO. However, the concentration cannot build up too high in the cracker recycle stream because of the continual dumping of a portion of the cracker recycle stream.

As shown in Figure 12, the products removed from the CO_2-reduction system are methane and carbon, which are equivalent in chemical content to acetylene:

$$0.2\ CH_4 + 0.6\ C = 0.4\ C_2H_2 \quad .$$

Disposal of products with a C/H_2 ratio of 1 results in a balanced system if the food supply has the same C/H_2 ratio. This is shown in the overall material balance for the system of Figure 12 for the assumed metabolic ratio of 0.8:

$$0.4\ C_2H_2 + O_2 = 0.4\ H_2O + 0.8\ CO_2 \quad .$$

Acetylene appears to be a desirable product of methane decomposition. (This is the basis of the exploratory studies of microwave decomposition of methane discussed earlier in this report.) Gaseous acetylene would provide a simpler product of methane decomposition for venting overboard to avoid carbon-handling problems. Also, acetylene might be a desirable intermediate for regeneration of food from waste products.

Figure 13 is a similar schematic flow diagram of an integrated Bosch system for comparison with Figure 12. A comparison of the flow diagrams and material balance of Figures 12 and 13 indicates some relative disadvantages of the Bosch system compared to the new system:

(1) The Bosch system produces one-third more elemental carbon to be handled and stored.

(2) The Bosch system vents excess hydrogen overboard (Figure 13) whereas the new system (Figure 12) vents some methane overboard, providing a continual purge of the CO_2-reduction system.

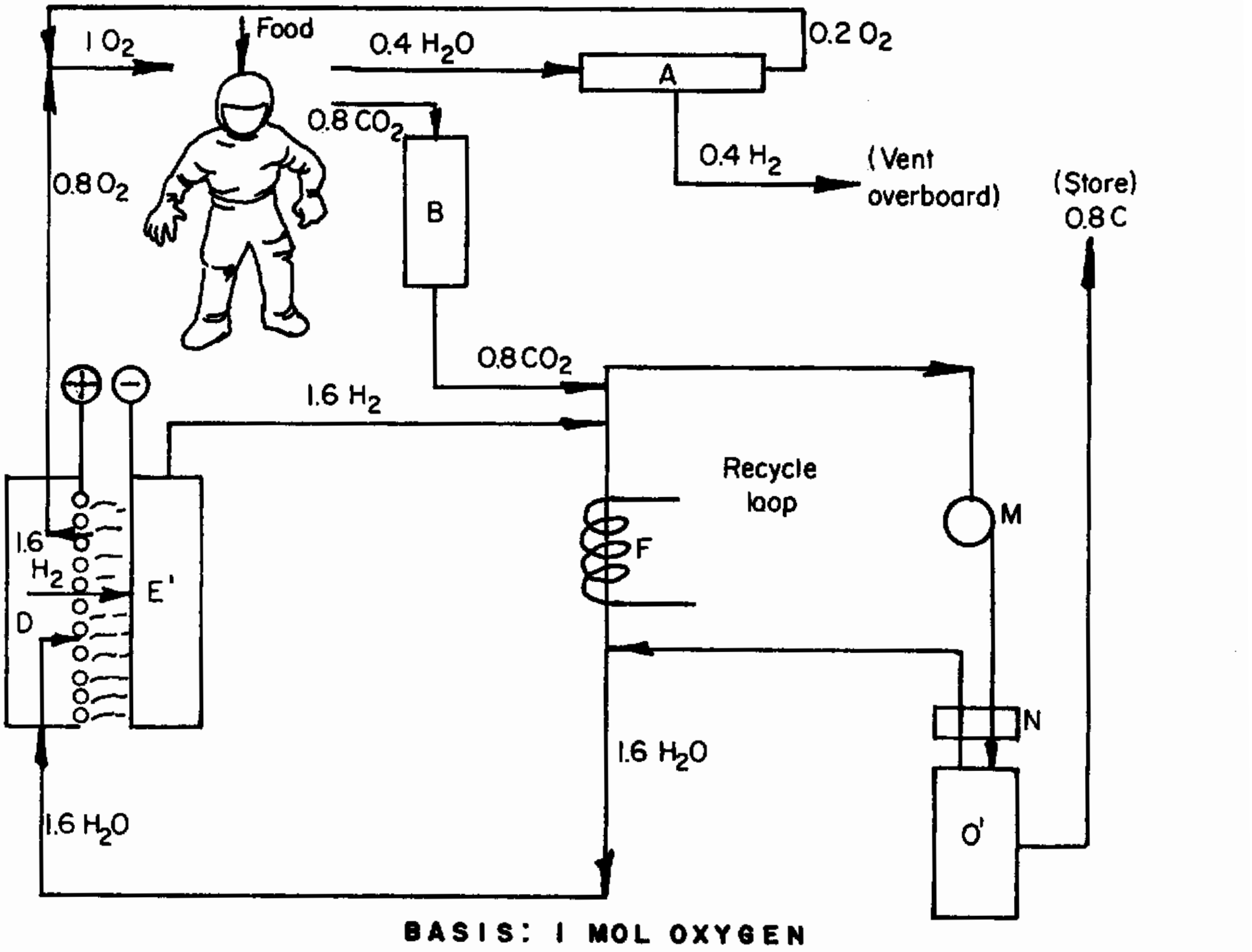
(3) The Bosch system (Figure 13) requires a recycle loop containing a water condenser and water separator. The new system (Figure 12) does not require a water condenser or separator in the recycle loop. Under conditions providing 75 percent methane cracking, no recycle loop would be required, and a single-pass CO_2-reduction system would be possible.

Preliminary estimates of hardware weight and power indicated that the new system and the Bosch system are practically equal. Table II shows the comparative estimates for a three-man system (1-year operation), emphasizing only the distinguishing differences. Weight and power estimates for all other components of the complete oxygen-recovery system are common to both systems.

TABLE II. COMPARATIVE ESTIMATES OF WEIGHT AND POWER FOR BOSCH SYSTEM AND NEW SYSTEM EXCLUDING COMMON COMPONENTS

Basis: O_2 production for three men for 1 year.

Item	Bosch System Weight, kg	Bosch System Power, watts	New System Weight, kg	New System Power, watts
Bosch reactor	32	355		
Methane-cracking reactor			24	288
Reactor heatup		103		77
Catalyst plus canister	71		64	
Sabatier catalyst			3	
H_2-stripper unit			10	64
Comparative totals	103	458	101	429



E') Pd-25Ag cathode only
O') Bosch reactor
Other symbols same as Figure 12

FIGURE 13. SCHEMATIC FLOW DIAGRAM OF INTEGRATED BOSCH SYSTEM FOR COMPARISON WITH FIGURE 12

The basis for the weight and power estimates was detailed calculations for the integrated Bosch system prepared on a concurrent study at Battelle. A batch-type operation was assumed with two Bosch reactors operating alternately on a 48-hour cycle for carbon removal and catalyst replacement. For the same operating temperature of 700 C and similar reactor design, the reactor for methane cracking would be smaller, with only 75 percent of the weight corresponding to the reduced amount of carbon to be handled in the methane cracker of the new system. The estimated power for the Bosch reactor corresponds to the net heat loss, taking into account the exothermic Bosch reaction, heat loss from insulated reactor, and sensible heat loss of recirculated gases. For the smaller methane cracker, the heat loss from the reactor would be 25 percent less, and the net heat loss took into account the smaller amount of gas recycled and the endothermic heat of reaction for methane cracking.

The average power for heatup of the reactor based on the 48-hour-cycle batch operation for 1 year would be 25 percent less for the smaller methane-cracking reactor.

The expendable weight for a 1-year mission was based on the assumption of a catalyst-consumption ratio of 0.1 gram of catalyst per gram of carbon and 200 grams per batch for disposable canister containing carbon and spent catalyst. The smaller expendable weight for the new system reflects only the 25-percent reduction in elemental carbon formed.

The additional Sabatier catalyst for the new system was estimated from the experimental results on this project for a nickel catalyst (bulk density of 1 g/cm^3) packed in Pd-25Ag tube cathodes (0.63-cm diameter) and a design current density of 37 ma/cm^2.

The estimate for the hydrogen-stripper unit was based on a design current density of 37 ma/cm^2 and Pd-25Ag tubes (0.63-cm OD x 0.013-cm wall) for both anodes and cathodes. The electrodes accounted for 2.5 kg of the total estimated stripper-cell weight of 10 kg. The power estimate of 64 watts was based on a stripper-cell voltage of 0.2 volt.

The results of the comparison in Table II show that there would be no significant difference in weight and power for the new system compared to the Bosch system for the assumptions used in the estimates. However, an important factor is the catalyst-consumption ratio that is assumed. This and other factors such as simplicity of operation and instrumentation, and operational reliability, would determine a preferred system. Extended operation of prototype systems is needed to provide data that cannot be estimated accurately.

SECTION VI

EXPERIMENTAL BREADBOARD SYSTEM

Introduction

The experimental breadboard system was constructed to evaluate extended operation of the new integrated system for oxygen recovery from CO_2. The breadboard-system design was based on the best results obtained with various components of the system in the experimental studies discussed earlier in this report. Also, the breadboard system was designed to evaluate two aspects of the proposed system not covered in previous experimental work, namely:

(1) Use of matrix-type water-electrolysis cell with Pd-25Ag cathodes containing Sabatier catalyst

(2) Use of a recycle pump for closed-loop operation of hydrogen stripper and methane cracker.

The matrix-type water-electrolysis cell would be needed for gravity-independent operation to recover oxygen. Although no problem was anticipated in operating a matrix-type cell with an integrated Sabatier reaction, the feasibility remained to be demonstrated. Mass transfer of water vapor to the matrix and heat transfer away from the matrix is required for electrolysis-cell operation. In addition to the heat produced by water electrolysis, there would be the exothermic heat of the Sabatier reaction (same order of magnitude as electrolysis heat) to be transferred from inside the Pd-25Ag tube, through the tube and matrix/electrolyte, to the oxygen/water-vapor gas phase.

The closed-loop operation of the methane cracker was needed to study the effect of builup of CO, hydrocarbons, and other trace contaminants on methane cracking and the influence of the degree of water removal from the Sabatier-product feed to the methane cracker. Also, the closed-loop operation would allow study of the interrelation of recycle rate, percent methane decomposition per pass, hydrogen-stripper-cell power and efficiency, methane-cracking temperature, catalyst consumption, and possibly operation without catalysts for methane cracking.

Design

Figure 14 is a photograph of the experimental breadboard system and Figure 15 is a schematic flow diagram. The breadboard unit was designed primarily for experimental studies with flexibility of operation in replacing components and changing gas-flow paths. The critical piping and control values were designed for a tenfold increase in capacity, from the startup

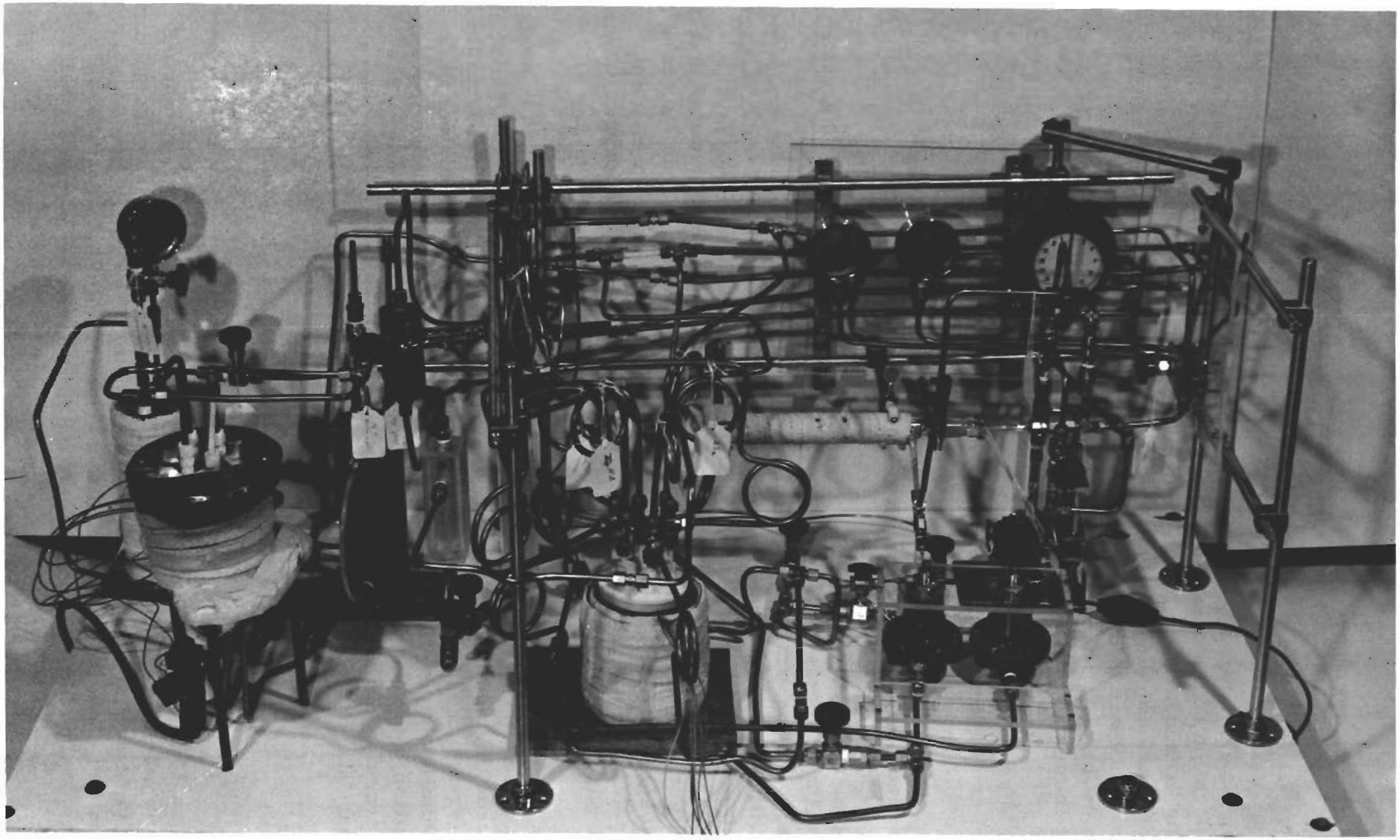


FIGURE 14. PHOTOGRAPH OF EXPERIMENTAL BREADBOARD SYSTEM

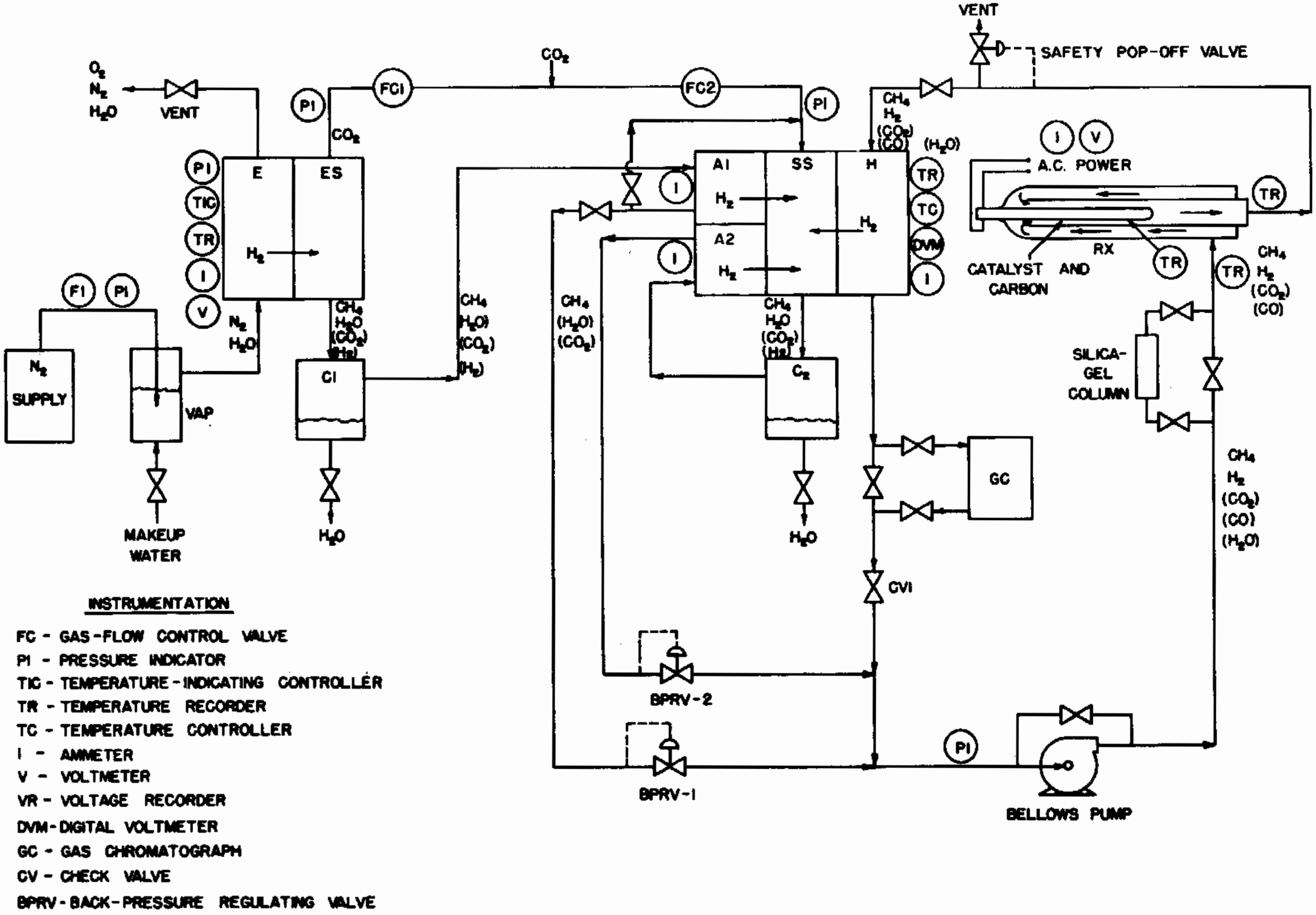


FIGURE 15. SCHEMATIC FLOW DIAGRAM OF EXPERIMENTAL BREADBOARD SYSTEM

capacity of about 0.02 man to about 0.2 man. The later tenfold increase would require an increase in the number of Pd-25Ag tubes above that provided in the initial system for a design current density of 37 ma/cm^2.

The three important components — water-electrolysis unit, hydrogen-stripper unit, and methane-cracking unit — were each designed for experimental studies (i.e., designed for operation on a gravity-independent principle, but not necessarily the mechanical design anticipated for a prototype of optimum size and weight).

Methane-Cracking Unit

Figure 16 is a cross-sectional drawing of the experimental methane-cracking unit constructed of Vycor. An integral heat exchange is provided by the design at the end and where gases enter and exit. The opposite end contains the heated zone for methane cracking provided by the internal glow-bar heater made of quartz. The available volume for carbon in the heated section is about 37 cm^3 (i.e., about 48 hr of carbon accumulation at a rate corresponding to a 0.02-man system).

Hydrogen-Stripper Unit

Figure 17 is a schematic of the hydrogen-stripper-cell unit for the breadboard system. Table III contains a description of the Pd-25Ag electrodes used including the activation, surface treatment, or catalyst loading for the initial experimental evaluation.

The hydrogen-stripper unit was designed with an excess of electrolyte common to the various individual electrolysis cells connected electrically in a series/parallel arrangement, as shown in Figure 17. The design provides for replacement or addition of electrodes in experimental studies but does not represent the anticipated prototype design because of the large excess of electrolyte used. However, a free-electrolyte type of electrolysis cell represents a practical principle for gravity-independent operation applicable to the electrolysis cells of the hydrogen-stripper unit. In operation, no gas is evolved on the electrolyte side of the electrodes (no gas-liquid separation necessary). There is no net consumption of water in the electrolyte, and the electrolyte compartment can be sealed.

The electrode design and operation of the Pd-25Ag cathodes (containing Sabatier catalyst) in a free electrolyte is directly comparable to prior experimental studies discussed in this report. Also, the hydrogen-stripper anodes for operation in a free-electrolyte correspond to prior experimental studies. Thus, the integration of the electrolysis cell containing hydrogen-stripper anodes and Sabatier reactor cathodes was shown to be feasible from prior experimental studies.

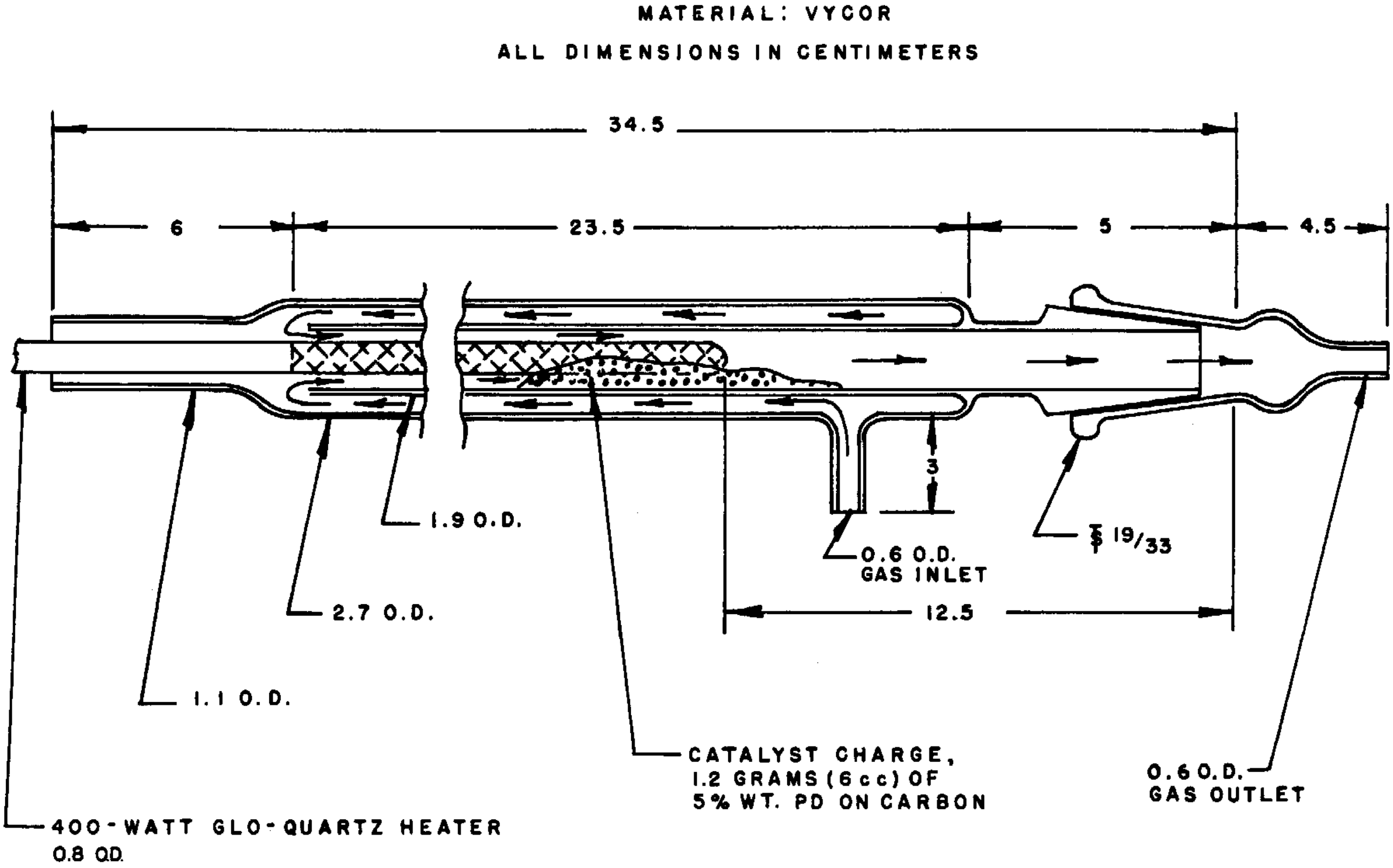


FIGURE 16. CROSS-SECTIONAL DRAWING OF EXPERIMENTAL METHANE-CRACKING UNIT OF BREADBOARD SYSTEM

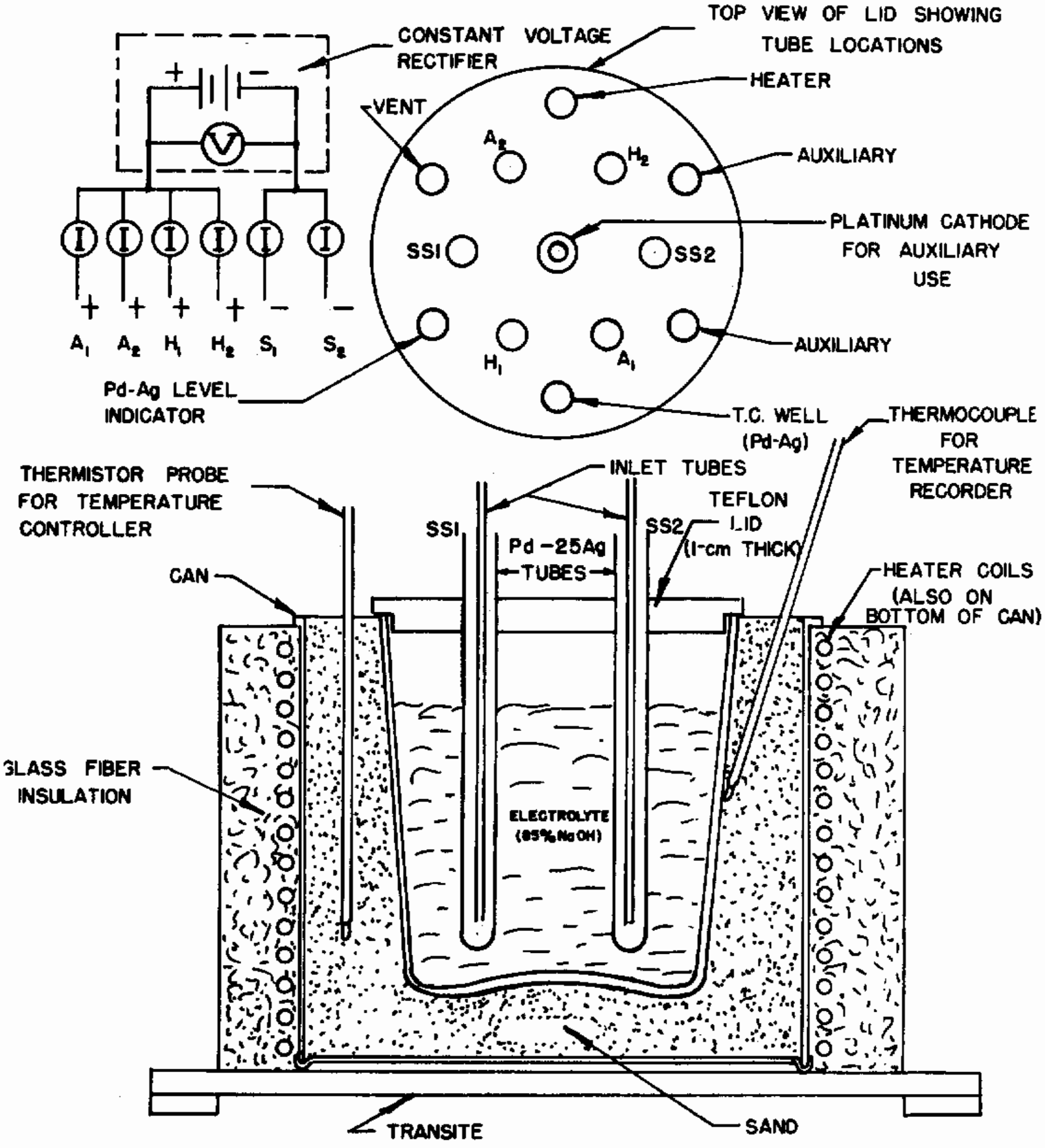


FIGURE 17. SCHEMATIC OF HYDROGEN-STRIPPER-CELL UNIT OF BREADBOARD SYSTEM

TABLE III. SUMMARY OF TREATMENT OF Pd-25Ag TUBES IN HYDROGEN-STRIPPER CELL OF BREADBOARD SYSTEM

Tube			Catalyst (inside)		Inlet	Outlet	
Number	Polarity	Treatment	Type	Amount, grams	from	to	Function (Figure 15)
A1	Anode	Acid(a)	Ru-asbestos(b)	0.4	C1	Pump	Analyze for excess H_2 from Sabatier reactors
A2	"	"	"	0.4	C2	Pump	
H1	Anode	Rh-black(c)	Ru-asbestos(b)	0.25	Rx	Pump	Anodic removal of H_2 from product gas from reactor (Rx)
H2	"	"	"	0.25			
SS1	Cathode	Activated(d)	Sabatier(e)	3.0	CO_2 feed	C2	Stripper cathode/Sabatier reactor (SS)
SS2	"	"	"	3.0		C2	

(a) Anodic treatment of tube (inside only) with 37 wt percent HCl, 37 ma/cm^2, 75 sec.

(b) Ruthenium metal powder (-325 mesh), 6 wt percent on acid-washed asbestos fiber.

(c) Rhodium-black plated (1-2 mg/cm^2) on inside of tube only; no subsequent heat treatment.

(d) Tube activated by standard procedure outlined on page 7 prior to adding Sabatier catalyst.

(e) Harshaw N-0104 nickel on kieselguhr catalyst, -20 +40 mesh.

Water-Electrolysis Unit

Figure 18 is a cross-sectional drawing of the water-electrolysis unit constructed for experimental studies while integrated in the breadboard system. The Pd-25Ag cathodes containing Sabatier catalyst were similar to those used in prior experimental studies with the exception of design for unidirectional gas flow (i.e., CO_2 feed at one end and Sabatier-reaction products removed at the opposite end of the Pd-25Ag tube).

The matrix/electrolyte/anode combination was based on prior studies of matrix-type, Pd-25Ag cathode water-electrolysis cells.(2) In the prior work, a matrix consisting of a mechanical mixture of Teflon threads (machined from a solid block of Teflon) and $Ca(OH)_2$, initially impregnated with 76 percent NaOH and wrapped around the cathode tube with a 45-mesh, 7.5-mil-wire platinum screen anode, had operated satisfactorily (100 percent hydrogen transmission) for 24 hr at 80 ma/cm^2 and a cell temperature of 145 C with a static water-vapor feed at 100 C. The latter matrix was the best available for high-temperature operation. (The use of 80-mesh, 3-mil-wire, platinum screen was not considered a significant design change.) However, matrix-cell operation at about 200 C, required for integration with the Sabatier reaction, had not been attempted previously. A water-vapor feed at a partial pressure above 760 mm Hg was required for operation at 200 C. The electrolysis unit was designed for study of total pressure (oxygen plus water vapor) up to 1500 mm Hg (gage). A high pressure on the anodic side minimizes the amount of water removed with the product oxygen that would have to be separated and recycled. The unit shown in Figure 18 was designed with an inner Teflon liner to minimize electrolyte contamination and possible alternate use as a free-electrolyte-type water-electrolysis cell.

The electrolysis unit was originally designed for a static water-vapor feed from a separate water-vapor generator. After preliminary experiments, the system was modified for a dynamic water-vapor feed. Nitrogen gas was used as the water-vapor carrier bubbled through the water-vapor generator) in a one-pass feed for convenience in experimental studies. A practical system would use a recirculated oxygen stream as the water-vapor carrier. Components for water-vapor feed and water-vapor separation from gas streams were not designed for gravity-independent operation in the experimental breadboard system.

Operational Checkout

The water-electrolysis unit was checked out first with one of the three electrolysis cells. A current of 750 ma provided a current density of 37 ma/cm^2 on the 10-cm length of 0.63-cm-OD Pd-25Ag cathode. The

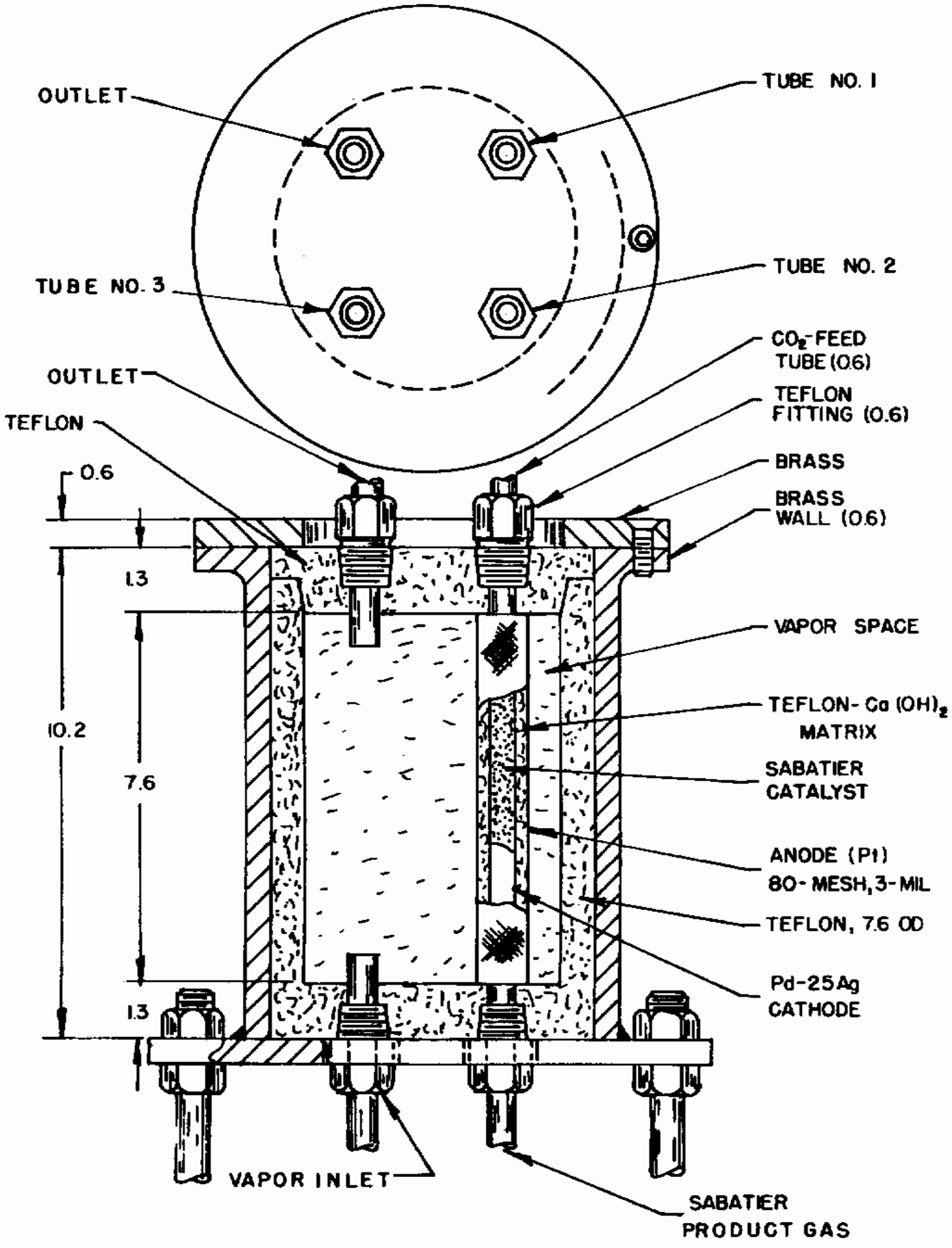


FIGURE 18. CROSS-SECTIONAL DRAWING OF EXPERIMENTAL WATER-ELECTROLYSIS UNIT OF BREADBOARD SYSTEM

All dimensions in centimeters.

electrolysis unit was maintained at 200 C, and water vapor was supplied initially by a static system. With the water-vapor generator set at 110 C, the water-vapor pressure was 1075 mm Hg absolute. The electrolyte concentration in the matrix that exists at steady-state conditions is not known. If the concentration remained at the value of initial impregnation (76 percent NaOH), the water-vapor pressure of the electrolyte would be 975 mm Hg at the cell temperature of 200 C, which would mean a driving force of about 100-mm-Hg differential water-vapor pressure.

During the first 3 hr of operation, 100 percent hydrogen transmission was obtained with the total electrolysis-unit pressure at 1065 mm Hg (mostly water-vapor pressure). The expected increase of cell pressure as oxygen accumulated was not obtained because of leakage of the unit. Overnight the pressure decreased to 812 mm Hg because of leakage, and the hydrogen transmission decreased to 89 percent because of drying-out of the matrix and possible solidification of the electrolyte.

After the fittings around the cathode tube were tightened, the unit pressure increased to 1020 to 1380 mm Hg, and the hydrogen transmission increased to a value of 100 percent, which was maintained for the next 7 hr.

Operation was continued over a weekend and measurement 64 hr later showed the hydrogen transmission to be about 50 percent, with the unit pressure at 960 mm Hg, due to leakage. The fittings were again tightened so that the unit pressure increased to 1065 mm Hg and the hydrogen transmission increased to 100 percent, which was maintained for 4 hr. The run was then terminated to modify the water-electrolysis unit.

The total operating time for the above checkout run of the water-electrolysis unit was 100 hr, and there was no evidence of permanent poisoning of the Pd-25Ag-tube cathode with the Teflon-$Ca(OH)_2$ matrix. A total of 14 hr of satisfactory operation at 100 percent hydrogen transmission was obtained when adequate water-vapor pressure was maintained (i.e., 1050 mm Hg partial pressure of water for electrolysis-cell operation at 200 C and 37 ma/cm^2). The cell voltage was 1.9 to 2.1 volts during periods of normal operation. Polarization to 2.5 to 3.0 volts and partial loss of hydrogen transmission occurred when the matrix was deficient in water. Normal operation of the electrolysis cell was resumed when adequate water-vapor feed was restored.

The electrolysis unit was modified to incorporate a dynamic water-vapor feed. Nitrogen was used as the carrier gas for experimental studies. With nitrogen bubbled through the water-vapor generator, both the nitrogen flow rate and water temperature could be used to control the water-vapor feed to the electrolysis unit.

During a subsequent checkout of the water-electrolysis unit, a leak developed at the connection to the Pd-25Ag tube cathode so that nitrogen and water vapor entered the inside of the tube with hydrogen. Further modification of the electrolysis unit is required to provide pressure-tight seals for operation at 200 C with a positive pressure on the water-vapor-feed circuit.

One Pd-25Ag anode tube in the hydrogen-stripper unit was found to have a defective weld at the closed end that resulted in leakage of electrolyte to the inside of the tube. This anode tube was replaced. The delays caused by mechanical-leakage problems prevented a complete operational checkout of the experimental breadboard system.

SECTION VII

CONCLUSIONS

The new integrated system of oxygen recovery from CO_2 appears to be competitive with the Bosch system in terms of estimated weight and power. Certain features of the new system indicate simpler control of CO_2-reduction reaction for extended operation. Experimental evaluation has shown that all of the component reactions for the integrated system are technically feasible at rates required for design of a practical system.

Further development of the new system is required to determine the optimum operating parameters for the small breadboard model of the integrated system now available. Design and development of prototype components and extended operational testing of an automated laboratory model of the new system should be undertaken to obtain data for comparison with other oxygen-recovery systems that are being developed. Operational reliability for extended missions is expected to be the important factor in the ultimate choice of a preferred oxygen-recovery system.

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13. ABSTRACT

A new integrated system for oxygen recovery from carbon dioxide was investigated. Experimental studies indicated that it was feasible to integrate water electrolysis with carbon dioxide hydrogenation in an electrolysis cell using Pd-25Ag hydrogen-diffusion cathodes containing Sabatier catalyst. A closed system producing carbon appeared feasible from experiments on catalytic methane cracking followed by hydrogen separation from unreacted methane in an electrolytic hydrogen-concentration cell using Pd-25Ag electrodes. A small experimental breadboard system was designed and constructed.

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Oxygen recovery						
Water electrolysis						
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