

FOREWORD

This study was initiated by the Biomedical Laboratory of the 6570th Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. The research was conducted by Isomet Corporation of Palisades Park, New Jersey, under Contract No. AF33(657)-8066, Project No. 6373, "Equipment for Life Support in Aerospace," and Task No. 637302, "Respiratory Support Equipment." Dr. H. Chandler was the principal investigator for the Isomet Corporation. Mr. Richard E. Bennett of the Respiratory Equipment Branch, Biotechnology Division, was the contract monitor for the Aerospace Medical Research Laboratories. This study was started in January 1962 and was completed in January 1964.

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ABSTRACT

An automatically operated carbon dioxide reduction system was developed, fabricated and tested. The system was designed to reduce the carbon dioxide equivalent to that produced by one man, and to produce carbon and oxygen. A system such as this is required for providing respiratory support for man on extended space missions. The program was conducted in three phases: (1) development of system components, (2) experimental determination of system design parameters, and (3) fabrication and testing of an engineering model. Successful operation of the engineering model demonstrated the feasibility and ease of operation of the system. Recommendations are made for improving the system and for future work.

PUBLICATION REVIEW

This technical documentary report is approved.

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SECTION 1

INTRODUCTION

Program Objectives

This report summarizes the research, development, design, fabrication and testing of an engineering model of a solid electrolyte system to convert carbon dioxide to carbon and oxygen for advanced aerospace vehicles. The scope of this program has been to develop the components essential to the operation of the solid electrolyte system and, by constructing and operating an engineering model containing these components, to demonstrate the engineering feasibility and ease of automatic operation of the system. Operating characteristics of the system were also to be studied.

SECTION 2

THEORETICAL STUDY

Overall System Analysis

A number of methods for regenerating oxygen from carbon dioxide have been proposed. Among these are:

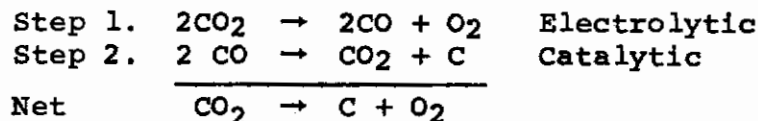
Direct reduction of CO₂ to carbon and water using hydrogen, followed by electrolysis of the water.

Conversion of CO₂ to methane and water using hydrogen, followed by thermal decomposition of the methane to carbon and hydrogen and electrolysis of the water to yield oxygen.

Electrolytic reduction of CO₂ to CO and oxygen followed by disproportionation of the CO to CO₂ and carbon.

The last system appears to have a number of attractive features. No water is formed in the process, thereby eliminating the need for liquid-gas separations in a zero-gravity field. Electrolytic conversion of CO₂ to CO and O₂ can be accomplished in two different types of cell, the molten carbonate and the solid electrolyte. The molten carbonate, because of the potential mechanical problems associated with the handling of corrosive, molten carbonates in a zero-gravity field and difficulties associated with operation of the cell, was not studied extensively at Isomet but is being investigated by others. The solid electrolyte cell, because of its simplicity of operation and potential for producing high purity oxygen, was felt to be a more suitable system for a space application.

The free energy of formation of carbon dioxide at 25°C is 94 kcal/g mole. This, therefore, is the minimum amount of energy required to decompose a gram mole of carbon dioxide to carbon and oxygen. In the system under study, the overall reaction is carried out in two separate steps, the net result of these steps being the conversion of one gram mole of carbon dioxide to one gram mole of carbon and one gram mole of O₂.



The free energy change in Step 1 is about +123 kcal/g mole of oxygen formed at 25°C. This means that a minimum of 123

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kcal. must be supplied in the electrolytic process per gram mole of oxygen formed. The free energy change in Step 2 is about -29 kcal/g mole of carbon formed, meaning that about 29 kcal are liberated per gram mole of carbon formed. In practical terms, at the one-man level, the minimum electrolysis power requirement is about 140 watts and the minimum heat dissipation requirement for the catalytic reactor is about 35 watts. The catalytic reactor could, therefore, be self supporting if properly insulated to restrict the heat loss to 35 watts.

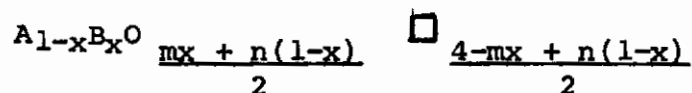
Since the minimum power requirement in the cell would be that required for operation just at the decomposition potential of the CO_2 , a potential greater than this must be used for a current to flow. The extent of this "over potential" is directly dependent on the electrical resistance of the cell which is in turn related to the electrolyte surface area. This is a consideration of vital importance, for it supplies the basis of trading weight for power in the electrolysis cell. As the surface area of the solid electrolyte increases, the electrical resistance decreases and the power required to produce a given amount of oxygen decreases. Using a weight penalty for power, optimum-size systems for a given rate of oxygen production can be specified. Examples of this procedure will be given in a later section.

The system under study, therefore, is one consisting of a solid electrolyte cell, a catalytic reactor and a gas recycle pump. Figure 1 shows a block diagram of the simplest embodiment of this system. Gas recirculates between the cells and the reactor. In the cells, the CO_2 is electrolyzed to CO and O_2 . The gas, enriched in CO and depleted in CO_2 , emerges from the cells and passes to the catalytic converter where the CO is disproportionated to CO_2 and carbon. The exit gas from the reactor, enriched in CO_2 and depleted in CO , then picks up fresh CO_2 from the cabin removal system thus further enriching the gas in CO_2 . This gas is then recycled to the cell. The net behaviour of the system is such as to produce carbon and oxygen from CO_2 .

Solid Electrolytes

A number of oxide systems are known which conduct electricity at elevated temperatures by virtue of oxygen ion migration through the lattice structure under the influence of an applied electric field. These oxide systems have several features in common, all being solid solutions of two oxides, the solid solution having the cubic fluorite crystal lattice structure. The two oxides have different valence metallic ions. The general formula for the solid solution can be represented as

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where m and n represent the valence of B and A respectively. The symbol \square represents the vacancies in the anion lattice caused by the requirement for electrical neutrality in the lattice. As a lower valence metal is substituted for a higher valence metal in the crystal lattice, it is necessary to remove oxygen ions from the anionic lattice to maintain electrical neutrality. This leaves ionic vacancies in the oxygen lattice, through which oxygen ions can migrate under the influence of an electric field.

We thus have what amounts to a semipermeable membrane, permeable only to oxygen ions, provided that the solid electrolyte has no pores large enough to allow molecular gases to flow through. The cell can be treated thermodynamically as an oxygen concentration cell whose reversible EMF is calculated by the following equation:

$$E = \frac{RT}{nF} \ln \frac{p_{2O_2}}{p_{1O_2}} = \frac{2.303RT}{nf} \log \frac{p_{2O_2}}{p_{1O_2}}$$

where E = reversible cell EMF, volts

n = 4 for the case of an oxygen concentration cell

F = 96,500

R = 8.3 joule/°C, mole

p_{2O_2} = 1 atmosphere, since oxygen is produced at 1 atmosphere pressure

$$p_{1O_2} = \left(K \frac{p_{CO_2}}{p_{CO}} \right)^2$$

K = equilibrium constant for reaction
 $CO_2 \rightarrow CO + 1/2 O_2$

The variation of K with temperature is given by the relation

$$F = -RT \ln K$$

where F = free energy of reaction

For the above reaction, as written, the variation in F with temperature is shown in Table 1.

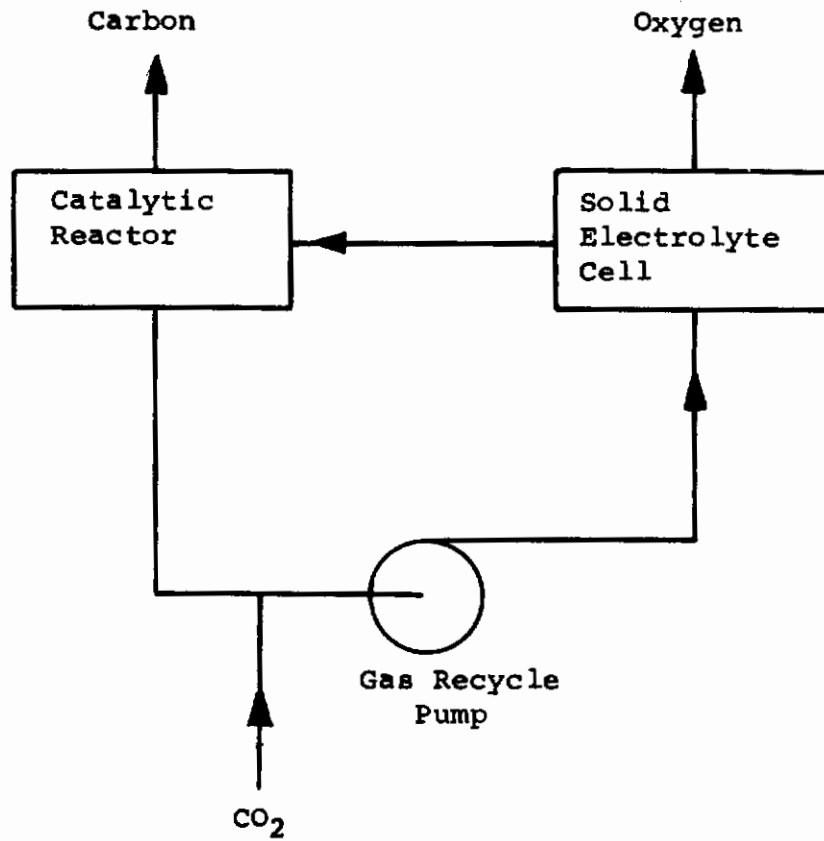


Figure 1
Block Diagram of Oxygen Regeneration System

TABLE 1

VARIATION OF FREE ENERGY CHANGE FOR REACTION
 $\text{CO}_2 \rightarrow \text{CO} + 1/2 \text{O}_2$ WITH TEMPERATURE

T, °C	F, kcal/g mole
200	57.5
400	53.5
600	49.5
800	45.5
1000	41.0
1200	37.0

Using the free energy data at 1000°C, since the solid electrolyte cell operates at about 1000°C, we calculate the variation of the reversible cell EMF with CO₂ concentration in the negative electrode compartment of the cell as shown in Table 2.

TABLE 2

VARIATION OF REVERSIBLE CELL EMF WITH CO₂ CONCENTRATION AT 1000°C

% CO ₂	$\frac{P_{\text{CO}_2}}{P_{\text{CO}}}$	E, volts
90	9.0	0.768
80	4.0	0.812
60	1.5	0.866
50	1.0	0.888
40	0.67	0.910
20	0.25	0.963

We thus see that the reversible cell EMF varied from about 0.75 to 0.95 volts as the CO₂ concentration decreased. In practice, the applied potential is always greater than the reversible cell EMF, the actual value depending on the internal ohmic resistance and polarization of the cell.

Conductivity data for a number of solid electrolytes known to conduct almost exclusively by oxygen ion migration are shown in Figure 2. Examination of these curves indicates that the specific resistivity of a solid electrolyte having the composition 8.75 mole % Y₂O₃ - 91.25 mole % ZrO₂ is about 4 ohm-cms. at 1000°C. On the basis of these data, it was decided that all work to be carried out with solid electrolytes would utilize this composition material. Different investigators report different values for the same compositions. Although the reasons for these differences are not known in these specific instances, it is generally known that differences in porosity and density and

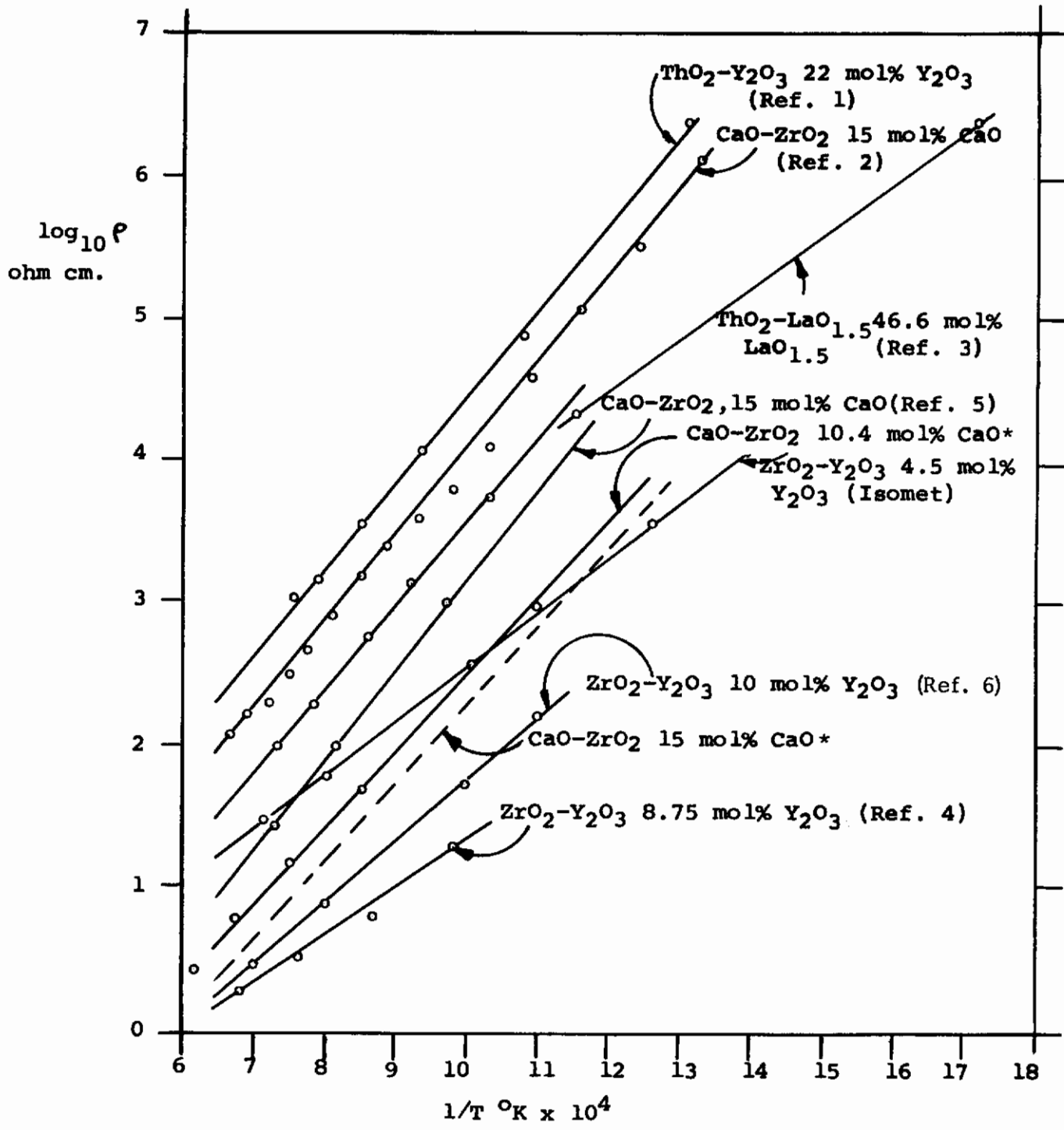


Figure 2
 Variation of Specific Resistivity of Solid Electrolytes
 With Temperature

*Personal communication from Zirconium Corporation of America.

the presence or absence of small amounts of impurities in the samples can cause variations in the sample resistance. Based on the value of 4 ohm-cms., it is calculated that for a solid electrolyte 2 mm. thick, a current density of 1.25 amps/cm² should be obtained for every volt applied above the reversible cell EMF. This value neglects cell polarization and lead resistances and is equivalent to 4.79 cc. of O₂ produced per cm. of area per volt applied above the reversible cell EMF.

Based on the nature of the electrolyte, the basic constructional features of the solid electrolyte cell can be visualized. It consists of the solid electrolyte, the electrodes attached to both surfaces of the solid electrolyte, a means for maintaining the solid electrolyte at about 1000°C, and inlet and exit lines for the CO₂ and O₂. The CO₂ side of the cell must be sealed from the oxygen side to prevent leakage of one gas into the other. The practical means for satisfying these requirements will be described in Section 3.

Catalyst Requirements

The reaction occurring in the catalytic reactor is the disproportionation of carbon monoxide to carbon and carbon dioxide. Variation of the free energy change of this reaction with temperature is shown in Table 3 while the equilibrium composition of a mixture of CO₂ and CO as functions of temperature and total pressure are shown in Figure 3.

TABLE 3

VARIATION OF FREE ENERGY CHANGE FOR REACTION
2CO → CO₂ + C WITH TEMPERATURE

T, °C	F, kcal/g mol
200	-21
300	-17
400	-12
500	- 8
600	- 4
700	0
800	+ 4
900	+ 9
1000	+13

Examination of Figure 3 shows that operation at temperatures up to 500°C should yield a product gas that is almost completely CO₂ provided that equilibrium is reached in the reactor. In addition it is seen that an increase in pressure raises the equilibrium concentration of CO₂ at a given temperature or allows

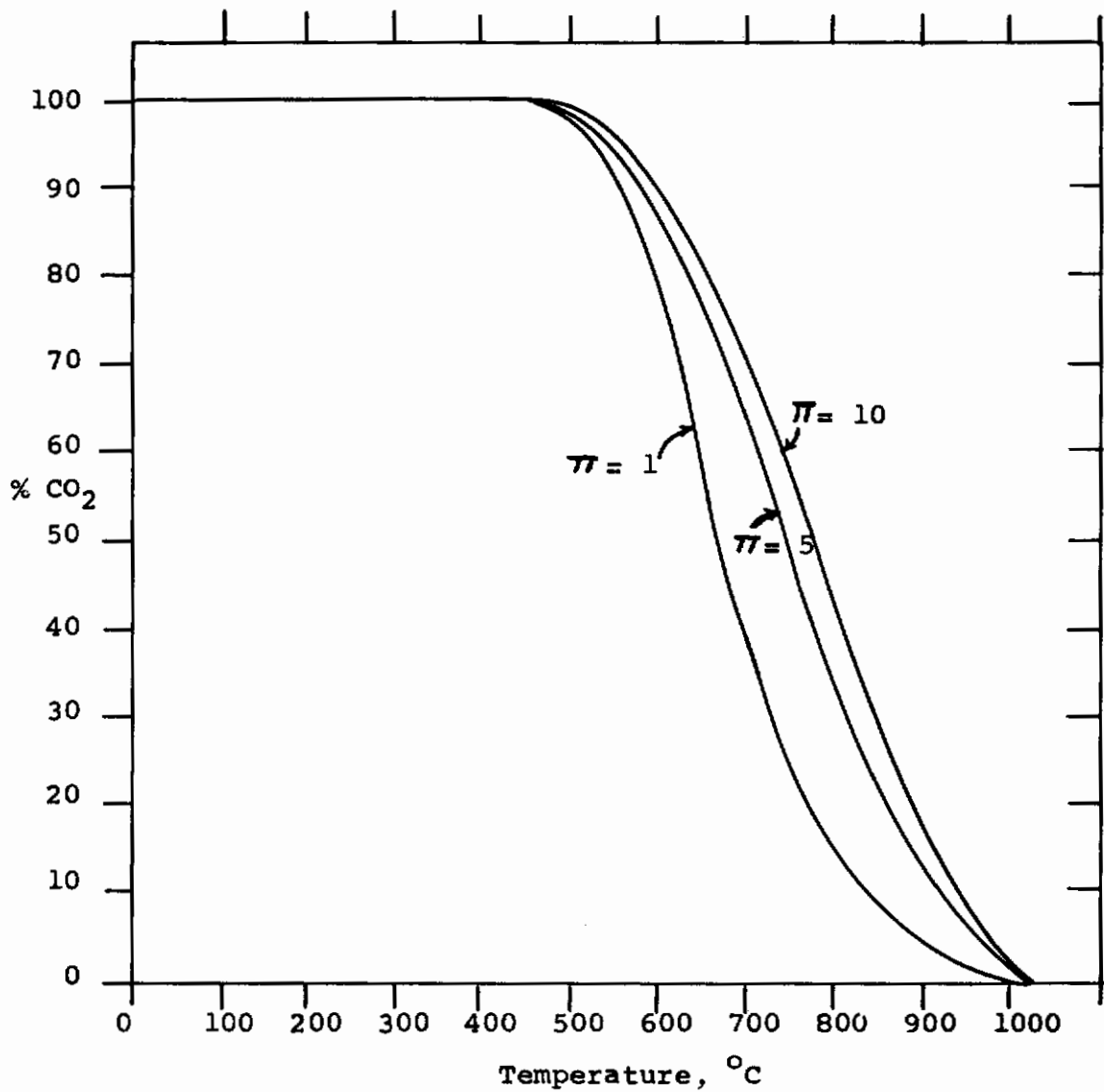


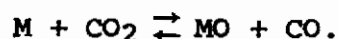
Figure 3

Variation of Equilibrium Gas Composition in
Catalytic Reactor as a Function of Temperature
and Pressure

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an increase in the temperature at which a given CO₂ concentration can be attained. This is an important factor in trade-off studies. While the detailed kinetics of this reaction are not known, generally, a temperature increase will increase the rate of reaction. In addition, a rise in pressure usually increases the rate of reaction. It is, therefore, to be expected that an increase in pressure at a fixed temperature in a given size reactor will result in a greater conversion of CO to CO₂. Similarly, an increase in pressure will allow the use of a higher temperature in a smaller reactor to attain a higher degree of CO conversion. Balanced against these effects would be the possible increase in reactor weight caused by the required increase in wall thickness to accommodate the higher pressures, and/or the increased heat losses resulting from an increase in reactor temperature. A trade-off study has not been made because of lack of detailed kinetic data for this reaction. Additional considerations would be the increase in frequency of emptying carbon from the reactor as the reactor volume decreased, and the increase in pumping power required to pressurize the incoming CO₂.

The disproportionation of carbon monoxide to form carbon and carbon dioxide is a slow reaction unless carried out in the presence of a catalyst. The catalysts normally used for this reaction are either iron, cobalt or nickel although it is by no means certain whether the metals themselves, the carbides of the metals or perhaps even the metal oxides are the catalytic species during the course of the reaction. It is generally known that carbon formation from carbon monoxide is most rapid in the temperature range from 500° to 600°C using an iron catalyst(ref. 7). Selection of the proper catalyst for the proposed system required consideration of several criteria. Important among these was the desire to maintain the carbon dioxide level in the system as high as possible since this would lead to a more efficient solid-electrolyte cell operation. The metals potentially useful as catalysts in this reaction are susceptible to oxidation by carbon dioxide according to the reaction



It appears necessary, therefore, to use as a catalyst that metal which is least susceptible to oxidation by this reaction. Free energy changes for this reaction at 500°C for the three metals under consideration are shown in Table 4.

TABLE 4

FREE ENERGY CHANGE FOR REACTION $M + CO_2 \rightleftharpoons MO + CO$ AT $500^\circ C$.

<u>Metal</u>	F
Fe	+ 0.5
Co	+ 8.5
Ni	+11.5

Because these data showed that nickel is least susceptible to oxidation by this reaction, it was decided to use nickel as the catalyst. Available information indicating that iron and nickel behaved similarly in respects other than their susceptibility to oxidation, provided a basis for predicting some of the operating characteristics of the catalytic reactor. Of particular interest are the maximum rate of carbon deposition, the amount of carbon that can be formed from a given weight of catalyst, and the effect of gas flow rate on the rate and extent of reaction.

Data for iron as a catalyst and a pure CO feed to the reactor indicated the following:

The most rapid reaction rate was obtained in the temperature range from $500^\circ C$ to $530^\circ C$.

About 3 grams of carbon were deposited per gram of catalyst per hour using the space velocity and feed composition described in reference 6.

About 30 to 50 grams of carbon were formed per gram of catalyst before carbon deposition ceased.

These data for decomposition of pure CO over an iron catalyst indicated that operation in the range from 500° to $530^\circ C$ would be suitable and that under these conditions a total deposition of at least 10 grams of carbon per gram of nickel catalyst could be expected. The best type and form of nickel catalyst must be determined experimentally.

An additional consideration in the design of the reactor is that the carbon is stored in the reactor as it forms and eventually fills the reactor. Since no method has yet been found to separate the carbon from the catalyst at the end of the reaction, provision must be made for removing the entire contents of the reactor and inserting fresh catalyst.

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Summary

The theoretical portion of this study of the solid electrolyte CO₂ reduction system consisted of a thermodynamic analysis of the effect of temperature, pressure and gas composition on the reversible cell potential and on the equilibrium concentration of the gas emerging from the catalytic reactor. Results indicate that the reversible cell potential increases as the carbon monoxide concentration in the gas increases and also as the pressure of the oxygen product increases. An increase in pressure on the CO₂ side of the cell would have little or no effect on cell operation. The catalytic reactor operates best in the temperature range from 500° to 530°C and uses a nickel catalyst. Increasing the total pressure in the reactor increases the equilibrium CO₂ concentration in the effluent gas, and allows the use of a smaller volume reactor and a higher temperature for a given equilibrium concentration of CO₂ in the effluent.

SECTION 3

EXPERIMENTAL PROGRAM

Cell Development

Previous work (ref. 8) indicated the possibility of using a solid oxide electrolyte to decompose carbon dioxide to oxygen. To test the feasibility of operating a completely closed cycle system, it was first necessary to determine the operating characteristics of a cell having a reasonable size and to develop techniques for constructing a rugged, mechanically sound, leak-proof cell.

To meet this requirement, several decisions were made on the basis of past experience. Both CaO-ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ were commercially available in a number of different compositions and shapes. To be of use in this program, these shapes would have to be highly dense, nonporous and impermeable to gas flow. Since these two compositions corresponded to those having maximum conductivity as shown in Figure 2, it was decided that these two compositions would be used in the course of this program.

The shape of the solid electrolyte would be of critical importance. Attempts had been made during the previous work (ref. 8) to construct cells utilizing the solid electrolyte in the form of flat discs between two electrodes. Extreme difficulties were encountered in trying to develop high-temperature seals between the two sides of the disc cell. In addition, the thermal stresses set up in the cell by the unequal expansion of the metal and ceramic parts almost invariably resulted in cracking of the solid electrolyte. For this reason, the use of flat discs was discontinued and, because of their ready availability and potential advantages in ease of cell construction, it was decided to use the solid electrolyte in the form of a hollow tube closed at one end. In this form, the seal could be made at one end in a relatively cool portion of the cell while the closed end of the cell could be lightly supported. Thus a minimum thermal stress would be placed on the tube. All experimental cells were constructed in this general manner and are shown schematically in Figure 4.

To describe the development of the solid electrolyte cell, the experimental program is described in chronological fashion showing the steps leading up to the development of the final cell.

In the first experiments, a closed-end tube made from 90 weight % ZrO_2 - 10 weight % Y_2O_3 was used as the solid elec-

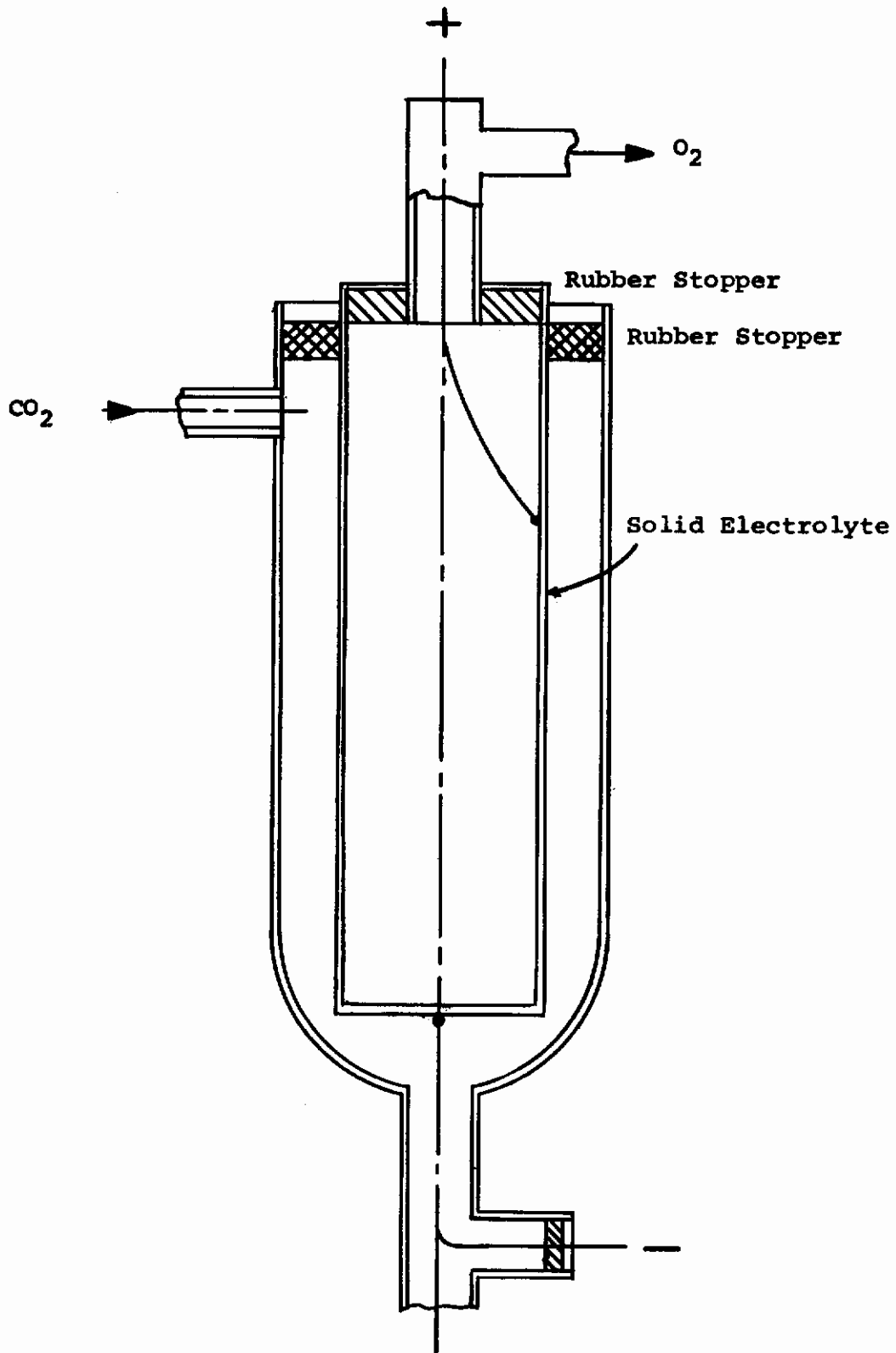


Figure 4. Solid Electrolyte Cell

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trolyte. The tube was tested before use and found to be vacuum tight and pinhole free. This tube was placed concentrically in a closed-end Vycor tube and both the annular space between the ceramic and Vycor tube and the space inside the ceramic tube were filled with 100-200 mesh unsintered platinum powder. The platinum powder served as the electrodes, and platinum wires were inserted into the powder to serve as electrical leads. The whole assembly was found to be gas tight.

The CO₂ compartment of the cell was kept under a constant pressure of 4 mm. Hg. with the CO₂ flowing into the cell at a rate of 18 cc/min. The O₂ compartment of the cell at the beginning of the experiment was at 1 atm. pressure. The whole O₂ side of the cell was maintained as a closed system with the exit from the cell being connected directly to a closed-end Hg. manometer. The oxygen produced as a result of the electrolysis raised the Hg. level in the manometer. The amount of oxygen produced in a given time was measured by withdrawing the O₂ with a hypodermic syringe so as to return the Hg level to its initial value.

The cell was heated to 505°C ± 5°C and a D.C. potential of 35 volts was applied across the cell. Under these conditions, a current of 200 mamps. was allowed to flow for 28 minutes, during which time 4.5 ± 0.05 ml. of O₂ were produced at 760 mm Hg pressure and 300°K. The terminal voltage dropped to 22 volts during the course of the run, probably because of self-heating of the solid electrolyte caused by passage of current. The gas produced on the O₂ side of the cell was found by chromatographic analysis to be pure O₂ while the effluent gas on the CO₂ side of the cell was found to be a mixture of CO₂ and CO.

From this information, the efficiency of the process was calculated. 0.0933 amp. hrs. were required to produce 4.5 ml of O₂. Since 26.804 ampere hours are equivalent to 1 Faraday and 4 Faradays are required for the passage of 1 mole of O₂, 0.0933 ampere hours should have produced 20.8 cc of O₂. Since only 4.5 cc of O₂ were produced, the conductivity under these conditions was only 21.5% ionic, the remainder of the current being carried by electronic flow.

Prolonged operation under these conditions resulted in a gradual decrease in O₂ production and the run was discontinued when only 1 ml of O₂ was produced in 28 minutes. The platinum powder was then removed from the cell, sintered at 800°C for 3 hours, and used to refill the cell. The cell was then operated at 505°C with a terminal voltage of 27 volts and a current of 300 mamps. for 8.5 minutes. During this time, 4.5 ml of O₂ were collected. Repeating the calculation, it can be shown that 47.5%

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of the current flowing through the solid electrolyte was carried by O_2 ions while the remainder of the current was carried by electron migration.

Under these conditions, an increase in carbon dioxide flow rate beyond a certain point did not improve the results; however, decreasing the flow rate below this point did result in poorer O_2 production.

It was believed that one of the reasons for the decline in efficiency of the cell with time was the sintering of the platinum powder and its resultant pulling away from the solid electrolyte, thereby giving poorer electrical contact. In an effort to overcome this difficulty, liquid Platinum Alloy No. 130 (Engelhard Industries) was painted on the solid electrolyte and fired at $800^\circ C$ for 30 minutes. As a result of this treatment, cell performance decreased further with O_2 yields based on current declining to about 15% or 20%. This was probably caused by the formation of an impermeable platinum film over the electrolyte, preventing access of the gas.

On the basis of previous experiments, it appeared that the positive electrode (electrode at which oxygen is discharged) was functioning satisfactorily as far as the speed of the electrode reaction was concerned. To improve cell operation, steps were taken to modify the negative electrode.

A cell similar to the others was constructed, except that the negative electrode consisted of powdered Fe_3O_4 which was loosely pressed against the solid electrolyte. Electrical contact was made with platinum lead wires. Experimental results appear in the following table.

<u>Duration of Run</u> <u>Minutes</u>	<u>Current</u> <u>Mamps</u>	<u>Voltage</u> <u>Volts</u>	<u>Temperature</u> <u>$^\circ C$</u>	<u>O_2 Volume</u> <u>cc</u>
35	60	2.8	550 ± 5	4.4
27	100	3.0	550 ± 5	4.4
30	200	4.0	540 ± 5	4.5

The cell was run continuously for 48 hours with a current of 200 mamps. and further tests were then carried out.

70	300	4.4	475 ± 5	4.2
52	400	4.8	485 ± 5	4.2

From these experiments, it appeared that the electrode-electrolyte contact was poor and an effort was made to improve this contact by actually rubbing fine Fe_3O_4 powder on to the surface of the electrolyte. Results of these experiments appear

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in the following table.

Run Duration, Minutes	Current Mamps.	Voltage Volts	Temperature °C	O ₂ Volume cc	Current Efficiency, %
6	200	3.3	600 ± 5	4.3 ± 0.05	96.0
6	200	3.3	600 ± 5	4.2 ± 0.05	94.0
6	200	3.3	600 ± 5	4.2 ± 0.05	94.0
10	200	4.0	555 ± 5	5.0 ± 0.05	67.0
10	200	4.0	555 ± 5	5.0 ± 0.05	67.0
10	200	4.0	555 ± 5	4.8 ± 0.05	64.5
10	100	3.7	555 ± 5	3.2 ± 0.05	86.5
10	100	3.7	555 ± 5	3.2 ± 0.05	86.5
6	300	5.2	555 ± 5	4.8 ± 0.05	70.0

The cell was operated continuously for 72 hours at 200 mamps. after which the results were as follows:

6 minutes, 200 mamps., 4.6 volts., 640°C, 4.2 ± 0.05 ml. O₂, 94% efficiency

After a further 48 hours of continuous operation, the following results were obtained:

6 minutes, 200 mamps., 4.4 volts., 625°C, 2.6 ± 0.05 ml. O₂, 58.2% efficiency

At this point, the cell was disassembled and observed to determine if visible changes had occurred in the electrolyte or the electrodes.

Over the 7-day period of the run, the top 2 cms. of the Fe₃O₄ powder had been oxidized to Fe₂O₃ through the reaction of the entering CO₂ with the Fe₃O₄. From this reaction and the cell reaction, enough CO is formed so that the CO₂-CO mixture is in equilibrium with the Fe₃O₄ and no oxidation of the Fe₃O₄ occurs in the lower portion of the Fe₃O₄. The Fe₂O₃ formed is non-conducting and thus the active area of the cell decreased. To avoid oxidation of the Fe₃O₄, about 2 cms. of platinum powder was put above the Fe₃O₄ to produce enough CO so that the CO₂-CO-Fe₃O₄ system is in equilibrium. It was also found that the layer of Fe₃O₄ that had been rubbed on the electrolyte had started to peel away.

To further improve the long-term operating efficiency of the cell, a paste of fine Fe₃O₄ and water was painted on the electrolyte and dried. The performance of the cell is shown in the following table:

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Run Duration, Minutes	Current Mamps.	Voltage Volts	Temperature °C	O ₂ Volume cc	Current Efficiency, %
6	60	3.0	600 ± 5	1.2 ± 0.05	88.5
16	100	3.6	600 ± 5	5.4 ± 0.05	90.5
5	200	4.9	600 ± 5	3.7 ± 0.05	99.0
4	300	6.1	600 ± 5	4.0 ± 0.05	89.2
7	100	3.05	670 ± 5	2.4 ± 0.05	92.0
5	100	3.05	670 ± 5	1.7 ± 0.05	91.0
5	200	4.0	670 ± 5	3.8 ± 0.05	99.0
5	200	4.0	670 ± 5	3.6 ± 0.05	99.0
4	300	4.9	670 ± 5	4.3 ± 0.05	96.0
4	300	4.9	670 ± 5	4.35 ± 0.05	97.0

After continuous operation for a week at a current of 200 mamps. with repeated heating and cooling of the cell, the current efficiency started to drop, apparently because of separation of the Fe₃O₄ from the electrolyte.

To achieve a large and highly active surface area at which the three-phase (gas, electrode, solid electrolyte) electrochemical reaction can occur and at the same time to obtain a firm bonding of the electrode to the electrolyte, several commercially available platinum paints and suspensions were tried in addition to a suspension of ammonium chloroplatinate in water. Of these preparations the most satisfactory one was the ammonium chloroplatinate suspension. This was painted on the solid electrolyte surfaces, air-dried, then ignited at 800°C in a furnace to form a spongy, well-bonded layer of platinum on the electrolyte surfaces. This could be handled with ease and was quite porous.

A solid electrolyte tube having the composition 15 mole % CaO - 85 mole % ZrO₂ was used. This tube was 1 cm in diameter, about 12 inches long, closed at one end, and had a 1 mm wall. This tube was painted in the above manner and inserted in a Vycor tube, and platinum powder was packed into the ceramic tube and into the annular space between the ceramic and Vycor tubes. Appropriate lead wires were inserted in the platinum powder. Pure CO₂ was passed into the annular space and the oxygen produced inside the ceramic tube was collected and measured. The cell performance is shown in the following table:

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Terminal Voltage D.C. Volts	Current Mamps.	Temp. °C	Run Duration, Minutes	Oxygen Collected, cc.	Oxygen Collected Theoretical, cc
1.5	200	955-968	5	3.8	3.8
1.65	300	968	5	5.7	5.7
1.75	360	968	5	7.0	6.84
1.85	400	968	4	6.0	6.08
1.90	500	968	4	7.65	7.6
2.0	600	968	3	6.9	6.84
2.15	700	968	3	8.0	7.98
2.2	800	968	2.5	7.7	7.6
2.3	900	968	2	6.8	6.84
2.4	1000	968	2	7.7	7.6
2.5	1100	968	2	8.4	8.36
2.7	1400	972	1	5.45	5.32
2.9	1500	972	-	-	-
3.25	2000	986	5	39.8	38.0
3.7	2500	986	5	49.0	47.5
4.3	3000	986	5	57.6	57.0
4.8	3400	961	5	67.0	64.6
5.75	4000	970	5	78.4	76.0
6.3	4600	980	5	89.6	87.4
6.7	5000	984	5	97.0	94.0

During the measurements, the flow of CO₂ was at such a rate that the carbon dioxide content in the effluent gas did not drop below about 50%. The theoretical oxygen collected was based on the assumption that all of the current flowing was carried by O⁻ ions, and was calculated at 25°C and 760 mm. Hg using the measured values of current flow.

This cell was operated for 100 hours at 2500 mamps. with an average of 3.5 volts applied at temperatures from 960°C to 990°C and with the oxygen production equated to the theoretical production. The cell was run for 24 hours at 6.7 volts and 5000 mamps. at temperatures from 965° to 985°C, again with theoretical oxygen production. In both cases, shutdown was for convenience rather than for failure of the cell in any way.

A cell was constructed identical to the one described above, except that the electrolyte was a ZrO₂-Y₂O₃ tube containing 4.75 mole % Y₂O₃. This tube was identical in length and diameter to the other, but the wall thickness was 2 mm rather than 1.5 mm. Heavier lead wires were used so that overheating did not occur.

The performance of this cell is shown in the following table:

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Terminal Voltage D.C. Volts	Current Mamps.	Temp. °C	Run Duration, Minutes	Oxygen Collected, cc	Oxygen Collected Theoretical, cc
2.1	2000	930	10	76.4	76.0
2.6	3000	960	5	56.4	57.0
3.2	4000	965	4	61.8	60.8
3.7	5000	970	3	57.6	67.0
4.4	6000	978	3	69.2	68.4
5.05	7000	983	3	80.7	79.8
6.2	8000	973	3	91.5	91.2
6.8	9000	978	2	69.2	68.2
7.6	9600	985	2	74.8	73.0
8.3	10000	981	2	76.6	76.0

The cell was run for 4 hours at a current of 10 amps. and measurements made at roughly 30-minute intervals showed a drop in production rate of oxygen from 76.6 cc in 2 minutes to 74.8 cc in 2 minutes. During this period, the carbon dioxide content of the exhaust gas was 34.8%. The carbon dioxide in the effluent stream at other values of the current, using a constant input of pure carbon dioxide, was as follows:

Current, Mamps.	% CO ₂ in Exhaust
6000	61.7
7000	55.5
8000	47.5
9000	42.3

Since it appeared that there was a slight decline in cell performance when the carbon dioxide concentration in the effluent gas decreased beyond a certain value, it was decided to make a study of this variation in performance so that limits could be placed on the amount of carbon dioxide converted in any cell. The value of carbon dioxide concentration, below which the performance starts to drop, is strongly dependent on the cell construction details and will change as these fabrication details change. In addition, it may change as the temperature changes. For the cell construction used in these experiments and using the ZrO₂-Y₂O₃ solid electrolyte, the following results were obtained:

Current Mamps.	Temp. °C	O ₂ Volume cc	O ₂ Volume Theoretical cc	Duration of Run, Mins.	% CO ₂ in Exhaust
2000	950	76.0	76.0	10	44.0
3000	960	80.3	79.8	7	24.2
4000	960	73.0	76.0	5	8.7
4000	960	72.8	76.0	5	8.7
4000	960	70.8	76.0	5	8.7

Contrails

At both 2000 and 3000 mamps., there was no change in cell performance during one-hour runs. There was a clear indication that a decline in performance occurred at 4000 mamps. when the effluent gas contained only 8.7% CO₂. After the last reading was taken at 4000 mamps., the carbon dioxide flow was doubled and at once the voltage drop across the cell decreased from 3.8 to 3.3 volts while the current increased from 4000 to 4200 mamps. The current was readjusted to 4000 mamps. and the oxygen production rate measured. Under these conditions, the oxygen production rate was equal to the theoretical oxygen production rate and the exhaust gas contained 80.05% CO₂.

Another series of runs was made at higher current values with the following results:

Current Mamps.	Temp. °C	O ₂ Volume cc	O ₂ Volume Theoretical cc	Duration of Run, Mins.	% CO ₂ In Exhaust
4000	970	77.0	76.0	5	50.0
5000	970	77.8	76.0	4	38.5
6000	973	81.4	79.8	3.5	28.0
7000	973	80.0	79.8	3	21.5
7000	973	77.4	79.8	3	-
7000	973	77.0	79.8	3	-
7400	980	81.8	84.4	3	18.7
7400	980	81.4	84.4	3	-
7400	980	81.2	84.4	3	-

At 7000 mamps. and 21.5% CO₂, the cell performance began to drop. Again, the carbon dioxide flow rate was increased and the oxygen production rose to the theoretical value. It is apparent that the higher the current, the higher the value of the CO₂ concentration at which performance starts to decline.

In addition to ammonium chloroplatinate as a material for applying a thin layer of platinum to the solid electrolyte, a commercially available platinum preparation was tried. This is in the form of a platinum metal suspension in an organic vehicle which also contains other unknown oxides to assist in the bonding of the platinum to the ceramic oxide. In all other respects, the cell construction and operating conditions were the same as those described previously. The solid electrolyte used was a Y₂O₃-ZrO₂ tube. The data are shown in the following table.

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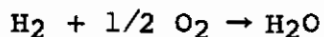
Volts	Current M/amps	Temp. °C	Run Duration <u>Minutes</u>	O ₂ Volume cc	O ₂ Volume Theoretical cc	% CO ₂ in Exhaust
1.85	1000	965	11	43.4	41.8	
2.35	2000	965	11	85.2	83.6	
3.5	5000	970	4.25	77.0	80.75	60

Comparison of these results with those shown earlier indicated that this method of applying the platinum layer was inferior to the use of the ammonium chloroplatinate. The oxygen production dropped below the theoretical oxygen production at much lower currents and a much higher concentration of CO₂ in the effluent. This might have been caused by a lower porosity of the platinum layer or the presence of the unknown oxides in the platinum preparation.

A study was made of the effect the presence of small amounts of impurities in the CO₂ has on operation of the cell. Two possibilities exist. The cell electrodes may be poisoned and the trace impurities may react or interact in the cell to yield undesirable products. In one series of runs, small amounts of water were introduced into the CO₂ by passing the CO₂ through a water bubbler before passing it into the cell. The operating conditions and results are shown in the following table for a cell temperature of 977°.

Terminal Voltage, <u>Volts</u>	Current Mamps	CO ₂ Input cc/min.	Test Duration Minutes	O ₂ Produced cc	O ₂ Produced cc <u>Theoretical</u>
3.3	2000	43	10	83.6	76.0
3.3	2000	43	9	75.4	68.4
3.3	2000	43	10	81.2	76.0
3.3	2000	43	11	85.0	83.6

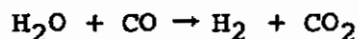
The total duration of the run was 52 hours and the above readings were taken at 7- or 8-hour intervals. The results indicate that the oxygen production was not affected by the presence of the water vapor, but the terminal voltage and thus the power were slightly higher than required when no water was present in the CO₂ feed. An analysis of the effluent gas from the cell showed the presence of a small but definite amount of H₂ in the effluent from the cell. This would explain the increase in the applied voltage, since an increase would be necessary to overcome the back E.M.F. of the cell caused by the reaction:



Other than the formation of small amounts of hydrogen and a slight increase in the cell terminal voltage, no other effect of water introduction was noted. It is not known whether the

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hydrogen was formed by direct electrolysis of water in the cell or by the water-gas reaction:



To this point, solid electrolyte cells had been constructed with platinum powder packed both inside the tube and around the outside of the tube. This represented both an appreciable weight and cost penalty. To reduce these penalties, a solid-electrolyte tube containing 15 weight per cent yttria and 85 weight per cent zirconia was coated with a layer of platinum paste on both the inside and outside surfaces. Several thin platinum wires were run along the length of the outside of the tube and securely fastened flat against the tube by lengths of platinum wire fastened tightly around the circumference of the tube. Platinum wires were pressed tightly against the inside surface of the tube by filling the tube with Fibrefrax which acted to press the wires against the surface. The outside surface of the tube was painted with a second layer of platinum paste.

This tube was then mounted in a Vycor tube in a manner similar to that previously used, and connected to a power source. Pure CO_2 was fed to this cell, and currents as high as 8 amperes were passed through the cell with the theoretical oxygen production being obtained at all times. It appeared that the use of platinum powder was unnecessary, thereby eliminating both the high cost and the weight penalty.

To further improve the cell, a new cell was constructed by coating both surfaces of a 15% Y_2O_3 - 85% ZrO_2 tube with 3 layers of ammonium chloroplatinate, firing each layer before application of the following one. A platinum-rhodium gauze was then wrapped against the outer surface and held tightly against it by a platinum wire tied around the tube. Similarly, a platinum-rhodium gauze was pressed against the inner surface of the tube by filling the tube with lightweight Fibrefrax insulation. Platinum lead wires were attached to the gauze.

This cell was operated continuously for two weeks in a closed-cycle system with a catalytic converter. During this period, the measured oxygen production rate was exactly equivalent to the current flowing in the cell, indicating 100% utilization of the current for oxygen production. The energy requirements for this cell were the lowest of any cell yet constructed, 4 volts being necessary to pass 8 amperes through the cell.

After two weeks of operation, the power requirements started to increase rapidly as the voltage drop across the cell rose from 4 volts to 8 volts, at which time the cell was shut

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down. Based on previous experience with these cells, it was believed that the increase in cell resistance was caused by some alteration in the electrode-electrolyte contact rather than any change in the electrolyte itself. A careful examination of the cell indicated that some change had occurred at the CO₂ electrode but that the oxygen electrode appeared to be intact. Although the nature of the change at the carbon dioxide electrode was not known, it was thought that contact of the platinum electrode with mixtures of carbon dioxide and carbon monoxide at temperatures of the order of 1000°C might be injurious to the platinum. It was not known, however, over what interval of time this damage would develop.

It was not known whether the failure of the cell was caused by the action of the CO₂-CO mixture on the electrode or whether it was caused by a mechanical loss of contact between the gauze and the platinum coating. A study was made of improved materials (alloys) which would be unaffected for longer periods of time by the action of carbon monoxide. There was evidence in the literature that platinum-iridium alloys had better resistance to carbon monoxide than did platinum.

The degradation of the platinum coating on the CO₂ side of the cell over a prolonged period of operation led to the construction of the final experimental cells in a modified fashion. A test cell was constructed from a 15 wt. % Y₂O₃ - 85 wt. % ZrO₂ tube with a 3/4" O.D. and a 2 mm. wall thickness. The tube was 12 inches long and closed at one end. The internal heating element consisted of a 1 cm. O.D. ceramic core on which was wound a Kanthal Al resistance wire. The inside of the solid electrolyte tube where the O₂ is liberated was coated with platinum as in previous models. Coating was accomplished by filling the inside of the tube to a depth of 8 inches with an aqueous suspension of (NH₄)₂ PtCl₆, then draining the tube. The coating was air-dried, then fired to decompose the (NH₄)₂ PtCl₆ to a highly-porous Pt coating. This procedure was repeated 3 or 4 times until the resistance of the 8-inch-coated length was about 5 ohms.

The outer electrode, which is where the CO₂ is fed, is the one at which degradation of the platinum coating was found to have occurred. A coating of platinum-iridium was substituted for the pure platinum. This was based on past experience by others with the use of platinum-iridium alloys in spark plugs where the operating conditions are similar to those encountered in the solid electrolyte cell. The coating on the CO₂ side consisted of a suspension of (NH₄)₂ PtCl₆ and (NH₄)₂ IrCl₆ to yield a 20 wt. % iridium alloy. The aqueous suspension was applied for an 8-inch length, air-dried and fired to decompose the mixture. This procedure was repeated 3 or 4 times until a resistance of about 5

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ohms was obtained for the 8-inch length. Formation of the Pt-Ir alloy was confirmed by x-ray analysis.

A 52-mesh platinum screen was wrapped tightly around the solid electrolyte tube and tied with platinum wire to serve as one current distributor. Four platinum lead wires 0.035 inches in diameter were attached to the outer screen as electrical leads. A platinum screen was pressed tightly against the inner electrode by means of Fibrefrax. The Fibrefrax was filled between the Kanthal heating element and the platinum screen and a Pt, Pt-10% Rh thermocouple was inserted into the hole running through the center of the ceramic heating core. Using this type of construction, the solid electrolyte tube was heated internally, thereby making more efficient use of the heat, and the inside screen was pressed tightly against the inside Pt coating.

The assembled tube was then inserted into a Vycor tube, the proper electrical and gas leads were attached, and the system was insulated. Tests were made to assure that the cell was gastight. A second Pt, Pt-10% Rh thermocouple was pressed against the surface of the outer screen to measure temperature at this point. Pure CO₂ was fed to the cell at 300 cc/min. The following data were obtained:

<u>Temperature</u> <u>(inner), °C</u>	<u>Temperature</u> <u>(outer), °C</u>	<u>Amps.</u>	<u>Volts</u>	<u>O₂ Production</u> <u>cc/min</u>
1010	700	8	3.5	30.4
1010	700	10	4.15	38.0
1010	700	12	4.85	45.6

The CO₂ feed rate was raised to 800 cc/min. and the following data were obtained:

1215	850	20	4.6	76.0
1215	850	25	5.4	95.0
1215	850	30	6.0	114.0 *

It will be noted that all of the measured oxygen production rates are those predicted from theory. The cell was run for 24 hours at a current of 25 amps. and a temperature of 1215° to 1260°C with oxygen production equal to the theoretically predicted rate. The cell was then run at 30 amps. Within the limits of measurement, the oxygen production was equal to the theoretical rate for 6 hours. After 6 hours of operation, the oxygen production rate had definitely fallen below the theoretical rate. The run was interrupted at this point, and careful examination of the solid electrolyte tube revealed dark spots indicating electrolysis of the tube itself with its resultant destruction.

* Initial reading.

The platinum-iridium alloy did not appear to have degraded noticeably.

Based on the performance of the above cell, construction of the cells for the final one-man model was started. The solid electrolyte tubes, 2-foot long with a 1-inch O.D. and a 2 mm. wall thickness were prepared in the same manner as described above. The internal heating element was 14 inches long and 1 cm. in diameter wound with 1 mm. diameter Kanthal A1 wire. Because the diameter of the solid electrolyte tube was increased to 1 inch, the layer of Fibrefrax between the heater and the platinum mesh next to the inside surface of the solid electrolyte tube had to be increased from about 2 mm. to 5 mm. This resulted in an increase in the Kanthal heating wire temperature and subsequent burnout of the Kanthal heating wire. The cell was disassembled, and reassembled using platinum heating wire rather than Kanthal. The platinum heating wire also burned out, leading to the final modification of the cell to be described in a later section.

Catalytic Reactor Development

As described in Section 2, theoretical considerations lead to the selection of nickel as the most suitable catalyst for the disproportionation of CO. Temperatures ranging from 500^oC to 550^oC were thought to be suitable. Experimental evaluation of various iron and nickel catalysts was required to select the most active one.

The catalyst screening experiments, using various catalysts and temperatures, were performed in a 25-mm. O.D. Vycor tube, 24 inches in length. The internal volume of the reactor was about 150 cc. The results are shown in the following table.

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Catalyst	Feed Rate cc/min.	% CO ₂ in Feed	% CO ₂ in Effluent	Temp. °C
1	96.8	26.7	46.7	590
	99.5	28.7	46.7	588
	97.2	28.0	46.7	593
	100.5	29.3	44.0	635
	98.2	30.7	41.3	535
	47.4	24.0	46.7	585
2	96.4	27.3	28.6	590
	98.1	28.6	28.6	600
3	99.4	28.6	56.5	607
	100.5	29.2	58.3	575
	99.4	28.6	52.4	525
	101.4	31.0	52.4	625
	39.7	11.9	69.2	565
	54.5	35.7	57.7	580
	20	0	68	590-605
	15	0	64	590-605
4	27	0	59.5	615
	20	0	45.5	615
	20	0	45.5	595
	20	0	47.7	590
	36	0	13.1	585
	64	0	4.0	605
	5	103.5	32.4	51.8
100.0		33.5	53.5	575
51.5		27.1	57.6	569
48.6		30.0	58.8	582
49.4		31.2	60.0	560
47.6		30.6	60.0	543
46.9		31.8	60.0	520
49.7		30.6	58.8	500
48.3		30.6	58.3	479
49.4		31.2	57.0	454
49.4	31.2	61.3	490	

A description of the catalysts is as follows:

- Catalyst 1. One gram of ferrous oxalate distributed uniformly along the length of the tube. Heated to 600°C in a stream of CO₂.
- Catalyst 2. 2.8 grams of commercial steel wool distributed loosely in the tube.
- Catalyst 3. Quartz wool coated with iron deposited by decomposition of iron carbonyl. 10 grams of catalyst containing about 8 grams of iron distributed loosely in the tube.

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Catalyst 4. Quartz wool coated with nickel deposited by decomposition of nickel carbonyl-2.6 grams of catalyst containing about 1.6 grams of nickel distributed loosely in the tube.

Catalyst 5. 25 grams of nickel oxalate spread uniformly in the tube. Heated to 600°C in a H₂ stream to decompose the oxalate to iron powder.

Large amounts of catalyst gave better results than small amounts. Catalyst 5, appeared to give the best results when a feed containing about 30% CO₂ was used with a residence time of 3 minutes. Under these conditions, variation of the temperature in the range from 500°C to 600°C did not seem to affect the conversion significantly. Conversion dropped both above and below this temperature range. A decrease in residence time caused a decrease in conversion. At 600°C, the equilibrium gas mixture should contain about 75% CO₂. The concentration of CO₂ in the effluent from the reactor was considerably below this value, indicating that a better conversion was possible. To improve CO conversion, several nickel catalysts were evaluated on a comparative basis to determine which gave the highest conversion and maintained its activity over the longest period of time. Of these catalysts, all of which were commercially available from Girdler Corporation* (Catalyst No. G-56, G-15, G-49A, H-219), the H-219 appeared to give the highest conversion and to maintain its activity over the longest period of time.

Further experiments were carried out to determine the effect of operating conditions on the conversion obtained in the catalytic reactor. The following factors were investigated:

- Reactor Volume
- Amount of Catalyst
- Feed Composition
- Linear Flow Rate

The results obtained were summarized as follows. All other operating conditions remaining the same, the conversion obtained with 10 grams of G-49A catalyst was the same as that obtained with 5 grams of G-49A catalyst, provided that the catalyst was spread along the bottom of the reactor the same way in both cases. Cutting the reactor volume in half by cutting the length of the reactor in half but keeping the amount of catalyst used constant, lowered the conversion. For a given reactor volume, the conversion obtained in a long, thin reactor where the velocity is relatively high, was greater than that obtained in a reactor where the linear velocity was low. This indicated a

*Girdler Catalysts, Chemical Products Division, Chemetron Corporation, Louisville 1, Kentucky.

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diffusion effect and pointed out the possible benefits to be obtained by distributing the catalyst more uniformly in the entire volume of the reactor, rather than merely spreading it along the bottom of the reactor.

To improve the handling characteristics of powdered nickel, attempts were made to impregnate Fibrefrax with nickel formate or nickel oxalate, then to thermally decompose and reduce these to powdered nickel. Results did not show any better performance than obtained with the Girdler G-49A catalyst.

In another procedure, attempts were made to impregnate a highly porous, lightweight, rigid, ceramic catalyst carrier made at Isomet with a nickel-nitrate solution. The nickel nitrate was then reduced to nickel. The hope was that this catalyst would retain its shape as carbon deposited on it, and not break up as others do. The activity of the catalyst was, however, low and the indications were that the ceramic was starting to disintegrate as the carbon deposited.

Experiments in which Girdler G-49A catalyst was encapsulated in closed-end Fibrefrax cylinders gave low conversions, indicating that the reaction was being limited by the rate at which the gases could diffuse through the Fibrefrax to reach the catalyst.

Experiments showed that the nickel catalyst was still magnetic at the 500°C operating temperature, indicating the possibility of utilizing magnetic fields to control the movement of the catalyst.

As a result of these screening experiments and preliminary tests on a small-scale, closed-cycle system, the Girdler H-219 nickel catalyst was selected for use in a reactor to be described in Section 4.

Closed Cycle System Development

Prior to the construction of the final engineering model and in conjunction with the tests run separately on the solid electrolyte cell and the catalytic reactor, small scale experiments were carried out on complete closed-cycle systems to observe the operating behaviour and to determine the controls necessary for automatic operation of the system.

The closed cycle oxygen regeneration system consisted of the following essential parts:

A solid electrolyte cell using a solid electrolyte containing 15 weight % Y_2O_3 - 85 weight % ZrO_2 and having the

configuration described in Section 3.

A floating ball flowmeter

A continuous thermal conductivity cell connected to a power supply and recorder and calibrated to read the composition of CO-CO₂ mixtures flowing through the cell.

A catalytic converter having a 3-inch I.D. and a heated length of 18 inches. The converter was provided with a thermowell for a thermocouple to measure the reactor internal temperature. A steel, wire-mesh cylinder with a fine, wire-mesh base on which was spread 8 grams of the nickel catalyst was inserted into the tube. The carbon builds up inside the wire-mesh cylinder and is removed at the end of the run.

A recirculating pump (diaphragm-type)

A constant-pressure, CO₂ feed system. Figure 5 is a schematic drawing of this system.

The system was purged of air by closing valve A, opening valve B and starting the recirculating pump. The flow in the system was adjusted to 300 cc./minute by regulating the flow in the bypass around the pump with a needle valve. A carbon dioxide-carbon monoxide mixture was fed to the system through the constant-pressure feed system. While the system was being purged with this mixture, the catalytic converter was brought up to 500°C and the solid electrolyte cell to 1000°C. When these temperatures were reached, the CO was shut off, valve A was opened, valve B was closed and the electrolysis current in the cell was brought to 8 amperes. Under these conditions, the applied voltage to the cell was 5.5 volts. The theoretical O₂ production under these conditions is 30.4 cc./min. at room temperature and pressure, and the cell was found to be producing this amount within plus-or-minus 1 per cent. With recycle rate maintained at 300 cc./min. and with 8 amperes flowing in the cell, the effluent from the cell contained on the average about 65% CO. The oxygen produced in the cell was analyzed chromatographically and found to contain no detectable impurities.

Operation of the closed-cycle oxygen regeneration system continued for a total of 72 operating hours, with shutdown and cooling during the nights. At the end of this period, the oxygen production was not equal to the theoretically predicted oxygen production and the voltage drop across the cell had increased. The run was terminated. It appeared that the platinum powder in the cell had sintered sufficiently to pull away from the solid electrolyte tube, increasing the contact resistance and causing a higher voltage drop across the cell. In addition, since the contact was poor, electrolysis could not occur properly and the oxygen production rate declined.

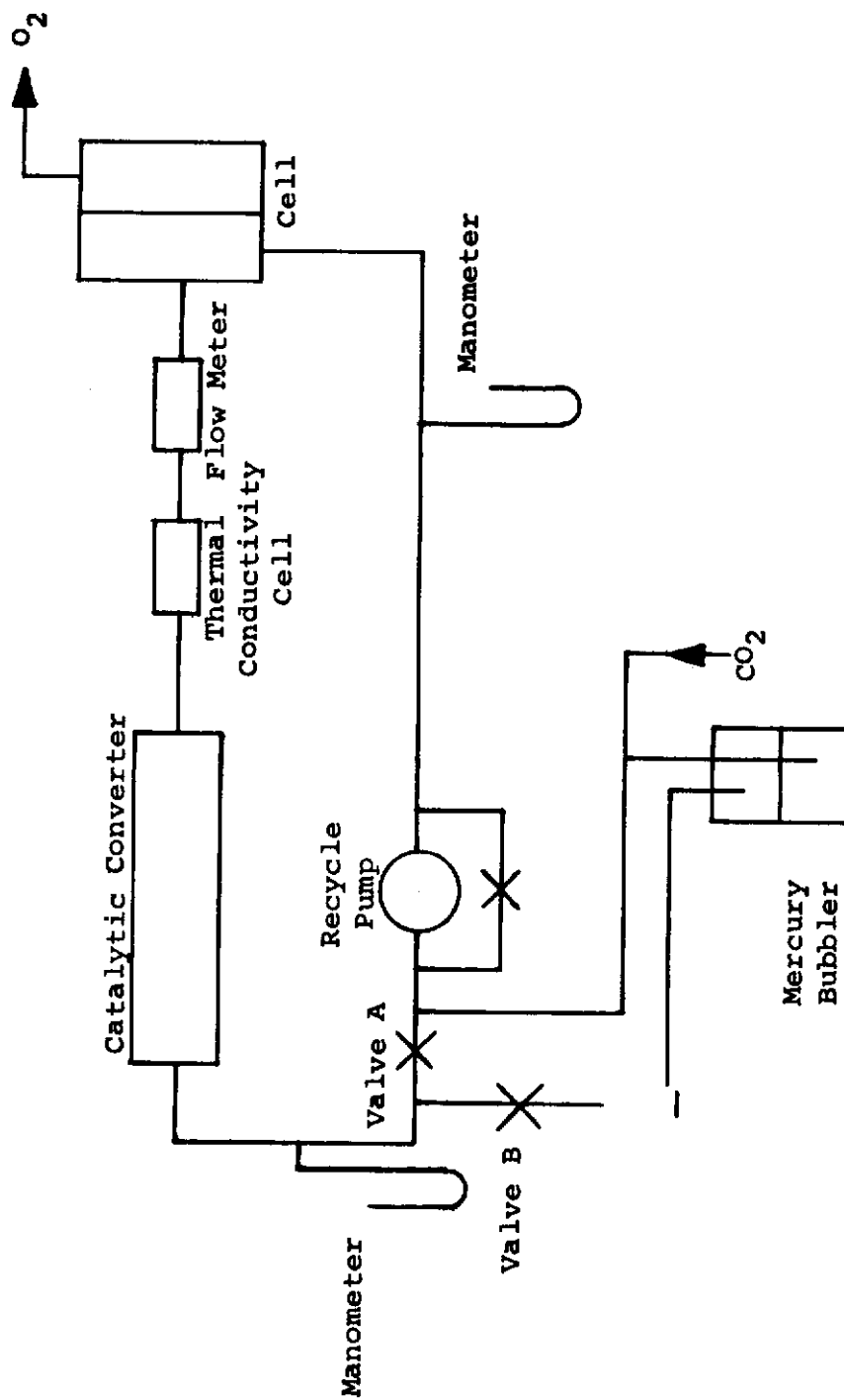


Figure 5. Small Scale Laboratory Solid Electrolyte System

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Based on a current flow of 8 amperes, it was calculated that 0.9 grams of carbon are deposited per hour so that approximately 65 grams of carbon should have been deposited in the 72-hour run. When the catalytic reactor was opened and the catalyst and carbon removed, it was found that their total weight was 72 grams. Since 8 grams of catalyst had been used, it appeared that 64 grams of carbon had been deposited. This constituted excellent agreement with the theoretical prediction. The density of the carbon deposit was found to be 0.35 with no attempt being made to pelletize or compress the carbon deposit. The ratio of carbon-to-catalyst in the final carbon product was 8:1 and the catalyst was by no means exhausted. It appeared quite feasible to attain carbon-catalyst ratios of at least 10:1 with no appreciable decline in catalyst activity.

After repair of the solid electrolyte cell and replacement of the catalyst with 5 grams of Girdler G-49A catalyst spread along the bottom of the converter, the run was continued for another 137 hours of operating time broken up into approximately 8-hour operating periods with overnight shutdowns. In a few cases, runs were allowed to continue throughout the night. Operating conditions were the same as previously described.

Over the total duration of the run, 112 grams of carbon collected in the reactor, giving a final carbon-to-catalyst ratio of 22.4:1. Although it was difficult to determine the practical density of the final carbon product as collected in the reactor, it was determined that the density was greater than 1 and probably around 2. The attainment of such high densities offered the possibility of allowing the carbon to collect in the reactor for extended periods of time without removal.

A condensed log of the run is shown in the following table. The table shows the duration of each portion of the run, the average concentration of CO₂ in the gas entering the cell, and the average concentration of CO₂ in the effluent from the cell.

<u>Duration of Run,</u> <u>hours:minutes</u>	<u>CO₂ Concentration In,</u> <u>%*</u>	<u>CO₂ Concentration Out,</u> <u>%*</u>
35:15	55	34
24:30	48	33
28:15	46	32
16:30	44	32
10:05	43.5	31
7:05	41	29
7:00	41	23
4:15	40	22
3:20	40	22
1:35	38	20

*All percentage readings \pm 2%

Conclusions

Between each successive operation period, the catalytic reactor was cooled from 500°C to room temperature. One interesting and most important result of this periodic cooling was that the catalyst recovered a great part of its activity during this cooling period. It had previously been noted that the catalyst declined in activity during the course of the run. However, as a result of this intermittent cooling procedure, it was found that the useful life of the catalyst could be markedly extended. One promising mode of operation would be to have two catalytic reactors in parallel with one operating, and one cooling down and restoring the catalytic activity. Eventually, however, the duration of catalyst activity became so low that the practical limit of operation was reached.

There was a gradual decline in catalyst activity over the total duration of the run as indicated by the gradual decline in CO₂ concentration in the gas streams. There was also a decline in the useful lifetime of the catalyst from one period to the next.

Summary of Test Results

From the experimental tests performed on the solid electrolyte cell, the catalytic reactor and small scale closed-cycle systems utilizing both of these components the following results were determined:

The solid electrolyte cell could be constructed from a closed end tube made of 8.75 mole % Y₂O₃ - 91.25 mole % ZrO₂, this material having the highest anionic conductivity of any known solid electrolyte.

Best results were obtained with the solid electrolyte cell using a platinum-iridium coating on the CO₂ surface of the solid electrolyte and a platinum coating on the O₂ surface of the solid electrolyte.

Platinum screen electrodes applied to both surfaces of the electrolyte were found to be satisfactory.

A suitable cell-operating temperature was 1000°C.

The oxygen produced in a leak-free cell contained no detectable impurities.

The CO₂ concentration in the cell must be kept above a certain level for the cell to function properly. This critical concentration is dependent on the cell dimensions and on the current flowing.

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A nickel catalyst is most suitable for use in the catalytic reactor.

Of those catalysts tested, Girdler H-219 nickel catalyst gave the best results.

Higher linear flow rates gave higher rates of CO conversion in the catalytic reactor.

Temperatures ranging from 500° to 530°C gave highest conversion in the catalytic reactor.

Ratios of carbon-to-catalyst of at least 20:1 were obtained in the final product before deactivation of the catalyst.

Carbon product densities of about one could be obtained without compression or pelleting.

Operation of the complete closed-cycle system was simple with feed of CO₂ being by demand. Carbon dioxide could be automatically fed into the system to balance the oxygen production.

SECTION 4

ENGINEERING MODEL

Design Requirements

In the engineering model of the solid electrolyte CO₂ conversion system, there were several requirements to be met. These were:

The system should demonstrate the technical feasibility of reducing carbon dioxide to carbon and oxygen using the solid electrolyte system.

The contents of the catalytic reactor should be easily removable and replaceable.

Power, size and weight requirements should be as low as possible.

The system should demonstrate a capability for operation under normal and zero-gravity conditions.

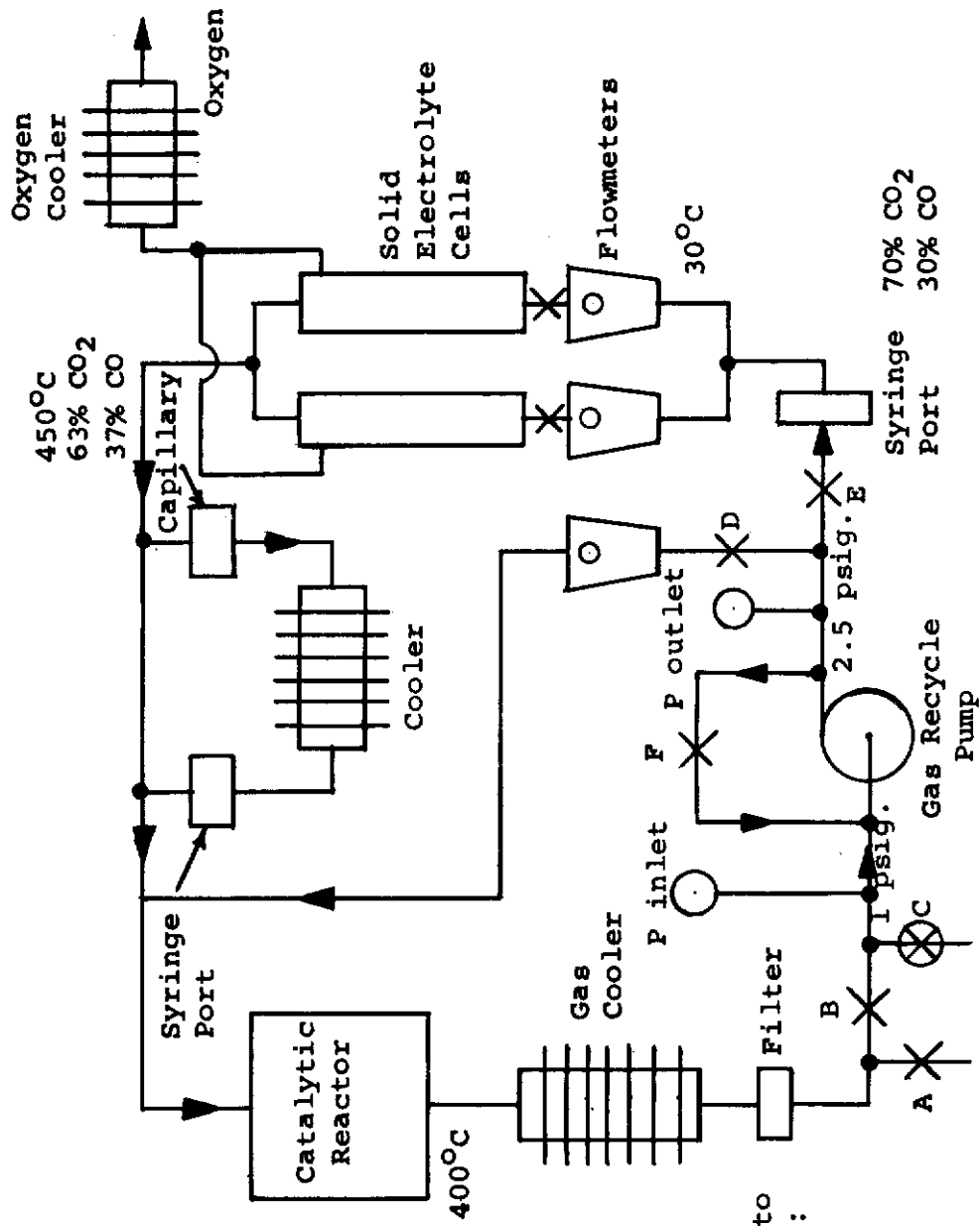
The system should demonstrate a capability for automatic control and operation.

Overall System and Flow Diagrams

Based on the information obtained in the preliminary experimental program, it was possible to specify the components required for the engineering system. In general, the system was to consist of the solid electrolyte cells, the catalytic converter, a recycle gas pump, a gas cooler on the reactor exit, provision for obtaining samples of the product oxygen and recirculating gas from different points in the system, an automatic CO₂ feed system, and system controls and instrumentation.

Figure 6 is a block diagram of the engineering model showing typical temperatures, pressures, and gas compositions at various points in the system.

Starting at the entrance to the solid electrolyte cells, the gas passes into the cell at room temperature and about 2.5 psig. The gas entering the cell emerges at about 450°C. Under a typical set of operating conditions, the gas entering the cell is about 70% CO₂ and 30% CO. In the cell the CO₂ is electrolyzed to CO, and O₂ is produced which leaves the cell at the ambient pressure. Composition of the effluent gas will vary depending on the oxygen



Letters on Figure refer to valves shown in Figure 7:

- A. Purge out
- B. Purge
- C. Pressure Control
- D. Cell Bypass
- E. Cell Inlet
- F. Pump Bypass

Figure 6
Block Diagram of Engineering Model

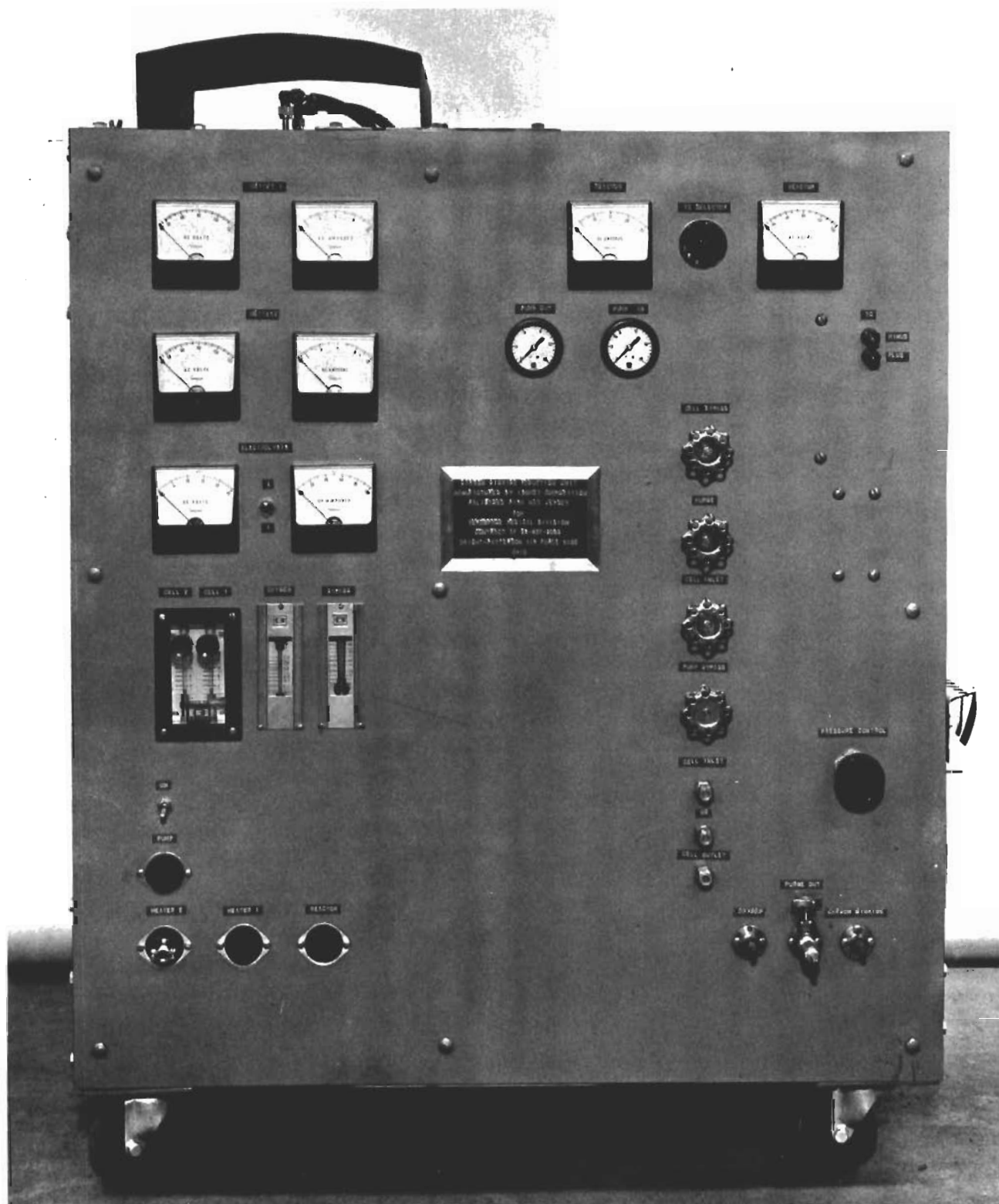


Figure 7. Front View of CO₂ Reduction System

Contrails

production rate and the gas flow rate. The effluent composition shown on the block diagram is 63% CO₂ and 37% CO, a typical number.

The gases leaving the cell are cooled almost to room temperature by heat loss from the line leading from the cell exit to the reactor entrance. A small portion of this gas is bypassed through a cooler and a hypodermic syringe sampling port. A bypass line around the cells is also provided so that gas can be passed through the reactor at a faster rate than through the cells, thereby allowing improved performance of the reactor. This arrangement permits a wide variation in flow rates through the cells and reactor. It is desirable to maintain as low as possible a flow rate through the cell since the cool gas entering the cell throws an additional heating load on the cells. The gas leaving the cells mixes with the bypassed gases and enters the catalytic converter which operates at about 500°C. The carbon formed in the converter is mixed intimately with the catalyst and retained in the catalyst bed which itself acts like a carbon filter. The gases leave the reactor at about 400°C and are cooled to room temperature prior to admission to the recirculation pump. The replacement CO₂ is admitted to the system at the inlet to the pump which is at a pressure of 1 psig. Admission of CO₂ is by means of a pressure control valve, set to maintain a pressure of 1 psig. at the pump entrance. Carbon dioxide is admitted when the pressure drops below this value as a result of conversion of CO₂ to carbon and oxygen.

The recycle pump has a bypass line around it so that the amount of gas circulating through the cell-reactor system can be controlled by opening or closing the valve in the pump recycle line. The incorporation of the various flow bypass lines into the system allows wide latitude in the flow of gas through the various parts of the system.

A detailed description of each of the major components is given in the following paragraphs.

Catalytic Reactor

The reactor consists of a 1/16-inch thick, 304 stainless steel cylinder 8 inches in diameter and 10 inches long. A 1/4-inch plate is welded to one end of this cylinder. The cylinder is heated internally by means of three Calrod heaters bent into the form of a U with the ends of the U coming up through the 1/4-inch plate through gastight Swagelok fittings. The gas inlet tube consists of a tube leading to the bottom of the cylinder and into a tubular ring to which are attached numerous small diameter tubes with holes drilled in them. These small tubes, reaching to the top of the cylinder, are all dead-ended and have numerous small

Contrails

holes drilled radially into them to distribute gas uniformly and to allow for possible plugging of holes by carbon formation. The gas exits through a small central tube with small holes drilled radially into it. A thermocouple can be inserted into a closed end thermowell welded into the top plate. Inlet and outlet gas tubes are equipped with Swagelok fittings for connection to gas circulating lines. The cylinder is filled loosely with 2 pounds of Girdler H-219 powdered nickel catalyst intimately mixed with loosely packed quartz wool. A 1/4-inch plate with several small holes drilled in it is bolted to the other end of the cylinder by means of a narrow flange on the cylinder. This serves to hold the catalyst in the reaction cylinder. This whole cylinder, which actually consists of a completely preformed reaction cartridge, is then inserted into a second cylindrical can surrounded by 4 inches of aluminum-foil coated Fibrefrax blanket insulation. The Fibrefrax insulation is also placed for a depth of 4 inches below the can to insulate the bottom. About 3 inches of the same Fibrefrax insulation is placed over the top of the can. The entire apparatus is enclosed in an outer jacket and a cover is placed over the top. Gas inlet and outlet tubes and the ends of the heating elements protrude through the top of the outer cover. The entire reaction chamber is insulated both peripherally and on the top and bottom.

Preliminary experiments were performed to determine the amount of power required to maintain the reactor at 500°C, its expected operating temperature. With 350 watts, the temperature could be maintained at 500°C with a small flow of nitrogen passing through the reactor. It was anticipated that the power requirement in actual operation would be slightly less than this because of the exothermic nature of the reaction. The greatest part of this heat loss is by free convection heat transfer from the jacketed surface. Since the jacket has a very low emissivity, the amount of heat lost by radiation is very small, only about 10% of the total heat loss. Under conditions where this reactor is in a gravity-free environment, heat loss by free convection would be eliminated, and the exothermic nature of the reaction should be sufficient to supply the heat loss by radiation. It was therefore anticipated that under actual zero-gravity operating conditions the reactor would be self-sustaining.

After construction and assembly of the reactor, a long-term test was performed to observe the behaviour of the reactor. The feed to the reactor was pure CO and the run was continuous except for a weekend shutdown between days 2 and 3. The following table is a record of the run.

Contrails

<u>Day</u>	<u>Time</u> <u>Hour</u>	<u>Temp.</u> <u>°C</u>	<u>Exit Flow,</u> <u>cc/min.</u>	<u>% CO₂ out</u>	<u>CO₂ formed,</u> <u>cc/min.</u>	<u>Power Input,</u> <u>Watts</u>
1	12:30	500		Start Run		
1	17:30	-	-	32	-	-
2	8:30	505	1050	33.2		-
3	16:00	505	1300	27.8	361	-
4	8:30	525	1215	27.8	338	395
4	17:15	520	1330	26.6	354	-
5	8:15	527	1330	27.9	371	382
5	10:30	525	1360	27.1	369	-
6	8:30	527	1272	31.5	401	328
6	16:00	525	1300	30.5	398	328
7	8:00	537	1560	26.8	418	300
7	11:30	518	990	37.3	370	293
8	8:30	543	880	47.0	413	281
8	15:30		Run over			

Contrails

At 15:30 on the eighth day, the supply of CO ran out. When the run was continued the following day it was noted that the power requirement was down to 277 watts and that the CO₂ production rate was 458 cc/min. Soon after starting up, the pressure rose to 1.8 cm. Hg., an indication that the reactor was beginning to fill. The run was discontinued, the reactor cooled, and the contents removed and weighed. The reactor had initially been filled with 2 pounds of Girdler H-219 nickel catalyst distributed on 4 ounces of quartz wool. After hydrogen reduction of the nickel catalyst, there were 1.5 pounds of nickel in the reactor. At the end of the run, the contents of the reactor weighed 6 lbs., 6 oz. It was calculated that 2100 grams of carbon had been deposited during the course of the run, approximately the equivalent of 7 man-days of operation. The final density of the product was 0.36 gr./cc.

Several observations were made, based on this run. It appeared that the conversion had increased slightly over the course of the run, probably resulting from "running in" of the catalyst. This effect had been noted in previous experiments with catalyst. The power required to maintain the reactor at temperature decreased over the course of the run, probably due to the buildup of carbon which acted like additional insulation in the reactor. Although the run was discontinued when the inlet pressure reached about 2 cms. Hg., the catalyst still retained its activity and the run could have been continued for a longer period of time, probably until the pressure built up to about 12 cms. Hg. The final product density of 0.36 gr/cc was well below that obtained in previous experiments and indicated that the reactor could be used for more than 7 man-days of operation. As a result of this test, it was decided that the reactor was functioning satisfactorily, and it was used without further modification in the final engineering tests of the system.

Solid Electrolyte Cells

Results of previous tests indicated that two 1-inch-diameter solid electrolyte tubes, two-foot long would allow operation of the cells at conservative values of current density even at the one-man level. The cells were, therefore, constructed from tubes of this size having a composition of 8.75 mole % Y₂O₃-91.25 mole % ZrO₂. The tubes were prepared as described in Section 3. They were then inserted in a Kanthal A1 heating coil wrapped with Fibrefrax insulation. A platinum, platinum -10% rhodium thermocouple had previously been attached to the outer surface of the solid electrolyte tube. The entire tube-heater assembly was then sealed at its upper end into a flange by means of a packing gland. The flange was equipped with electrical terminals to which heater leads, electrodes and thermocouple were attached. This assembly

Contrails

was then inserted in a casing having a mating flange at which the seal was made. The casing was equipped with inlet and outlet lines for gas. The two cells were identical in construction and the oxygen effluent lines were connected to a common line. Both cells were finally insulated with four inches of Fibrefrax blanket coated with aluminum foil.

Recycle Pump

Since gas is continually recycled through the system, a non-leaking pump capable of overcoming the pressure drop in the system is required. Based on an examination of pump characteristics, it was found that the smallest available pumping system would utilize a diaphragm pump. A sliding-vane, non-lubricated pump would also be suitable but would be heavier, require greater power, and cause more heating of the gas in its passage through the pump. The pump used a 1/6 HP., 110 volt, 60-cycle motor and had a pumping capacity of about 20 liters per minute under the pressure drop conditions encountered in the system. Since the pump had a plastic diaphragm, the gas entering the pump from the catalytic reactor was cooled by passage through a finned-tube cooler prior to admission to the pump. A filter was also placed in the pump entrance line to prevent entrance of any catalyst or carbon dust into the pump. A valved bypass line around the pump was also provided.

Controls and Instrumentation

The variables to be controlled in this system are as follows:

- Cell operating temperature
- Reactor operating temperature
- Electrolysis Current
- Gas flow through cells
- Bypass flow around cells
- System operating pressure

The cell and reactor temperatures are sensed by platinum, platinum-10% rhodium thermocouples and indicated on a potentiometer through a multipoint switch on the instrument control panel. Power inputs to the heaters are monitored by A.C. voltmeters and ammeters on the control panel and are controlled by variable transformers plugged into the control panel. The electrolysis current and voltage drops across the two cells are monitored by D.C. voltmeters and ammeters. The electrolysis current is controlled by a variable transformer on the D.C. power supply. Gas flows were monitored by floating ball flowmeters and controlled by needle valves in the appropriate lines. The system pressure

Contrails

is controlled by a standard pressure control valve that admits CO₂ only fast enough to maintain the desired pressure. Two pressure gauges indicate the pressure at the inlet and outlet of the recirculating pump. The CO₂ is admitted at the inlet of the pump and it is this pressure that is controlled by the pressure control valve. The recycle pump is operated by an on-off switch.

System Assembly and Preparation for Operation

The system used in the engineering model consisted essentially of two solid electrolyte cells, a catalytic reactor, and a recycle pump. The two cells are in parallel with respect to gas flow, and in series with respect to electrolysis current flow. Other features of the system have been described previously. All components of the system were assembled on a mobile Dexion frame, 33" x 30" x 36" in size. All connections were made by Swagelok fittings. The system was pressurized to 5 psig. with a mixture of nitrogen and freon and tested for leaks using a halogen leak detector. All connections were found to be leaktight but it was found that both solid electrolyte tubes had developed porosity during the platinum application procedure. This had not happened on any of the other tubes previously used and the reasons for the development of this porosity are not now known. Since the slight porosity of the tubes would not interfere with the system operation, these tubes were used with the understanding that the product oxygen would be monitored for the presence of CO₂ and CO.

The catalytic reactor was filled with two pounds of the Girdler H-219 nickel catalyst uniformly distributed on about six ounces of quartz wool. This catalyst required hydrogen reduction before use. The system was first purged with pure nitrogen to remove all freon. The hydrogen gas was introduced into the system at about 8 ft.³/hr. through the carbon dioxide feed line. The hydrogen passed through the cold cells into the catalytic reactor and out to a water collection tank attached to the reactor through a small auxiliary line and valve. The hydrogen emerging from the water collection tank was vented to the roof. The catalyst was reduced for 8 hours at slowly increasing temperatures up to 350°C. During this time, 210 grams of water were collected. After 8 hours, no more water collected, indicating completion of the reduction. The system, following purging with nitrogen, was now ready for operation.

System Operation

The whole system was purged with nitrogen through the water collector and the water collector was then valved off from the rest of the system. Purging was continued by feeding nitrogen into the system through the CO₂ feed line and out through the exit

marked "Purge out". The valve marked "Purge" was closed. A complete log of the Engineering Model test run is shown in the Appendix.

At several points during the run, the product oxygen was analyzed for carbon monoxide using a gas chromatograph. None was detected by sensitivity was inadequate for detection of low levels.

Engineering Model Test Results

The startup and operation of the system were without incidents and the system performed as expected. Other than the porosity of the solid electrolyte tubes, which based on previous experience was a unique experience, no defects were detected in the system. It is of interest to note for future reference that even though the tube did leak, little or no carbon monoxide was detected in the oxygen. Cell and reactor construction techniques appeared to yield gastight units.

Electrolytic cell resistance were higher than anticipated on the basis of previous tests and heat losses from the reactor were slightly high. The pressure drop in the system was low, only about 1.5 psig. The catalyst activity appeared to increase during the course of the run, as shown by the higher CO₂ concentrations in the gas stream on the second day of operation. There was a noticeable heat effect from passage of the electrolysis current and from the exothermic reaction in the catalytic reactor.

Control of the system was simple, and carbon dioxide feed to the system was automatic. The technical feasibility of the system was demonstrated by this model, and the ease of operation confirmed the results obtained in previous small scale tests.

Weight, Power and Volume

Each of the cells weighed about 30 pounds and the fully loaded reactor weighed about 30 pounds. The recirculating pump weighed about 16 pounds. Piping, wiring, instruments, and controls weighed about 20 pounds. The whole system, including the Dexion frame, occupied a volume of 30" x 33" x 36" and weighed about 150 lbs.

The power requirements at a production rate of 150 cc. of O₂ per minute were as follows:

Electrolysis Cell 1.

Heating power (A.C.)	237 watts	
Electrolysis power (D.C.)	90	
Total Power		327 watts

Electrolysis Cell 2.

Heating power (A.C.)	189	
Electrolysis power (D.C.)	86	
Total Power		275

Reactor	580	
Recycle Pump, (1/6 H.P.)	<u>125</u>	
Total		1307 watts

Summary on the Engineering Model

The engineering model consists of a catalytic reactor, two solid electrolyte cells, a gas recycle pump, and associated instrumentation and controls. Figures 7 and 8 show two different views of the system. The catalytic reactor operates at 500°C while the solid electrolyte cells are run at 1000°C. The system operates at essentially atmospheric pressure with a recycle rate of about 1 CFM.

The cells are 1-inch-diameter, solid electrolyte tubes, two-foot long with appropriate heaters, thermocouples, and insulation. The reactor is an insulated, internally heated canister filled with two pounds of Girdler H-219 catalyst spread on about 6 ounces of quartz wool. The recycle pump is an electric-motor-driven diaphragm pump. The system operated with automatic "demand" feed of CO₂ which is directly related to the oxygen production rate.

Tests showed the system to operate simply with a minimum of attention. Unexplained porosity of the solid electrolyte tubes allowed CO₂ to leak into the product oxygen, but no CO was detected in the oxygen.

The system weighed about 150 pounds, occupied a volume of 30" x 33" x 36", and required about 1300 watts at an oxygen production rate of 150 cc./min.

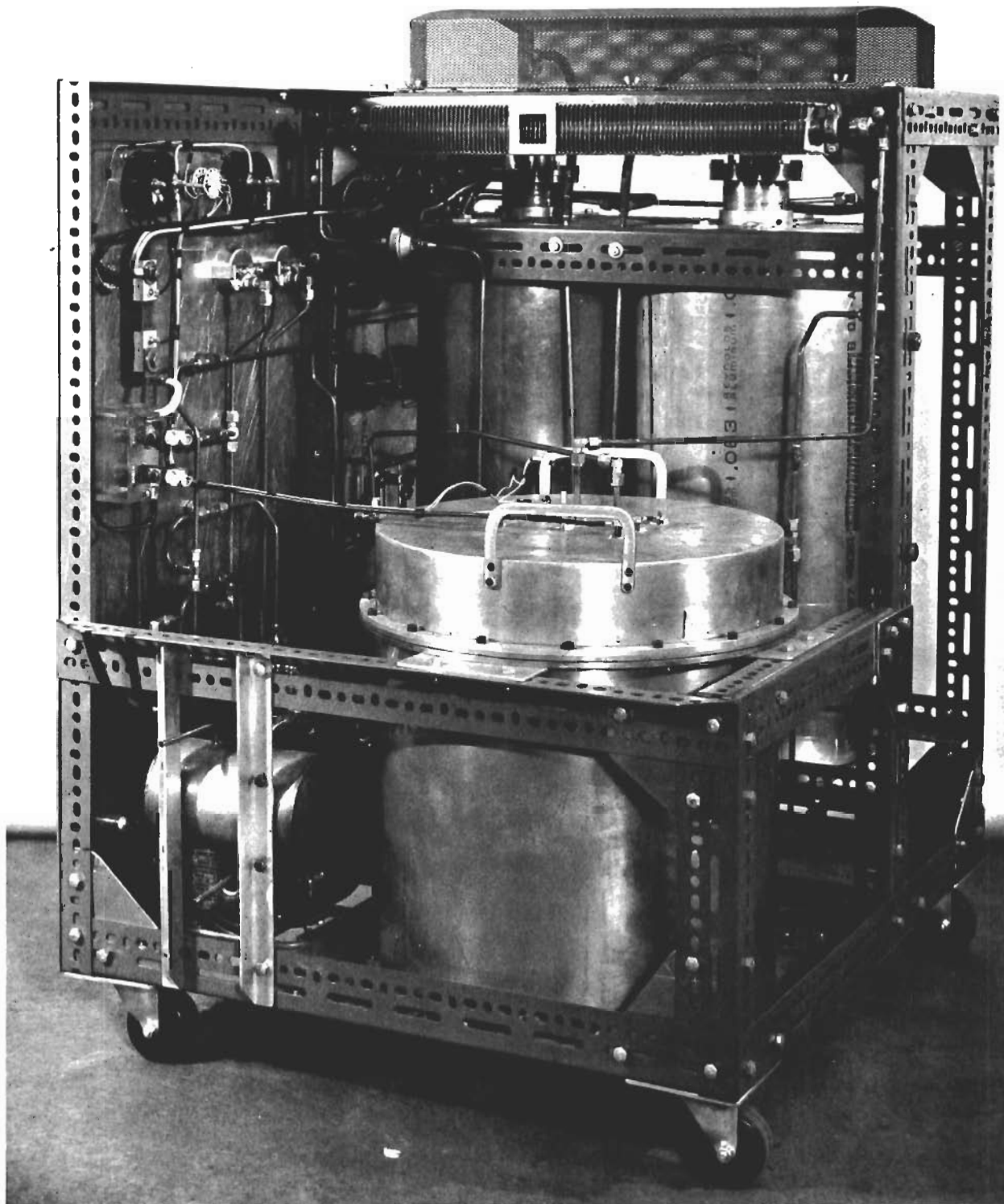


Figure 8. Side View of CO₂ Reduction System

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on the results of this program involving preliminary experiments and the construction and operation of the engineering model, the following conclusions can be drawn:

Operation of the system is simple and requires a minimum of attention.

Nickel is a suitable catalyst for the carbon monoxide disproportionation reaction.

Higher pressures increase conversion in the catalytic reactor but do not appreciably affect cell operation.

Hydrogen reduction of the catalyst at 300°C yields an active catalyst.

A suitable reactor operating temperature range is 500° - 530°C.

The reactor is capable of holding a minimum of 7 man-days of carbon.

The catalytic reaction liberates a detectable amount of heat.

The solid electrolyte cell operates at about 1000°C.

The solid electrolyte used in the engineering model cells contained 8.75 mole % Y_2O_3 , 91.25 mole % ZrO_2 .

Cell resistances in the engineering model were about 0.2 ohms.

Recommendations

This study led to the development of the first operating engineering prototype of the solid electrolyte system for carbon dioxide reduction to carbon and oxygen. Although operation of the system was satisfactory from all points of view with the exception of the unexplained development of porosity in the solid electrolyte tube, the experience gained in this program makes it realistic to expect marked reductions in weight, volume, and power require-

ments of the system.

As an example, assuming a power penalty of 300 pounds per kilowatt and changes in cell and reactor construction that are possible with further development, an optimum one-man system would be conservatively estimated to consume about 625 watts and weigh about 100 pounds exclusive of the support frame and power source; while an optimum 3-man system would consume about 1000 watts and weigh about 120 pounds.

To reach these or even more favorable goals, the following recommendations for further development are made:

A more active, lightweight catalyst should be developed. This would allow the use of a smaller reactor for a given rate of conversion, resulting in weight and power saving. Isomet has carried out preliminary experiments on catalyst preparation techniques which indicate that such improved catalysts can be prepared.

Methods for continuously introducing fresh catalyst into the reactor and removing a mixture of carbon and spent catalyst should be studied concurrently with the catalyst development program. Such a technique will be required if the full benefits of an improved catalyst are to be realized.

Modification of the reactor construction to eliminate metal-metal contacts, which it is believed are responsible for the high heat losses, should be studied.

Possibilities of utilizing heat exchange between various streams in the system should be investigated. There is a possibility of utilizing hot streams, which must be cooled to heat cold streams which must be heated. Such an arrangement is capable of potential savings of about 300 watts.

Realization of the above-mentioned power savings depend on the development of suitable improved cell construction techniques, with particular importance being attached to improved high temperature seals. Recent developments in ceramic-metal sealing techniques make this technically feasible.

Improved solid-electrolyte cell fabrication techniques make it probable that cell resistances lower by a factor of ten than those in the present unit can be achieved. Such a development is vitally important to the ultimate success of this system and should receive maximum attention.

Methods for minimizing heat losses from the cells

Conclusions

should be studied. Such savings can be realized by changes in cell construction.

The possibility of electrolyzing water in the solid electrolyte cell should be investigated extensively. Preliminary results reported in this paper indicate its feasibility. The effect of introduction of water on the operation of the whole system should also be studied in detail.

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Contrails

APPENDIX

LOG OF ENGINEERING MODEL TEST RUN* CELL 1

Day	Time	Flow	ACV	ACA	DCV	DCA	MV	°C
	Hour							
1	8:30	0	10	1.0	0	0	-	25
	9:00	0	10	1.0	0	0	0.31	52
	9:30	0	15	2.0	0	0	0.75	115
	10:00	0	21	3.0	0	0	1.60	220
	10:30	0	30	4.0	0	0	3.00	375
	11:45	2	30	4.0	0	0	4.71	550
	13:00	2	30	4.0	0	0	5.35	613
	13:30	9	38	5.0	0	0	6.34	707
	14:00	9	42	5.5	0	0	7.15	782
	14:30	9	46	6.0	0	0	7.95	855
	15:00	9	46	6.0	1.8	5	8.86	937
	15:30	9	46	6.0	2.8	11	9.13	962
	16:00	9	46	6.0	3.7	15	9.43	990
	16:30	9	46	6.0	4.5	20	9.83	1023
	17:00	9	43	5.5	4.5	20	9.67	1010
	17:30	-	-	-	3.6	15	-	-
	18:00	-	-	-	-	10	-	-
	18:30	-	-	-	-	5	-	-
	19:00	-	-	5.0	-	0	-	-
	19:40	-	-	-	-	-	-	-
2	8:30	9	37	4.9	0	0	7.90	850
	9:00	9	46	6.0	0	0	8.84	938
	9:30	9	46	6.0	1.8	5	9.20	968
	10:00	9	46	6.0	2.8	10	9.47	992
	11:00	9	46	6.0	3.7	15	9.93	1032
	12:00	9	42	5.5	4.5	20	9.85	1025
	13:00	9	41	5.4	4.5	20	9.80	1020
	14:00	9	42	5.4	4.5	20	9.73	1016
	15:00	-	-	-	-	15	-	-
	16:00	-	-	-	-	0	-	-
	17:00	-	-	-	-	-	-	-
	17:30	-	-	-	-	-	-	-

* The column symbols are identified as follows:

Flow - Gas flow in ft.³/hr measured as air

ACV - A.C. volts on heater

ACA - A.C. amps. through heater

DCV - D.C. electrolysis volts on cell

DCA - D.C. electrolysis current through cell

MV - Thermocouple millivolts

°C - Temperature

Contrails

CELL 2

Day	Time Hour	Flow	ACV	ACA	DCV	DCA	MV	°C
1	8:30	0	10	1.0	0	0	-	25
	9:00	0	10	1.0	0	0	0.29	51
	9:30	0	18	2.0	0	0	0.78	120
	10:00	0	27	3.0	0	0	1.15	165
	10:30	0	36	4.0	0	0	2.89	365
	11:45	2	36	4.0	0	0	5.15	593
	13:00	2	36	4.0	0	0	5.98	696
	13:30	9	46	5.0	0	0	6.96	763
	14:00	9	46	5.1	0	0	7.69	832
	14:30	9	50	5.4	0	0	8.45	902
	15:00	9	50	5.5	1.8	5	9.33	980
	15:30	9	50	5.3	2.7	11	9.53	997
	16:00	9	50	5.3	3.5	15	9.80	1020
	16:30	9	46	5.0	4.3	20	9.87	1025
	17:00	9	44	4.8	4.3	20	9.78	1018
	17:30	-	-	-	3.4	15	-	-
	18:00	-	-	-	-	10	-	-
	18:30	-	-	-	-	5	-	-
	19:00	-	-	4.5	-	0	-	-
	19:40	-	-	-	0	-	-	-
2	8:30	9	40	4.4	0	0	8.10	870
	9:00	9	50	5.4	0	0	9.07	957
	9:30	9	50	5.4	1.7	5	9.46	990
	10:00	9	50	5.4	2.7	10	9.79	1020
	11:00	9	46	5.0	3.5	15	9.84	1025
	12:00	9	44	4.7	4.3	20	9.85	1025
	13:00	9	42	4.6	4.3	20	9.78	1018
	14:00	9	42	4.5	4.3	20	9.70	1012
	15:00	-	-	-	-	15	-	-
	16:00	-	-	-	-	0	-	-
	17:00	-	-	-	-	-	-	-
	17:30	-	-	-	-	-	-	-

Contrails

REACTOR

Day	Time Hour	ACV	ACA	MV	°C
1	8:30	40	5.8	2.62	337
	9:00	40	5.8	2.55	327
	9:30	40	5.8	2.52	324
	10:00	40	5.8	2.47	318
	10:30	40	5.8	2.52	323
	11:45	50	7.6	2.77	350
	13:00	50	7.6	3.12	387
	13:30	60	9.0	3.42	420
	14:00	60	9.0	3.59	438
	14:30	67	10.0	3.94	474
	15:00	67	10.0	4.14	493
	15:30	67	10.0	4.28	506
	16:00	67	10.0	4.40	520
	16:30	61	9.1	4.27	505
	17:00	62	9.2	4.25	504
	17:30	-	-	-	-
	18:00	-	-	-	-
	18:30	-	-	-	-
	19:00	-	-	-	-
	19:40	-	-	-	-
2	8:30	61	9.0	4.05	483
	9:00	66	9.9	4.28	507
	9:30	66	9.9	4.32	510
	10:00	66	9.9	4.37	515
	11:00	62	9.2	4.25	504
	12:00	62	9.2	4.22	501
	13:00	63	9.3	4.23	502
	14:00	63	9.2	4.24	503
	15:00	-	-	-	-
	16:00	-	-	-	-
	17:00	-	-	-	-
	17:30	-	2	-	-

Contrails

MISCELLANEOUS

Time Day	Hour	Bypass Flow	% CO ₂ into cell	% CO ₂ out of cell	% CO ₂ in O ₂	Press. into Pump (psig)	Press. out of Pump (psig)
1	8:30	-	-	-	-	-	-
	9:00	-	-	-	-	-	-
	9:30	-	-	-	-	-	-
	10:00	-	-	-	-	-	-
	10:30	-	-	-	-	-	-
	11:45	0	-	-	-	-	-
	13:00	0	-	-	-	-	-
	13:30	20	-	-	-	1.2	2.5
	14:00	20	-	-	-	1.2	2.3
	14:30	20	-	-	-	-	-
	15:00	20	93.3	89.7	30	-	-
	15:30	20	77.3	69.0	16.5	1.1	2.3
	16:00	20	63.8	58.3	10.8	0.9	2.2
	16:30	20	56.7	52.6	9.3	0.9	2.2
	17:00	20	62.8	53.0	12.4	-	-
	17:30	20	-	-	-	-	-
	18:00	20	-	-	-	-	-
	18:30	20	-	-	-	-	-
	19:00	20	-	-	-	-	-
	19:40	20	-	-	-	-	-
2	8:30	20	-	-	-	0.9	2.3
	9:00	20	-	-	-	-	-
	9:30	20	81.5	78.1	-	0.9	2.3
	10:00	20	73.2	68.5	15.7	0.9	2.3
	11:00	20	69.5	64.7	15.7	0.9	2.3
	12:00	20	70.3	63.0	12.6	0.9	2.3
	13:00	20	67.7	61.0	12.6	-	-
	14:00	20	68.8	58.3	12.95	0.9	2.3
	15:00	-	-	-	-	-	-
	16:00	-	-	-	-	-	-
	17:00	-	-	-	-	-	-
	17:30	-	-	-	-	-	-

Contrails

NOTES

Day	Hour	Comments
1	8:30	Turn on Heaters 1 & 2, 1 amp. each. N ₂ purging
	9:00	Heaters 1 & 2, 2 amp. each
	9:30	Heaters 1 & 2, 3 amp. each. Switch to CO ₂ purge
	10:00	Heaters 1 & 2, 4 amp. each
	10:30	---
	11:45	Reactor to 50 volts, 7.6 amps.
	13:00	Heater 1 to 4.5 amps.
	13:30	Heater 1 to 5.5 amps., Heater 2 to 5 amps.
	14:00	Reactor to 10 amps
	14:30	Heater 1 to 6 amps. Heater 2 to 5.5 amps. Electrolysis to 5 amps.
	15:00	Electrolysis to 10 amps
	15:30	Electrolysis to 15 amps.
	16:00	Reactor to 9 amps. Heater 2 to 5 amps.
	16:30	Electrolysis to 20 amps. Heater 1 to 5.5 amps. Heater 2 to 4.8 amps.
	17:00	---
	17:30	Electrolysis to 15 amps.
	18:00	Electrolysis to 10 amps.
	18:30	Electrolysis to 5 amps.
	19:00	Electrolysis off. Heater 1 to 5 amps. Heater 2 to 4.5 amps.
19:40	Leave for night. Pump on.	
2	8:30	Heater 1 to 6 amps., Heater 2 to 5.4 amps., reactor to 10 amps.
	9:00	Electrolysis to 5 amps.
	9:30	Electrolysis to 10 amps.
	10:00	Heater 2 to 5 amps., Reactor to 9.2 amps. Electrolysis to 15 amps.
	11:00	Heater 1 to 5.5 amps., Heater 2 to 4.8 amps., Electrolysis to 20 amps.
	12:00	---
	13:00	Heater 1 to 5.4 amps. Heater 2 to 4.6 amps.
	14:00	---
	15:00	Electrolysis to 15 amps.
	16:00	Electrolysis from 15 to 0 amps. over 1-hour period.
	17:00	---
	17:30	All heaters off. Pump overnight.