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CHEMICAL AND STRUCTURAL PRODUCTS DIVISION

RESEARCH ON PROCESSES FOR UTILIZATION OF LUNAR RESOURCES

A REPORT TO

NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

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AEROJET
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RESEARCH ON PROCESSES FOR UTILIZATION OF LUNAR RESOURCES

a report to

OFFICE OF ADVANCED RESEARCH AND TECHNOLOGY
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C.

S. D. Rosenberg, G. A. Guter, F. E. Miller, and R. L. Beegle, Jr.

Contract NAS 7-225

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AEROJET-GENERAL CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

Report No. 3049

This report is submitted in partial fulfillment of Contract NAS 7-225. The period covered by the report is 22 April 1963 through 15 July 1965.

AEROJET-GENERAL CORPORATION

L. R. Rapp, Manager
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Report No. 3049

ABSTRACT

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Laboratory apparatus was designed, fabricated, and operated for studying the reduction of up to 1 lb of igneous rock with carbon, hydrogen, and methane. Several experiments demonstrated that with the use of specially designed inlet tubes, methane reacts with natural silicate materials at 1600°C to form carbon monoxide, hydrogen, silicon, trace metals, and slag. Nearly quantitative carbon balances were achieved. Reactor materials were found which allow the reaction to run at 1600°C for long time periods.

Laboratory apparatus for studying the catalytic reduction of carbon monoxide with hydrogen was designed, fabricated, and operated. Three different nickel-containing catalysts were evaluated. In addition, a determination was made of the effects on catalyst activity of several impurities in the reactant gas and of the feasibility of achieving the reduction reaction without catalyst. Virtually quantitative reduction of carbon monoxide with hydrogen to form methane and water was obtained using Catalyst C-0765-1001 under the following conditions: H_2/CO mole ratio, 3:1; space velocity, 1000 hr^{-1}; catalyst bed temperature, 250°C; and catalyst bed pressure, 6.1 atm. Two continuous long-duration runs were made (60 and 90 days, approximately) using a single catalyst charge. No measurable decline in catalyst activity was noted; quantitative yields of methane and water were obtained.

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I. OBJECTIVE

The objective of this program was to demonstrate the feasibility of the Aerojet Carbothermal Process for the manufacture of oxygen from lunar resources. The program objective was achieved by (a) a study of the reduction of natural silicates with methane, carbon, hydrogen, and mixtures of methane and hydrogen, and (b) a study of the reduction of carbon monoxide with hydrogen, under a variety of conditions, to yield methane and water. Sufficient data were obtained to permit a preliminary evaluation of these reactions to be made; the feasibility of the carbothermal process for lunar oxygen manufacture was demonstrated.

II. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A. SUMMARY

1. Task 1, Carbothermal Reduction of Silicates

Task 1 was devoted to the design and operation of bench-scale equipment for use in determining the feasibility of the first step of the Aerojet Carbothermal Process for the manufacture of oxygen from lunar materials. This equipment consisted of an induction-heat rock reactor (50 cu cm capacity) and a resistance-heated rock reactor (450 cu cm capacity), together with their auxiliary flow systems. Modifications in the design and operation of the reactant gas inlet systems occurred throughout the program.

A total of 31 runs was made in the induction-heated rock reactor using granite, an acidic basalt, and tektites as the silicate material. Eighteen runs were made in the resistance-heated rock reactor using granite and an acidic basalt as the silicate material. The reducing agents were methane and/or elemental carbon. The significant achievements attained are summarized below.

a. Reduction of Silicates

Reduction of silicates with carbon resulted in as high as 96% conversion to carbon monoxide. When methane was used, somewhat lower conversions were obtained; the remainder of the methane-carbon was recovered as elemental carbon. Significant amounts of metal, containing as high as 62.4% elemental silicon, were formed.

b. Inlet Tube Design

The design of the inlet tube for introducing methane into the silicate melt was a major problem throughout the course of this research. Clogging of the inlet tube due to deposition of carbon limited the duration of the experiments. Two methods of preventing carbon buildup were investigated: (1) removal of deposited carbon by reaction with the molten silicate, and (2) removal of deposited carbon by a tungsten carbide reamer. Method (1) worked well for carbon removal; however, the action of the molten silicate caused excessive corrosion of the zirconia inlet tubes. The reamer (Method 2) worked successfully and permitted runs of much longer duration.

c. Material Compatibility

It was found that at the high operation temperatures, compatibility was a problem with the reactor materials, the methane gas, the silicate melt, and the reaction products. Carbon formed from freshly cracked methane was found to be particularly corrosive to the zirconia inlet and crucible materials. In addition, it was found that the zirconia was attacked by the silicate melt when continuous agitation of the melt was effected.

d. Methods of Carbon Addition

The addition of carbon was accomplished in most of the runs by the direct addition of methane into the melt. This method resulted in up to 60% conversion of the methane to carbon monoxide. In those runs in which the reactor was charged with a mixture of carbon and silicate, up to 100% of the carbon was converted to carbon monoxide before methane was added to the melt. Slow, continuous addition of carbon to a silicate melt was undertaken in one run; 96% conversion of carbon to carbon monoxide was obtained - a highly significant result.

e. Heating Methods

The induction-heated reactor, which could handle 0.25 lb of rock, operated most successfully with hydrogen cooling of the methane inlet tube. Experiments with this apparatus gave quantitative carbon balances. However, difficulties were encountered with this apparatus due to problems associated with induction-heating of the reactor.

The larger scale, resistance-heated furnace was found to be more reliable in operation. The reactor employing this method of heating was operated for 18 runs with no furnace failures.

f. Carbon Balances

Excellent carbon balances were achieved with the induction-heated reactor. The methane-carbon could be quantitatively recovered as carbon monoxide, carbon dioxide, and elemental carbon. With the resistance-heated reactor, the best carbon balance was 96% (recovered as CO). This was achieved by the gradual addition of elemental carbon to a silicate melt over a 28-hour period.

When methane was used, a considerable amount of this reducing agent was converted to elemental carbon. This carbon could not be recovered from this reactor.

2. Task 2, Carbon Monoxide Reduction, Methane Synthesis

a. Design, Construction and Testing

Two bench-scale test units were designed, fabricated, and tested to determine the feasibility of the second step of the Aerojet Carbothermal Process.

(1) A small, manually operated reactor (10 scfh of reactant gas) was designed, built, and tested for the reduction of carbon monoxide with hydrogen. Maximum flexibility of operation was stressed to provide the ability to operate at temperatures of 200 to 900°C, at pressures of 1 to 7 atm, and at hydrogen/carbon monoxide mole ratios ranging from 1:1 to 4:1. The catalyst chamber was fabricated from a Type 316 stainless-steel fin-tube in

order to withstand the high temperatures and high heat fluxes required. Air cooling was used to remove the heat of reaction. Tests were made which demonstrated that the equipment can be operated successfully at temperatures ranging from 200 to 900°C, and at pressures varying from 1.0 to 7.0 atm. The temperatures of the three catalyst bed sections were controllable to ±2°C with a differential of ±200°C. An initial charge of catalyst was successfully reduced and activated by flowing hydrogen through it at temperatures up to 450°C for 5 hours. Three preliminary runs demonstrated that the equipment was capable of yielding excellent data for the intended research.

(2) This carbon monoxide reduction reactor was modified in a number of ways to achieve automatic operation for long-term catalyst life studies of 60- to 90-day duration. Greater flexibility in the choice of operating conditions was also made possible by the modifications. Water cooling, which was used to remove the heat of reaction, greatly improved and simplified catalyst-bed temperature control. Multi-feed injection of the gaseous reactants provided a more uniform catalyst-bed temperature and resulted in long catalyst life at high space velocities. Automatic pressure, temperature, flow, level-control, and shutdown devices were used which permitted unattended operation. After leak-testing and reduction of the catalyst with hydrogen, preliminary tests were made which demonstrated the suitability of the equipment for extended catalyst life tests.

b. Data Acquisition

The manually operated test unit was used to obtain data on the reduction of carbon monoxide with hydrogen over a wide variety of reaction conditions. Three different catalysts were evaluated. In addition, a series of runs was made to determine (1) how various impurities in the reactant gas affect catalyst activity, and (2) the feasibility of accomplishing the reduction without a catalyst. The automatic test unit was used to demonstrate that the best of catalysts had a useful life in excess of 6 months.

(1) Catalysts Tested

The three catalysts tested gave good conversions of carbon monoxide to methane and water. Catalyst C-0765-1001 (25% nickel on kieselguhr) was selected for further testing because it was more active than the others, giving complete carbon monoxide conversion to methane and water at high space velocity (1000 hr^{-1}) and low temperature (250°C). A series of four runs was made without catalyst (bare tube) in the reactor. These runs showed a maximum carbon monoxide conversion of only about 44%, 15 to 25% of which went to carbon dioxide rather than to methane and water.

(2) Temperature

Catalyst bed temperatures of 200 to 500°C were tested. The best catalyst (C-0765-1001) was found to operate satisfactorily at 250°C, whereas the other catalysts were found to require 350 and 425°C, respectively, for optimum conversion.

(3) Pressure

Catalyst bed pressures of 1 to 7 atm were used. Although the catalysts were found to operate successfully at 1 atm, increasing the pressure to 6.1 atm was found to triple the usable space velocity and to decrease greatly the unwanted yield production of carbon dioxide.

(4) Space Velocity

Space velocities of 500 to 3000 hr^{-1} were investigated. Usable space activities of about 1000 hr^{-1} were found for the two less active catalysts, whereas a space velocity of 2500 hr^{-1} gave satisfactory conversions and yields for Catalyst C-0765-1001.

(5) H_2/CO Mole Ratio

Mole ratios of 2.98:1 to 4.1:1 were investigated. The less active catalysts were found to require H_2/CO ratios of 3.5:1 to 4.0:1 for satisfactory conversions, whereas Catalyst C-0765-1001 was found to give excellent conversion at a 3.1:1 ratio, yielding a product gas composition averaging 88.7% CH_4, 10.8% H_2, 0.08% CO_2, 0.00% CO, and 0.4% H_2O for a 92-day continuous run.

(6) Material Balances

Good to excellent (100% ±5%) material balances were obtained in almost all runs. A negligible amount of carbon was lost (deposited on the catalyst) with the C-0765-1001 catalyst. No impurities were found in the water or product gases.

(7) Heat Balances

Heat balances made on the automatic test unit gave a heat of reaction of 54 kcal/mole of carbon monoxide (theoretical, 51.3 kcal/mole CO).

(8) Multiple Feed Lines

The feed gas to the catalyst bed was split into five equal streams which were fed into the catalyst bed at 3-in. intervals. This method of addition lowered the maximum catalyst bed temperature and made possible high space velocities without carbon deposition or catalyst deactivation.

(9) Pressure Drop

The pressure drop across the catalyst bed was found to be quite low (i.e., 0.15 in. Hg at 1000 hr^{-1} space velocity). No appreciable pressure drop increase occurred during a 92-day continuous run.

(10) Catalyst Poisons

Sulfur and phosphorus were found to poison the nickel catalyst and thus must be removed from the feed gases to the carbon monoxide reduction unit. Nitrogen oxide (NO) was found not to damage the catalyst; it was reduced to NH_3 (75 wt%) and N_2 (25 wt%). Carbon dioxide and water in the amounts normally present in the catalyst bed were not found to be harmful. A low concentration of nitrogen (0.5% N_2) present in the carbon monoxide feed gas did not harm the catalayst.

(11) Catalyst Life

Catalyst C-0765-1001 gave excellent conversion and yields after a total of 154 days of operation in the automatic unit. No measurable change in catalyst activity had taken place during that length of time even though space velocities as high as 3000 hr^{-1} and H_2/CO mole ratios as low as 2.97:1 were tested for substantial time periods during the long-duration runs.

B. CONCLUSIONS

1. Task 1, Carbothermal Reduction of Silicates

a. The objective of the program has been achieved. The feasibility of the near-quantitative recovery of carbon when it is reacted with molten silicates was demonstrated. Most of this carbon was obtained as carbon monoxide. When methane was used as the reducing agent, some of the methane was converted to carbon which was difficult to recover and caused corrosion of the zirconia inlets and reactors.

b. The continuous addition of methane to the silicate melt can be achieved over a 48-hour period when a tungsten carbide reamer is used to prevent the clogging of the inlet tube. Mechanical means can be used to overcome the inlet-tube clogging. However, corrosion problems due to attack of carbon on zirconia became serious using this technique. These corrosion problems may be eliminated by the use of properly designed protective molybdenum liners placed on the inside wall of the inlet tube.

c. Operation of the Aerojet Carbothermal Process may require some make-up carbon as quantitative carbon balance is not easily achieved. This is not a serious problem as carbon will be present at a manned lunar base as waste material.

d. The low-temperature cracking of methane (1000° to $1200^\circ C$) can be introduced into the process as a fourth step. This would give satisfactory carbon balances and solve the materials compatibility problems associated with the methane-zirconia system.

e. In the design of experimental apparatus used for studying this reaction, high-temperature resistance-heating of reactors is superior to induction-heating. The problems encountered appear to be inherent in the use of induction-heating for this particular reaction system.

f. The first step of the Aerojet Carbothermal Process can use a variety of silicate material. Three types of naturally occurring silicates were used in this study: granite, acidic basalt, and tektites.

2. Task 2, Carbon Monoxide Reduction, Methane Synthesis

a. The objective of the program has been achieved. The feasibility of the quantitative reduction of carbon monoxide with hydrogen to form methane and water utilizing a modified Fischer-Tropsch synthesis was unequivocally demonstrated.

b. Reaction conditions were found which yield (1) virtually quantitative conversion of carbon monoxide to methane and water, (2) carbon dioxide in less than 1.0%, (3) negligible carbon formation, (4) methane as the exclusive organic product, and (5) an 89% methane concentration in the product gas.

c. A nickel-containing catalyst was found which achieves these excellent results at low catalyst bed temperature, low pressure, and high space velocity (250°C, 1.0 to 6.0 atm, and 100 hr^{-1}, respectively).

d. The uncatalyzed reduction of carbon monoxide with hydrogen does not produce sufficiently high yields of methane and water to warrant further consideration. Maximum carbon monoxide conversion was only 44% at 700°C, and the yield of carbon dioxide was intolerably high (15 to 25%).

e. Sulfur and phosphorus compounds must be completely removed from the reactant gases prior to contact with the catalyst bed to obtain suitable catalyst life.

f. Two continuous, long-duration runs using Catalyst C-0765-1001, totaling 154 days of operation, proved that there was no measurable decline in catalyst activity in that length of time. It should be possible to design methanation units that will have sufficiently long life-times to support permanent lunar bases.

g. A water-cooled reactor allowed higher space velocities while maintaining excellent conversions and product yield. This method of heat transfer is superior to that provided by air cooling.

C. RECOMMENDATIONS

The Aerojet Carbothermal Process for lunar oxygen manufacture has three essential steps: (1) the reduction of metallic silicate with methane to form carbon monoxide and hydrogen; (2) the reduction of carbon monoxide with hydrogen to form methane and water; and (3) the electrolysis of water to form hydrogen and oxygen. The process is cyclic in nature, with the methane and hydrogen returned to the system. The feasibility of Steps 1 and 2 of the process was demonstrated on Contract NAS 7-225.

1. Further research is required on Step (1), the reduction of silicates with methane, to devise methods for the quantitative introduction of methane into silicate melts to achieve quantitative conversion of methane-carbon to carbon monoxide. This research should be continued.

2. The incompatibility of the methane-zirconia system at 1600°C, which results in severe corrosion of the zirconia, is a serious problem in the design of the silicate reactor; the effort to devise a solution to this problem should be continued.

3. A modification of the process by the introduction of another step, the low temperature (1000 to 1200°C) cracking of methane, followed by the slow addition of carbon to the silicate melt, is feasible and should be investigated. This complicates the process by the addition of the extra step, but avoids many of the problems encountered in the three-step process associated with Recommendations 1 and 2 above.

4. A larger carbon monoxide reduction unit should be designed and tested utilizing a multi-catalyst tube assembly with multi-feed line design. This unit will be used to provide engineering data for the design of a lightweight lunar plant.

5. The separation of water into its elements is required for many of the chemical cycles which will find use in extraterrestrial applications, including Step (3) of the Aerojet Carbothermal Process. Electrolysis appears to be the only practical method for the decomposition of water. Unfortunately, commercially available equipment cannot be utilized in cases where light weight is required for payload savings. Electrode efficiency can be improved by judicious choice of electrode materials and electrolysis methods. The importance of this reaction requires that it be supplied promptly.

III. TECHNICAL DISCUSSION

Research on Contract NAS 7-225 was initiated on 22 April 1963 and completed on 15 July 1965. The first research period, 22 April through 15 November 1963, was devoted to a study of the second step of the Aerojet Carbothermal Process. This research is reported in detail in Reference 1 and is summarized herein. The second research period, 16 November 1963 through 15 July 1964, was devoted to a study of the first step of the process. This research is reported in detail in Reference 2 and is summarized herein. The third and last research period, 16 July 1964 through 15 July 1965, was devoted to studies of both the first and second steps of the process. This research is reported in detail herein. The overall program was divided into two major tasks: Task 1, Carbothermal Reduction of Silicates; and Task 2, Carbon Monoxide Reduction, Methane Synthesis.

A. THE AEROJET CARBOTHERMAL PROCESS FOR LUNAR OXYGEN MANUFACTURE

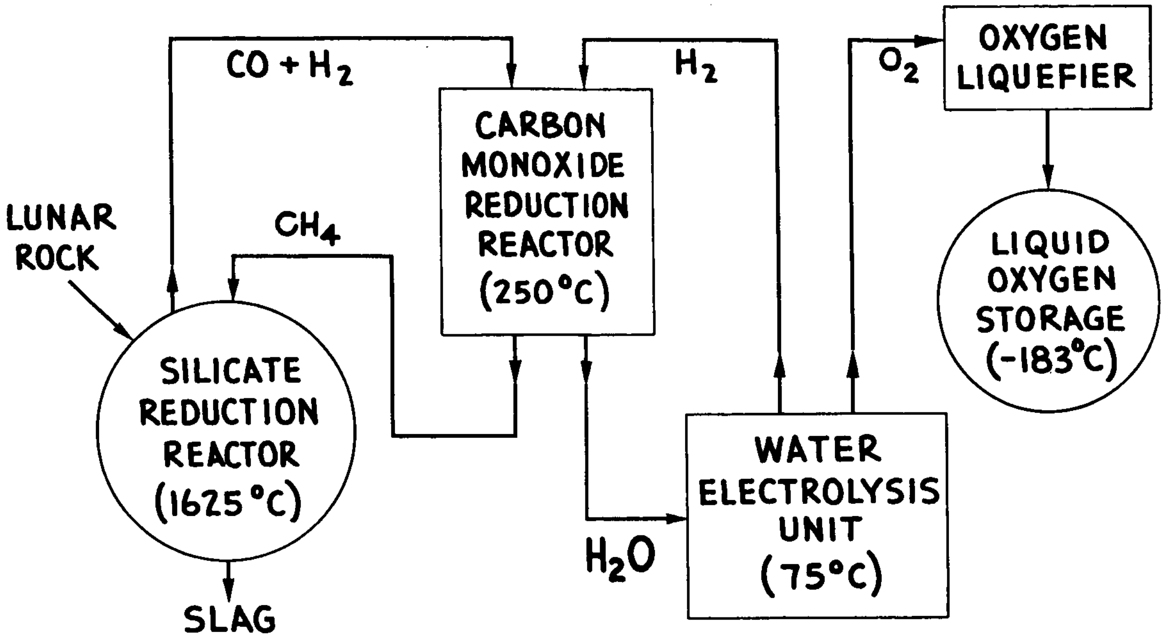
The Aerojet Carbothermal Process for manufacturing propellant oxygen from lunar silicates is presented in the flow chart at the top of the following page and is expressed by the following equations (magnesium silicate, $MgSiO_3$, typifies lunar rock):

Step (1) $$MgSiO_3 + 2\ CH_4 \xrightarrow{1625^\circ C} MgO + Si + 2\ CO + 4\ H_2$$

Step (2) $$2\ CO + 6\ H_2 \xrightarrow{250^\circ C} 2\ CH_4 + 2\ H_2O$$

Step (3) $$2\ H_2O \xrightarrow{75^\circ C} 2\ H_2 + O_2$$

In Step (1), the silicate is reduced to carbon monoxide, silicon, and slag using methane as a reducing agent. In Step (2), the carbon monoxide is catalytically reduced with hydrogen to form methane and water. The methane is recycled to Step (1); the water is electrolyzed in Step (3) where the oxygen is obtained as a product. The hydrogen formed in Step (3) is recycled into Step (2). Silicate rock is the only material consumed in the process. If water is present in any form in the raw material, it will also be obtained as a product.



Ideally, only metallic silicates and energy are required as expendables. Hydrogen and methane are required initially for process start-up, but these materials are regenerated by the process and are recycled continuously. This fact is emphasized by combining the three steps of the process to give the following chemical equation which represents the sum of the process:

$$MgSiO_3 \longrightarrow O_2 + Si + MgO$$

B. TASK 1, CARBOTHERMAL REDUCTION OF SILICATES

1. Basis for Choice of Silicate Material

In the development of a chemical process for utilizing lunar raw materials, it is necessary to choose a material representative of the lunar surface. The mineral composition of an extremely small fraction of the lunar surface will be known after its examination by various probes and by the men of the Apollo missions; however, the detailed report of composition will have to await the establishment of lunar bases and geological exploration.

Insofar as the processing of lunar rock for the production of water and oxygen is concerned, it is useful to consider the bulk composition of lunar material. The gross composition of the Moon can probably be best represented by a mixture of metallic silicates with the iron in an unknown oxidation state (Reference 3). This conclusion is drawn from observational data and is consistent with cosmogenic theories of the solar system. Earth, Moon, and meteoritic matter may be thought to have the same general composition, except for iron content (Reference 3). The Moon does not appear to have an iron core; from its mean density of 3.34 g/cu cm, it may be concluded that only small percentages of free iron may be found. If the iron were removed from the Earth or from meteorites, the composition of these bodies would then more closely resemble that of igneous rock. In a recent paper, Kopal (Reference 4) suggests that the Moon is of approximately the same composition as the terrestrial mantle. The terrestrial mantle has a much higher density (approximately 4.5 g/cu cm) than that of lunar rock; this may be accounted for by pressure-compression of presumed mantle rockets. Unfortunately, samples of mantle rock are not available to test this hypothesis.

In choosing a terrestrial sample representative of lunar rock, crustal or igneous rock is a logical choice for two major reasons: (a) the composition resembles both meteoritic material and the bulk of the Earth with iron removed, and (b) the density of igneous rock (3.3 g/cu cm) is close to the mean density of the Moon.

Representative lunar material may also be found among materials having extraterrestrial origin. A recent paper by Chapman and Larson (Reference 5) presents a basis for the belief that tektites have a lunar origin. If this be true, then either the lunar composition is high in silica, or material has been differentiated in the lunar crust with lighter, silica-rich, tektite material concentrated on the surface.

The naturally occurring materials used in this research were samples of granite and acidic basalt, as representative of igneous rock, and Indochinites, as representative of tektites. Chemical analyses of the granite and basalt are given in Table 1 where their composition can be compared to the estimates of the maria regions according to Urey and of the terrae regions according to Kuiper (Reference 6). The granite was obtained in the Cactus Flats regions of the San Bernardino Mountains near San Bernardino, California. The acidic basalt was obtained from the Pisgah Crater in San Bernardino County and from the Columbia River Basin (CRB). The Indochinites are from Thailand, and were purchased from the Wards Natural Science Establishment. The approximate range of composition of Indochinite tektites (taken from Reference 7) is shown in Table 2.

2. Research Using an Induction-Heated Reactor

This research on the reaction of methane with molten, natural silicates, using an induction-heated reactor, was carried out under the second research period of Contract NAS 7-225 (Reference 2). The results of this work are summarized below.

a. Bench-scale equipment was designed and fabricated for use in determining the feasibility of the first step in the Aerojet Carbothermal Process. This equipment consisted of an induction-heated rock reactor (50 cu cm capacity) together with its auxiliary flow system. Modifications in the design, especially of the gas inlet tubes, occurred throughout the program. Schematic flow diagrams of the apparatus are shown in Figure 1. Standard industrial and laboratory equipment and materials were used wherever possible in the fabrication of the unit in order to speed and simplify construction. The fabricated unit and its components are shown in Figures 2, 3, and 4. Ten runs were devoted to the testing of the apparatus. Temperatures as high as 1900°C were reached while excellent heat control was maintained. Table 3 summarizes the ten test runs.

b. Data obtained from a total of 22 runs indicate that the first step of the carbothermal process can be adapted to lunar silicates. The reaction conditions and results are summarized in Table 4.

(1) Reduction of silicates with carbon or with methane produced carbon monoxide and significant amounts of silicon. Near-quantitative recoveries of carbon were achieved. It is most significant that these results were obtained with all of the natural silicates used (i.e., tektites, basalt, and granite).

(2) An inlet tube design which was evolved during the program allowed the delivery of methane into molten rock for extended time periods without the loss of carbon or the premature cracking of methane in the inlet tube. This design consists of a triple-walled inlet tube terminating in a "bell" which extended into the molten rock. Cooling hydrogen can circulate in the outer jacket to cool the rapidly flowing methane which enters the "bell" via the center tube. The "bell" provides a lower linear velocity for the methane, permitting methane cracking to occur above the melt surface. No methane escaped through the melt when this type of inlet was used, and quantitative recoveries of carbon (as either CO or elemental carbon) were achieved.

(3) With the use of zirconia crucibles and inlet tubes fabricated from zirconia, alumina, and Zircoa Cast, it was determined that the optimum temperature for the silicate reduction was near 1600°C. Below this temperature, carbon monoxide production was low due to formation of carbides; above this temperature, carbon reacted with the ceramic materials of the inlet tube and crucible.

3. Research Using a Resistance-Heated Reactor

This section contains a report of the research performed on the silicate reduction step during the third research period of Contract NAS 7-225.

a. Design, Fabrication, and Testing of the Resistance-Heated Reactor

The silicate reduction unit was designed to contain a charge of approximately 1 lb of silicate material (granite or acid basalt), utilizing a resistance-heated furnace. The gas inlet tubes were designed utilizing the information gained during the preceding research period.

Figure 5 is a cross-sectional assembly drawing of the silicate reduction furnace which was fabricated for this part of the program. The steel case is 20 in. OD by 26 in. deep, and is designed to withstand a full vacuum. Approximately 6.5 in. of insulation is provided to minimize heat losses and to keep the steel case cool. High-grade zirconia was used to fabricate the gas inlet bells (0.75-in. OD), crucible (2.5-in. OD), heater core (4-in. OD), and outer shield (6-5/8-in. OD). Pure alumina (99%+) was used to fabricate the gas inlet tubes (3/8-in. OD, 7/32-in. OD, and 1/8-in. OD). Molybdenum was used for the heater element. Vacuum-tight seals were fabricated from rubber stoppers for the optical pyrometer sight tube, electrical heater leads, and gas inlet and outlet tubes. The 9.5-in. ID opening in the furnace top is sealed with a rubber O-ring. Zirconia blocks (not shown) are used to support the crucible and shields.

Figure 6 is a flow diagram for the silicate reduction unit. Provisions were made to evacuate and purge the system with argon, to meter methane or methane-hydrogen mixtures into the rock, and to meter and analyze the product gases. Hydrogen-cooling of the inlet tubes was used in the early runs. A time-cycle-controller was provided on some runs to control the gas flow into and out of the inlet tubes. A precision optical pyrometer was provided to measure the temperature at the middle of the crucible and at the top of the inlet bells. Several Chromel-Alumel thermocouples (not shown) were installed to measure the temperature at various locations in the inlet tubes. The product gas rate was measured by a wet-test meter. Water and carbon dioxide in the product gas were measured by absorption tubes. Gas analysis was provided by the on-stream gas chromatograph. In addition, these gas analyses were checked periodically by mass spectrophotometry.

The initial heating test of the furnace was made with a small crucible and a single inlet tube. This run demonstrated that the furnace was capable of attaining temperatures of 1800°C or higher. However, several modifications were made to improve the furnace operation. The heater which was fabricated from molybdenum wire wound on a zirconia crucible required larger conductive leads to the heating coil. Several water-cooling coils were installed on the outside of the case. The zirconia shield, zirconia heating crucible, and the melting crucible were shortened so that additional shielding and insulation could be installed to reduce heat loss from the top of the furnace.

In addition, covers were made from zirconia for the melting crucible and for the heating crucible. A cooling coil of 1/4-in. stainless-steel tubing was installed in the top of the furnace in order to maintain the top several inches of the inlet gas tubes below the cracking temperature of methane.

The inlet tubes, melting crucible, cooling coil, and furnace outlet tube were fabricated as a unit attached to the furnace cover (see Figure 5). This permitted the unit to be assembled from the top. Final insulation was achieved by pouring alumina bubbles through holes in the furnace cover.

Several modifications of the rock reduction furnace were made throughout the research effort. These modifications are described below.

(1) A small rod or wire was installed in the product gas outlet tube after Run 7. This rod entered through a packing gland in one leg of a tee so that the rod could be periodically raised and lowered (1 to 2 in.) in order to prevent the outlet tube from becoming clogged with sublimate.

(2) Zirconia tubes (1/2-in.-OD by 18-in.-long) were used for inlet tubes for Runs 8 and 9 rather than the 3/4-in.-OD bells sealed to 1/8-in. tubes used earlier. This change eliminated the troublesome seal problem.

(3) A 0.003-in.-thick molybdenum liner was installed in the reactant gas inlet tube for Run 9. This prevented carbon from reacting with the zirconia tube, and thereby eliminated the embrittlement previously experienced.

(4) The cycle timer operation for feed gas was modified from a "20 min on, 10 min off" cycle to an "8 min on, 2 min off" cycle, and finally to an "8 min on, 50 sec off, 10 sec surge" cycle. This was done in an effort to find a means of removing carbon from the reactant gas inlet tube.

(5) A filter was installed in the outlet gas line from the furnace to remove dust and/or carbon from the outlet gas stream.

(6) A 4-liter surge bottle was installed in the outlet gas lines downstream of the juncture of the furnace outlet line to the outlet line from the inlet bells. This permitted the outlet gas streams to mix thoroughly so that the total outlet gas composition could be accurately measured.

b. Reduction of Igneous Rock

Eighteen runs were made with the larger rock reduction furnace. All but three (Runs 1, 16, and 17) resulted in some useful data. The runs have been divided into three categories: (1) runs in which the rock was reduced with carbon, (2) runs in which the rock was reduced with methane and carbon, and (3) runs in which the rock was reduced with methane only.

(1) Runs with Rock and Carbon

Three runs were made starting with mixtures of rock and carbon in the crucible (Runs 6, 7, and 10). One run was made with continuous addition of carbon to the rock (Run 18).

Run 6 was made with 1 lb of basalt (-6 to +28 mesh) mixed with 60.5 g of pure graphite (emission spectrograph electrodes) ground to -6 to +28 mesh size. The purpose of this run was to determine if essentially 100% of the carbon could be recovered (as CO) when enough graphite was added to the rock to react with 50% of the silicate.

The data for Run 6 are presented in Table 5 and Figure 7. Although the data points were taken every 30 min, the data are reported in the table at 4-hour intervals due to the length of the run (68 hours). The crucible was heated at the rate of about 60°C/hour, up to about 1400°C (see Figure 7). Carbon monoxide started to evolve at about 1040°C. The basalt melted at about 1200°C. At 1400°C, carbon monoxide started to evolve rather rapidly; the rate of heating was then decreased. Trouble was experienced after 31 hours of operation, at which time the product gas outlet tube (1/2-in. ID) became clogged with sublimate. The furnace heater was turned off for several hours while an alternate gas outlet tube was installed; heating was then resumed. The crucible temperature was gradually increased as the rate of carbon monoxide evolution declined. The run was terminated after 68 hours, at which time 86% of the graphite charged had been recovered as carbon monoxide and a crucible wall temperature of 1785°C had been attained. At shutdown, carbon monoxide was being evolved very slowly (i.e., at a rate of 0.25%/hour).

Inspection of the crucible after the run (see Figures 8 and 9) showed that while it had been severely blistered and somewhat deformed, it had not cracked. Metal and a small amount of slag remained in the crucible. A very small amount of sublimate was found deposited in the outlet tube. The slag was absorbed by the crucible and/or volatilized out of the crucible, and was deposited in the insulation of the furnace.

Run 7 was made with 1 lb of basalt (-6 to +28 mesh) mixed with 60.5 g of finely ground graphite (-28 to +48 mesh). This run was a duplicate of Run 6 except that the graphite used was more finely ground. The purpose of this experiment was to determine whether the more finely ground carbon would react faster than the Run 6 carbon and provide a higher carbon monoxide yield.

The results of this run are shown in Table 6 and Figure 10. The reaction did indeed go faster with the more finely ground carbon; 36% of the carbon was recovered as carbon monoxide in 12 hours in Run 7, as compared with 22 hours for the same carbon recovery in Run 6. It soon became apparent that there is an inherent limitation on the rate of gas production using the current apparatus. If this rate is exceeded, foaming or frothing of the melt will result. Shortly after 12 hours of operation, the gas outlet tube clogged. Another gas outlet from the furnace was opened, but thereafter the rate of carbon monoxide production dropped off rapidly.

Examination of the crucible after the run showed that the first outlet tube was clogged with froth from the melt. In addition, there was a layer of solidified foam about 1/2-in. thick at the top of the crucible. Calculations showed that the maximum rate of carbon monoxide production prior to clogging was 0.49 scfh (i.e., 22 scfh per sq ft of crucible cross-sectional area). This production velocity should vary with the melt viscosity, type of rock, size of crucible, etc. Prolonged heating of the crucible at temperatures up to 1800°C did not result in full recovery of the carbon; 74%

was recovered over a period of 60 hours. The low carbon recovery was caused by the foaming of the carbon and rock out of the crucible (i.e., out of the hot zone). The reduction reaction cannot take place out of the hot zone of the furnace.

Inspection and analyses of the furnace insulation (alumina bubbles) after the run showed the presence of carbon. This carbon could have been deposited by the decomposition of carbon monoxide on the hot insulation after the gas outlet tube clogged.

The spectrographic analyses of the alumina bubbles from Run 7 are presented in Table 7. Figure 11 is a photograph of the bubbles as taken in reverse order from the furnace. Virgin bubbles are composed of nearly pure alumina with about 1.6% silicate as Si. The used bubbles were found to contain more silicon (silica) as their position approached the top of the crucible. The bubbles were also found to be contaminated with appreciable quantities of molybdenum (from the furnace winding), sodium (sublimed from the reduced melt), and lesser quantities of magnesium and iron.

Table 7 presents data on the spectrographic analyses of the metal obtained from Runs 6 and 7. The silicon content of the metal from Run 6 was 62.4%. A material balance shows that the silicon in the metal corresponds to nearly a 50% reduction of the silica in the basalt charged. Sufficient graphite had been added to the crucible to reduce just 50% of the silicate. In Run 7, the silicon content of the metal was only 15.1%; this low content probably came about because the metal found in the bottom of the crucible was formed early in the run (i.e., before the melt foamed over). The metal samples, in addition, contained appreciable quantities of aluminum, manganese, and titanium, and lesser quantities of copper and nickel.

The clogging of the gas outlet tube in Run 7 caused the crucible to swell and adhere to the furnace wall. This necessitated a virtually complete rebuilding of the interior parts of the furnace.

Run 10 was to be a duplicate of Run 6. One pound of basalt mixed with 60.5 g of graphite was used. The basalt and graphite were crushed to the same size as in Run 6. Approximately the same rate of heating was used in Run 10 as in Run 7. However, after about 32 hours of operation, it became apparent that something had gone wrong. First of all, the carbon monoxide content in the product gas began to fall off. After 46 hours of operation, the heating unit shifted in the furnace and broke off the optical pyrometer sight tube. The run was terminated after 47.5 hours of operation with a carbon recovery of only 54.5%. Although some carbon monoxide was still being produced, it was impossible to determine the crucible wall temperature. Inspection of the furnace showed that the melt crucible had broken and allowed some of the molten rock to run into the heating crucible. The reason for failure was not determined.

One positive result obtained from Run 10 was that it was found that the product gases did not contain any sulfur and only a trace of phosphorus. In this run, all of the product gases were bubbled through a 0.1 N NaOH solution. The solution was then analyzed for sulfur and phosphorus. No sulfur and only 1.6 ppm of phosphorus was found. This confirms the results obtained in Run 3.

Run 18 was made with 1 lb of basalt to which carbon black was slowly and continuously added after the rock had been heated to 1540°C. The data for this run are given in Table 8 and Figure 12. The carbon black (12-16 mesh pelletized furnace black) was dropped upon the top of the molten rock at the average rate of 1.42 g/hr. The 3/8-in.-ID alumina inlet tube through which the carbon was added was terminated at the top of the crucible. An alumina outlet tube and an alumina crucible cover were used. The crucible cover and inlet and outlet tubes were carefully cemented onto the crucible with a zirconia castable refractory.

Figure 12 is a plot of crucible temperature and carbon recovery vs time. For the first 6 hours of operation the crucible temperature was not high enough; thus the carbon did not react as fast as it was fed (the interval CO recovery was less than 100%). As the crucible temperature was raised from 1560 to 1600°C, the carbon started to react faster than it was being fed, and thus the interval CO recovery was over 100% for several hours. Thereafter, the crucible temperature was maintained so that the interval CO recovery was approximately 90-100%. After 27.5 hours, when 34.2 g of carbon (or 7.6 g C/100 g rock) had been charged, the carbon addition was stopped. At this point the cumulative carbon recovery had risen to 86%. By maintaining the heat on the crucible for an additional 9.5 hours, more carbon in the melt reacted to bring the cumulative carbon recovery up to 96%. It appears that prolonged heating would have brought the recovery up to near 100%. Although the crucible was recovered intact without severe erosion from the melt, its appearance and analysis showed that considerable interaction with the melt had taken place.

(2) Runs Using Carbon and Methane

Run 2 was quite successful. The data for Run 2 are reported in Table 9 and Figure 13. In this run, 392 g of basalt and 8 g (2%) of carbon were charged into a 0.25-in.-wall zirconia crucible that was 2.5 in. in diameter and 8 in. deep. The three inlet tubes were fabricated from alumina, and mullite tubes were cemented to 0.75-in.-dia by 12-in.-long zirconia bells. The bells extended to the bottom of the crucible which was filled with the basalt. The depth of the molten basalt was estimated to be about 3 in. at the start of the run; it was only about 1.5 to 2.0 in. deep at the end of the run. The crucible was placed in the furnace and heated at the rate of about 60°C/hour (see Figure 13) to 1600°C and was then maintained at 1550 to 1600°C until most of the carbon charged (87%) was given off as carbon monoxide. An argon purge was used to protect the molybdenum furnace winding and to transport the product gas through the analytical train. Nitrogen (25°C) cooling in the stainless-steel coil was used to maintain the top several inches of the gas inlet bells below the methane cracking temperature.

After the carbon monoxide content in the product gas had dropped to below 0.5%, the methane feed gas (95.2% CH_4, 4.4% H_2, 0.4% N_2) was introduced at the rate of 0.10 g mole/hour. There was no sign of carbon dust in the exit gas stream after a few hours had elapsed, so the methane rate was increased to 0.20 g mole/hour. After this was done, there was an indication of a very small amount of carbon dust in the product gas. Methane flow was turned off after approximately 7 hours of operation. The gas inlet lines had <u>not</u> clogged, and the conversion rate had not fallen appreciably when the unit was shut down (see Figure 13).

The last column in Table 9 gives the cumulative recovery, as carbon monoxide and carbon dioxide, of the carbon charged. About 87% of the carbon charged with the basalt was recovered as carbon monoxide before the methane feed gas was turned on. The overall carbon recovery was 79%, which is better than the recoveries which were achieved on the previous program when both carbon and methane were used (Reference 2).

Inspection of the apparatus after the run showed the following:

(a) The crucible remained intact throughout the run. There were no bulges, internal cracks, or serious penetration of the walls by the melt (see Figure 14).

(b) The inlet tubes (alumina surrounded by mullite) were in excellent condition. There were no cracks, bulges, or carbon deposition.

(c) The inlet bells were in fair condition (see Figure 14). One of the three inlets was shut off during the run because the seal between the inlet tube and bell opened. The other two bells operated throughout the run without failure. There was, however, an appreciable amount of carbon deposited on the inside of the bells from 5 to 8.5 in. above the outlet end. The unreacted carbon may be explained by assuming that the melt did not contact it (i.e., the pressure difference between the bell inlet and the outlet from the furnace was not great enough to force the melt to the top of the bell during the "vent" cycle) or that the "vent" cycle (3 min out of every 30 min) was not long enough to allow the melt to react with all of the carbon that was formed during the "on" cycle. The first supposition is much more likely to be the case.

(d) The bells cracked while cooling after the run was terminated. The inlet tubes were raised 5 in. out of the furnace over a period of 20 min after termination of methane flow in an attempt to salvage the inlet bells for another run. A slower withdrawal rate was indicated for future runs.

(e) Some of the alumina balls which were used for insulation fell into the melt when the inlet bells were withdrawn. This was the result of the crucible cover sticking to the inlet bells as they were lifted out of the furnace. In the next run, the cover was wired to the crucible, preventing a recurrence of this problem.

(f) Some trouble was experienced during the early part of the run with sublimate (a very fine white dust probably composed of sodium compounds and other low-melt materials from the basalt) clogging the product gas filter. This filter was redesigned; a second filter was installed in series with the first so that the first filter could be bypassed and cleaned during a run.

(g) The product gas outlet line from the furnace (5/16-in. alumina tube) was found to be nearly clogged with sublimate. This line was increased to 3/8-in. size and brought straight up from the furnace so it could be easily cleaned during a run or could be used to add more rock to the reactor during future runs.

(3) Runs Using Methane Only

Ten runs were made in which the rock (granite or acid basalt) was reduced by methane only. During this series of runs, numerous changes were made in the inlet tube to prevent the tubes from cracking and leaking and to prevent carbon from building up in the tubes.

(a) Run 3

The data for Run 3 are reported in Table 10 and Figure 15. In this run, a charge of 454 g of granite was placed in a 2.5-in.-dia by 8-in.-deep, 0.25-in.-wall zirconia crucible. Inlet tubes similar to the ones in Run 2 were used. The crucible was placed in the furnace and heated at the rate of about 75°C/hour up to 1550°C. Argon was purged through the furnace and through the inlet bells during the warmup. A very small amount of carbon monoxide (0.2%) appeared in the exit gas as the crucible temperature approached 1550°C. About 2 g of water and 0.3 g of carbon dioxide were found in the product gases up to this time. Gas samples were taken and analyzed by mass spectrophotometry (see Table 11). Samples 1 and 2, taken when the crucible was at

1150°C and 1350°C, respectively, did not show any impurities such as sulfur or phosphorus compounds. The argon flow through the bells was stopped and methane feed started when the crucible temperature reached 1550°C. The methane flow was then maintained at 0.2 g/mole/hour and the crucible temperature was held at 1550 to 1650°C for 15.2 hours. The run was terminated because bells 1 and 3 were becoming clogged, with the conversion of methane to carbon monoxide dropping gradually.

The rate of conversion of methane to carbon monoxide (see Table 10) increased slowly from about 40% for about 9 hours after the run was started to about 57%. Then it slowly declined throughout the rest of the run to 49%. Some carbon monoxide continued to be given off after the methane flow was shut off. An overall conversion of methane to carbon monoxide of 54% was obtained.

1 Methane in the Product Stream

A small amount of methane was present in the product gas stream (see Figure 15). This was due, at first, to the back flow of methane out of the bells after each cycle change. The residual methane in the bells was displaced into the product gas stream by the carbon monoxide which was generated by the rock reacting with the carbon in the bells. However, as the run progressed, the refractory cement seal between the inlet tube and inlet bells gradually opened and allowed increasing amounts of methane to bypass the bells. Part of this methane was cracked and lost as carbon deposited in the furnace; the remainder appeared in the product gas stream.

2 Carbon Balance

Table 12 presents the carbon balance obtained from Run 3. Of the 36.2 g of carbon charged as methane, only 53.6% of it was recovered as carbon monoxide and 0.6% as carbon dioxide; 7.2% was recovered as methane in the product gas. Carbon deposited in the inlet bells accounted for 20.4% of the methane charged, and carbon filtered from the outlet gas for 3.0%. The remainder, 5.5 g (15.2%), was not accounted for quantitatively; it was deposited as carbon on the insulation in the furnace. The alumina and the Fiberfrax insulation in the furnace were quite black.

3 Metal and Slag Recovered

The slag recovered from the run was a light greenish-gray glass. Microscopic examination of the slag showed that it contained <u>many</u> very small (less than 0.001-in.-dia) nodules of metal. In addition to these nodules, there were a few larger nodules of metal (up to about 1/8-in. dia). The larger ones were collected and found to weigh 0.34 g. The analysis of this metal is given in Table 13. The average of two spectrographic analyses showed that the metal was 58.3% Fe and 38.4% Si, the balance being Ni, Cu, and Ag.

4 Silica Reduction

The above results prove that some silica was reduced to silicon. However, the amount that was completely reduced was much smaller than expected. The amount of iron metal found was also small (3% of the total expected). About 1.6 g mole of carbon monoxide was recovered from the run. The potassium and sodium oxides in the granite required only 0.46 mole of carbon for reduction; the iron actually reduced required only 0.01 mole; this left 1.13 moles of carbon to reduce silica. The results indicate that suboxides of iron and silica were formed and remained in solution. Apparently, granite is much more difficult to reduce to the free metals than is basalt.

(b) Run 4

Run 4 was made with 1 lb of granite in a 2.5-in.-OD by 8-in.-deep zirconia crucible. Three zirconia inlet bells, 3/4-in. OD by 12-in. long, were used. The upper ends of the bells were joined to 1/8-in.-OD alumina inlet tubes. The joint was made with Zircoa Cast (-100 mesh size). The cams on the timer were also changed so that the melt would be forced into the bells for approximately 2 min out of every 10 min of operation. This was done in an effort to get better removal of the carbon deposited in the bells.

The crucible was heated to 1580°C with an argon purge. The methane (95.0% CH_4, 4.5% H_2, 0.5% N_2) was then turned on at a rate of 0.2 g mole/hour. The crucible temperature was maintained at about 1600°C. The carbon monoxide content of the product gas rose slowly to a maximum of 5.2%

after 4.5 hours of methane addition. This value corresponds to a 41% carbon recovery. Thereafter, the carbon monoxide content of the product gas fell slowly; after 11 additional hours, the carbon recovery was only 21%. Appreciable quantities of methane were present in the product gas; the amount gradually increased as the run progressed.

Examination of the furnace and inlet bells after the run showed that the seals between the bells and 1/8-in. inlet tubes were leaking. Apparently, a large part of the methane by-passed the crucible during the run and cracked inside the furnace or escaped unreacted with the product gases.

(c) Run 5

Run 5 was made with 1 lb of -6 to +28 mesh basalt in a 2.5-in.-OD by 8-in.-deep zirconia crucible. Three 3/4-in.-OD by 12-in.-long zirconia inlet bells were used. The joints between the bells and the 1/8-in. inlet tubes were modified to give a thicker seal of Zircoa Cast than that previously used. In addition, the exterior of the joint was covered with several coats of Sauereisen Binder No. 32 (a high-temperature ceramic sealing compound). The same cams on the timer were used as for Run 4, except that an additional valve and timer were added to surge the melt up and down in the bells once a minute for 2 min out of every 10 min of operation.

The crucible was heated to about 1570°C while the system was purged with argon. Carbon monoxide was formed during this warm-up period from the carbon deposited in the furnace insulation during the previous run. Approximately 12 hours of heating at 1570°C was required to eliminate the carbon monoxide from the product gas. During this time, the cycle timers were operated with a low argon flow to test the system and the seals in the inlet tubes and bells. Two of the three bell seals held up perfectly all during this time; the third bell seal opened up almost complete (this was indicated by a large flow in the off-gas rotameter). The methane feed was turned on using the remaining two bells. However, in a short time (1 to 2 hours), one of the bell seals started leaking and the other bell started to clog; the run was then terminated.

Inspection of the bells after the run showed that surging of the melted basalt up and down for 6 hours at about 1570°C had eroded or dissolved more than one-half of the zirconia wall (approximately 0.020 in. penetration). One bell made of a special Zircoa mixture (No. 1027) appeared to hold up no better than the standard impervious zirconia. Figure 16 is a top view of the crucible from Run 5. Small beads of metal can be seen embedded in the top of the solidified melt.

(d) Run 8

Run 8 was made with 1.0 lb of basalt in a 2-in.-ID, 8-in.-high zirconia crucible. In this run, one-piece inlet tubes made from impervious zirconia were used for the methane inlets. The tubes were approximately 0.52-in. OD, 0.35-in. ID, and 18-in. long. Twisted tungsten wires (three 0.050 in. wires) were installed in two of the three tubes. The third tube, used as a blank, was open in the usual manner. The wire in one of the tubes was rotated at about 60 rpm during the run, while the other wire was raised and lowered a distance of 2 in. about 30 times per minute during the run. The moving wires were used in an attempt to prevent carbon from clogging the gas inlet tubes. The crucible was heated to approximately 1550°C with a low argon purge before the wire stirrers were turned on. The rotating wire became tangled soon after its rotation began; it was then stopped. The reciprocating wire became stuck and inoperable after 2.5 hours. The open tube operated for 10 hours with methane flow before it became clogged with hard carbon.

A 3/8-in.-ID alumina tube was used as the gas outlet from the crucible. A 1/8-in.-OD alumina rod was installed inside of the gas outlet tube to keep it free of sublimate and dust. Raising and lowering the 1/8-in. rod several inches at 15- to 30-min intervals prevented the outlet line from clogging.

Complete data for Run 8 are not reported because of the run's brief duration and low carbon monoxide recoveries. The carbon monoxide recovery rate was 41.6% shortly after the methane was turned on at 1580°C; the rate of carbon monoxide recovery increased to a minimum of 66%

approximately 3 hours after the methane was turned on. The carbon monoxide recovery thereafter fell to 36% (13 hours), and then to 27% when the run was terminated.

(e) Run 9

Run 9 was made with 1.0 lb of basalt in a 2-in.-ID, 8-in.-high zirconia crucible. In this run, only one 1/2-in.-OD, 18-in.-long zirconia inlet tube was used. The top 15 in. of the zirconia tube was lined with a piece of molybdenum sheet 0.003-in. thick by 2.5-in. wide. The sheet, formed into a spiral shape, was inserted into the tube and expanded to make a reasonably tight inner lining. Three 0.050-in. tungsten wires twisted together were inserted into the inlet tube extending to within 6.5 in. of the bottom of the crucible. After the methane feed was turned on, the tungsten wires were rotated at about 60 rpm for 8 sec out of each minute. The differential pressure surging mechanism was not used during this run.

The crucible was heated at a rate of 800°C/hour with an argon purge up to 1550°C, and then the methane feed was turned on at a rate of 0.20 mole/hour. The wire rotating timer was also turned on at this time. The conversion of methane to CO rose to about 36% shortly after the methane was turned on, and then slowly fell off. No methane was detected in the product gas. After only 2.25 hours, the inlet tube clogged off with carbon stopping the methane flow.

Inspection of the inlet tube (see Figure 17) after the run showed that the tube was totally clogged with carbon about 6.5 to 8.5 in. above the crucible bottom. The tungsten wires had caught and twisted off at a level of about 8 in. above the crucible bottom. The molybdenum liner was effective in preventing the carbon from attacking the zirconia tube. However, the lower 0.5 in. of the molybdenum liner had been corroded away by the melt (to a level of 4.5 in. above the crucible bottom). The movement of a 1/8 in. alumina rod in the product gas outlet tube again prevented this line from clogging with sublimate. These results show that reaming, or some other method of removal, will be required to dislodge the carbon from the inlet tube.

(f) Run 11

Run 11 was made with 1 lb of acidic basalt (-6 to +28 mesh) in a special (No. 1027) zirconia crucible (2.62-in. OD, 2.29-in. ID, 8.03-in. long). An impervious zirconia inlet tube (0.53-in. OD, 0.41-in. ID, 18-in. long) was lined with two layers of 0.003 in. molybdenum sheet. The crucible and rock were heated to 1500°C at the rate of about 100°C/hour with an argon purge; then the methane feed was turned on at the rate of about 0.2 mole/hour. The inlet tube was reamed every 10 min with a tungsten carbide reamer during the run. The reamer was fabricated from solid tungsten carbide (overall length, 6 in.); it had six flutes measuring 5/16-in. dia by 1-1/2-in. long. A stainless-steel extension shank was attached to the reamer to give an overall shaft length of 18-1/2 in. A packing gland was attached to the top of the inlet tube so that the reamer could be used while the methane was flowing. The reamer was attached to a 3/8-in. (700 rpm) portable electric drill which was mounted on a Black & Decker drill stand. The drill stand provided a 4-7/8 in. vertical movement for the reamer.

The run lasted for a total of 4 hours, during which time the conversion of methane to carbon monoxide dropped from 64 to 27%. Inspection of the equipment after the run showed that the inlet tube had broken at the top of the crucible cover - probably because of mechanical stress. However, the reaming operation appeared to be successful and the reamer was not dulled, clogged with carbon, or damaged in any way.

(g) Run 12

Run 12 was made in the same manner as Run 11 except that the 1/2-in.-OD zirconia inlet tube was lined with two layers of platinum foil 0.001-in. thick. This run was terminated 10 min after the methane feed was turned on because the platinum foil caught on the reamer and broke the inlet tube. Apparently, the platinum foil was too soft at 1525°C (only 250°C below its melting point) to provide the required mechanical properties. Unfortunately, this inlet tube had a slightly smaller ID than the one for Run 11; there was very little clearance between the platinum foil and the tungsten carbide reamer.

(h) Run 13

Run 13 was made with 1 lb of acidic basalt obtained from the Columbia River Basin (-6 to +28 mesh). It was contained in an impervious zirconia crucible (2.40-in. OD, 2.00-in. ID, 8.0-in. long). The inlet tube was a specially constructed impervious zirconia tube. This tube was on hand for use in the pressure-surging technique utilized to remove the carbon which deposits on the inside of the inlet tube. It was not the optimum shape for the reaming technique now being used (the reamer had to be modified to fit it). The inlet tube was 0.75-in. OD by 0.59-in. ID for 12 in., tapered down to 0.39-in. OD by 0.20-in. ID for 6.4 in. The 0.59-in. ID section was lined with two layers of 0.003 in. molybdenum foil. A 0.312-in.-OD tungsten carbide reamer, 1.0-in. long with an 0.187-in. OD shaft, was used. The drill stand was modified to give a 6.5-in. movement of the reamer and was set so that the lower end of the reamer came to within 4.75 in. of the crucible bottom. The reamer was operated once every 5 min after the methane feed was turned on. Each reaming operating took about 8 to 10 sec.

The data for Run 13 are presented in Table 14 and Figure 18. A methane flow of about 0.20-g mole/hour was used throughout the run. The crucible temperature was slowly increased from 1500 to 1650°C during the run. The conversion rate of methane to carbon monoxide (taken each half hour) varied from a low of 21% to a high of 78%; the trend was from about 40% at the start to about 65% at the end of the 13.75-hour run. The cumulative conversion of methane to carbon monoxide gradually increased throughout the run from about 52% at the time the methane was turned off, to a maximum of 55.6% some 7 hours later.

The reamer was effective in maintaining the inlet tube open until a few minutes before the methane feed was turned off. This was evident from a constant ΔP on the inlet tube (0.60 to 0.65 in. of Hg) into the crucible of molten rock. A surging in the inlet gas rotameter indicated that the inlet tube was not broken and that gas was bubbling through the molten rock. Fifteen minutes before the run was terminated, the ΔP on the inlet line started to increase (to 1.7-in. Hg). This indicated that carbon was building up in the inlet tube below the maximum travel point of the reamer. An attempt to lower the reamer an additional 1.0 in. caused the top of the reamer to break off and also the inlet tube to break.

A total of 5.0 g of carbon was collected in the outlet filter throughout the run. This corresponds to 16.7% of carbon in the methane feed. In addition, 55.6% of the methane was converted to carbon monoxide. The remaining 27.7% of the methane, corresponding to 8.3 g of carbon, was apparently deposited as carbon in the inlet tube. A total of 13.5 g of material was found in the inlet tube. The precise composition of this material was not determined because of the presence of molybdenum carbide.

Inspection of the crucible after the run showed that (1) the crucible was in excellent condition, (2) the inlet tube was not severely corroded, and (3) the melt depth was only about 2.5 in. The results of the run are very encouraging in that the reaming technique was found to be effective in maintaining an open inlet tube. Modification of the inlet tube and reamer should permit runs of almost any desired duration to be made.

(i) Run 14

Run 14 was made with the standard size impervious zirconia crucible (2.4-in. OD, 2.0-in. ID, 8-in. long). This crucible was charged with 1 lb of acidic basalt from the Columbia River Basin. The inlet tube was the same size as the one used in Run 13 except that it was lined with three layers of 0.003 in. molybdenum sheet instead of two layers. In an attempt to eliminate the long time period in which a solid layer of carbon is built up in the inlet tube surrounding the reamer, a graphite tube was installed in the inlet tube on the inside of the molybdenum liner. This graphite tube was 0.531-in. OD by 0.344-in. ID by 8.5-in. long, and weighed 28.5 g. It was cemented into the inlet tube using 100 mesh Zircoa Cast. A tungsten carbide reamer, similar to the one used in Run 13, was used but with the following modifications: (1) the end of the shank was gradually tapered up to the diameter of the reamer; (2) the length of the stroke was increased from 6.5 to 7.0 in.; (3) the bottom of the stroke was lowered from 4.75 to 3.5 in. above the bottom of the crucible; (4) the reamer was operated once every 3 min instead of once every 5 min; and (5) the reamer operation was changed from manual to automatic.

The reamer's operation was controlled by a cycle timer which opened and closed two 3-way solenoid valves. These valves furnished air to an air cylinder which raised and lowered the reamer. The cycle timer also turned the drill motor on and off.

The crucible filled with basalt was placed in the furnace and heated to approximately 1500°C at the rate of about 90°C/hour. An attempt was then made to add more basalt to the crucible in order to increase the depth of molten rock through which the methane feed would bubble. The gas outlet tube (0.5 in. ID) through which the rock was being added clogged after 0.16 lb of basalt was added. After clearing the outlet line, the crucible was heated to about 1600°C and the methane feed gas was turned on. After about 1.5 hour, a part of the carbon liner in the inlet tube fell into the melt, and the carbon monoxide produced far exceeded the methane input. Eleven hours after the methane was turned on, the reamer became stuck and the inlet tube was broken, allowing the remainder of the carbon liner and the tip of the reamer to fall into the melt. The run was continued for 46 hours without the inlet tube clogging. The inlet tube had broken off near the top of the crucible, and the end of the reamer shaft apparently prevented the inlet line from clogging with carbon. No meaningful carbon recovery data could be calculated because of the large quantities of carbon which had fallen into the melt from the inlet tube liner, and because large quantities of carbon were deposited in the furnace insulation.

(j) Run 15

Run 15 was made with the maximum amount (1.31 lb) of acidic basalt that could be charged into the standard 2.0-in.-ID by 8-in.-long crucible. The inlet was an impervious zirconia (lime stabilized) tube 3/8-in. ID by 5/8-in. OD by 18-in. long lined with three layers of 0.003-in. thick molybdenum sheet. The inlet tube was reamed automatically every 2.4 min. The reamer was 5/16-in. OD by 18 in. overall length. The reamer had a 7 in. stroke starting 4 in. above the bottom of the inlet tube. The duration of the reaming operation varied from 7 to 9 sec each cycle.

The data for Run 15 are given in Table 15 and Figure 19. The crucible was heated to 1535°C at the rate of about 80°C/hour with an argon purge. Then the methane feed and the reamer were turned on. The interval carbon monoxide recovery quickly increased to about 55% and then slowly dropped to 32%. Increasing the crucible wall temperature to 1630°C did not increase the carbon monoxide recovery. The methane feed was turned off after 25-1/3 hours when appreciable amounts of methane appeared in the product gas. The argon purge was continued and the crucible temperature was slowly increased to 1740°C. The increase in temperature produced some additional carbon monoxide, but the crucible and heater were very badly damaged.

Inspection of the furnace and crucible showed the following developments:

1 The reamer had functioned perfectly and was not damaged, even though it had contacted molten rock for a short time. During the warmup period, some molten rock was forced up into the gas inlet tube, shutting off the argon purge for a few minutes. This rock did not completely drain out of the inlet tube and was partially caught on the reamer flutes when it was turned on.

2 The inlet tube was found to be carbonized and cracked an inch or two above the crucible cover and just below the crucible cover.

3 The crucible was badly damaged and the lower 3 in. of the inlet tube was missing. There was a 1 in. by 3 in. hole in the crucible. This is believed to have developed when the temperature was raised after the methane feed was stopped.

The crack below the crucible cover is believed to have occurred near the beginning of the run when the carbon monoxide production first started to drop. The crack above the crucible cover is believed to have occurred near the end of the run when methane started to show up in the product gas. Apparently, installing the spirally rolled molybdenum liner in the zirconia inlet tubes slows down but does not stop carbonization and cracking.

The temperatures reported are those read on an optical pyrometer without correction for emissivity. They are believed to be low by 20 to 40°C at a reading of 1600 to 1700°C. Apparently, the calcium-stabilized zirconia crucibles and inlet tubes will not stand up in contact with the silicate slags at temperatures above 1650°C (as read on the optical pyrometer).

Metal from the run was found to weight 26.4 g and was found to contain mostly iron (96%).

(4) Material Balances

(a) Carbon Balances

Because it is imperative that nearly 100% of the carbon charged to the rock reactor be recovered, changes in materials and techniques were made throughout the program in order to improve the carbon recovery. Table 16 gives the carbon recoveries achieved in the larger rock reduction unit. In each run the major part of the carbon recovery was carbon monoxide. In all runs the amount of carbon recovered as CO_2 was very low - 2% or less. In one run, 18.7% of the carbon charged was recovered in the outlet gas lines and filters; however, the carbon in the outlet lines and filters was almost negligible in most cases. In most runs there was an appreciable amount of carbon deposited in the inlet tube, but this was difficult to separate and weigh accurately. In all the runs in which methane was charged, a great deal of the carbon was deposited (due to leaky inlet tubes) on the furnace insulation and could not be recovered.

Of the three runs with mixtures of graphite and rock (Runs 6, 7, and 10), Run 6 was the most successful (86% recovery). In all three of these runs, most of the unaccountable carbon is believed to have been deposited in the furnace insulation when the outlet lines became clogged. This forced the outlet gases out into the insulation where cracking or reduction occurred.

Run 18 gave the best carbon recovery (96% as CO). In this run, extremely active carbon (carbon black) was dropped directly into the crucible of molten rock at such a rate that it was consumed nearly as fast as it was fed. This did not allow an excess of carbon to accumulate, so large quantities of carbides were not formed. The crucible cover and outlet line were kept sealed so that the outlet gases did not leak into the furnace lining.

(b) Water Recovery Data

Water recovery data were determined on four runs (Runs 2, 3, 6, and 7) in which basalt was charged to the furnace. Amounts of 0.1 to 0.9 wt% water (average wt%, 0.4) in the basalt were recovered. These values are believed to be more accurate than the one (1.7% av) obtained in the smaller (45 cu cm) unit. It is believed that there may have been a very small leak in the induction coil water heater which leaked into the bell jar of that unit.

(c) Metal Recovery Data

In all runs where there was appreciable reduction of the rock, a metal phase separated from the slag. Table 17 gives an emission spectrographic analysis of the metal obtained. Care was taken so that no slag was included in the metal samples. In each case the metal was largely iron and silicon, with small amounts of Cu, Ni, Al and other elements. The silicon content of the metal was found to vary from 15 to 62 wt%. However, this would vary both with the degree of completion of the reduction and with the amount of metal in the original rock.

In all runs, some lower boiling metals or elements were found to collect in the outlet lines and filters. Table 18 gives emission spectrograph analyses of several samples of this material. The material in the outlet line was found to be largely sodium and potassium (potassium was not determined in these emission spectrographs), with small amounts of many lower boiling elements. This material caught fire and burned upon exposure to the air.

The material in the outlet line from Run 18 (still in the hot zone) contained mostly iron and silicon and was similar in composition to the crucible metal.

(d) Gas Impurities in Product Gas

Because the second step of the Aerojet Carbothermal Process uses a nickel catalyst which is known to be poisoned by various impurities (including sulfur and phosphorous), the outlet gases were carefully tested for the presence of these impurities.

Gas samples from Run 3 were taken at various times throughout the run and were analyzed by mass spectrometry (see Table 11). No impurities containing sulfur or phosphorus were found. However, the mass spectrometer used for these analyses could not detect traces (less than 0.01%) of these components. Special gas scrubbers were set up to absorb trace amounts of acidic gas impurities. The results of wet chemical analyses are given in Table 19. The outlet gases were passed through fritted glass disks immersed in 0.1 N NaOH solutions. These solutions were then analyzed by wet methods. The results were calculated on the basis of parts per million of rock. (The results would be nearly equivalent to grains/100 scf of CO, i.e., it is assumed that 100 lb rock will yield 14 lb of CO). The results were found to be somewhat erratic, varying from below the detectable limit for sulfur (0.27 ppm) to 50 ppm, and from 0 to 5 ppm for phosphorus. Apparently a more sensitive method of detection will have to be developed.

If the higher values found for the impurities are correct, they will have to be removed before the CO can be reduced with nickel catalyst. The attempt to segregate the impurities given off during the melting cycle (below 1500°C) and the reduction cycle (above 1500°C) was inconclusive. It seems probable that the largest part of the impurities would be given off below 1500°C; if so, the purification step could be simplified or perhaps eliminated.

4. Process Development Schemes

The results of the research on rock reduction, while demonstrating the feasibility of the process, indicated the need for more development work. Several areas where additional research is needed are described below.

a. Methane Inlet to the Furnace

To date it has not been possible to introduce the methane below the surface of the molten rock. On a larger scale pilot plant this may be possible by use of a liquid-cooled lance similar to an oxygen lance used in a modern steel furnace. However, for a lunar plant this may cause more complications than it solves - frothing, heat regulation, etc.

The last run (Run 18) indicates that it may not be necessary to add the methane below the molten rock surface. A much simpler inlet can be developed which discharges methane (or carbon and hydrogen) onto the rock surface. Gas-cooled concentric tubes and/or the reaming technique can be used.

A third approach may be taken: methane pre-cracking. This has the following advantages: (1) the cracking can be done at lower temperatures (1400°C or below); (2) all or part of the hydrogen can be separated from the carbon (this may permit a much higher carbon feed rate); and (3) carbon black appears to be less corrosive to the zirconia crucibles than methane or partly cracked methane.

b. Heating Method

The resistance heater used on the larger rock furnace (2-in. ID) was found to be quite satisfactory. However, it does have the disadvantage that all the heat has to be transferred through the crucible walls. This may be a serious problem on a plant sized unit. Several alternative heating methods should be tried including (1) electric arc, (2) microwave heating, and (3) solar heating.

c. Product Lines

The outlet gas line design should be investigated in order to overcome the tendency to clog with foamed, splattered, or sublimed materials. Some form of a reamer or moving chain should be developed to overcome this problem.

A solution must be found to the problem of dumping the slag and metal. This could involve either a system of filtering and dumping the whole furnace (similar to a modern oxygen steel furnace) or the development of a valving system.

d. Furnace Construction

The materials of construction of the furnace are very critical. A development program should be undertaken to determine the most suitable materials and design for the furnace (i.e., crucible walls, insulation, shape, etc.).

C. TASK 2, CARBON MONOXIDE REDUCTION, METHANE SYNTHESIS

1. Research Using Air-Cooled Reactor

This research on the reduction of carbon monoxide with hydrogen using an air-cooled reactor was carried out during the initial research period on Contract NAS 7-225 (Reference 1). The results of this work are summarized below.

a. A small reactor (10 scfh of reactant gas) for the reduction of carbon monoxide with hydrogen was designed and fabricated. A schematic flow diagram of the apparatus is shown in Figure 20. Maximum flexibility of operation was stressed to provide the ability to operate at temperatures of 200 to 900°C, at pressures of 1 to 7 atm, and at hydrogen/carbon monoxide mole ratios ranging from 1:1 to 4:1. The catalyst chamber was fabricated from a Type 316 stainless-steel fin-tube in order to withstand the high temperatures and high heat fluxes required. Standard industrial and laboratory equipment were used wherever possible in order to simplify and speed construction.

b. Tests were made which demonstrated that the equipment can be operated successfully at temperatures ranging from 200 to 900°C, and at pressures varying from 1.0 to 7.0 atm. The temperatures of the three catalyst bed sections were controllable to ±2°C with a differential of ±200°C. An initial charge of catalyst was successfully reduced and activated by flowing hydrogen through it at temperatures up to 450°C for 5 hours. Three preliminary runs demonstrated that the equipment was capable of yielding excellent data for the intended research.

c. Three different catalysts were evaluated. In addition, a series of runs was made to determine how various impurities in the reactant gas affect catalyst activity, and the feasibility of accomplishing the reduction without a catalyst.

(1) A series of 26 successful data-producing runs was made with Catalyst C-0765-1005 (25% Ni on 4- to 8-mesh silica gel). Optimum operating conditions for this catalyst were found to be as follows: space velocity, approximately 1000 hr^{-1}; hydrogen/carbon monoxide mole ratio, 4:1; catalyst bed pressure, 6 atm; and catalyst bed temperature, approximately 425°C. Under these conditions, carbon monoxide conversions were greater than 99.8%, yields of water and methane were greater than 99%, and yields of carbon dioxide were less than 1%. No other hydrocarbons or oxygenated compounds were found in either the product water or gases. Less than 0.1% of the carbon monoxide was deposited on the catalyst as carbon.

(2) A series of 12 data-producing runs was made with Catalyst C-0765-1001 (50% nickel on Kieselguhr, 1/8-in.-dia pellets). This catalyst was greatly superior to Catalyst C-0765-1005. Nearly complete conversions were obtained under the following conditions: space velocities of 2000 hr^{-1}; hydrogen/carbon monoxide mole ratio of 4:1; atmospheric pressure; and a reaction temperature of only 250°C. The hydrogen/carbon monoxide mole ratio could be reduced to 3:1 at 6.1 atm, 1000 hr^{-1} space velocity, and 250°C, while still maintaining nearly complete conversions (CH_4 and H_2O yields of 99%+, CO_2 yield of less than 1%). At the 3:1 hydrogen/carbon monoxide mole ratio, the product gas contained more than 90% methane and less than 0.5% carbon dioxide. Pressure drop across the catalyst was low (less than 1 in. of water ΔP with 1000 hr^{-1} space velocity and 6.1 atm). The pressure drop did not build up with time, and no carbon was found deposited on the catalyst. The catalyst was still active when it was removed after 110 hours of operation. A deep (38.5 in.) catalyst bed was required to obtain nearly complete conversion of the carbon dioxide (produced in the top of the catalyst bed) when the low hydrogen/carbon monoxide mole ratio was used.

(3) Catalyst C-0765-1003, which contained about 15% nickel deposited on kieselguhr (5/32-in. extruded pellets), was found to be intermediate in activity between the first two catalysts tested. The catalyst was not active at 250°C, but was quite active at 350°C. Increasing the catalyst bed temperature to 400°C did not increase the conversion of carbon dioxide into methane and water at a hydrogen/carbon monoxide mole ratio of 3:1.

(4) A series of four runs was made without catalyst (bare tube) in the reactor. These runs were made under the following conditions: space velocity of 550 hr^{-1}; pressure of 6.1 atm; hydrogen/carbon monoxide mole ratio of 3.7:1; and temperatures of 500 to 900°C. The data show that the maximum carbon monoxide conversion was only about 44% at 700°C; about 15 to 25% of the conversion was to carbon dioxide rather than to methane and water.

d. Three series of runs (described below) were made with the best catalyst (C-0765-1001) in which impurities were purposely added to the reactant hydrogen gas.

(1) A run of 22 hours duration was made with 59 grains of sulfur/100 scf (as COS) in the hydrogen stream. In this time more than 3 g of sulfur (equivalent to 3.9 wt% of the nickel in the catalyst) was charged to the reactor. Although the top third of the reactor had absorbed nearly all of the sulfur and was nearly deactivated, the remaining two-thirds of the reactor continued to operate with only a small decrease in conversion and yields.

(2) A run of 10 hours duration with 1 vol% nitrogen oxide (NO) in the hydrogen reactant gas demonstrated that this nitrogen oxide does not damage the catalyst. However, the oxide is reduced (75 wt% to NH_3, 25 wt% to N_2); this ammonia would have to be removed from the product gases and the hydrogen recovered for a lunar process.

(3) A run of less than 3 hours duration with 0.5 mol% phosphine (PH_3) in the hydrogen reactant gas demonstrated that phosphorus is an active catalyst poison which will have to be removed from the reactant gases. Approximately one-half of the catalyst bed was deactivated and its pressure drop increased greatly during the short run.

Carbon dioxide and water in the amounts normally present in the catalyst bed were not found to be harmful. A low concentration of nitrogen (0.5% N_2) present in the carbon monoxide reactant gas did not harm the catalyst.

2. Research Using an Automatic Water-Cooled Reactor

This section contains a report of the research performed on the carbon monoxide reduction step during the third research period of Contract NAS 7-225.

a. Design and Construction

The carbon monoxide reduction reactor was modified to operate automatically for long-term catalyst life studies of 60- to 90-day duration. The revised unit was much simpler to operate and provided closer temperature control and a greater flexibility in the choice of operating conditions than the one developed during the first program period. As described below, provisions were made to measure temperatures at any catalyst bed level. Multiple entry for reactant gas was another notable modification which provided a more uniform bed temperature throughout the reaction zone. These changes resulted in extended catalyst life and permitted the use of higher space velocities.

Figure 21 is a flow diagram of the automatic carbon monoxide/hydrogen reduction unit. A constant pressure (200 psig) was provided on the orifice meters by standard gas-cylinder pressure-reducing regulators. Line filters were provided to remove dirt from the gases. All lines and fittings were of stainless steel to prevent corrosion and contamination. Solenoid valves were installed in both feed lines to automatically shut down the unit in case of high catalyst bed temperature, low gas pressure (line break), or failure of electrical power or water. Gas rates were measured and controlled by calibrated flow-recording controllers.

Uniform and controlled catalyst bed temperatures were provided by a water jacket (2-in. ID) around the catalyst bed. The exothermic reaction between the gases entering the bottom of the reactor generated steam bubbles in the water which rose to maintain a uniform jacket temperature. The jacket temperature was very closely controlled by means of a pressure controller which maintained a constant temperature in the jacket by regulating the flow of water in the cooling coil.

Heat for catalyst regeneration, startup, and/or isothermal operation was provided by two 3/16-in. OD heater tubes (not shown) extending up throughout the length of the water jacket. The carbon monoxide or mixed carbon monoxide/hydrogen stream was distributed as desired at the 0, 3, 6, 9, and 12.5-in. level (from the bottom of the catalyst bed) by means of rotameters and needle valves. The outlet gases were cooled and condensed in a coil of 0.25-in. stainless-steel tubing immersed in cooling water. Safety pressure release was provided by a relief valve on the water jacket and by a mercury release bubbler on the low-pressure product gas line.

The product water was separated from the gas in a 250-ml stainless-steel sample container. The level in the water separator was maintained constant by a solenoid valve (not shown) which was actuated by a relay connected to a mercury contact in a manometer. The pressure in the catalyst bed could be controlled accurately at 1 to 10 atmospheres by means of a pressure controller and motor valve installed in the product gas line. The product gas from the 12.5-, 19-, 25.5-, 32-, and 39-in. catalyst bed levels was analyzed by an on-stream gas chromatograph, an Orsat apparatus, or a mass spectrometer. A manometer (50 in. of mercury) was used to measure the pressure drop across the catalyst bed. The product gas flow rates were measured by a wet-test meter.

Figure 22 is a photograph of the catalyst tube before assembly. The unit is fabricated from a 5/8-in.-OD stainless-steel tube with 1.25-in.-OD stainless-steel fins. The inlet tubes, sample lines, drain line, vent line, jacket thermocouple tube, cooling coil, and lower and upper flanges are welded to the catalyst tube.

Figure 23 is a photograph of the catalyst tube with the water jacket installed. The connections are shown, as are the 2-in. stainless-steel pipe water jacket, the 3/16-in. OD heater tubes, and the AN fittings on the ends of the catalyst tube.

Figure 24 is a photograph of the completed carbon monoxide/hydrogen reduction unit. On the panel board can be seen the pressure and flow controllers, the multipoint temperature recorder, Variacs for jacket and line heater control, and pressure gages. The reactor (complete with a 3-in. layer of insulation) and the insulated condenser and water separator are also visible. The muffle-type furnace was installed for hydrogen reduction of the catalyst; this furnace was removed during carbon monoxide reduction runs.

Figure 25 is a photograph of the back side of the unit showing the gas cylinder, pressure-reducing regulators, manometers, differential pressure transfer cells, and the gas chromatograph.

b. Testing

The equipment was leak-tested and the catalyst reduced with hydrogen at about 400°C. The first shakedown test run was then started. This run was made under the following conditions: (1) Catalyst C-0765-1001 (nickel on kieselguhr) crushed to -9 to +16 mesh; (2) 1000 hr^{-1} space velocity (based on 119 cu cm of catalyst); (3) 4:1 H_2/CO mole ratio; (4) 6 atm pressure in catalyst bed; (5) 220°C jacket temperature; and (6) feed entry split equally at 0, 3, 6, and 9 in. Under these conditions, 100% conversion of the carbon monoxide was obtained (no CO or CO_2 in outlet gas) with about 0.1 in. mercury pressure drop across the catalyst bed and a catalyst-bed-temperature profile as shown in Figure 26. There was a rapid increase in temperature at each point of feed entry, after which the gases tended to cool to the temperature of the water jacket. After the last feed entry, the gas temperature equilibrated with that of the water jacket.

c. Long-Duration Runs

Two long-duration runs were made using the water-cooled automatic unit. The first run was of 62 days duration made under nine different sets of conditions - each more stringent than the preceding one. The second run was of 92 days duration with all variables held constant. Catalyst C-0765-03-1001 was chosen for these runs because previous results of a 110-hour run indicated that this catalyst had the required long-life characteristics (Reference 1). The same change of catalyst was used for the two long-duration runs. No attempt was made to reactivate the catalyst.

(1) Conversions and Yields

The first long-duration carbon monoxide reduction run operated virtually without interruption for 1495 hours (62 days) with no indication of a change in performance. The data for the complete 60-day test are reported in Tables 20, 21, and 22. Data collected under each set of reaction conditions are grouped together.

The carbon monoxide conversion remained at 100% throughout the run. The percent yields of products averaged over the entire run are as follows: methane, 99.8; water, 98.1; and carbon dioxide, 0.4. The carbon dioxide yield became significant only toward the end of the run when a high space velocity (3000 hr^{-1}) was used. These data served to indicate that the activity of the catalyst remained high throughout the run, and also to indicate the conditions under which quantitative conversion of carbon monoxide to methane and water was obtained.

The second long-duration carbon monoxide reduction run was made at a space velocity of 1000 hr^{-1}. The reactor was operated for 2217 hours (92 days) with no indication of a decrease in catalyst performance as measured by product gas yields. The conditions and product yields for Run 2 are listed in Tables 20 and 21; the product gas analyses are given in Table 22. The carbon monoxide conversion remained at 100%. For all of Run 2, the average percent yield of products is as follows: methane, 102.7; water, 99.7, and carbon dioxide, 0.09. The carbon material balance is 103.6%, while the oxygen material balance is 101.1. The pressure drop did not increase during this time. The catalyst analyses after a 3712-hour operation showed that the carbon deposition on the catalyst was almost nil (new catalyst: 5.1 wt% Ni; catalyst after 3712 hours: inlet 6.3% Ni, middile 5.3% Ni, and outlet 4.4% Ni). After the 3712 hours of testing, the sulfur content of the catalyst near the gas inlet had increased from 0.07 to 0.63%, indicating a very small amount of sulfur in the feed gas.

(2) Multiple Feed Entry

The CO was split into four and later into five equal parts and injected at 3-in. intervals up the catalyst bed. This resulted in a saw-toothed temperature profile (Figures 26 and 27) but spread the heat out from 3 to 15 in. along the bed length. This is believed to have made possible the achievement of the extremely high space velocities (3000 hr^{-1}) and long catalyst life (154 days) without appreciable loss in catalyst activity in this equipment.

After Run 1-7 was completed, the hydrogen and carbon monoxide were premixed and introduced through the five feed inlets for about 3 hours. There was no apparent difference between the two methods of gas introduction; the carbon monoxide conversion, carbon dioxide production, and temperature profile remained relatively constant (Figure 28).

(3) Effect of Space Velocity

Figure 29 shows how the CO_2 content in the product gas slowly increases as the space velocity increases. Even at a space velocity of 2500 hr^{-1}, the H_2O and CH_4 yieldsare excellent and the CO_2 yield is acceptably low. The better catalyst performance at high space velocity in the automatic test unit than in the air cooled unit (Reference 1) is ascribed to the much better catalyst temperature control made possible by the water cooling and by the multifeed entry. Figure 30 shows how increasing the space velocity increases the maximum catalyst bed temperature. (These were the maximum temperatures measured with a thermocouple in the center of the catalyst tube at any height.) High space velocities tend to be hard on the catalyst due to the high temperatures which tend to promote carbon deposition on the catalyst.

(4) Effect of H_2/CO Mole Ratio

Complete CO conversion with 0 percent CO_2 yield was achieved at H_2/CO mole ratios of 4:1 and 3.51. At 3.1:1 ratio the CO conversion remained 100% throughout runs 1-3 to 1-9 and 2-1 to 2-64, and it was only at very high space velocities that the CO_2 yield became appreciable.

(5) Heat Balances

It was possible to get some approximate heat of reaction data. The unit was fairly well insulated and the amount of heat required to maintain the catalyst bed at 250°C with no gas flow was found to be about 100 watts or 86 kcal/hour. The equipment was in an air-conditioned laboratory which was held at $\pm 3^{\circ}$C, so the heat loss should vary only about ± 1.2 kcal/hour. The heater input was measured with an ammeter and wattmeter, and the catalyst-bed cooling-water heat removal was measured by thermocouple and rotameter readings.

For Run 1-10 an average of 42.0 kcal/mole of CO was removed by the cooling water. The gases entering at 25°C and leaving at 250°C removed 12 kcal/mole, making the calculated heat of reaction 54.0 kcal/mole CO. This compares favorably with the theoretical value of 51.3.

(6) Pressure Drop

The pressure drop across the catalyst bed did not go up with time even at H_2/CO mole ratios as low as 3:1. Run No. 2-1 to 2-64 was continued for 92 days without shutdown; the pressure drop did not increase a measurable amount during this prolonged period. The absence of a pressure buildup indicated no carbon deposition, and also a long, useful catalyst life. Tripling the space velocity (1000 to 3000 hr^{-1}, Run 1-3 to Run 1-9, Table 20) increased the pressure drop from 0.15 to 0.50 in. Hg.

(7) Carbon Dioxide Surveys

A series of catalyst bed surveys for CO_2 were taken for Runs 1-1 to 1-9 (see Table 23). At 4:1 H_2/CO, no CO_2 was found 19 in. above the gas inlet; at 3.5:1 H_2/CO, no CO_2 was found 25.5 in. above the inlet, and at 3.1:1 H_2/CO ratio and 1000 hr^{-1}, no CO_2 was found 32 in. above the gas inlet. In Runs 1-4 through 1-9, the CO_2 in the gas gradually built up as the space velocity was increased to 3000 hr^{-1}. The maximum CO_2 concentration at 19 in. (approximately halfway up the bed) was 4.8%. No CO was found in any of these tests. This would indicate that for less stringent requirements, such as commercial methane production, half of the bed depth could be used or the space velocity could be increased to 6000 hr^{-1}, while still maintaining 100% CO conversion. The bed survey made during Run 2-68 after 154 days of operation showed a small buildup of CO_2 over the one taken during Run 1-3. This indicated a small decrease in catalyst activity, bu the outlet gas was still within specificiations.

3. Process Development Scheme

The automatic water-cooled CO reduction unit proved to be capable of continuous automatic control with little attention. Temperature control, pressure control, flow control, and liquid level controls with minor improvements could be adopted for a lunar prototype plant. A multi-tube catalyst bed unit having at least ten times (100 scfh/hour) the capacity of the present unit should be tested. The multi-feed inlet system should be checked out on the larger scale unit.

IV. PERSONNEL

The senior staff assigned to this program was comprised of S. D. Rosenberg (Project Manager), G. A. Guter, F. E. Miller, and R. L. Beegle, Jr.

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TABLE 1

ELEMENTAL COMPOSITIONS

Element	Maria According to Urey	Basalt	Terrae According to Kuiper	Granite
O	43-46	45.45	47-51	49.58
Si	21-24	21.73	31-35	33.46
Al	4-9	8.61	6-10	8.24
Fe	8-11	8.29	1.5-4	1.43
Mg	3-15	5.13	0.1-1	0.37
Ca	5-8	6.47	1-3	0.50
Na	0.5-3	2.77	2-4	2.30
K	0.2-2	-	2-4	4.07
H	0.1-0.3	0.07	0-0.2	0.05
C	1-3	-	<1	-
S	<0.5	-	<1	-
Ni	<0.5	-	-	-

TABLE 2

APPROXIMATE RANGE OF COMPOSITION OF INDOCHINITE TEKTITES

Constituent	Wt%
SiO_2	71.2 - 77.5
Al_2O_3	11.59 - 13.68
Fe_2O_3	0.37 - 0.82
FeO	3.25 - 4.88
MgO	1.62 - 2.96
CaO	1.57 - 2.08
Na_2O	1.06 - 1.58
K_2O	2.10 - 2.62
TiO_2	0.63 - 0.81
MnO	0.08 - 0.10

TABLE 3

SUMMARY OF ROCK REDUCTION REACTOR IMPROVEMENTS

Run No.	Maximum Temperature Achieved °C	Major Problems Encountered	Modifications to Solve Problems
1	635	Induction unit tube burned out; it operated on half load	Installed new tube
2	974	Heat cracked bell jar neck	Replaced bell jar and installed heat shield made of tungsten crucible cover, 1/8" alumina spacer, and 1/2" alumina dish filled with 14-28 mesh zirconia.
3	985	(a) Quartz cylinder, 1/8" extruded wall with drilled port holes for radiameter and optical pyrometer, broke	(a) Installed new cylinder of same material but without holes
		(b) Heat shield broke	(b-1) Cast 1-5/8" thick x 2-1/4" dia. zirconia heat shield with ports for top of tungsten crucible (b-2) Cast secondary zirconia heat shield with ports and diameter of quartz cylinder
		(c) Induction heat was insufficient	(c) Removed transformer
4	1330	(a) Quartz cylinder broke	(a) Installed new 1/4-in. wall cintered quartz cylinder
		(b) Induction heat was insufficient	(b) Installed new induction furnace leads, 3/8" tubing, 2" x 1/16" silver soldered copper flanges with 1/16" Teflon separator
		(c) Induction power heated (150°F) structural members near leads	(c) No correction
		(d) Bell jar was too hot considering susceptor temperature level	(d-1) Fiberfrax dome cover 1/2" thick, with quartz windows, fabricated (d-2) In the 1-7/8" annular insulation space between susceptor and quartz cylinder, replaced outside 1/2-in. of 14-28 mesh zirconia with 325 mesh zirconia, GGC type

TABLE 3 (Cont.)

Run No.	Maximum Temperature Achieved °C	Major Problems Encountered	Modifications to Solve Problems
5	1579	(a) Induction unit burned out bulbs, heat was insufficient (b) Induction power heating steel adjacent to leads	(a) Revised tank grid coil support so that it could be raised out of tank coil (b) Installed copper shield
6	1792	(a) Induction power continued to heat steel near leads (b) Rear section of bell jar lower cooling-ring picked up induction field, causing heating and arcing (c) Pyrex base plate broke due to Item b (d) Too much heat came through quartz cylinder to bell jar wall	(a) Removed steel and copper shield in areas of induction leads (b) Replaced rear half of ring with plastic tubing drilled for air dispersion (c) Installed new Pyrex base (d) Installed molybdenum radiation shield midway within annular insulation space; alumina split-tube heat shield liner for quartz cylinder, 14-28 mesh zirconia refractory
7	1502*	(a) Thermocouple at tip of gas injection nozzle picked up induction heat (b) Quartz cylinder red, refractory passing too much heat (c) Too much heat reaching upper portion of bell jar (d) Basalt fogged quartz windows in heat shield	(a) Removed thermocouple (b) Replaced quartz cylinder with rigidized Fiberfrax shell, 1/16", and 4 layers of 1/16" Fiberfrax felt, replaced 14-28 mesh GGC zirconia with GGA, same mesh. (c) Used Fiberfrax blanket to pack between heat shields (d) Windows cleaned

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* Maximum desired temperature for melt.

TABLE 3 (Cont.)

Run No.	Maximum Temperature Achieved °C	Major Problems Encountered	Modifications to Solve Problems
8	1822	(a) Milky deposit formed on shield windows; low temperature readings resulted	(a) Windows easily cleaned for following run
		(b) Alumina crucible melted, allowing molten quartz to run into tungsten crucible	(b) Replaced tungsten crucible with new one; zirconia crucible used for next run
		(c) Fiberfrax cylinder red; refractory passed more heat than desired for bell jar grease seal for long runs	(c) Outside 1/2-in. of refractory space for length of susceptor filled with -48 + 150 mesh GGA zirconia, balance of area, next to susceptor -14 + 28 mesh
9	1916**	(a) A major portion of the carbon released by bubbling methane into molten quartz passed out of the melt into bell jar	
		(b) Carbon in upper portion of bell jar closed over windows for temperature reading	(b) Moved optical pyrometer to lower port to sight on mid-section of susceptor
		(c) Induction coil arced due to buildup of carbon on coil; Pyrex base cracked by arcing	(c) Pyrex base replaced; inlet induction post insulated with Teflon
		(d) Zirconia inlet jacket tube atacked by carbon	(d) Use alumina tube for lower temperature melts, thoria 1900°C and above
		(e) Zirconia crucible in one piece but fused to tungsten crucible	(e) Position away from susceptor
		(f) Tungsten crucible damaged in removal of zirconia discs for crucible support	(f) Replaced with tungsten cylinder, same dimensions as tungsten crucible, and tungsten disc for bottom radiant heat shield
10	1707*	Considerable carbon passed through melt into bell jar; inlet tubes plugged	

** Fiberfrax cylinder shield remained white, showing excellent heat insulation. Bell jar top and bottom remained under 70°C. Induction furnace automatically controlled at ± 10°C; ample power reserve for higher future temperatures if desired.

* Maximum desired temperature for melt.

TABLE 4

CARBOTHERMAL REDUCTION OF NATURAL SILICATES
(Reaction Conditions and Results)

Run No.	Crucible Charge	Crucible	Inlet Tube	Inlet Gas	Maximum Temperature (°C)	Results
11	55.8 g granite	1-1/2" OD, 3-1/2" high, Al_2O_3	Single, 1/4" OD, Al_2O_3	argon; H_2	1800	Pyrex base cracked, crucible cracked, could not maintain 1800° with H_2 flow.
12	54.8 g granite	1-1/2" OD, 3" high ZrO_2	Double 1/4" ZrO_2, 1/8" Al_2O_3	H_2; argon	1800	Pyrex base cracked, crucible cracked, inlet tube broke.
13	72.9 g granite	1-1/2" OD, 3" high ZrO_2	Single 5/16" ZrO_2	argon; CH_4 + H_2 + A	1800	Inlet tube cracked off when CH_4 + H_2 was turned on, crucible OK, base OK.
14	97.9 g granite	1-1/2" OD, 3" high ZrO_2	Single 1/4" thoria	argon, CH_4 + H_2 + A	1800	Inlet tube broke off and dissolved in melt; inlet tube broke and plugged 5 min after CH_4 + H_2 turned on.
15	99.1 g basalt + 3.0 g carbon	1-1/2" OD, 3" high ZrO_2	Triple Al_2O_3 (H_2 cooled)	argon, H_2, CH_4 + H_2	1520	CO evolution started at 1100°C, CH_4 + H_2 flow for 43 min before inlet tube plugged. Iron was reduced in melt and some silica.
16	50.1 g basalt + 5.0 g carbon	1-1/2" OD, 3" high ZrO_2	None	argon purge	1670	Temperature increased too rapidly and frothing of melt occurred, white sublimate noted which deposited on bell jar; iron reduced;crucible intact; transite base OK.
17	50.1 g basalt + 5.0 g carbon	1-1/2" OD, 3" high ZrO_2	None	argon purge	1730	90% of carbon evolved as CO and CO_2. Considerable reaction at 1400-1500°C noted. Tungsten not compatible with melt; it dissolved in metal;most of material sublimed out of crucible.
18	50.0 g granite + 5.0 g carbon	1-1/2" OD, 3" high ZrO_2	None	argon purge	1646	73% C recovered as CO and CO_2, 20% C in melt, 7% C lost; crucible intact, but with grey discoloration. Slag contained droplets of metal. Appreciable quantities of white powder sublimed on bell jar.
19	50.0 g basalt + 5.0 g carbon	1-1/2" OD, 3-1/2" high Al_2O_3	None	argon purge	1645	Al_2O_3 crucible sagged and broke. Only 78% C recovered as CO and CO_2.
20	42.0 g granite + 4.2 g carbon	1-7/8" OD, 2" high ZrO_2	None	argon purge	1675	Used coarse grained ZrO_2 crucible with heavier wall; crucible in good shape. Only 72% C recovered as CO and CO_2.
21	Slag from Run 20	Same as Run 20	None	argon purge	1770	CO + CO_2 recovery increased to 88%; C in slag about 10%; crucible intact but badly corroded and attacked by melt.
22	37.5 g granite + 12.5 g SiC	1-7/8" OD, 2" high ZrO_2	None	argon purge	1755	83% of C recovered as CO + CO_2. Crucible intact but covered with flux. Most of melt had sublimed (only 12.4 g left). Slag contained most of missing C.

TABLE 4 (Cont.)

Run No.	Crucible Charge	Crucible	Inlet Tube	Inlet Gas	Maximum Temperature (°C)	Results
23	70.9 g basalt + 2.1 g carbon	1-1/2" OD, 3" high, Impervious ZrO_2	Triple walled with 1" x 4-1/2" ZrO_2 bell	94.4% CH_4 + 5.2% H_2	1550	Bell cracked and allowed CH_4 to escape reaction zone; 44% of CH_4 reacted to form CO
24	65.8 g basalt 2.0 g carbon	1-1/2" OD, 3" high, Fine grain ZrO_2	Triple walled with 1" x 4-1/2" ZrO_2 bell	94.4% CH_4 + 5.2% H_2	1540	Bell functioned well; 50% of methane reacted to form CO.
25	50.0 g granite	1-1/2" OD, 3" high, Fine grain ZrO_2	Triple walled with 1/2" x 5" ZrO_2 bell	94.4% CH_4 + 5.2% H_2	1520	CH_4 was inadvertently allowed to enter purge line and immediately cracked in bell jar; run aborted.
26	50.0 g granite	1-1/2" OD, 3" high, Fine grain ZrO_2	Triple walled with 1/2" x 5" ZrO_2 bell	94.4% CH_4 + 5.2% H_2	1570	CH_4 flow maintained for 3 hours;carbon deposited in inlet bell. Inlet tube did not clog.
27	Slag from Run 24	1-1/2" OD, 3" high, Fine grain ZrO_2	None	Argon purge	1730	An insignificant amount of CO was produced.
28	70 g basalt + 1.46 g carbon	1-1/2" OD, 3" high, Impervious ZrO_2	Triple walled with 1" x 7/8" impure ZrO_2 bell	94.4% CH_4 + 5.2% H_2	1565	Run lasted for 47 min before inlet tube clogged.
29	69.9 g basalt + 1.4 g carbon	1-1/2" OD, 3" high, Impervious ZrO_2	Triple walled with 1" x 5" bell	94.4% CH_4 + 5.2% H_2	1700	CH_4 flow maintained for 4.5 hours. Carbon appeared to react with inlet bell.
30	70.0 g granite	1-1/2" OD, 3" high, Impervious ZrO_2	Triple walled with 1" x 5" bell	94.4% CH_4 + 5.2% H_2	1700	CH_4 flow lasted for 3 hours before inlet clogged. Carbon deposited in inlet bell.
31	70.0 g tektite	1-1/2" OD, 3" high, Impervious ZrO_2	Triple walled with 1" x 5" bell	94.4% CH_4 + 5.2% H_2	1610	CH_4 flow maintained for 3 hours. Carbon deposited inside inlet bell. Inlet tube remained open.
32	70.0 g basalt	1-1/2" OD, 3" high, Impervious ZrO_2	Triple walled with 1" x 6" bell	94.4% CH_4 + 5.2% H_2	1600	CH_4 flow maintained for 7.67 hours. Carbon deposited in inlet bell. Inlet tube remained open.

TABLE 5

REDUCTION OF BASALT WITH GRAPHITE*
RUN 6

Time (hours)	Crucible Temp (°C)	Product Gas Rate (gram mole/hour)	Carbon Monoxide in Product Gas (mole %)	Carbon Recovered as CO (g carbon)	Cumulative** Recovery of Carbon (%)
0	1020	1.32	1.4	0	0
4	1310	1.31	4.6	2.56	4.2
8	1400	1.25	7.6	6.71	11.1
12	1560	1.26	10.3	11.30	18.7
16	1560	1.16	4.3	15.26	25.2
20	1640	1.28	10.4	19.72	32.6
24	1580	1.21	7.0	23.26	38.4
28	1615	1.23	7.1	26.67	44.1
32	1500	0	0	30.98	51.1
36	1590	1.14	0.3	31.02	51.3
40	1690	1.28	8.8	34.13	56.4
44	1690	1.19	6.7	39.32	65.0
48	1690	1.12	7.0	44.27	73.2
52	1680	1.07	4.0	46.82	77.4
56	1685	1.04	3.0	48.54	80.1
60	1700	1.05	2.3	49.82	82.4
64	1730	1.05	2.4	51.05	84.3
68	1785	1.10	2.0	52.13	86.1

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* 454 g of basalt mixed with 60.5 g of pure graphite in an impervious zirconia crucible and heated with an argon purge.

** In addition to the CO in the product gas, 0.54 g of H_2O and 0.15 g of CO_2 were recovered.

TABLE 6

REDUCTION OF BASALT WITH GRAPHITE*
RUN 7

Time (hours)	Crucible Temp (°C)	Carbon Monoxide in Product Gas (mole %)	Carbon Recovered as CO (g carbon)	Cumulative** Recovery of Carbon (%)
0	660	0	0	0
2	1070	4.2	0.37	0.6
4	1305	7.8	2.82	4.7
6	1445	7.4	4.85	8.0
8	1562	16.7	10.23	16.9
10	1575	30.8	17.35	28.7
12	1592	5.7	22.21	36.8
14	1658	5.4	23.66	39.1
16	1685	8.0	25.38	42.0
18	1715	6.0	27.15	44.9
20	1710	4.3	28.48	47.1
22	1705	2.2	29.27	48.2
24	1700	1.5	29.69	49.1
26	1725	1.8	30.09	49.7
28	1755	5.7	31.30	51.7
30	1755	4.4	32.61	53.8
32	1755	3.7	33.59	55.5
34	1755	3.6	34.54	57.1
36	1745	3.2	35.37	58.4
38	1750	3.3	36.18	59.8
40	1758	3.2	37.00	61.2
42	1755	3.6	37.95	62.8
44	1745	3.0	38.77	64.1
46	1760	2.8	39.49	65.2
48	1765	2.6	40.16	66.3
50	1782	2.9	40.87	67.7
52	1790	4.5	41.90	69.2
54	1765	3.0	42.86	70.9
56	1758	2.4	43.75	72.5
58	1765	2.2	44.32	73.4
60	1758	1.8	44.78	74.1

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* 454 g of basalt mixed with 60.5 g of pure graphite in an impervious zirconia crucible. The graphite was crushed to -28 mesh to +40 mesh.

** In addition to the CO in the product gas, 1.78 g of H_2O and 0.21 g of CO_2 were recovered.

TABLE 7

EMISSION SPECTROGRAPHIC ANALYSES

	Sample Analysis (Wt%)					
			Alumina Bubbles from Run 7			
Component	Metal from Run 6	Metal from Run 7	New Bubbles	1/4 way down to Crucible**	3/4 way Down to Crucible	Near Crucible Top
Si	62.4	15.1	1.6	7.8	6.9	15.1
Fe	23.5	75.4	-	1.1	0.2	0.2
Mg	0.8	0.1	-	1.0	2.4	2.3
Al	5.8	1.4	98.4	73.5	72.0	65.7
Cu	0.4	0.6	-	-	-	-
Mn	5.8	2.3	-	-	-	-
Ti	1.3	2.0	-	-	-	-
Ni	-	1.4	-	-	-	-
Mo	-	-	-	8.8	14.7	11.7
Na	-	-	-	7.8	3.8	5.0
Co	-	1.7	-	-	-	-
C*	-	-	-	-	0.2	-

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* Carbon analyses by furnace oxidation to CO_2 and subsequent absorption

** From top of insulation layer

TABLE 8

REDUCTION OF BASALT WITH CARBON

Run 18[a]

Time (Hour)	Crucible Temp (°C)	Gas Flow Rates g-mole/hr Argon Purge	N_2 Cooling	Product Gas	Carbon Charged[b] (g carbon) Per Interval	Cumulative	CO in Product Gas (Mole %)	CO Recovered (g carbon) Per Interval	Cumulative	Recovery of C as CO (mole %) Per Interval	Cumulative
-0.5-0	1540	0.66	72	0.107	0.166	0.166	0.89	0.011	0.011	6.6	6.6
0-1	1545	0.66	72	0.833	1.420	1.568	5.04	0.482	0.494	33.9	31.5
1-2	1565	0.66	72	0.923	1.420	3.006	7.65	0.880	1.374	61.9	45.7
2-3	1550	0.66	72	0.925	1.420	4.427	9.07	1.007	2.380	70.9	53.8
3-4	1558	0.66	72	0.900	1.420	5.847	9.06	0.978	3.358	68.8	57.4
4-5	1565	0.66	72	0.885	1.420	7.268	9.42	1.000	4.358	70.4	59.9
5-6	1587	0.66	72	0.860	1.420	8.688	8.84	0.913	5.271	64.2	60.7
6-7	1600	0.66	72	0.874	1.420	10.108	9.44	0.989	6.260	69.6	61.9
7-8	1610	0.66	72	0.834	1.420	11.529	12.48	1.397	7.657	98.3	66.4
8-9	1603	0.66	72	0.946	1.420	12.949	15.42	1.751	9.408	123.3	72.7
9-10	1603	0.66	72	0.912	1.420	14.370	14.66	1.606	11.065	113.1	76.6
10-11	1606	0.66	72	0.909	1.420	15.790	13.51	1.474	12.489	103.8	79.1
11-12	1610	0.66	72	0.896	1.420	17.210	12.82	1.379	13.868	97.1	80.6
12-13	1616	0.66	72	0.898	1.420	18.631	12.00	1.294	15.162	91.1	81.4
13-14	1620	0.66	72	0.896	1.420	20.051	12.66	1.362	16.524	95.9	82.4
14-15	1625	0.66	72	0.882	1.420	21.472	11.36	1.203	17.727	84.7	82.6
15-16	1625	0.66	72	0.874	1.420	22.892	10.50	1.103	18.830	77.6	82.3
16-17	1640	0.66	72	0.939	1.420	24.312	13.53	1.528	20.358	107.6	83.7
17-18	1635	0.66	72	0.907	1.420	25.733	12.27	1.337	21.693	94.1	84.3
18-19	1644	0.66	72	0.884	1.420	27.153	10.85	1.152	22.848	81.1	84.1
19-20	1645	0.66	72	0.913	1.420	28.574	11.90	1.305	24.152	91.9	84.5
20-21	1645	0.66	72	0.909	1.420	29.994	11.33	1.237	25.389	87.1	84.6
21-22	1667	0.66	72	0.902	1.420	31.414	11.06	1.198	26.587	84.3	84.6
22-23	1665	0.66	72	0.904	1.420	32.835	11.70	1.270	27.857	89.4	84.8
23-24	1580	0.66	72	0.913	1.420	34.255	12.14	1.329	29.186	93.6	85.2

TABLE 8 (Cont.)

Time (Hour)	Crucible Temp (°C)	Gas Flow Rates g-mole/hr			Carbon Charged[b] (g carbon)		CO in Product Gas (Mole %)	CO Recovered (g carbon)		Recovery of C as CO (Mole %)	
		Argon Purge	N_2 Cooling	Product Gas	Per Interval	Cumulative		Per Interval	Cumulative	Per Interval	Cumulative
24-25	1580	0.66	72	0.920	1.420	35.676	12.49	1.379	30.565	97.1	85.7
25-26	1590	0.66	72	0.921	1.420	37.806	12.80	1.412	31.977	99.4	86.2
26-27.5	1608	0.66	72	1.377	2.103	39.20[c]	11.29	1.864	33.842	88.7[c]	86.3
27.5-29	1590	0.66	72	1.269	0	-	8.02	1.223	35.064	-	89.4
29-31	1620	0.66	72	1.641	0	-	3.79	0.747	35.811	-	91.4
31-33	1610	0.66	72	1.592	0	-	3.24	0.624	36.435	-	92.9
33-35	1630	0.66	72	1.621	0	-	3.24	0.630	37.066	-	94.6
35-37	1650	0.66	72	1.605	0	-	2.81	0.541	37.607	-	95.9

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[a] Charge of 454 g basalt in 2.0 in. ID by 8 in. high zirconia crucible; 3/8-in. ID by 10-in. long alumina inlet tube; 3/4-in. ID by 4-in. long alumina outlet tube; alumina crucible cover cemented on with zircoa cast.

[b] 12-16 mesh pelletized carbon black.

[c] Carbon feed stopped at 27.5, heat and argon purge continued for an additional 9.5 hours.

TABLE 9

ROCK REACTOR DATA FOR RUN 2*

Time	Crucible Temp (°C)	Gas Flow Rates (gram mole/hour)				Graphite and Methane Charged (g carbon)	Carbon Monoxide in Product Gas (mole %)	Carbon Recovered as CO (g carbon)	Cumulative Carbon Recovery as CO and CO_2 (mole %)
		Methane Feed	Argon Purge	N_2 Cooling	Product Gas				
11:00	850	0	1.08	12	1.10	8.00	0	0	-
12:00	930	0	1.08	12	1.16	8.00	0.7	0.10	1.2
1:00	960	0	1.08	12	1.12	8.00	1.7	0.33	4.1
2:00	1040	0	1.08	12	1.17	8.00	2.7	0.71	8.9
3:00	1060	0	1.08	12	1.15	8.00	3.3	1.12	14.0
4:00	1130	0	1.08	12	1.21	8.00	6.3	2.03	25.4
5:00	1215	0	1.08	12	1.25	8.00	4.6	2.72	34.0
6:00	1315	0	1.08	24	1.20	8.00	2.1	3.02	37.8
7:00	1350	0	1.08	24	1.21	8.00	3.1	3.47	43.4
8:00	1340	0	1.08	36	1.18	8.00	4.0	4.04	50.5
9:00	1509	0	1.08	54	1.20	8.00	4.1	4.63	57.8
10:00	1545	0	1.08	60+	1.17	8.00	6.4	5.53	69.0
11:00	1595	0	1.08	60+	1.12	8.00	4.4	6.12	76.5
12:00	1555	0	1.08	60+	1.10	8.00	3.4	6.57	82.2
1:00	1595	0	1.08	60+	1.10	8.00	1.9	6.82	85.2
2:00	1600	0	1.08	60+	1.12	8.00	0.7	6.91	86.4
3:00	1575	0	1.08	60+	1.06	8.00	0.5	6.97	87.1
4:00	1540	0.10	1.08	60+	1.25	8.57	3.6	7.51	87.5
5:00	1565	0.10	1.08	60+	1.43	9.71	7.0	8.71	89.5
6:10	1555	0.20	1.08	60+	1.54	10.70	6.6	9.93	92.6
7:10	1565	0.20	1.08	60+	1.45	12.98	5.4	10.87	83.8
8:10	1560	0.20	1.08	60+	1.45	15.26	6.2	12.05	79.1
9:10	1565	0.20	1.08	60+	1.44	16.59	6.5	13.17	79.4
10:10	1579	0.20	1.08	60+	1.48	18.89	6.5	14.32	75.8
11:10	1620	0	1.08	60+	1.24	20.32	5.4	15.13	74.5
12:00	1445	0	1.08	60+	1.22	20.32	4.0	15.71	77.4
					(Carbon in CO_2 recovered 0.33 gram)			(16.04)	(79.0)

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* Two inlet tubes of alumina and mullite terminating in 0.75-in. OD by 12-in. long ZrO_2 bells; crucible - 2.5 in. OD by 8-in. deep impervious ZrO_2; charge - 392 g of basalt mixed with 8 g of graphite; CO_2 recovered = 1.20 g; H_2O recovered = 1.21 g; Methane feed = 95.2% CH_4, 4.4% H_2, 0.4% N_2.

TABLE 10

ROCK REACTOR DATA FOR RUN 3*

Time	Crucible Temp (°C)	Gas Flow Rates (gram mole/hour) Methane Feed	Argon Purge	N_2 Cooling	Product Gas	Methane Charged (g carbon)	Carbon Monoxide in Product Gas (mole %)	Carbon Recovered as CO (g carbon)	Cumulative Carbon Recovered as CO (mole %)
7:00	1600	0.20	1.08	60	1.64	.95	6.0	.47	50
7:30	1630	0.20	1.08	60	1.59	2.10	4.2	.87	41
8:00	1635	0.20	1.08	60	1.58	3.24	4.0	1.25	39
8:30	1640	0.20	1.08	60	1.56	4.37	5.5	1.76	40
9:00	1625	0.20	1.08	60	1.54	5.51	6.2	2.33	42
9:30	1625	0.20	1.08	60	1.53	6.65	7.0	2.98	45
10:00	1620	0.20	1.08	60	1.43	7.80	6.3	3.52	45
10:30	1620	0.20	1.08	60	1.43	8.94	6.9	4.11	46
11:00	1620	0.20	1.08	60	1.56	10.10	8.0	4.86	48
11:30	1615	0.20	1.08	60	1.58	11.21	7.9	5.61	50
12:00	1610	0.20	1.08	60	1.58	12.37	8.3	6.40	52
12:30	1640	0.20	1.08	42	1.57	13.50	8.0	7.15	53
1:00	1590	0.20	1.08	36	1.42	14.64	7.8	7.81	53
1:30	1595	0.20	1.08	36	1.52	15.80	8.0	8.59	54
2:10	1585	0.20	1.08	36	1.57	17.30	8.0	9.60	55
2:50	1605	0.20	1.08	36	1.56	18.83	7.8	10.58	56
3:30	1625	0.20	1.08	36	1.56	20.38	7.5	11.52	56
4:10	1630	0.20	1.08	36	1.54	21.86	7.1	12.40	57
4:50	1610	0.20	1.08	36	1.50	23.40	6.7	13.21	57
5:30	1615	0.20	1.08	36	1.47	25.00	6.4	13.96	56
6:10	1635	0.20	1.08	36	1.44	26.42	5.7	14.62	55
6:50	1610	0.20	1.08	36	1.43	27.98	4.8	15.17	54
7:30	1655	0.20	1.08	36	1.49	31.00	4.8	15.74	51
8:10	1625	0.20	1.08	36	1.46	32.30	4.5	16.27	50
8:50	1635	0.20	1.08	36	1.45	34.80	4.4	16.78	50
9:50	1670	0.20	1.08	36	1.43	35.80	4.1	17.48	49
10:15	1660	0	1.08	36	1.23	36.20	4.0	17.72	49
11:30	1635	0	1.08	36	1.18	36.20	3.2	18.28	50
1:00	1565	0	1.08	36	1.11	36.20	2.1	18.79	52
2:00	1560	0	1.08	36	1.08	36.20	1.1	19.03	53
4:00	1570	0	1.08	36	1.06	36.20	1.0	19.43	54

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*Three inlet tubes of alumina and mullite terminating in 0.75-in.-OD by 12-in.-long ZrO_2 bells; crucible - 2.5-in.-OD by 8-in.-deep impervious ZrO_2; charge 454 g granite; CO_2 recovered = 0.62 g; H_2O recovered = 3.99 g; feed = 95.2% CH_4, 4.4% H_2, 0.4% N_2.

TABLE 11

ANALYSIS OF PRODUCT GAS SAMPLES FROM RUN 3 BY MASS SPECTROMETRY*

	Sample Number				
	1	2	3	4	5
Feed Gas Flow (g mole/hour)	0	0	0.2	0.2	0.2
Temperature (°C)	1150	1350	1630	1595	1630
Argon (mole%)	98.1	84.6	81.8	68.8	68.6
O_2 (mole%)	0.2	2.6	0.2	0.2	0.1
N_2 (mole%)	1.1	12.3	0.7	0.6	1.5
H_2 (mole%)	0.2	0.3	11.1	21.9	23.3
H_2O (mole%)	0.3	0.2	0.2	-	-
CO_2 (mole%)	0.1	-	0.4	-	-
CH_4 (mole%)	-	-	0.3	0.6	1.4
CO (mole%)	-	-	5.3	7.9	5.1

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*In addition to the samples for mass spectrometry, a special gas sample was taken throughout the run in order to detect the presence of minor gas impurities. For six minutes of each hour, the product gas was bubbled through a gas CNGA absorption bottle containing 0.1 N NaOH. This liquid was then analyzed by wet methods for sulfur and phosphorus compounds. No sulfur (less than 1 ppm) was found; only a trace (0.7 ppm) of phosphorus was found.

TABLE 12

CARBON BALANCE FOR RUN 3

	Grams of Carbon	Percent
Carbon feed as CH_4	36.2	100.0
Carbon recovered as CO	19.4	53.6
Carbon recovered as CH_4 in outlet gas	7.2	7.2
Carbon recovered as CO_2 in outlet gas	0.2	0.6
Carbon recovered as carbon in inlet tubes	7.4	20.4
Carbon recovered as carbon in outlet filter	1.1	3.0
Estimated loss in furnace	5.5	15.2
Total	36.2	100.0

TABLE 13

ANALYSIS OF METAL RECOVERED FROM RUN 3 BY EMISSION SPECTROSCOPY

	Wt%	
Metal	Sample 1	Sample 2
Iron	58.5	58.0
Silicon	37.7	39.0
Nickel	2.1	1.8
Copper	1.3	0.8
Silver	0.4	0.4

TABLE 14

REDUCTION OF BASALT WITH METHANE

(Run 13[a])

Time (hr)	Crucible Wall Temp. (°C)	Gas Flow Rates (g mole/hr)				Methane Charged (g carbon)		CO in Product Gas (Mole %)	CO Recovered (g carbon)		Recovery of C as CO (%)	
		Methane Feed [b]	Argon Purge	Nitrogen Cooling	Product Gas	Per Interval	Cumulative		Per Interval	Cumulative	Per Interval	Cumulative
6:30	1490	0.20	1.08	60	1.62	0.52	0.52	2.4	0.11	0.11	21.3	21.3
7:00	1530	0.19	1.08	60	1.62	1.10	1.62	5.0	0.49	0.60	44.1	36.8
7:30	1535	0.19	1.08	60	1.55	1.10	2.72	5.7	0.53	1.13	48.0	41.4
8:00	1510	0.20	1.08	60	1.62	1.11	3.83	4.9	0.47	1.60	42.6	41.7
8:30	1520	0.19	1.08	60	1.54	1.10	4.94	4.7	0.43	2.03	38.9	41.1
9:00	1520	0.20	1.08	60	1.55	1.11	6.05	4.3	0.40	2.43	36.0	40.2
9:30	1550	0.20	1.08	60	1.51	1.12	7.17	4.5	0.41	2.84	36.3	39.6
10:00	1555	0.19	1.08	60	1.30	1.10	8.27	4.3	0.33	3.17	30.3	38.3
10:30	1555	0.20	1.08	60	1.74	1.12	9.39	4.4	0.46	3.63	41.0	38.6
11:00	1570	0.20	1.08	60	1.53	1.11	10.50	4.9	0.45	4.07	40.3	38.8
11:30	1565	0.19	1.08	60	1.62	1.10	11.60	8.8	0.86	4.93	77.7	42.5
12:00	1560	0.20	1.08	60	1.58	1.15	12.75	6.7	0.64	5.57	55.5	43.7
12:30	1590	0.20	1.08	60	1.60	1.11	13.86	6.5	0.63	6.20	56.7	44.7
1:00	1590	0.19	1.08	60	1.56	1.10	14.96	6.8	0.63	6.83	57.3	45.7
1:30	1550	0.20	1.08	60	1.56	1.11	16.07	7.1	0.67	7.50	60.2	46.7
2:00	1555	0.21	1.08	60	1.58	1.19	17.26	6.6	0.63	8.12	52.6	47.1
2:30	1575	0.19	1.08	60	1.58	1.10	18.36	6.6	0.62	8.75	56.6	47.6
3:00	1575	0.20	1.08	60	1.55	1.12	19.48	6.6	0.61	9.36	54.8	48.1
3:30	1595	0.20	1.08	60	1.52	1.11	20.59	6.3	0.57	9.94	51.9	48.3
4:00	1570	0.19	1.08	60	1.46	1.10	21.69	6.7	0.59	10.52	53.2	48.5
4:30	1595	0.19	1.08	60	1.55	1.10	22.80	7.2	0.67	11.19	60.7	49.1
5:00	1605	0.19	1.08	60	1.58	1.09	23.89	7.4	0.69	11.89	63.6	49.8
5:30	1625	0.19	1.08	60	1.55	1.10	24.99	7.1	0.66	12.55	60.2	50.2
6:00	1650	0.19	1.08	60	1.56	1.10	26.08	7.5	0.70	13.25	64.5	50.8
6:30	1630	0.20	1.08	60	1.56	1.11	27.19	7.0	0.65	13.91	58.8	51.1
7:00	1645	0.19	1.08	60	1.51	1.09	28.28	6.8	0.61	14.52	56.1	51.3
7:30	1650	0.19	1.08	60	1.53	1.07	29.35	7.9	0.73	15.25	67.9	51.9
7:48	1515	0.19	1.08	60	1.85	0.64	29.99	4.1	0.27	15.52	42.4	51.7
8:30	1570	c	1.08	60	1.16	c	29.99	2.1	0.21	15.72	c	52.4
9:30	1605		1.08	60	1.20		29.99	2.1	0.30	16.02		53.4
10:30	1600		1.08	60	1.22		29.99	1.5	0.22	16.24		54.2
11:30	1615		1.08	60	1.20		29.99	1.0	0.15	16.39		54.7
12:30	1610		1.08	60	1.19		29.99	0.8	0.12	16.51		55.0
1:30	1620		1.08	60	1.19		29.99	0.6	0.09	16.60		55.3
2:30	1640		1.08	60	1.17		29.99	0.5	0.07	16.67		55.6

[a] One inlet tube of impervious ZrO_2 lined with Mo, reamed every 5 min. with WC reamer; ZrO_2 crucible charged with 454 g of Columbia River Basalt.

[b] Methane Feed = 94.4 wt% CH_4, 5.6 wt% H_2. [c] Methane addition stopped.

TABLE 15

REDUCTION OF BASALT WITH METHANE

(Run 15[a])

Time (hr)	Crucible Wall Temp. (°C)	Gas Flow Rates (g mole/hr)				Methane Charged (g carbon)		CO in Product Gas (Mole %)	CO Recovered (g carbon)		Recovery of C as CO (%)	
		Methane Feed[b]	Argon Purge	Nitrogen Cooling	Product Gas	Per Interval	Cumulative		Per Interval	Cumulative	Per Interval	Cumulative
10:00	1535	0.107	1.08	30	1.32	1.01	1.01	2.9	0.39	0.39	39.1	39.1
11:00	1535	0.107	1.08	30	1.37	1.21	2.22	3.8	0.64	1.04	53.0	46.7
12:00	1535	0.107	1.08	26	1.35	1.21	3.43	4.1	0.66	1.70	54.7	49.5
1:00	1535	0.108	1.08	27	1.33	1.22	4.65	4.1	0.66	2.36	54.2	50.8
2:00	1540	0.108	1.08	27	1.24	1.22	5.87	4.1	0.61	2.97	50.0	50.5
3:00	1530	0.108	1.08	27	1.28	1.22	7.09	4.1	0.62	3.60	51.6	50.8
4:00	1535	0.108	1.08	27	1.32	1.22	8.31	4.0	0.62	4.22	51.4	50.8
5:00	1540	0.107	1.08	27	1.32	1.21	9.52	3.8	0.60	4.82	48.2	50.6
6:00	1540	0.106	1.08	27	1.32	1.21	10.73	3.6	0.56	5.38	46.7	50.2
7:00	1535	0.107	1.08	27	1.32	1.22	11.94	3.5	0.55	5.93	45.2	49.7
8:00	1530	0.107	1.08	27	1.32	1.22	13.16	3.2	0.59	6.53	48.8	49.6
9:00	1535	0.107	1.08	27	1.29	1.21	14.37	3.1	0.48	7.00	39.6	48.7
10:00	1575	0.107	1.08	30	1.31	1.22	15.59	3.1	0.48	7.49	39.4	48.0
11:00	1590	0.108	1.08	36	1.31	1.22	16.80	2.7	0.42	7.91	34.4	47.1
12:00	1580	0.107	1.08	36	1.30	1.22	18.02	3.0	0.47	8.39	38.6	46.5
1:00	1585	0.108	1.08	36	1.30	1.22	19.24	2.9	0.46	8.84	37.6	46.0
2:00	1595	0.108	1.08	36	1.29	1.22	20.46	2.9	0.44	9.29	36.4	45.4
3:00	1600	0.107	1.08	36	1.28	1.22	21.69	2.9	0.44	9.73	36.1	44.9
4:00	1600	0.107	1.08	36	1.28	1.22	22.90	2.9	0.45	10.18	36.9	44.5
5:00	1600	0.108	1.08	36	1.25	1.22	24.12	2.8	0.43	10.60	35.2	44.0
6:00	1600	0.108	1.08	30	1.26	1.22	25.34	2.8	0.42	11.02	34.4	43.5
7:00	1620	0.108	1.08	30	1.26	1.22	26.57	2.8	0.42	11.44	34.4	43.0
8:00	1600	0.108	1.08	24	1.26	1.22	27.79	2.8	0.42	11.86	34.4	42.7
9:00	1610	0.108	1.08	24	1.25	1.22	29.01	2.5	0.37	12.23	30.4	42.2
10:00	1630	0.108	1.08	24	1.26	1.22	30.23	2.6	0.41	12.64	33.6	41.8
11:00	1630	c	1.08	24	1.23	0.61	30.84	2.4	0.43	13.07	32.1	42.4
12:00	1660	-	1.08	10	1.20	c	c	1.8	0.27	13.33	c	43.2
2:00	1655	-	1.08	10	1.19	-	-	1.8	0.51	13.84	-	44.8
4:00	1680	-	1.08	18	1.23	-	-	3.2	0.94	14.79	-	47.9
6:00	1685	-	1.08	18	1.22	-	-	3.3	0.98	15.77	-	51.1
8:00	1685	-	1.08	18	1.21	-	-	3.1	0.91	16.68	-	54.1
10:00	1720	-	1.08	24	1.21	-	-	3.0	0.88	17.56	-	56.9
12:00	1730	-	1.08	36	1.07	-	-	2.2	0.53	18.09	-	58.6
2:00	1730	-	1.08	36	1.07	-	-	1.0	0.25	18.34	-	59.4
4:00	1740	-	1.08	36	1.07	-	-	0.7	0.18	18.52	-	60.0

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[a] One inlet tube of impervious ZrO_2 lined with 3 layers of 0.003 Mo, reamed every 2.4 min with a tungsten carbide reamer.

[b] Methane feed = 94.4% CH_4, 5.6 wt% H_2

[c] Methane feed stopped at 10:30

TABLE 16

CARBON BALANCES FOR RESISTANCE-HEATED ROCK REACTOR RUNS

Run No.	Feed Type	Amount of Carbon Charged (g C/100 g Rock)	Max Temp (°C)	Duration of Run (hr)	Carbon Recovered as CO (mol%)		Notes
					Maximum per Interval	Total or Cumulative	
6	6-28 Mesh graphite	13.3	1785	68	-	86	Outlet tube clogged with sublimate after 31 hours of operation.
7	28-48 Mesh graphite	13.3	1800	60	-	74	Outlet tube clogged when melt formed over after 12 hours of operation.
10	6-28 Mesh graphite	13.3	1685+	47.5	-	55	Crucible broke, tube shifted, temperature could not be measured.
18	12-16 Mesh carbon black	7.6	1650	37	-	96	Continuous carbon addition. Heating continued 9.5 hours after carbon feed stopped.
2	Methane + carbon	2C + 3.2 CH_4	1620	25	-	77	Carbon deposited in inlet bells; 2% C recovered as CO_2.
3	Methane only	8.0	1670	21	57	54	Carbon clogged inlet bells after 15 hours of operation.
4	Methane only	13.6	1660	21	41	(30 est)	Inlet bells leaked, carbon in bells, carbon deposited in furnace insulation.
5	Methane only	1.0	1550	2.2	70	(50 est)	One bell clogged, two bells leaked, carbon deposited in bells and in furnace.
8	Methane only	7.1	1610	16	66	(48 est)	One bell clogged, two bells broke and leaked.
9	Methane only	1.0	1580	2.2	36	(30 est)	Single tube clogged.
11	Methane only	1.8	1600	4.0	64	(47 est)	Inlet tube broke, carbon deposited in furnace insulation.
13	Methane only	6.6	1650	13.7	78	55.6	16.7% carbon recovered in outlet filters and liners, balance in inlet line.
14	Methane only	-	1675	46	-	-	Inlet tube cracked but not clogged. Carbon liner fell into melt - no carbon balance.
15	Methane only	5.2	1740	25.3	55	60	Inlet tube cracked, carbon deposited in furnace insulations.

TABLE 17

SPECTROGRAPHIC ANALYSES OF METAL OBTAINED FROM ROCK REACTOR MELTS

Run No.	Type Rock	Metal Composition (wt%) Al	Fe	Si	Cu	Ni	All Other
3-1	Basalt	-	58.5	37.7	1.3	2.1	0.4
3-2	Basalt	-	58.0	39.0	0.8	1.8	0.4
6	Basalt	5.8	23.5	62.4	0.4	-	8.9
7	Basalt	1.4	75.4	15.1	0.6	1.4	3.1
18	Basalt	-	90.4	7.0*	-	-	2.6

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*The density of this metal was found to be 6.0 g/cu cm. If the metal is assumed to be a mixture of Fe and Si, simple calculations show it to contain 35% Si.

TABLE 18

SPECTROGRAPHIC ANALYSES OF SUBLIMATE FROM ROCK REDUCTION RUNS

Element	Composition (wt%) at Selected Sample Locations Run No. 15 (Outlet Gas Filter)	Run No. 18 (Outlet Gas Filter)	Run No. 18 (Outlet Line)
Na	85.6	95.0	-
Mg	5.4	2.5	-
Ga	1.8	-	-
Fe	1.0	-	80.0
Si	0.8	1.2	14.0
Al	0.5	0.1	1.0
Mo	0.2	-	-
Cu	0.04	-	-
Ni	-	-	-
Zr	-	0.5	5.0

TABLE 19

PRODUCT GAS IMPURITIES BY GAS SCRUBBING

Run No.	Type Basalt Used	Impurities, Lb Per Million Lb Rock					
		Up to 1500°C		Over 1500°C		Total	
		P	S	P	S	P	S
3	B-1					0.19	<0.27
10	B-1					0.48	<0.27
11	B-1					0.00	50.00
13	CRB					5.38	2.72
14	CRB					0.66	0.80
15	CRB	0.09	0.0	0.16	0.20	0.25	0.20
17	B-4	0.26	8.5	0.12	1.2	0.38	9.60
18	B-4					0.20	0.08

TABLE 20

REDUCTION OF CARBON MONOXIDE WITH HYDROGEN

(Operating Data for Water-Cooled Automatic Unit)[a]

Sixty-Day Run

Run No.	Period of Operation (hours)	Reactant Flow Rate H_2 (g mole/hr)	Reactant Flow Rate CO (g mole/hr)	Product Flow Rate Gas (g mole/hr)	Product Flow Rate Liquid Water (g/hr)	Pressure Water Jacket (psig)	Pressure Catalyst Bed Static (psig)	Pressure Catalyst Bed ΔP (in.Hg)	Temperature Water Jacket (°C)	Temperature Catalyst Bed Maximum[b] (°C)
1-1a	26-75	3.93	0.986	1.86	-	350	76.0	0.1	220	275
1-1b	75-176	3.93	0.986	1.85	16.1	360	75.5	0.1	223	296
1-1c	176-238	3.93	0.986	1.62	16.6	355	76.0	0.1	222	299
1-2a	238-255	3.39	1.09	1.57	19.7	565	75.0	0.10	249	331
1-2b	255-279	3.39	1.09	1.67	18.2	565	75.5	0.12	248	328
1-2c	279-303	3.39	1.09	1.60	18.2	560	76.0	0.12	248	326
1-2d	303-320	3.39	1.09	1.62	18.3	575	76.0	0.11	250	327
1-2e	320-341	3.39	1.09	1.51	18.2	575	76.5	0.15	249	330
1-2f	341-386	3.39	1.09	1.50	19.1	600	77.0	0.18	253	335
1-2g	386-407	3.39	1.09	1.59	19.1	580	76.5	0.17	251	332
1-2h	407-432	3.39	1.09	1.59	19.2	570	74.5	0.13	250	331
1-2i	432-456	3.39	1.09	1.50	19.0	570	75.5	0.13	249	329
1-2j	456-475	3.39	1.09	1.52	19.4	580	75.5	0.16	250	331
1-2k	475-499	3.39	1.09	1.41	19.5	570	76.0	0.15	250	333
1-2l	499-573	3.39	1.09	1.57	19.2	580	76.0	0.16	247	330
1-3a	573-596	3.81	1.23	1.27	22.0	580	76.0	0.17	251	337
1-3b	596-619	3.81	1.23	1.27	22.1	585	76.0	0.16	252	338
1-3c	619-644	3.81	1.23	1.31	22.1	580	75.5	0.15	253	339
1-3d	644-666	3.81	1.23	1.28	22.2	580	76.0	0.15	253	339
1-3e	666-693	3.81	1.23	1.14	22.4	565	76.0	0.15	251	338
1-3f	693-714	3.81	1.23	1.31	22.5	550	76.0	0.15	249	337
1-3g	714-739	3.81	1.23	1.28	22.3	555	76.0	0.15	250	336
1-3h	739-755	3.81	1.23	1.27	22.3	580	76.0	0.15	253	337

TABLE 20 (cont.)

		Reactant Flow Rate		Product Flow Rate		Pressure			Temperature	
							Catalyst Bed			
Run No.	Period of Operation (hours)	H_2 (g mole/hr)	CO (g mole/hr)	Gas (g mole/hr)	Liquid Water (g/hr)	Water Jacket (psig)	Static (psig)	ΔP (in.Hg)	Water Jacket (°C)	Catalyst Bed Maximum[b] (°C)
1-4a	755-778	4.77	1.54	1.62	27.2	560	76.0	0.19	249	360
1-4b	778-801	4.77	1.54	1.65	26.5	560	76.0	0.20	250	357
1-4c	801-827	4.77	1.54	1.66	27.1	560	76.0	0.18	251	358
1-4d	827-851	4.77	1.54	1.63	27.4	555	76.0	0.15	250	360
1-4e	851-875	4.77	1.54	1.66	27.4	550	76.0	0.18	249	357
1-4f	875-899	4.77	1.54	1.65	26.6	555	76.0	0.17	249	356
1-4g	899-922	4.77	1.54	1.68	27.1	570	76.0	0.16	249	356
1-4h	922-997	4.77	1.54	1.66	25.8	570	76.0	0.17	249	357
1-4i	997-1016	4.77	1.54	1.71	27.4	550	76.5	0.19	249	359
1-4j	1016-1035	4.77	1.54	1.62	26.9	540	76.5	0.19	248	357
1-5a	1035-1059	5.49	1.85	2.02	32.3	560	76.0	0.22	248	374
1-5b	1059-1081	5.49	1.85	1.27[c]	31.3	580	76.5	0.22	248	374
1-5c	1081-1106	5.72	1.85	2.02	32.1	560	76.5	0.23	249	376
1-5d	1106-1146	5.72	1.85	2.02	32.2	570	76.5	0.23	249	377
1-6a	1146-1171	6.67	2.15	2.40	37.9	565	76.0	0.25	249	376
1-6b	1171-1196	6.67	2.15	2.38	37.6	580	76.0	0.25	251	376
1-6c	1196-1215	6.67	2.15	2.38	37.7	575	76.0	0.25	250	376
1-6d	1215-1242	6.67	2.15	2.41	37.9	565	76.5	0.25	249	376
1-6e	1242-1267	6.67	2.15	2.39	37.8	570	76.5	0.25	250	376
1-6f	1267-1284	6.67	2.15	2.39	37.6	570	76.5	0.25	250	377
1-7a	1284-1308	7.62	2.46	2.74	43.6	575	76.5	0.30	251	387
1-7b	1308-1333	7.62	2.46	2.74	43.4	580	76.5	0.30	251	388
1-7c	1333-1357	7.62	2.46	2.75	43.3	575	76.5	0.30	252	391
1-7d	1357-1373	7.62	2.46	2.75	43.6	570	76.5	0.30	251	393
1-8a	1373-1396	9.53	3.07	3.59	54.2	595	76.5	0.40	252	402
1-8b	1396-1419	9.53	3.07	3.50	54.5	595	76.5	0.39	252	402
1-8c	1419-1444	9.53	3.07	3.54	54.1	580	76.5	0.39	252	403

TABLE 20 (cont.)

		Reactant Flow Rate		Product Flow Rate		Pressure			Temperature	
							Catalyst Bed			
Run No.	Period of Operation (hours)	H_2 (g mole/hr)	CO (g mole/hr)	Gas (g mole/hr)	Liquid Water (g/hr)	Water Jacket (psig)	Static (psig)	ΔP (in.Hg)	Water Jacket (°C)	Catalyst Bed Maximum^b (°C)
1-9a	1444-1466	11.44	3.69	4.29	63.5	570	76.0	0.50	251	409
1-9b	1466-1494	11.44	3.69	4.31	64.2	575	76.0	0.50	250	407
				Ninety-Day Run						
2-1	0-24	3.81	1.23	1.36	21.6	615	75.5	0.14	255	345
2-2	24-66	3.81	1.23	1.38	21.7	600	75.5	0.14	254	344
2-3	66-89	3.81	1.23	1.37	21.6	555	76.0	0.14	249	343
2-4	89-127	3.81	1.23	1.36	21.9	585	76.0	0.14	253	346
2-5	127-144	3.81	1.23	1.39	22.1	570	75.5	0.14	251	350
2-6	144-168	3.81	1.23	1.36	22.0	570	76.0	0.14	250	348
2-7	168-190	3.81	1.23	1.36	20.8	565	76.0	0.14	250	348
2-8	190-214	3.81	1.23	1.37	21.9	565	76.0	0.14	250	348
2-9	214-239	3.81	1.23	1.35	22.4	575	75.5	0.15	251	346
2-10	239-262	3.81	1.23	1.37	22.2	555	76.0	0.15	250	349
2-11	262-280	3.81	1.23	1.35	22.1	555	76.0	0.15	250	352
2-12	280-304	3.81	1.23	1.33	22.4	555	76.0	0.15	250	352
2-13	304-327	3.81	1.23	1.36	22.0	560	76.0	0.15	250	350
2-14	327-351	3.81	1.23	1.36	22.0	560	76.0	0.15	250	348
2-15	351-375	3.81	1.23	1.35	22.3	550	76.0	0.15	249	347
2-16	375-400	3.81	1.23	1.36	22.0	550	76.0	0.16	249	347
2-17	400-423	3.81	1.23	1.35	22.1	570	76.0	0.16	251	349
2-18	423-456	3.81	1.23	1.41	22.2	575	76.0	0.16	252	350
2-19	456-495	3.81	1.23	1.41	22.3	565	76.5	0.16	252	350
2-20	495-519	3.81	1.23	1.43	22.3	565	76.5	0.16	252	349
2-21	519-543	3.81	1.23	1.43	22.4	560	76.5	0.16	252	348
2-22	543-574	3.81	1.23	1.40	22.1	560	76.5	0.16	251	346
2-23	574-599	3.81	1.23	1.42	22.1	560	76.0	0.16	250	345
2-24	599-623	3.81	1.23	1.42	22.3	565	76.0	0.16	251	347
2-25	623-664	3.81	1.23	1.43	22.4	570	76.5	0.16	252	349
2-26	664-688	3.81	1.23	1.44	22.1	565	76.0	0.16	252	349
2-27	688-732	3.81	1.23	1.43	22.0	560	76.0	0.16	252	349
2-28	732-766	3.81	1.23	1.42	22.2	560	76.5	0.16	252	349

TABLE 20 (cont.)

		Reactant Flow Rate		Product Flow Rate		Pressure			Temperature	
							Catalyst Bed			
Run No.	Period of Operation (hours)	H_2 (g mole/hr)	CO (g mole/hr)	Gas (g mole/hr)	Liquid Water (g/hr)	Water Jacket (psig)	Static (psig)	ΔP (in.Hg)	Water Jacket (°C)	Catalyst Bed Maximum[b] (°C)
2-29	766-786	3.81	1.23	1.43	22.2	570	76.5	0.16	252	349
2-30	786-816	3.81	1.23	1.41	22.3	585	76.5	0.16	253	350
2-31	816-831	3.81	1.23	1.42	21.9	575	76.5	0.16	253	350
2-32	831-855	3.81	1.23	1.41	22.4	560	76.5	0.16	252	345
2-33	855-878	3.81	1.23	1.39	21.9	560	76.5	0.16	251	341
2-34	878-931	3.81	1.23	1.39	22.3	560	76.5	0.16	251	341
2-35	931-979	3.81	1.23	1.41	22.1	570	76.5	0.16	252	341
2-36	979-997	3.81	1.23	1.44	22.3	565	76.5	0.16	251	342
2-37	997-1029	3.81	1.23	1.42	22.4	550	76.5	0.16	252	340
2-38	1029-1048	3.81	1.23	1.42	22.1	550	76.5	0.16	254	339
2-39	1048-1072	3.81	1.23	1.44	22.2	555	76.5	0.16	253	341
2-40	1072-1097	3.81	1.23	1.45	22.3	565	76.0	0.16	251	335
2-41	1097-1118	3.81	1.23	1.48	22.6	570	76.0	0.16	253	334
2-42	1118-1140	3.81	1.23	1.46	22.4	580	76.5	0.16	254	335
2-43	1140-1183	3.81	1.23	1.49	22.5	575	76.5	0.16	252	333
2-44	1183-1213	3.81	1.23	1.52	22.2	555	76.5	0.15	251	331
2-45	1213-1236	3.81	1.23	1.48	22.5	550	76.5	0.15	251	331
2-46	1236-1284	3.81	1.23	1.51	22.3	545	76.5	0.15	250	330
2-47	1284-1350	3.81	1.23	1.36	22.0	560	76.5	0.15	250	332
2-48	1350-1373	3.81	1.23	1.34	22.0	565	76.5	0.15	251	333
2-49	1373-1405	3.81	1.23	1.34	21.9	555	76.5	0.15	250	330
2-50	1405-1429	3.81	1.23	1.34	21.9	570	76.5	0.15	251	330
2-51	1429-1453	3.81	1.23	1.32	22.1	575	76.5	0.15	252	332
2-52	1453-1522	3.81	1.23	1.34	21.9	565	76.5	0.15	251	331
2-53	1522-1541	3.81	1.23	1.33	21.8	555	76.5	0.15	250	330
2-54	1541-1566	3.81	1.23	1.38	21.5	560	76.5	0.15	250	329
2-55	1566-1593	3.81	1.23	1.35	21.7	560	76.5	0.15	250	327
2-56	1593-1618	3.81	1.23	1.34	21.6	555	76.5	0.15	250	327
2-57	1618-1661	3.81	1.23	1.34	21.8	575	76.5	0.15	251	330
2-58	1661-1686	3.81	1.23	1.32	21.8	590	76.5	0.15	252	333
2-59	1686-1762	3.81	1.23	1.32	21.6	575	76.5	0.15	249	331
2-60	1762-1788	3.81	1.23	1.25	22.0	560	76.5	0.15	248	330
2-61	1788-1858	3.81	1.23	1.28	21.9	560	76.5	0.15	249	329
2-62	1858-1877	3.81	1.23	1.28	22.1	555	76.5	0.15	249	329

TABLE 20 (cont.)

Run No.	Period of Operation (hours)	Reactant Flow Rate		Product Flow Rate		Pressure			Temperature	
		H_2 (g mole/hr)	CO (g mole/hr)	Gas (g mole/hr)	Liquid Water (g/hr)	Water Jacket (psig)	Catalyst Bed Static (psig)	Catalyst Bed ΔP (in.Hg)	Water Jacket (°C)	Catalyst Bed Maximum[b] (°C)
2-63	1877-1953	3.81	1.23	1.27	21.8	560	76.5	0.15	249	330
2-64	1953-2021	3.81	1.23	1.29	22.1	555	76.5	0.15	250	330
2-65	2021-2066	3.81	1.23	1.43	21.9	550	76.5	0.15	250	330
2-66	2066-2121	3.81	1.23	1.43	22.1	565	76.5	0.15	250	330
2-67	2121-2197	3.81	1.23	1.41	22.2	585	76.5	0.15	250	330
2-68	2197-2217	3.81	1.23	1.43	22.1	585	76.5	0.15	250	330

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[a] Using Catalyst 0765-1001-1 with CO feed equally divided among the 0, 3, 6, and 9 in. feed lines for Run No. 1-1 through 1-5, and equally divided among the 0, 3, 6, 9, and 12.5 in. feed lines for Run No. 1-6 through 2-68.

[b] The catalyst bed maximum temperature as recorded 10 in. from the bottom of the bed unless otherwise noted.

[c] Hydrogen metering orifice partially clogged: H_2/CO mole ratio = 2.97:1.

TABLE 21

CARBON MONOXIDE CONVERSIONS AND PRODUCT YIELDS

Sixty-Day Run

Run No.	Nominal H_2/CO Mole Ratio	Space Velocity (hr^{-1})	Nominal Catalyst Bed Temp (°C)	CO Conversion (mole %)	Actual Product Yield (mole %)		
					H_2O	CH_4	CO_2
1-1a	4:1	1000	220	100	-	-	0.00
1-1b	4:1	1000	220	100	92.5	98.6	0.00
1-1c	4:1	1000	220	100	94.8	100.5	0.00
				average	93.4	99.6	0.00
1-2a	3.5:1	1000	250	100	101.5	105.6	0.00
1-2b	3.5:1	1000	250	100	94.4	97.8	0.00
1-2c	3.5:1	1000	250	100	94.3	89.8	0.00
1-2d	3.5:1	1000	250	100	94.3	93.3	0.00
1-2e	3.5:1	1000	250	100	94.3	102.2	0.00
1-2f	3.5:1	1000	250	100	98.5	95.4	0.00
1-2g	3.5:1	1000	250	100	98.5	95.6	0.00
1-2h	3.5:1	1000	250	100	94.2	99.5	0.00
1-2i	3.5:1	1000	250	100	97.6	101.8	0.00
1-2j	3.5:1	1000	250	100	100.1	94.7	0.00
1-2k	3.5:1	1000	250	100	100.8	87.7	0.00
1-2l	3.5:1	1000	250	100	99.0	99.7	0.00
				average	97.2	97.0	0.00
1-3a	3.1:1	1000	250	100	98.4	99.2	0.1
1-3b	3.1:1	1000	250	100	98.9	97.9	0.1
1-3c	3.1:1	1000	250	100	98.9	102.7	0.1
1-3d	3.1:1	1000	250	100	99.2	99.7	0.1
1-3e	3.1:1	1000	250	100	100.1	88.8	0.1
1-3f	3.1:1	1000	250	100	100.6	101.9	0.1
1-3g	3.1:1	1000	250	100	99.7	100.5	0.1
1-3h	3.1:1	1000	250	100	99.7	100.5	0.1
				average	99.4	99.5	0.1
1-4a	3.1:1	1250	250	100	100.2	100.3	0.1
1-4b	3.1:1	1250	250	100	97.7	98.7	0.1
1-4c	3.1:1	1250	250	100	99.9	99.3	0.1
1-4d	3.1:1	1250	250	100	101.0	100.1	0.1
1-4e	3.1:1	1250	250	100	101.0	100.9	0.1
1-4f	3.1:1	1250	250	100	98.0	101.2	0.1
1-4g	3.1:1	1250	250	100	99.9	102.3	0.1
1-4h	3.1:1	1250	250	100	95.1	97.8	0.1
1-4i	3.1:1	1250	250	100	101.0	97.9	0.1
1-4j	3.1:1	1250	250	100	99.2	98.8	0.1
				average	99.6	99.7	0.1

TABLE 21 (cont.)

Run No.	Nominal H_2/CO Mole Ratio	Space Velocity (hr^{-1})	Nominal Catalyst Bed Temp (°C)	CO Conversion (mole %)	Actual Product Yield (mole %)		
					H_2O	CH_4	CO_2
1-5a	3.1:1	1500	250	100	98.9[a]	101.6[a]	1.1[a]
1-5b	3.1:1	1500	250	100	95.9[a]	-	1.6[a]
1-5c	3.1:1	1500	250	100	96.7	99.2	0.3
1-5d	3.1:1	1500	250	100	97.4	96.2	0.2
				average	97.1	97.7	0.3
1-6a	3.1:1	1750	250	100	98.0	101.7	0.3
1-6b	3.1:1	1750	250	100	97.1	100.5	0.3
1-6c	3.1:1	1750	250	100	98.1	101.1	0.3
1-6d	3.1:1	1750	250	100	98.2	102.4	0.2
1-6e	3.1:1	1750	250	100	97.6	101.5	0.3
1-6f	3.1:1	1750	250	100	98.1	102.7	0.3
				average	97.9	101.7	0.3
1-7a	3.1:1	2000	250	100	98.6	102.2	0.3
1-7b	3.1:1	2000	250	100	98.3	102.4	0.3
1-7c	3.1:1	2000	250	100	97.7	102.4	0.4
1-7d	3.1:1	2000	250	100	99.4	102.9	0.3
				average	98.5	102.5	0.3
1-8a	3.1:1	2500	250	100	97.8	100.5	0.4
1-8b	3.1:1	2500	250	100	99.0	101.7	0.4
1-8c	3.1:1	2500	250	100	97.9	100.6	0.5
				average	98.2	100.9	0.4
1-9a	3.1:1	3000	250	100	96.1	99.8	1.7
1-9b	3.1:1	3000	250	100	97.1	101.7	1.7
				average	96.6	100.8	1.7
				Run 1 average	98.1	99.8	0.4

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[a] Discounting 1-5a and 1-5b: Hydrogen metering orifice partially clogged; H_2/CO mole ratio = 2.97:1.

TABLE 21 (cont.)

Ninety-Day Run

Run No.	Nominal H_2/CO Mole Ratio	Nominal Space Velocity (hr^{-1})	Nominal Catalyst Bed Temp (^oC)	CO Conversion (mole %)	Actual Product Yield (mole %)		
					H_2O	CH_4	CO_2
2-1	3.1:1	1000	250	100	97.8	100.0	0.25
2-2	3.1:1	1000	250	100	98.2	101.5	0.10
2-3	3.1:1	1000	250	100	97.8	101.1	0.05
2-4	3.1:1	1000	250	100	99.1	101.8	0.15
2-5	3.1:1	1000	250	100	100.3	101.7	0.10
2-6	3.1:1	1000	250	100	99.6	100.4	0.10
2-7	3.1:1	1000	250	100	94.5	100.8	0.15
2-8	3.1:1	1000	250	100	99.4	101.6	0.20
2-9	3.1:1	1000	250	100	100.9	101.7	0.25
2-10	3.1:1	1000	250	100	100.3	102.9	0.35
2-11	3.1:1	1000	250	100	99.7	101.2	0.40
2-12	3.1:1	1000	250	100	101.4	101.8	0.30
2-13	3.1:1	1000	250	100	99.3	100.3	0.10
2-14	3.1:1	1000	250	100	99.1	100.1	0.10
2-15	3.1:1	1000	250	100	99.8	100.6	0.15
2-16	3.1:1	1000	250	100	99.1	103.4	0.45
2-17	3.1:1	1000	250	100	99.7	102.4	0.50
2-18	3.1:1	1000	250	100	100.3	105.2	0.20
2-19	3.1:1	1000	250	100	100.5	103.8	0.05
2-20	3.1:1	1000	250	100	100.6	104.4	0.00
2-21	3.1:1	1000	250	100	101.2	104.3	0.00
2-22	3.1:1	1000	250	100	100.2	103.1	0.00
2-23	3.1:1	1000	250	100	99.7	104.0	0.00
2-24	3.1:1	1000	250	100	100.2	103.3	0.05
2-25	3.1:1	1000	250	100	100.2	103.1	0.05
2-26	3.1:1	1000	250	100	99.6	103.1	0.00
2-27	3.1:1	1000	250	100	99.3	103.0	0.00
2-28	3.1:1	1000	250	100	100.2	103.3	0.00
2-29	3.1:1	1000	250	100	100.3	103.8	0.00
2-30	3.1:1	1000	250	100	100.7	101.9	0.00
2-31	3.1:1	1000	250	100	98.7	102.7	0.00
2-32	3.1:1	1000	250	100	100.9	101.8	0.05
2-33	3.1:1	1000	250	100	99.0	100.9	0.10
2-34	3.1:1	1000	250	100	100.4	102.1	0.10
2-35	3.1:1	1000	250	100	99.8	103.7	0.00
2-36	3.1:1	1000	250	100	100.7	103.8	0.00
2-37	3.1:1	1000	250	100	101.2	103.2	0.00

TABLE 21 (cont.)

Run No.	Nominal H_2/CO Mole Ratio	Nominal Space Velocity (hr^{-1})	Nominal Catalyst Bed Temp (°C)	CO Conversion (mole %)	Actual Product Yield (mole %) H_2O	CH_4	CO_2
2-38	3.1:1	1000	250	100	99.9	104.4	0.00
2-39	3.1:1	1000	250	100	100.0	103.7	0.00
2-40	3.1:1	1000	250	100	100.7	102.4	0.65
2-41	3.1:1	1000	250	100	102.2	105.8	0.00
2-42	3.1:1	1000	250	100	100.9	104.6	0.00
2-43	3.1:1	1000	250	100	101.5	105.4	0.00
2-44	3.1:1	1000	250	100	100.4	105.8	0.05
2-45	3.1:1	1000	250	100	101.3	103.1	0.10
2-46	3.1:1	1000	250	100	100.4	105.2	0.05
2-47	3.1:1	1000	250	100	99.8	103.7	0.0
2-48	3.1:1	1000	250	100	99.6	102.5	0.0
2-49	3.1:1	1000	250	100	99.3	102.1	0.05
2-50	3.1:1	1000	250	100	99.3	103.2	0.05
2-51	3.1:1	1000	250	100	100.2	102.3	0.0
2-52	3.1:1	1000	250	100	99.3	102.0	0.05
2-53	3.1:1	1000	250	100	98.7	100.4	0.05
2-54	3.1:1	1000	250	100	97.5	103.9	0.0
2-55	3.1:1	1000	250	100	98.3	100.4	0.0
2-56	3.1:1	1000	250	100	98.0	101.4	0.0
2-57	3.1:1	1000	250	100	98.6	103.4	0.0
2-58	3.1:1	1000	250	100	98.8	102.2	0.05
2-59	3.1:1	1000	250	100	97.9	103.3	0.05
2-60	3.1:1	1000	250	100	99.6	99.5	0.05
2-61	3.1:1	1000	250	100	99.1	101.7	0.05
2-62	3.1:1	1000	250	100	100.0	105.0	0.0
2-63	3.1:1	1000	250	100	98.9	102.0	0.05
2-64	3.1:1	1000	250	100	100.0	103.6	0.05
2-65	3.1:1	1000	250	100	99.3	102.4	0.05
2-66	3.1:1	1000	250	100	100.0	103.0	0.05
2-67	3.1:1	1000	250	100	100.5	102.3	0.05
2-68	3.1:1	1000	250	100	100.0	103.8	0.00
				Run 2 average	99.7	102.7	0.09

TABLE 22

PRODUCT GAS ANALYSIS

Sixty-Day Run

Run No.	Composition of Product Gas (vol%)				
	H_2	CO	CH_4	CO_2	H_2O
1-1a	(49.7)[a]	0.0	(49.8)[a]	0.0	(0.5)[a]
1-2a	26.2	0.0	73.2	0.0	0.5
1-2b	35.6	0.0	63.7	0.0	0.5
1-2c	35.7	0.0	61.1	0.0	0.4
1-2d	36.5	0.0	62.6	0.0	0.4
1-2e	30.2	0.0	68.8	0.0	0.4
1-2f	34.7	0.0	64.6	0.0	0.4
1-2g	34.1	0.0	65.2	0.0	0.4
1-2h	31.4	0.0	67.8	0.0	0.4
1-2i	30.2	0.0	69.0	0.0	0.4
1-2j	31.9	0.0	67.5	0.0	0.4
1-2k	31.6	0.0	67.7	0.0	0.4
1-2l	30.3	0.0	69.1	0.0	0.4
1-3a	3.5	0.0	95.8	0.1	0.4
1-3b	4.7	0.0	94.5	0.1	0.4
1-3c	3.4	0.0	95.8	0.1	0.4
1-3d	3.7	0.0	95.6	0.1	0.4
1-3e	4.0	0.0	95.2	0.1	0.4
1-3f	4.2	0.0	95.0	0.1	0.4
1-3g	2.9	0.0	96.4	0.1	0.4
1-3h	2.2	0.0	97.0	0.1	0.4
1-4a	6.7	0.0	94.8	0.05	0.3
1-4b	7.6	0.0	91.7	0.05	0.3
1-4c	7.6	0.0	91.7	0.05	0.3
1-4d	5.2	0.0	94.1	0.05	0.3
1-4e	6.0	0.0	93.2	0.05	0.3
1-4f	5.3	0.0	94.0	0.05	0.3
1-4g	5.9	0.0	93.4	0.05	0.3
1-4h	9.0	0.0	90.2	0.05	0.3
1-4i	11.4	0.0	87.8	0.05	0.3
1-4j	5.6	0.0	93.4	0.05	0.3
1-5a	6.1	0.0	91.6	1.0[b]	0.3
1-5b	6.2	0.0	92.0	1.3[b]	0.3
1-5c	8.0	0.0	91.1	0.3	0.3
1-5d	7.8	0.0	91.25	0.25	0.3

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[a] Average value for this portion of the run.

[b] Hydrogen metering orifice partially clogged: H_2/CO mole ratio = 2.97:1.

TABLE 22 (cont.)

Run No.	Composition of Product Gas (vol%) H_2	CO	CH_4	CO_2	H_2O
1-6a	8.5	0.0	90.6	0.35	0.3
1-6b	8.1	0.0	90.8	0.35	0.3
1-6c	8.4	0.0	90.5	0.30	0.3
1-6d	8.2	0.0	90.8	0.25	0.3
1-6e	7.8	0.0	91.1	0.30	0.3
1-6f	7.9	0.0	90.9	0.35	0.3
1-7a	7.9	0.0	91.2	0.35	0.3
1-7b	7.7	0.0	91.4	0.35	0.3
1-7c	7.6	0.0	91.4	0.45	0.3
1-7d	8.1	0.0	91.0	0.35	0.3
1-8a	12.2	0.0	87.0	0.35	0.3
1-8b	12.1	0.0	86.9	0.35	0.3
1-8c	12.5	0.0	86.5	0.45	0.3
1-9a	10.2	0.0	86.3	1.55	0.3
1-9b	9.6	0.0	86.2	1.45	0.3
Ninety-Day Run					
2-1	8.5	0.0	90.5	0.25	0.4
2-2	8.4	0.0	90.8	0.10	0.4
2-3	8.7	0.0	90.6	0.05	0.4
2-4	7.0	0.0	92.0	0.15	0.4
2-5	8.9	0.0	89.8	0.10	0.4
2-6	8.0	0.0	90.6	0.10	0.4
2-7	7.2	0.0	91.4	0.10	0.4
2-8	7.0	0.0	91.5	0.15	0.4
2-9	6.3	0.0	92.7	0.20	0.4
2-10	6.6	0.0	92.4	0.35	0.4
2-11	6.8	0.0	92.2	0.35	0.4
2-12	7.3	0.0	91.7	0.30	0.4
2-13	8.1	0.0	90.8	0.10	0.4
2-14	8.4	0.0	90.2	0.10	0.4
2-15	6.6	0.0	92.2	0.15	0.4
2-16	5.0	0.0	93.9	0.40	0.4
2-17	5.6	0.0	93.2	0.45	0.4
2-18	7.4	0.0	91.7	0.15	0.4
2-19	8.9	0.0	90.3	0.05	0.4
2-20	9.4	0.0	89.7	0.0	0.4
2-21	9.5	0.0	89.6	0.0	0.4
2-22	8.7	0.0	90.3	0.0	0.4

TABLE 22 (cont.)

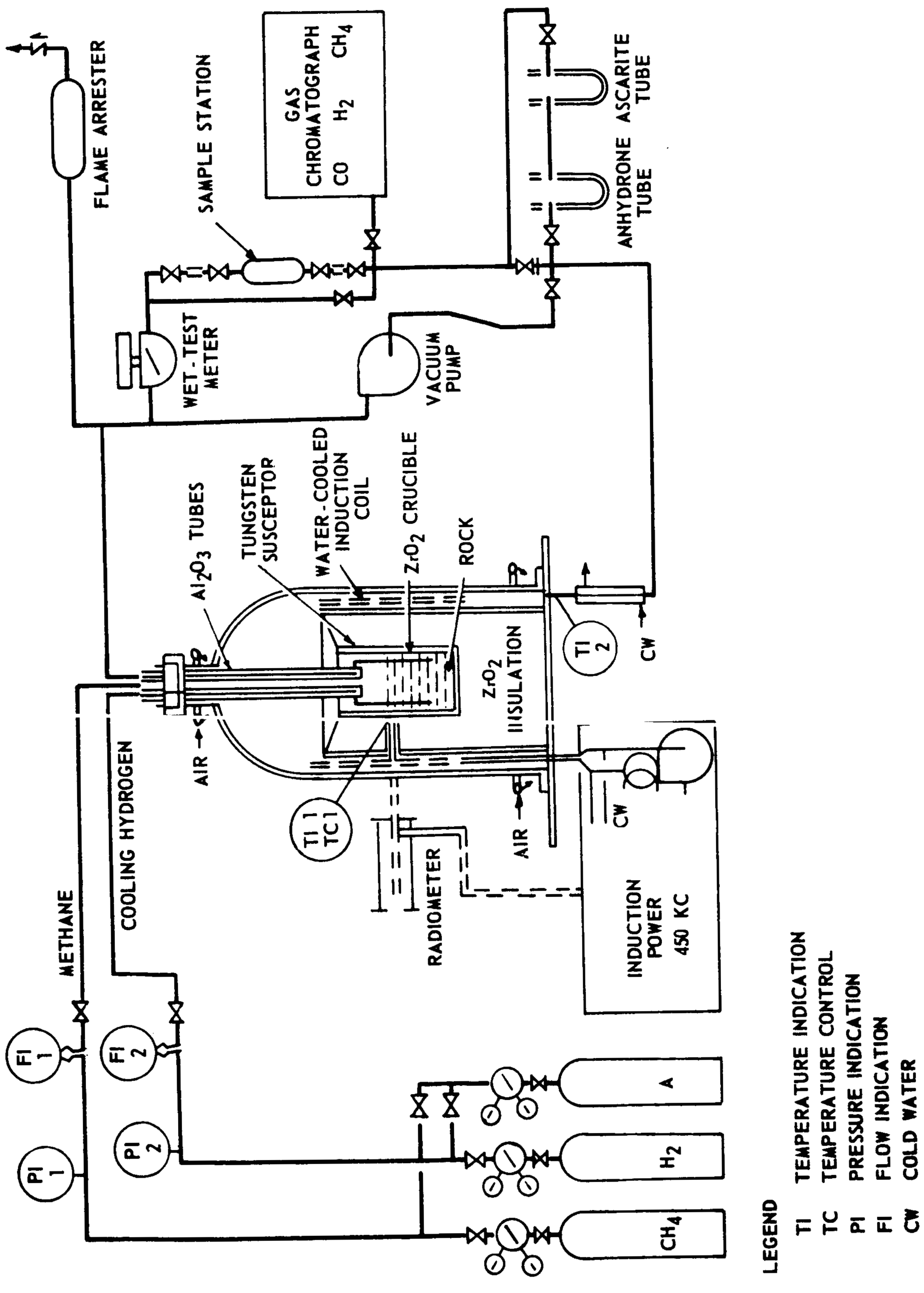
Run No.	Composition of Product Gas (vol %)				
	H_2	CO	CH_4	CO_2	H_2O
2-23	9.3	0.0	89.9	0.0	0.4
2-24	9.7	0.0	89.5	0.05	0.4
2-25	10.0	0.0	89.1	0.05	0.4
2-26	10.9	0.0	88.3	0.0	0.4
2-27	10.5	0.0	88.7	0.0	0.4
2-28	9.9	0.0	89.3	0.0	0.4
2-29	10.2	0.0	89.0	0.0	0.4
2-30	10.2	0.0	89.0	0.0	0.4
2-31	10.0	0.0	89.2	0.0	0.4
2-32	10.7	0.0	88.5	0.05	0.4
2-33	10.1	0.0	89.1	0.10	0.4
2-34	8.6	0.0	90.6	0.10	0.4
2-35	8.8	0.0	90.5	0.0	0.4
2-36	10.2	0.0	89.1	0.0	0.4
2-37	10.0	0.0	89.2	0.0	0.4
2-38	9.1	0.0	90.1	0.0	0.4
2-39	10.6	0.0	88.6	0.0	0.4
2-40	11.8	0.0	86.8	0.55	0.4
2-41	11.5	0.0	87.8	0.0	0.4
2-42	11.2	0.0	88.1	0.0	0.4
2-43	12.4	0.0	87.0	0.0	0.4
2-44	13.5	0.0	85.8	0.05	0.4
2-45	13.4	0.0	85.9	0.05	0.4
2-46	13.7	0.0	85.7	0.05	0.4
2-47	14.9	0.0	84.5	0.0	0.4
2-48	15.2	0.0	84.2	0.0	0.4
2-49	15.3	0.0	84.1	0.05	0.4
2-50	14.2	0.0	85.2	0.05	0.4
2-51	13.5	0.0	85.9	0.0	0.4
2-52	14.6	0.0	84.8	0.05	0.4
2-53	15.5	0.0	83.9	0.05	0.4
2-54	16.1	0.0	83.3	0.0	0.4
2-55	16.8	0.0	82.6	0.0	0.4
2-56	15.8	0.0	83.6	0.0	0.4
2-57	13.7	0.0	85.7	0.0	0.4
2-58	13.4	0.0	86.0	0.05	0.4
2-59	12.7	0.0	86.5	0.05	0.4
2-60	10.9	0.0	88.0	0.05	0.4
2-61	10.9	0.0	87.9	0.05	0.4
2-62	11.3	0.0	87.5	0.0	0.4
2-63	10.0	0.0	89.0	0.05	0.4
2-64	10.5	0.0	88.6	0.05	0.4
2-65	11.3	0.0	87.9	0.05	0.4
2-66	10.5	0.0	88.6	0.05	0.4
2-67	10.2	0.0	89.0	0.05	0.4
2-68	10.0	0.0	89.3	0.00	0.4
Average for Run 2	10.8	0.0	88.7	0.08	0.4

TABLE 23

CATALYST BED SURVEY FOR CARBON DIOXIDE (CATALYST C-0765-1001)

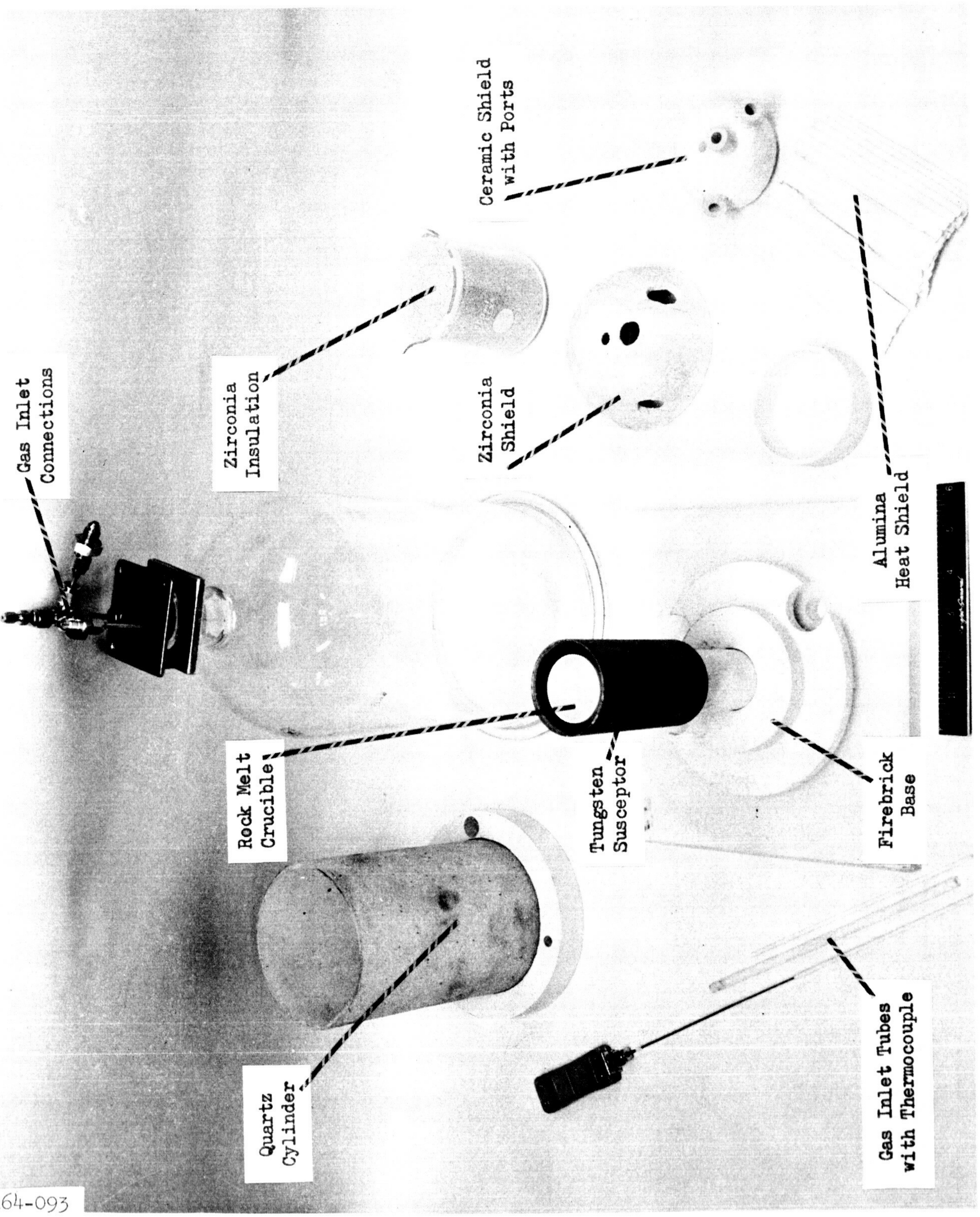
Run No.	Velocity (hr^{-1})	Nominal H_2/CO Mole Ratio	CO_2 Concentration (mol%) in Reactant Gas Sampled From Several Catalyst Bed Positions (in.)			
			12.5	19.0	25.5	32.0
1-1	1000	4.0:1	0.6	0.0	0.0	0.0
1-2	1000	3.5:1	1.0	0.2	0.0	0.0
1-3	1000	3.1:1	1.6	0.6	0.2	0.0
1-4	1250	3.1:1	-	1.1	0.1	0.1
1-6	1750	3.1:1		2.5	0.9	0.2
1-7	2000	3.1:1		4.0	1.5	0.8
1-8	2500	3.1:1		4.4	1.8	1.0
1-9	3000	3.1:1		4.8	2.7	1.8
2-68	1000	3.1:1	-	2.2	0.6	0.05

Note: In Runs No. 1-6 through 1-9, the 12.5-in. sample line was used as the fifth CO inlet.



Schematic Flow Diagram of Silicate Reduction Furnace

Figure 1



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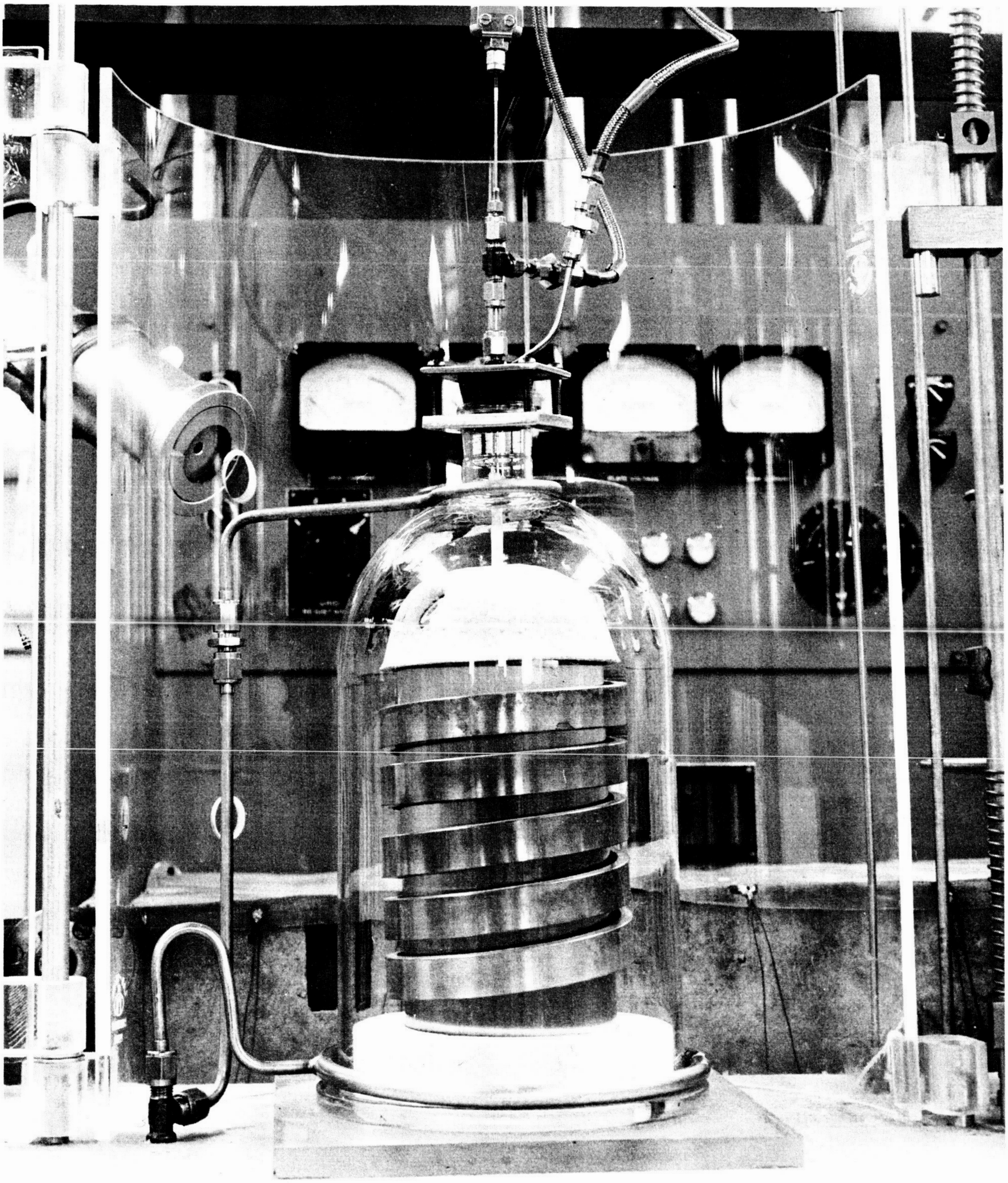
Reactor Parts
Silicate Rock Reduction Furnace

Figure 2



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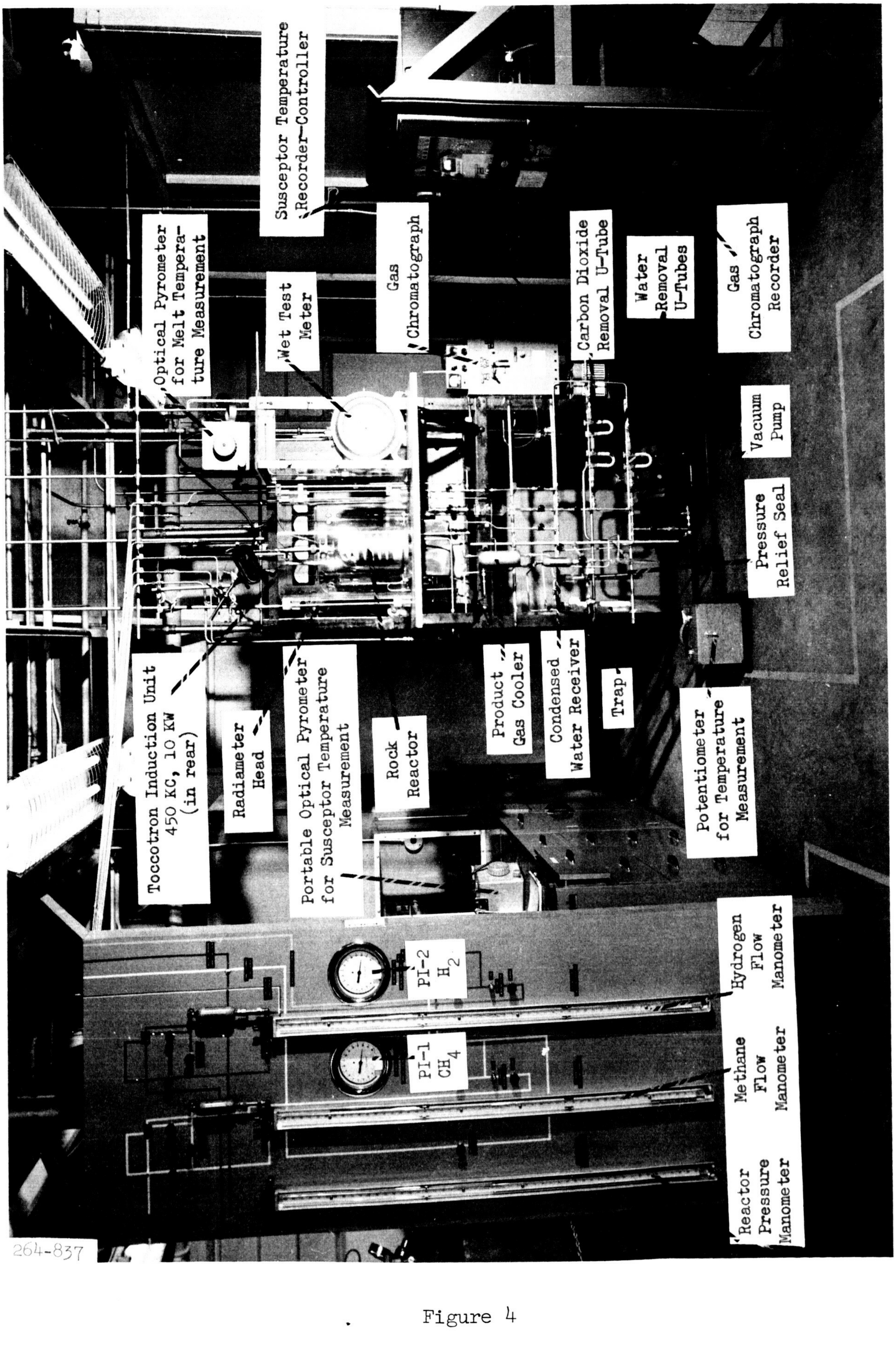
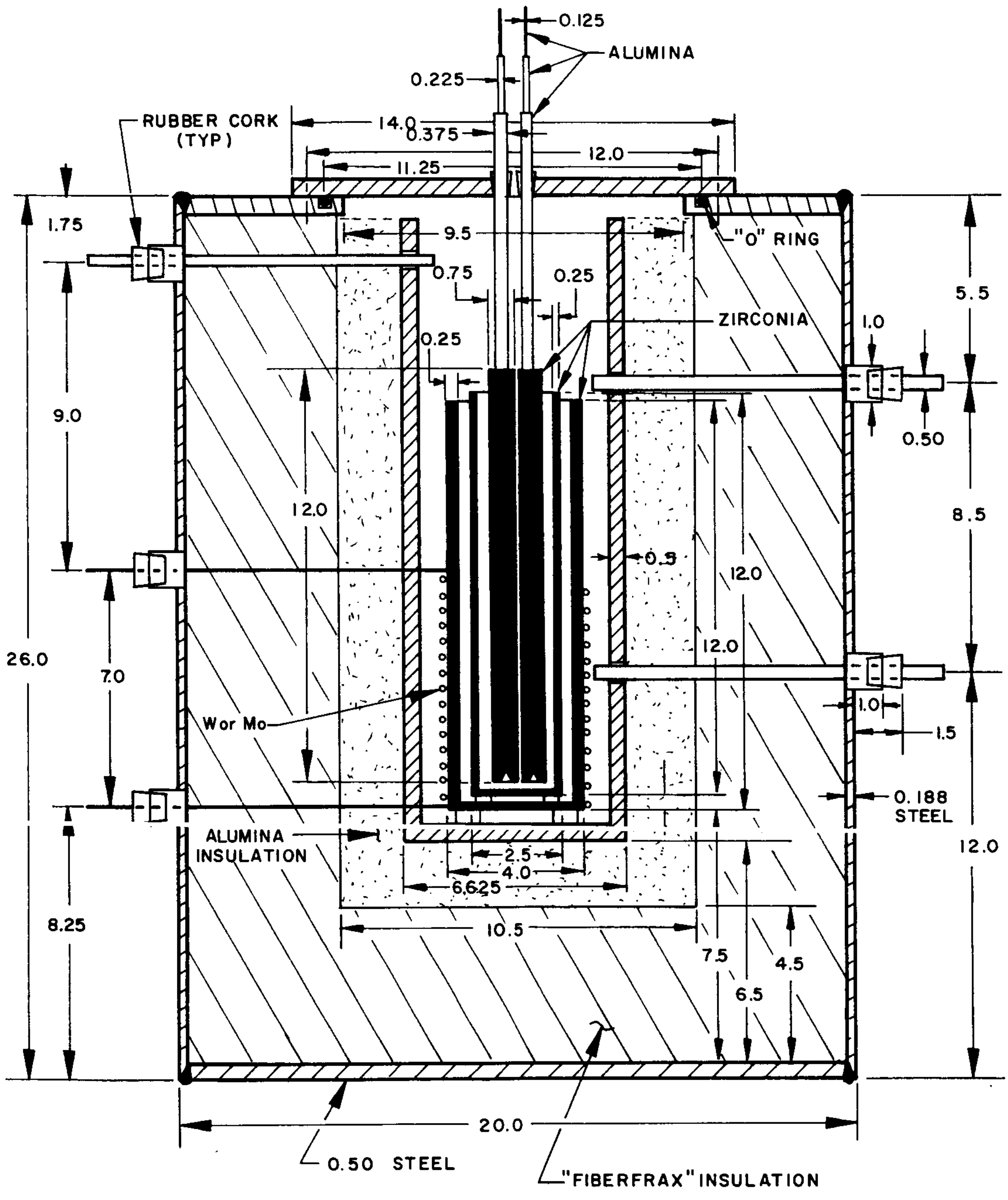
Assembled Rock Reduction Reactor, Silicate Rock Reduction Furnace

Figure 3



Silicate Rock Reduction Furnace

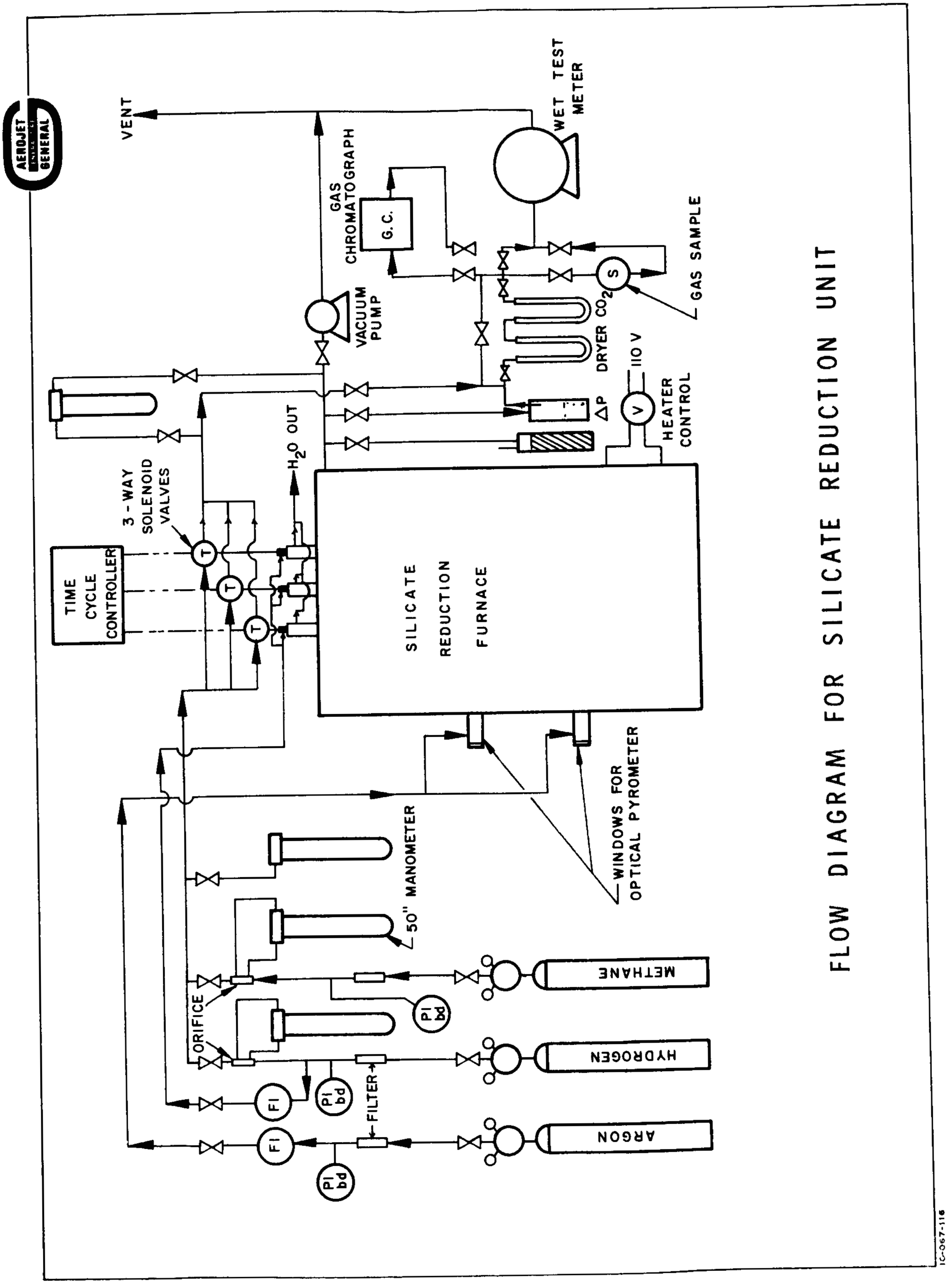
Figure 4



SILICATE REDUCTION FURNACE

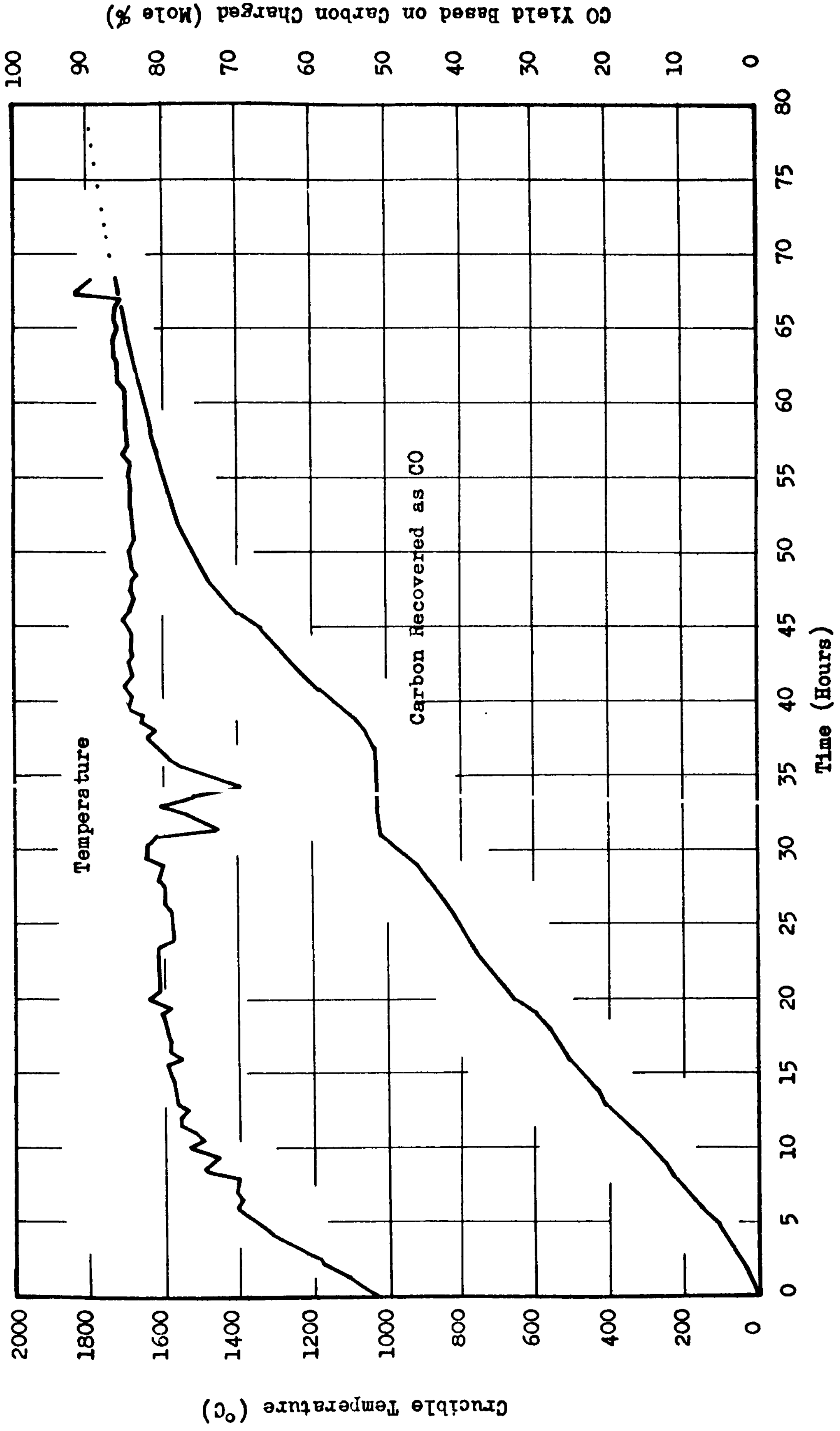
10-067-118-

Figure 5



FLOW DIAGRAM FOR SILICATE REDUCTION UNIT

Figure 6



LOG OF RUN 6, REDUCTION OF BASALT WITH CARBON

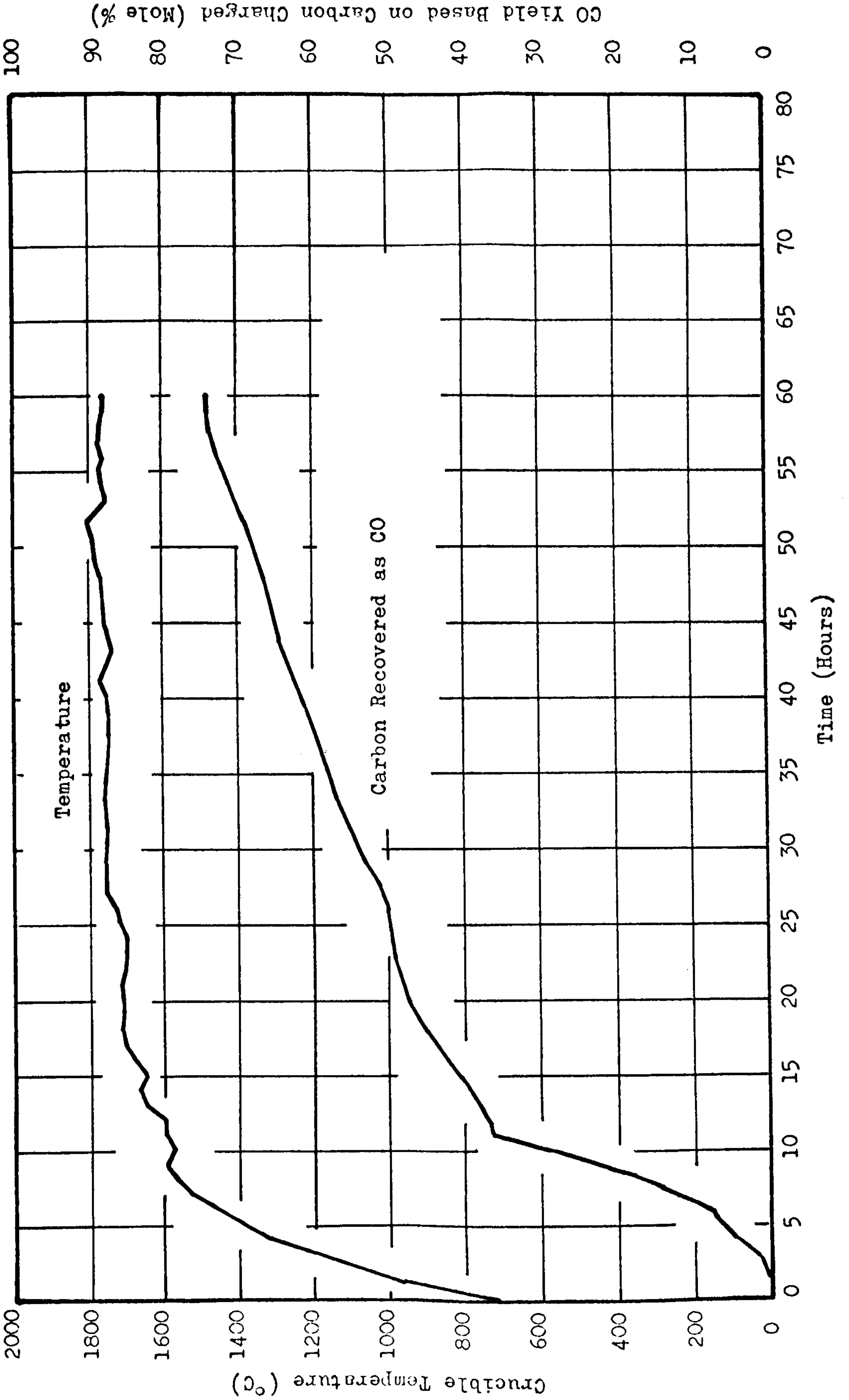
Figure 7

Inside View of Zirconia Curcible from Run 6
(large metal slug at bottom of crucible showed the following analysis:
Si, 62.4; Fe, 23.5; Al, 5.8; Mn, 5.8; Ti, 1.3; Mg, 0.8; and Cu, 0.4)

Figure 8

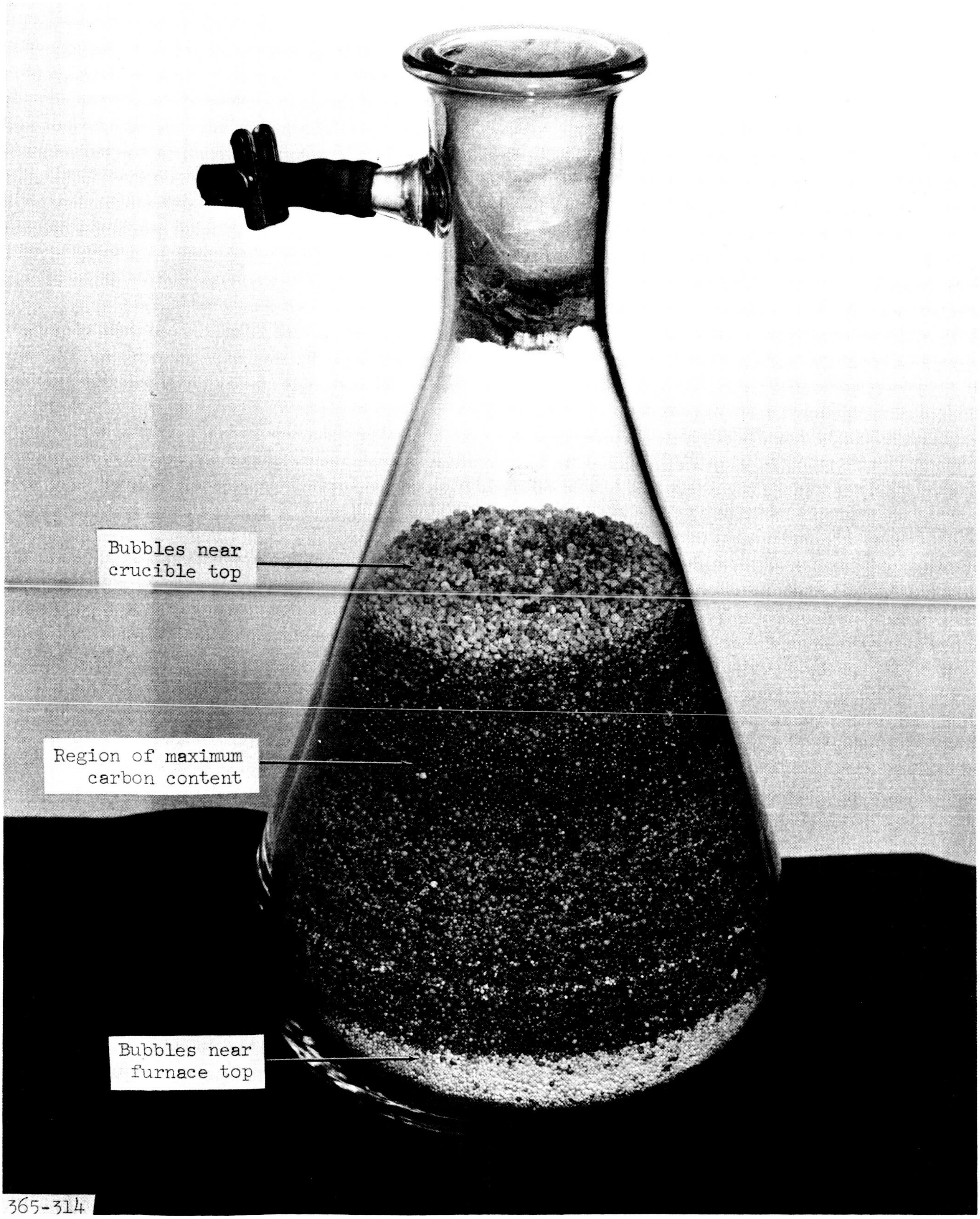
Zirconia Crucible from Run 6 - Outside View

Figure 9



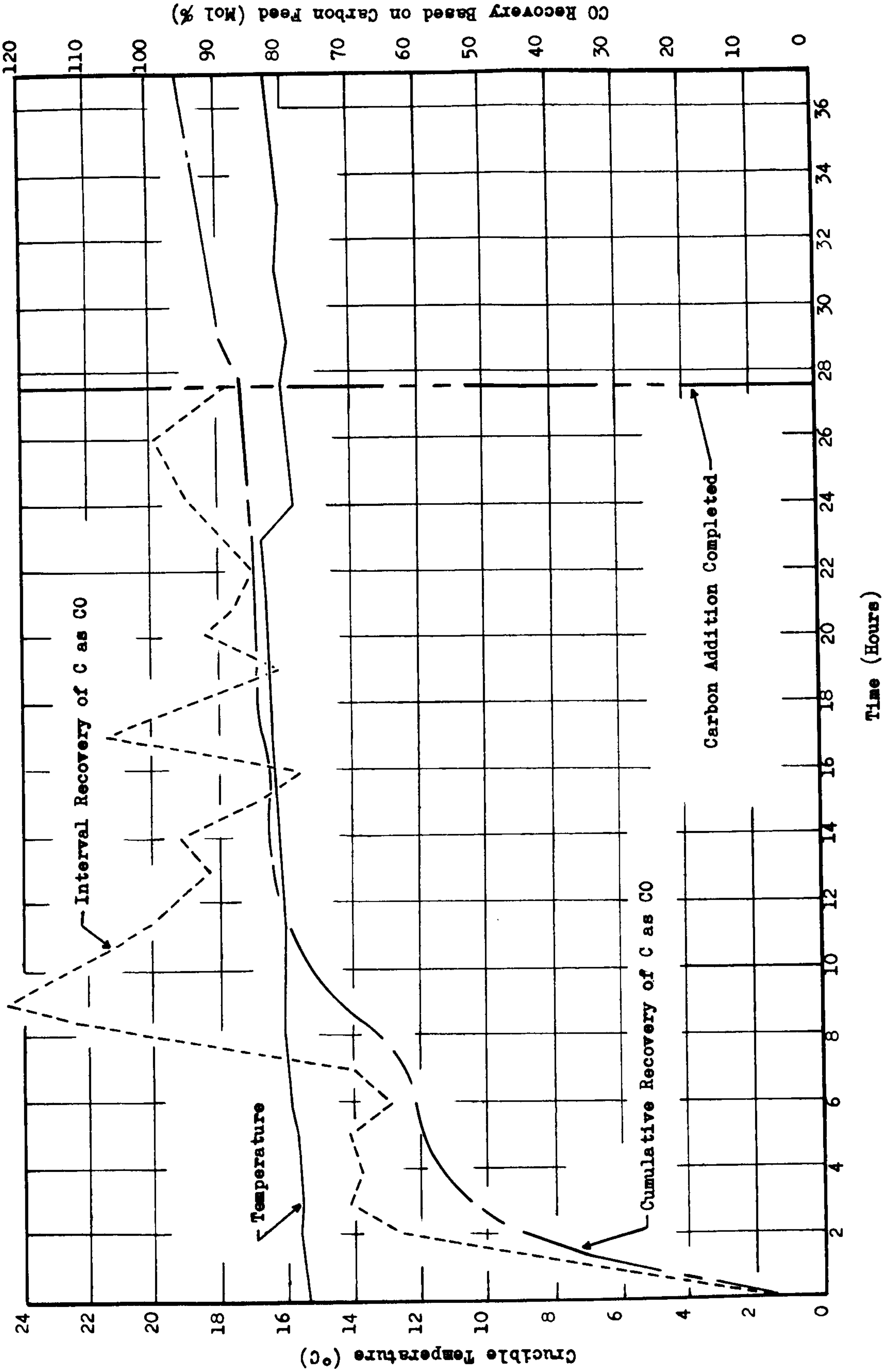
LOG OF RUN 7, REDUCTION OF BASALT WITH CARBON

Figure 10



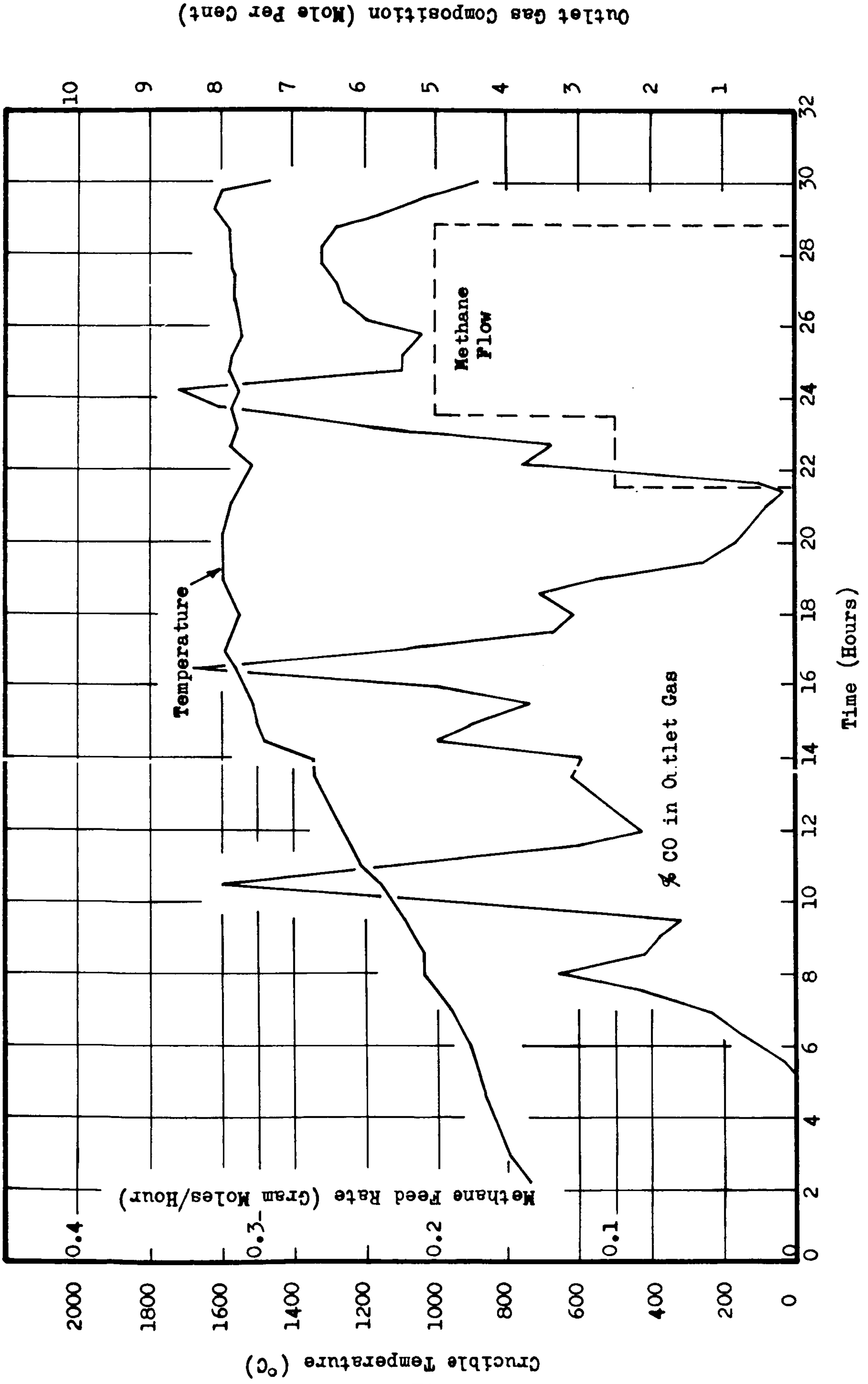
Alumina Bubble Furnace Insulation from Run 7

Figure 11



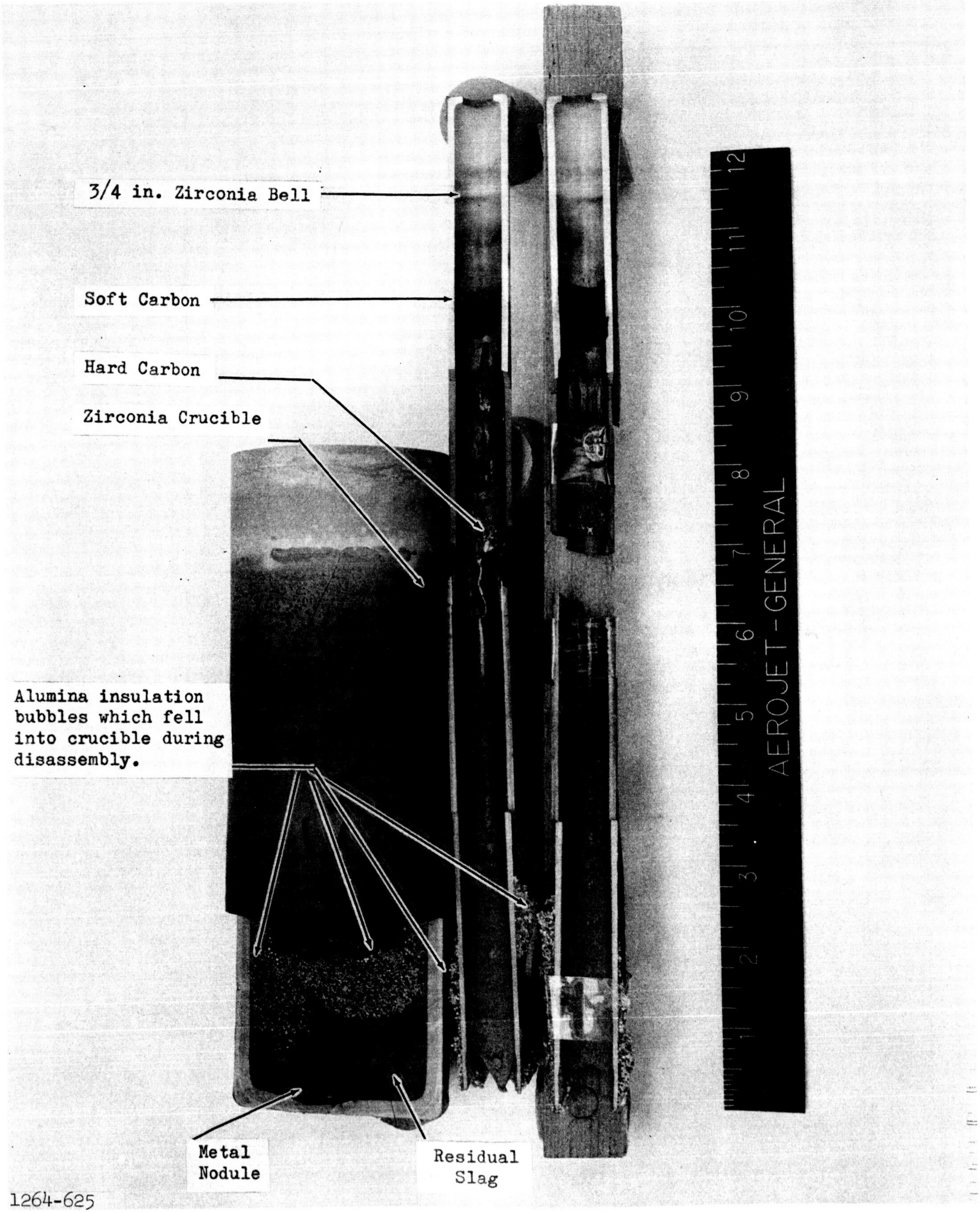
LOG OF RUN 18, REDUCTION OF BASALT WITH CARBON BLACK

Figure 12



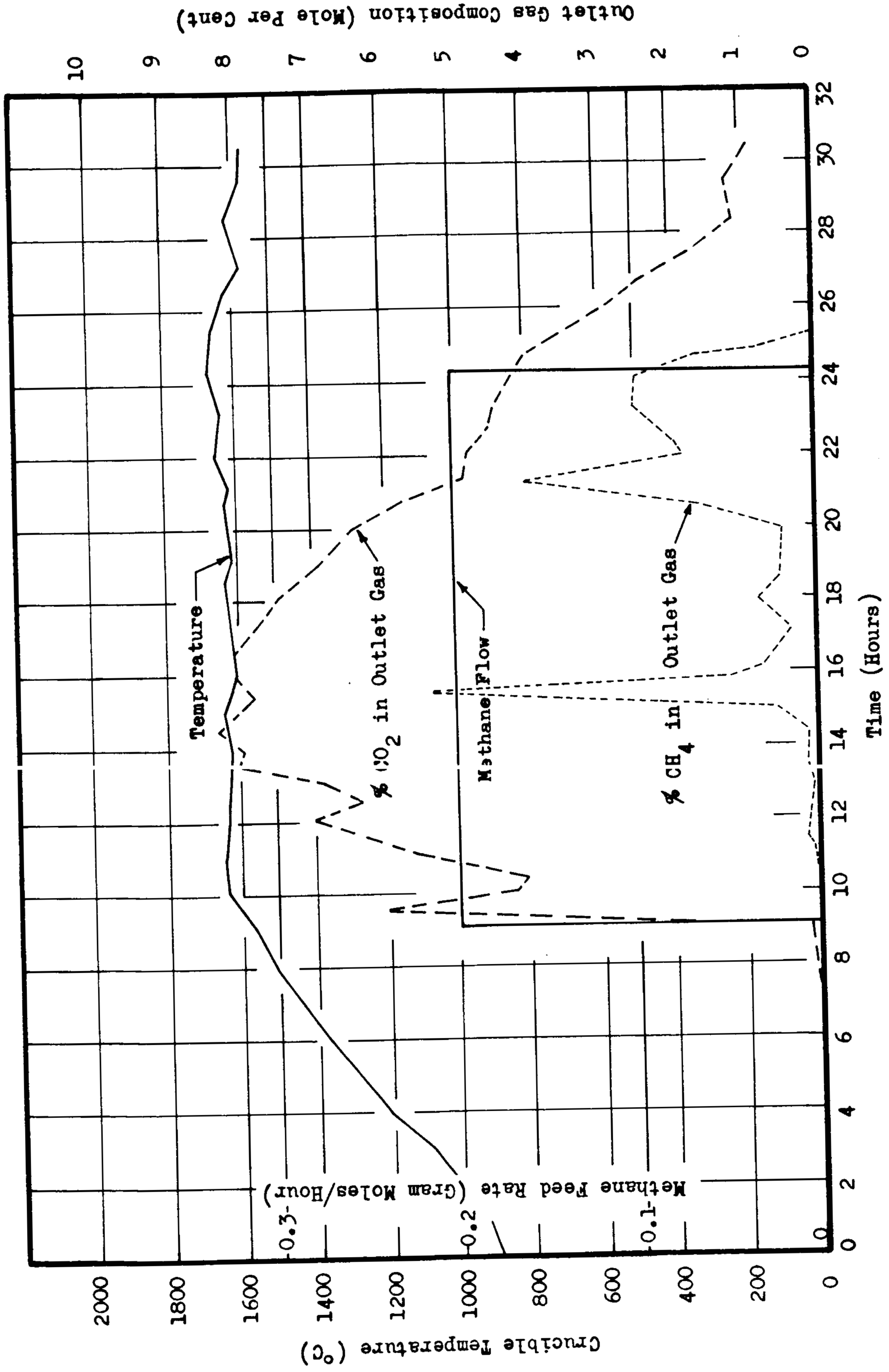
Log of Run 2, Reduction of Basalt with Carbon and Methane

Figure 13



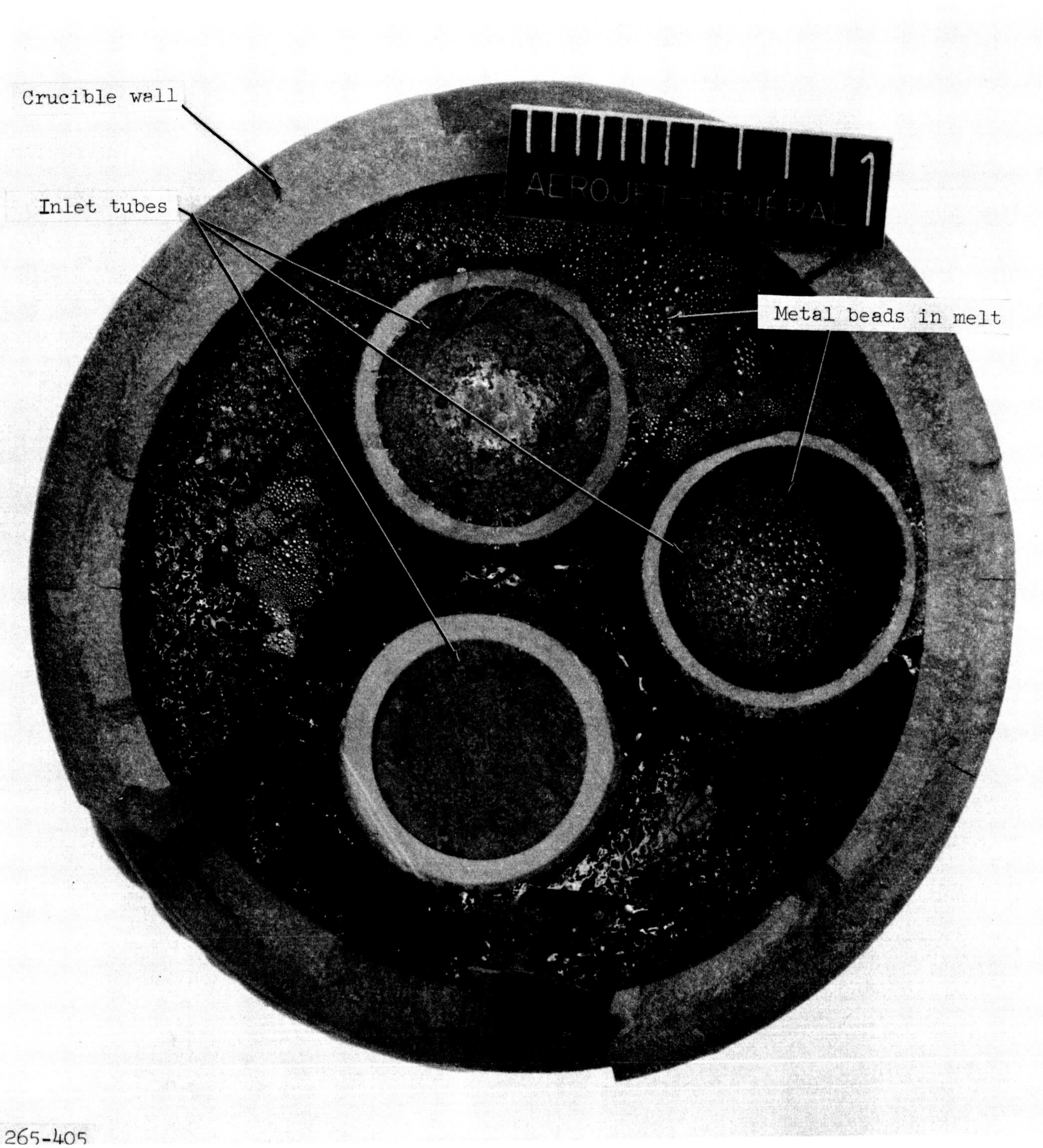
Zirconia Crucible and Inlet Bells from Run 2

Figure 14



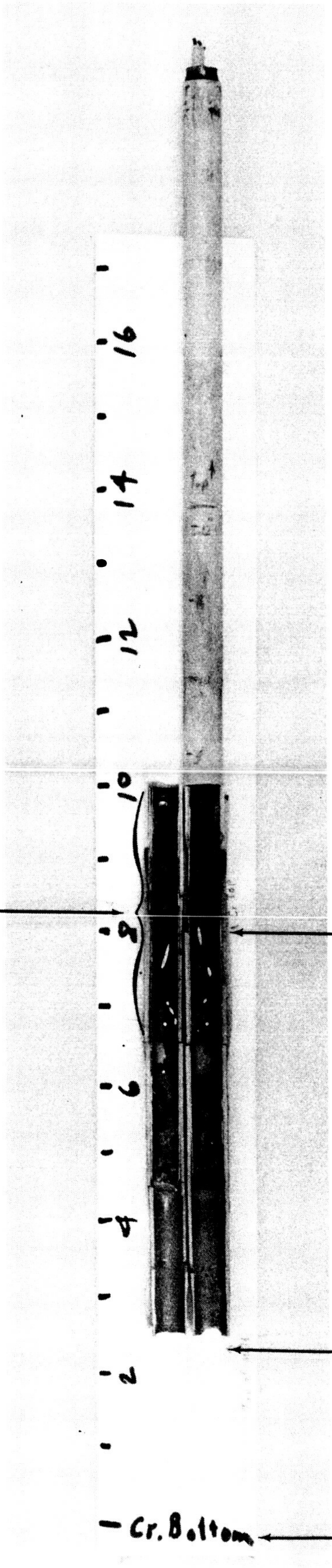
Log of Run 3, Reduction of Granite with Methane

Figure 15



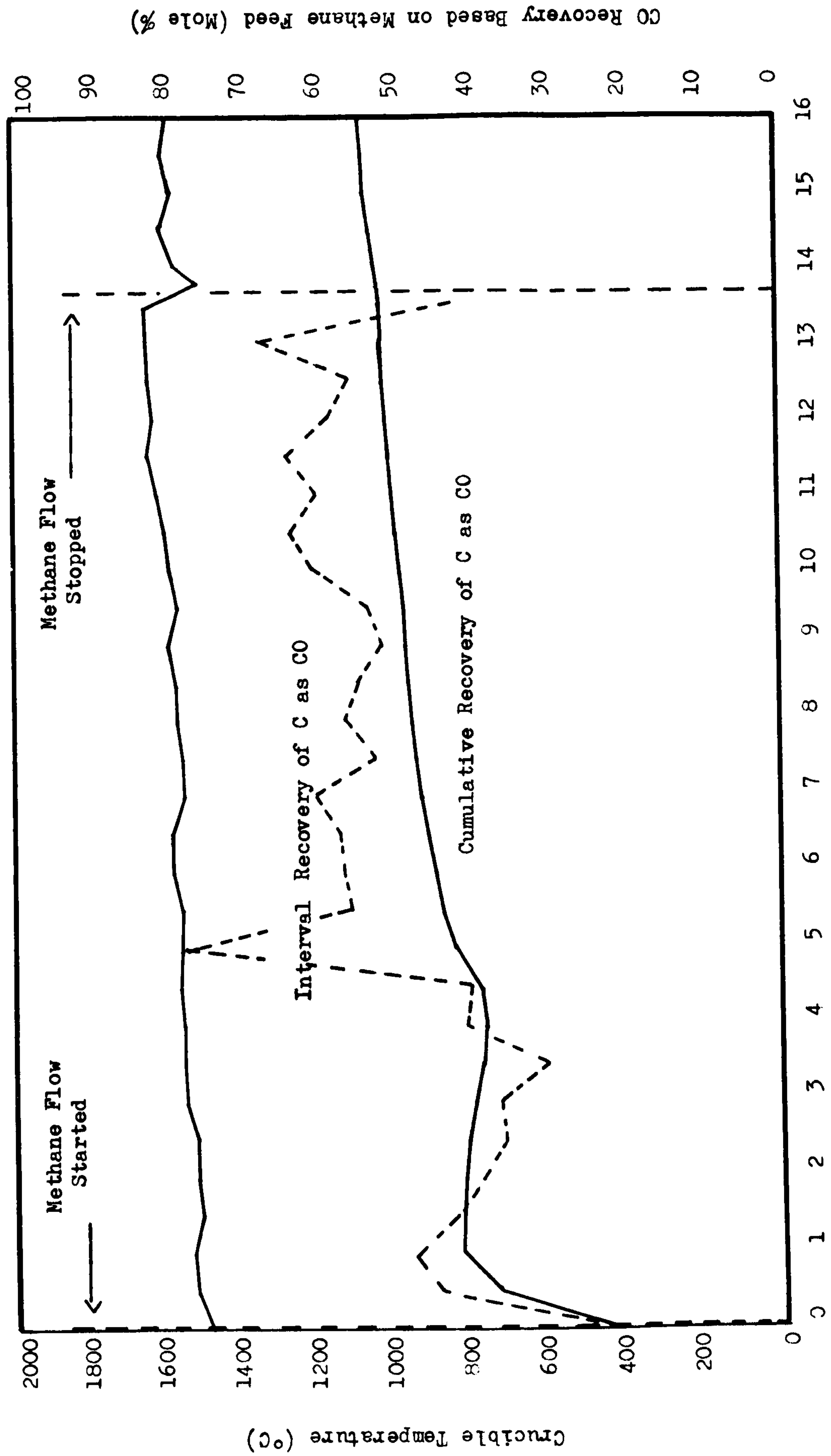
Zirconia Crucible from Run 5 - Top View

Figure 16



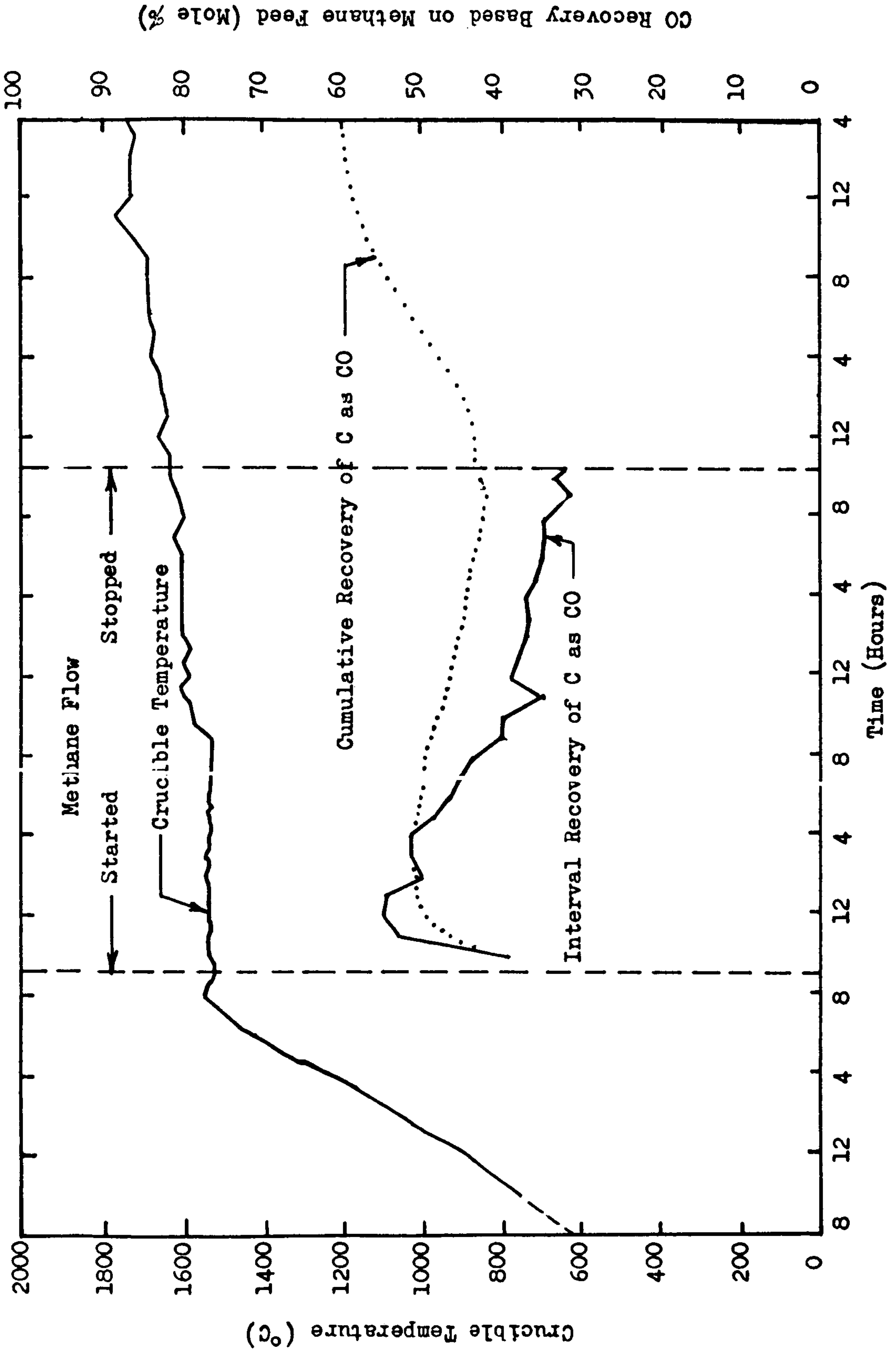
265-0050

Reactant Gas Inlet Tube from Run 9
Figure 17



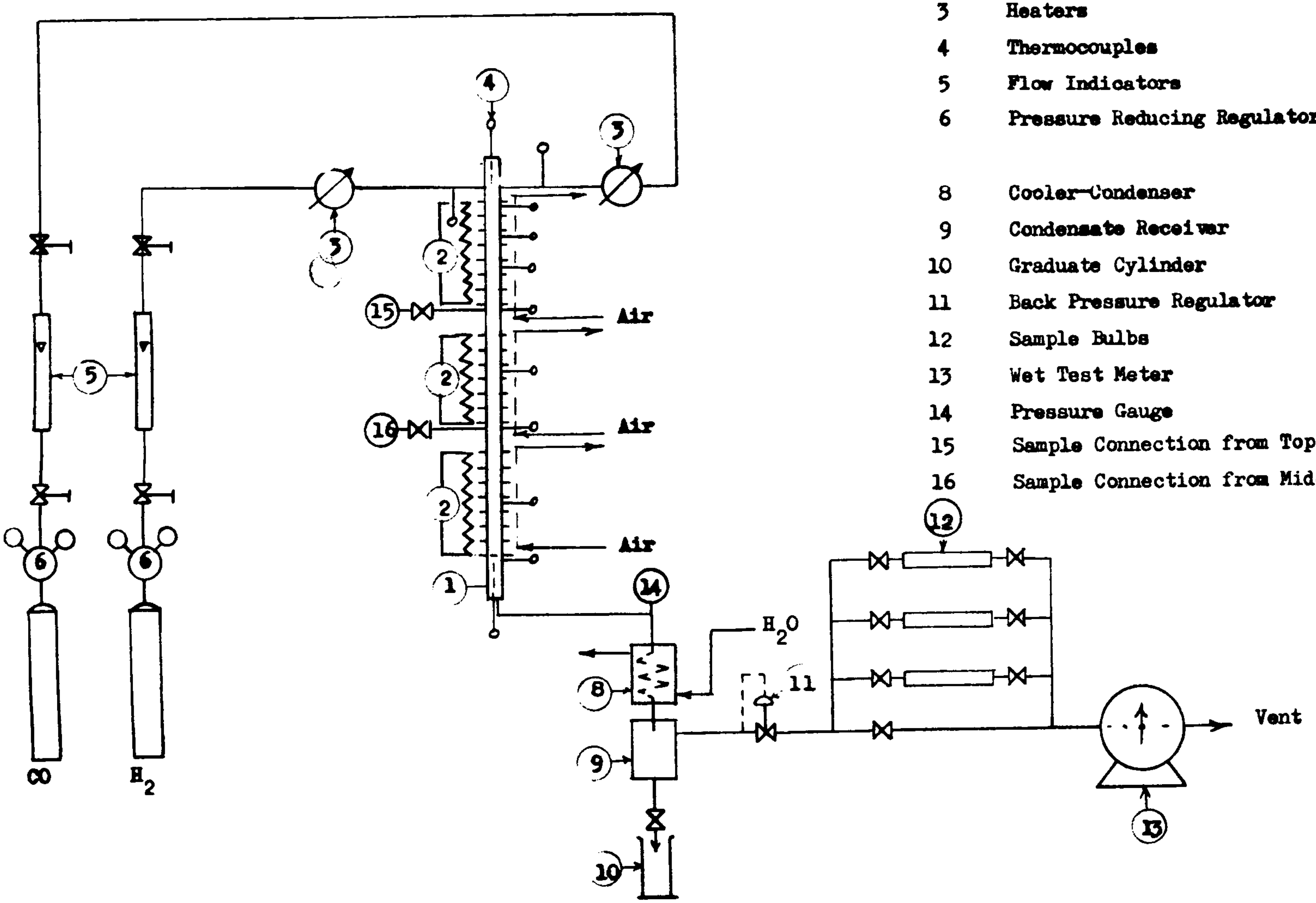
LOG OF RUN 13, REDUCTION OF BASALT WITH METHANE

Figure 18



LOG OF RUN 15, REDUCTION OF BASALT WITH METHANE

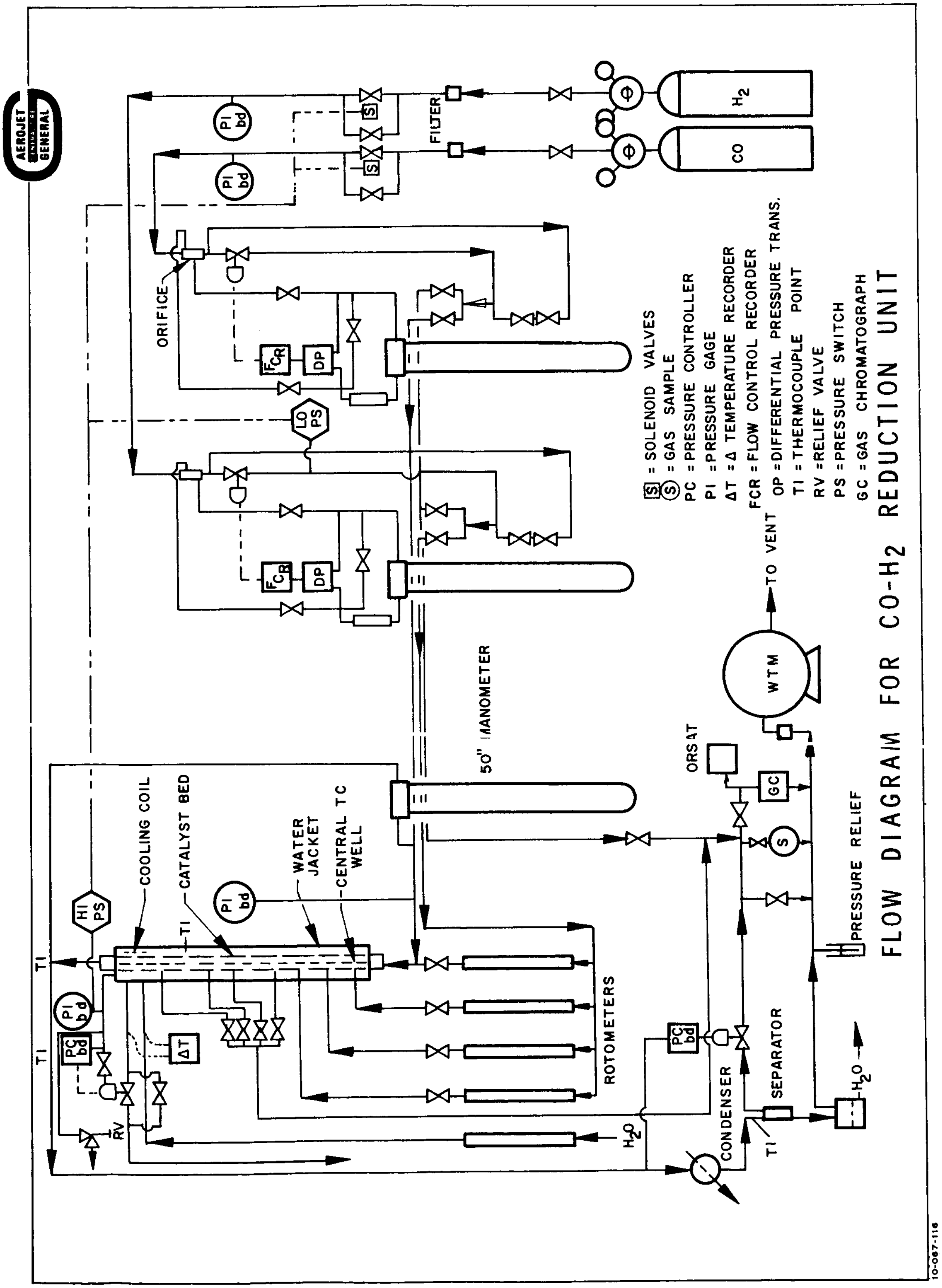
Figure 19



1	Stainless Steel Fintube, Reaction Chamber
2	Heaters
3	Heaters
4	Thermocouples
5	Flow Indicators
6	Pressure Reducing Regulators
8	Cooler-Condenser
9	Condensate Receiver
10	Graduate Cylinder
11	Back Pressure Regulator
12	Sample Bulbs
13	Wet Test Meter
14	Pressure Gauge
15	Sample Connection from Top 1/3 of bed
16	Sample Connection from Middle 1/3 of bed

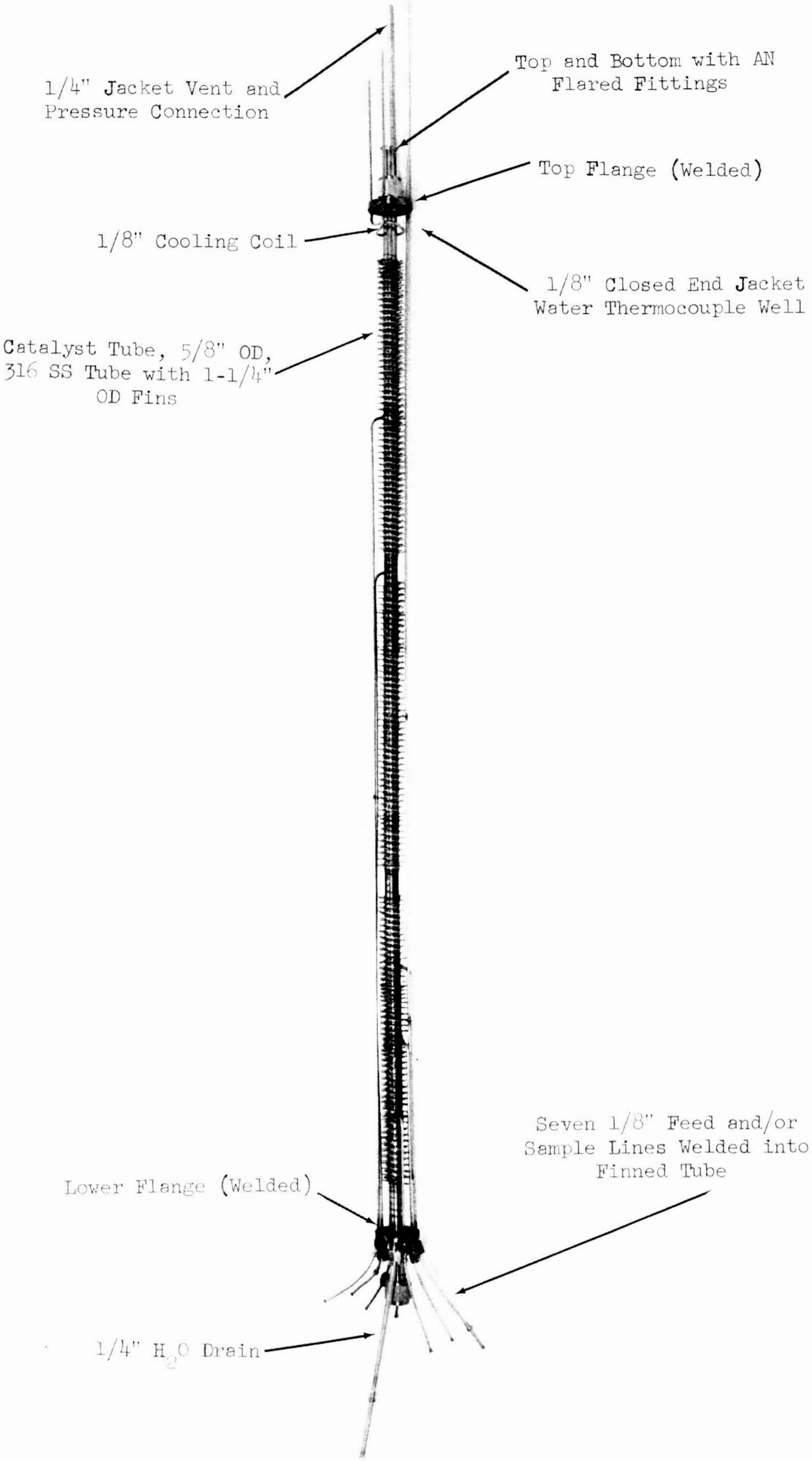
SCHEMATIC FLOW DIAGRAM OF H_2-CO REACTOR

Figure 20



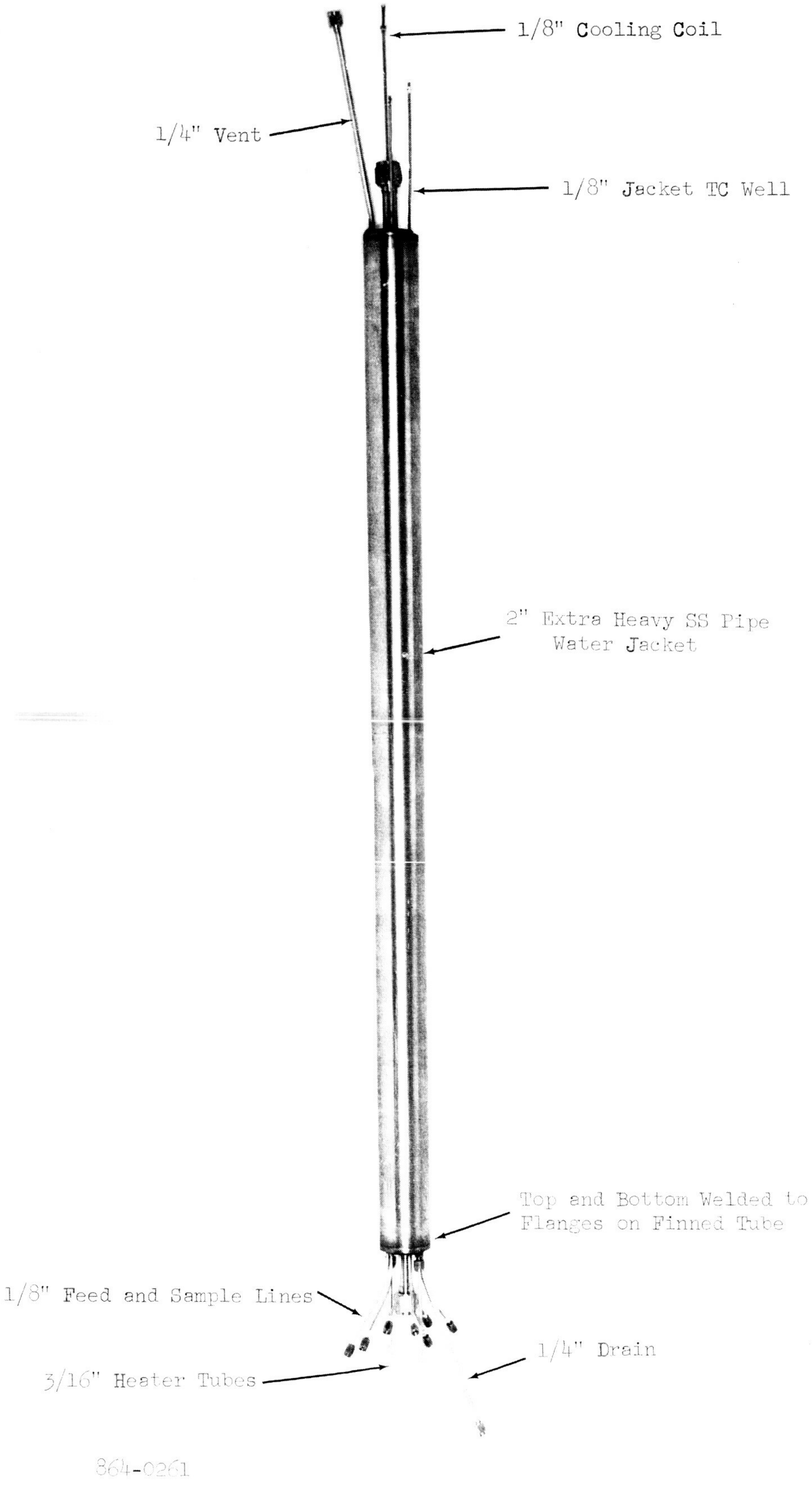
FLOW DIAGRAM FOR CO-H_2 REDUCTION UNIT

Figure 21



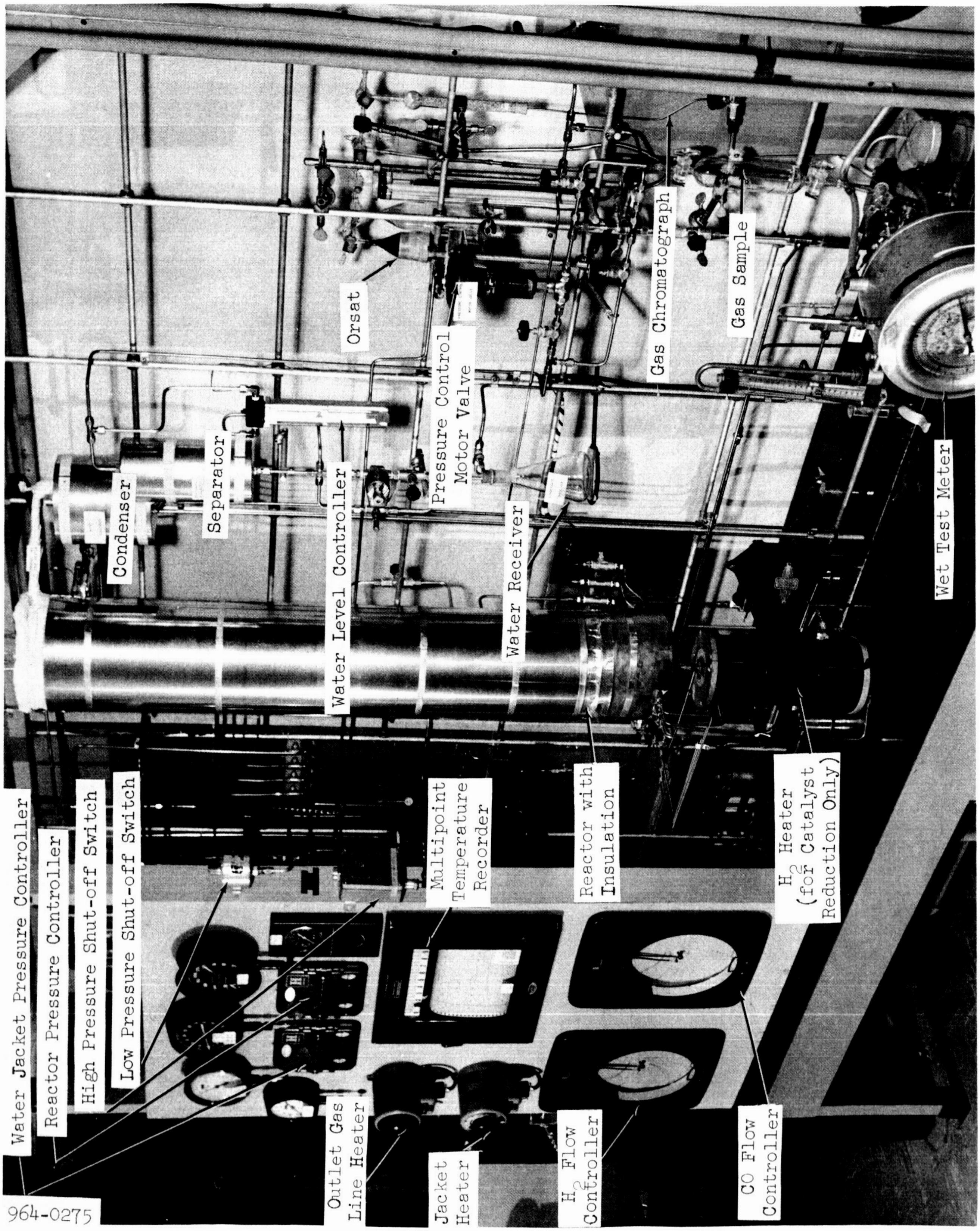
Catalyst Tube for Reduction of CO with H_2 Before Assembly

Figure 22



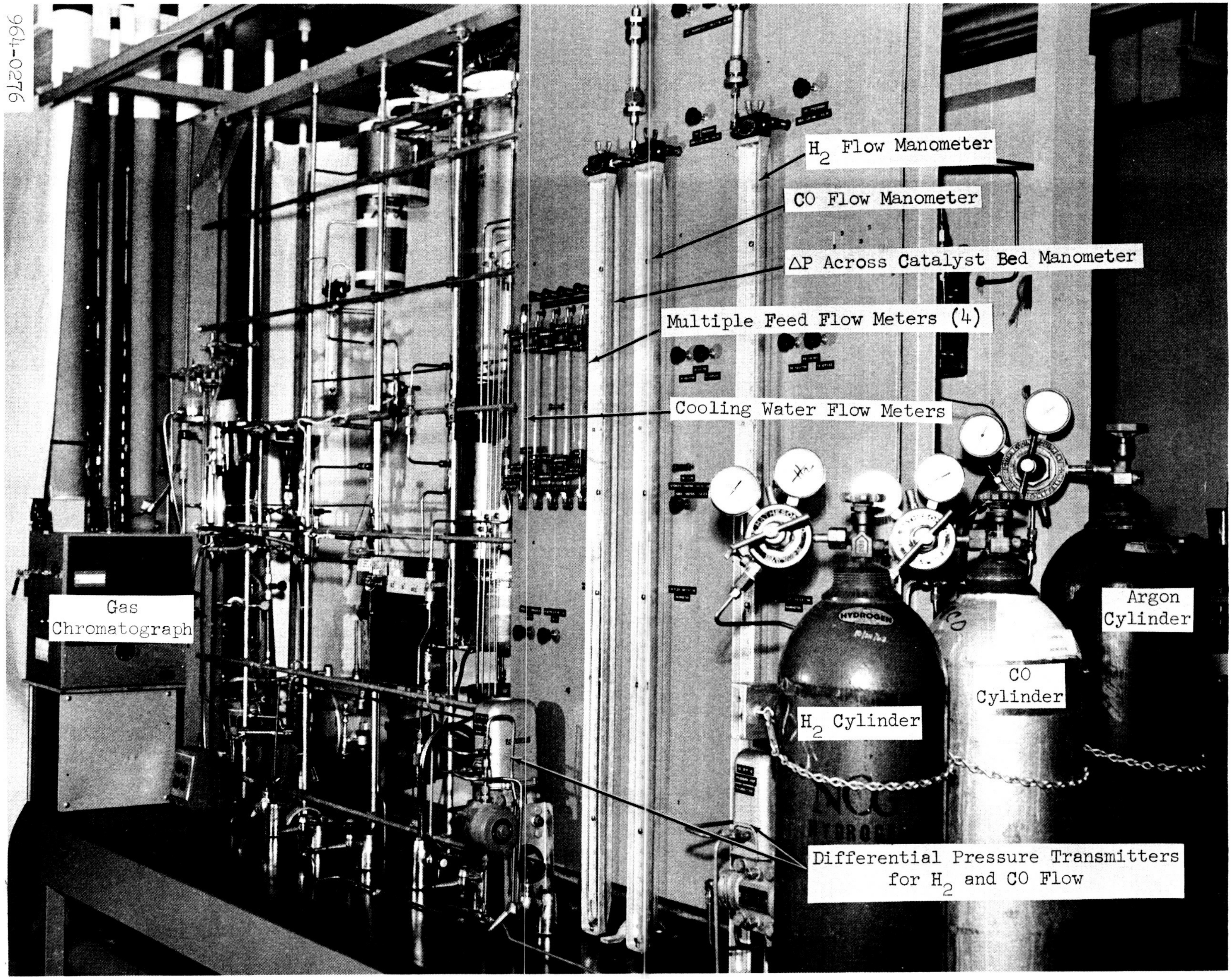
Catalyst Tube with Water Jacket

Figure 23



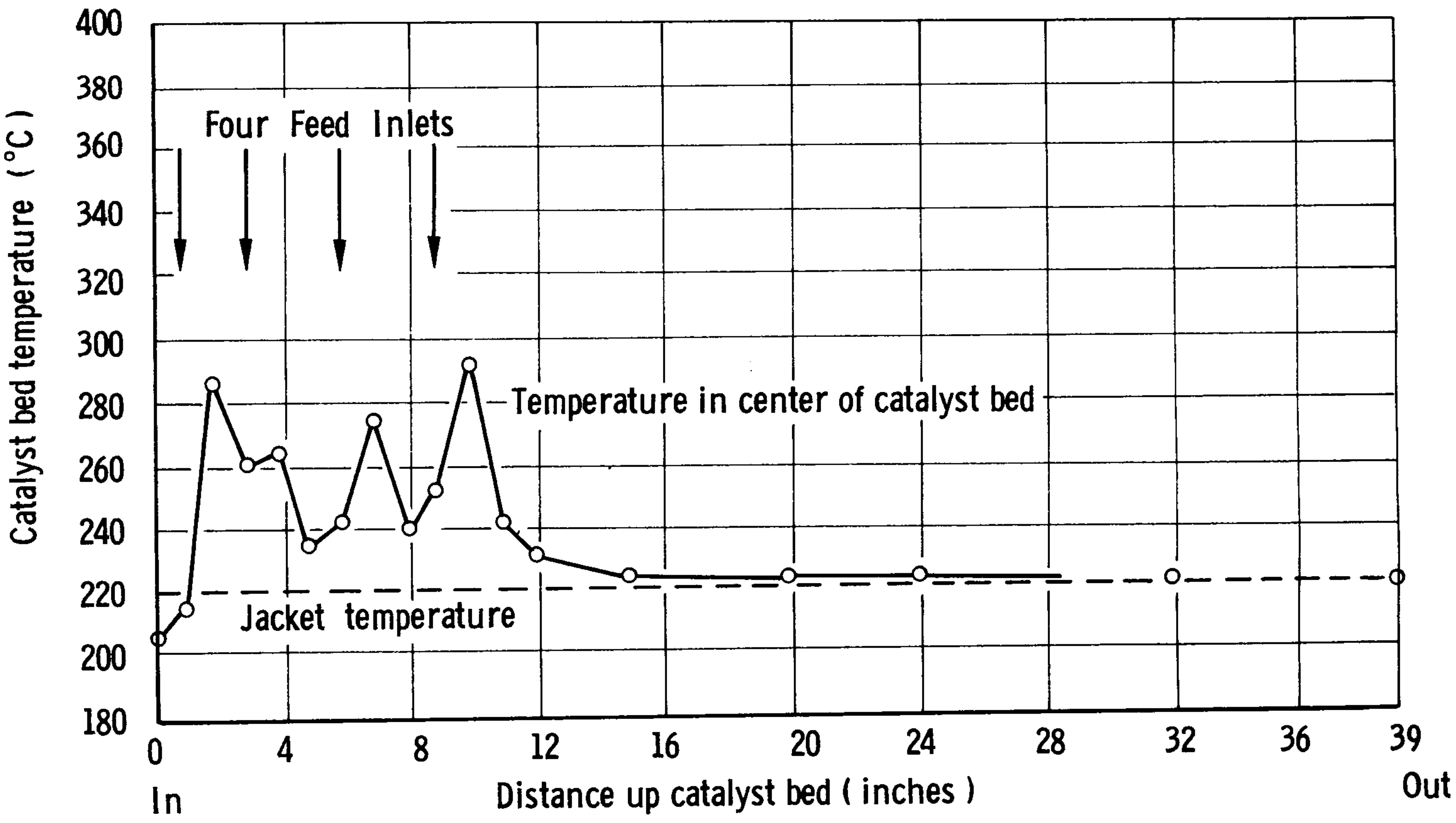
Unit for CO-H_2 Reduction for Long Term Operation

Figure 24



Back Side of CO-H_2 Reduction Unit

Figure 25

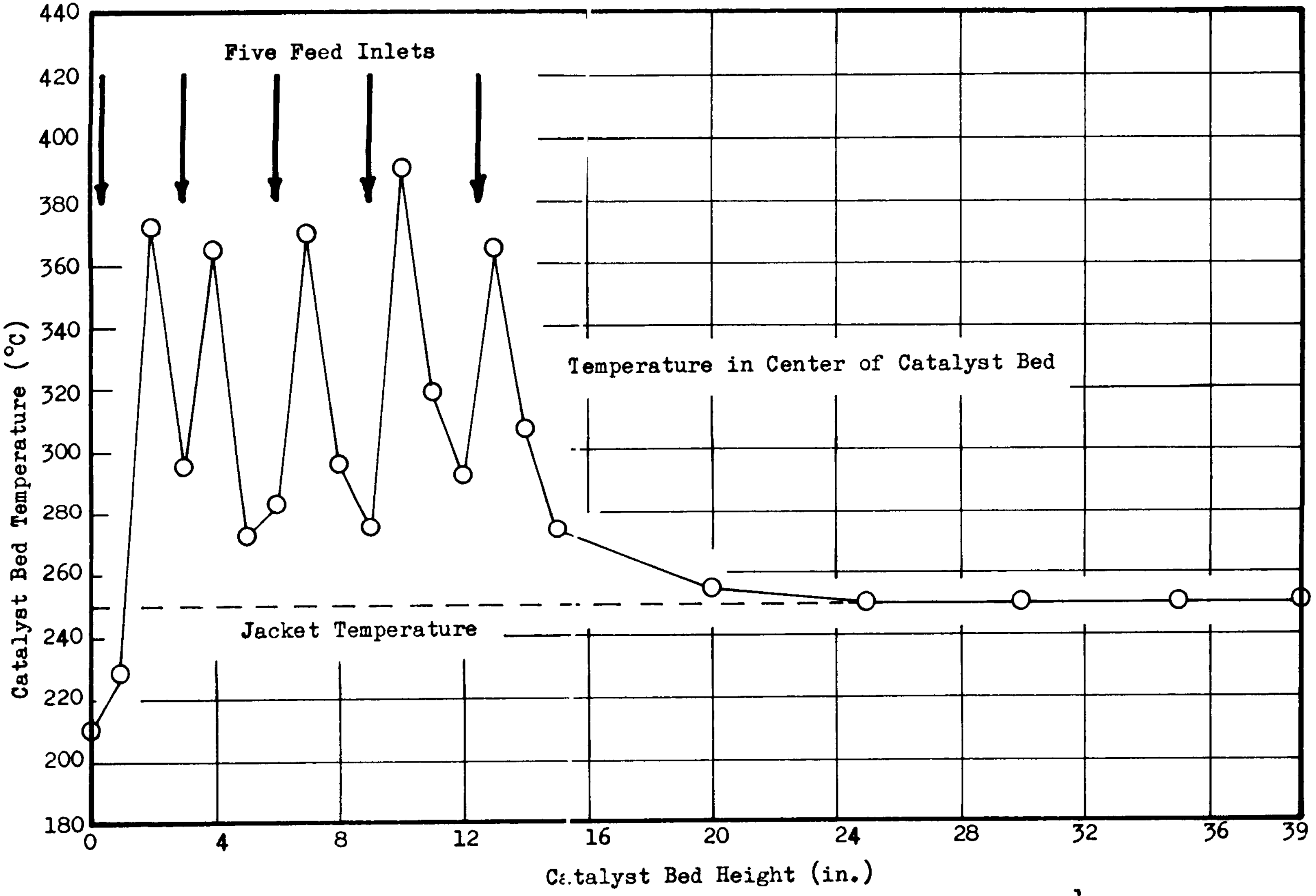


H_2 / CO = 4, Pressure = 6.0 Atm., Space Velocity = 1000, Catalyst 0765-1001-1, Feed Distribution : 0''-25%, 3''-25%, 6''-25%, 9''-25%, After 30 hr operation

CATALYST BED TEMPERATURE PROFILE

10-067-116

Figure 26

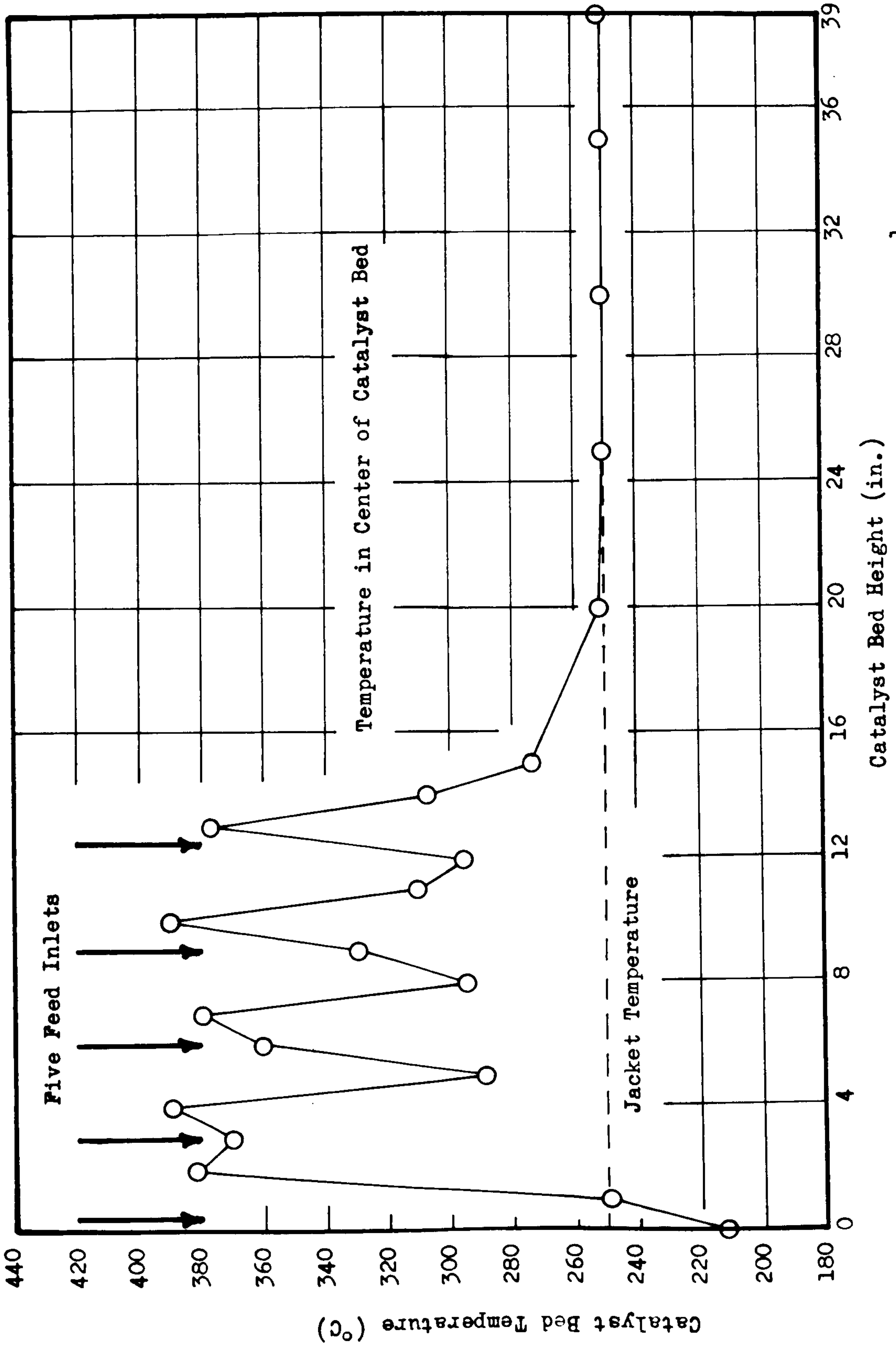


Date = 12-4-4, H_2/CO Mole Ratio = 3.1, Pressure = 6.0 atm, Space Velocity = 2000 hr^{-1}, Catalyst 0765-1001-1.

Feed Distribution: 0"-20%, 3"-20%, 6"-20%
9"-20%, 12.5"-20%

Catalyst Bed Temperature Profile After 1373 Hours Operation

Figure 27

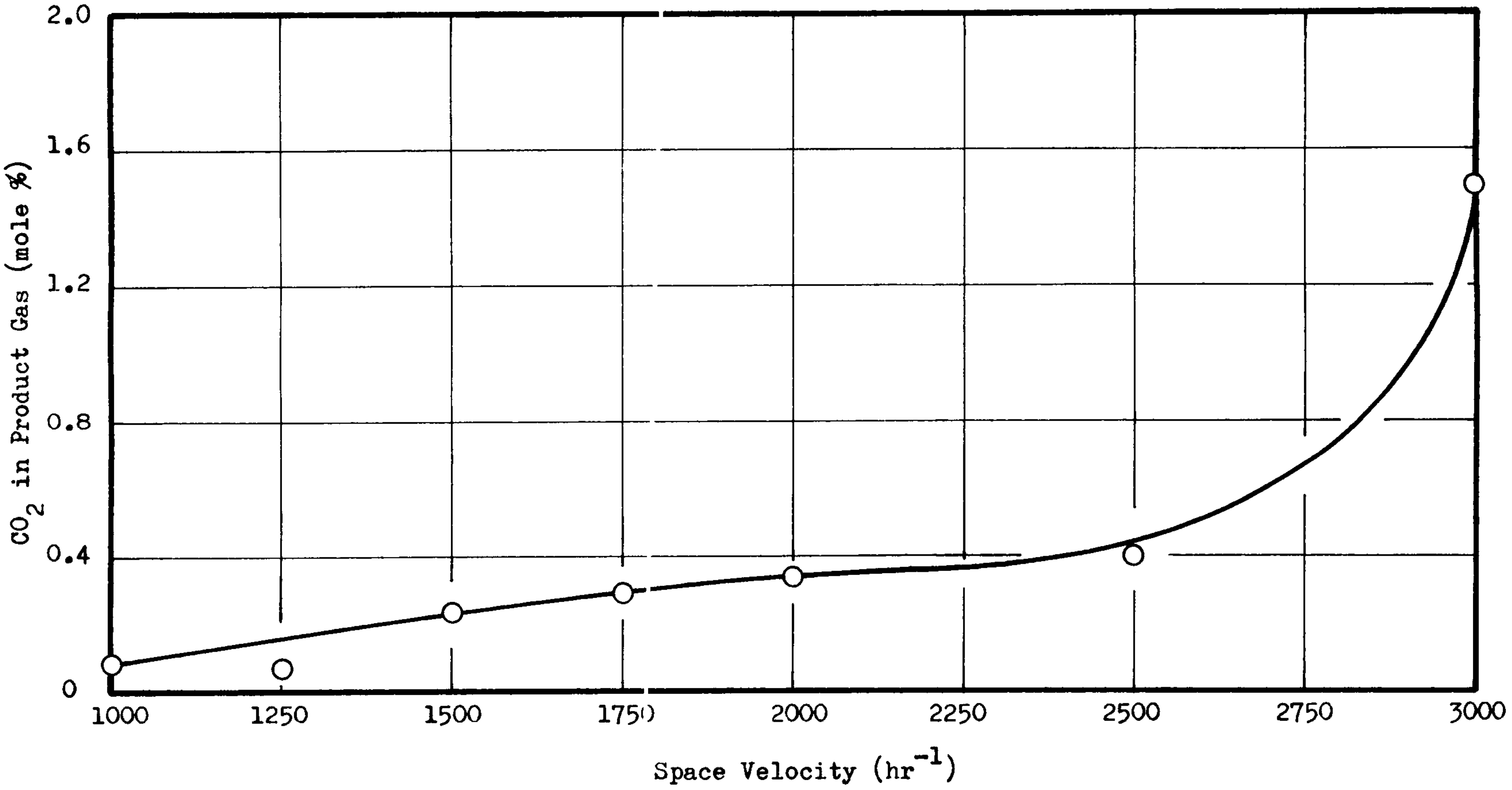


Date = 12-4-4, H_2/CO Mole Ratio = 3.1, Pressure = 6.0 atm, Space Velocity = 2000 hr^{-1}, Catalyst 0765-1001-1

Feed Distribution (H_2 and CO premixed): 0"-20%, 3"-20%, 6"-20%
q"-20%, 12.5"-20%

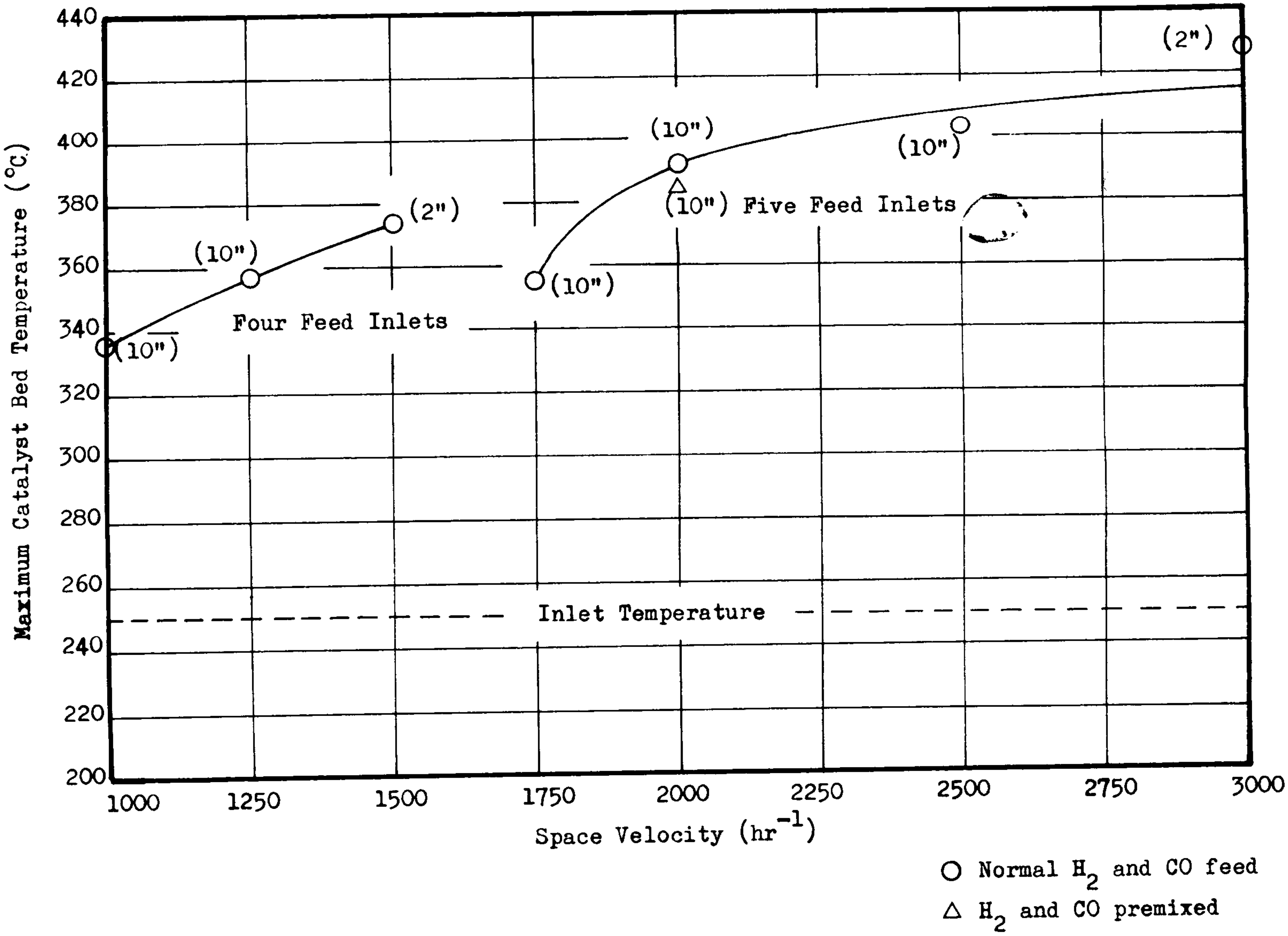
Catalyst Bed Temperature Profile After 1375 Hours Operation

Figure 28



Variation of CO_2 Concentration in Product Gas with
Space Velocity in the Water-Cooled Unit
(Catalyst C-0765-1001, 250°C Catalyst Temperature, 6.1 Atm Pressure, 3.1:1 H_2/CO Ratio)

Figure 29



Variation in Catalyst Bed Temperature with Space Velocity in the Water-Cooled
(Catalyst C-0765-1001, 250°C Catalyst Temperature, 6.1 Atm Pressure, 3.1:1 H_2/CO

Figure 30