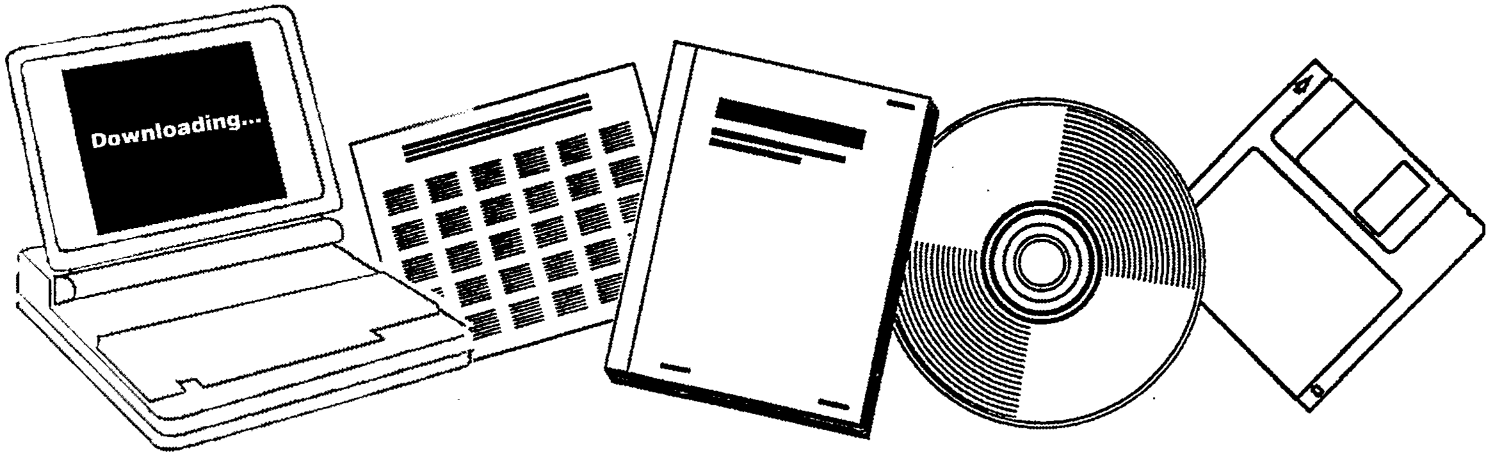
FE380T1

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS. MONTHLY PROGRESS REPORTS, AUGUST 31--DECEMBER 31, 1964

KELLOGG (M.W.) CO., HOUSTON, TEX.
RESEARCH AND DEVELOPMENT DEPT

1964



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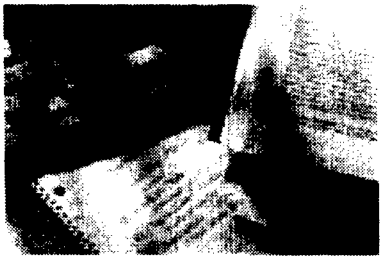

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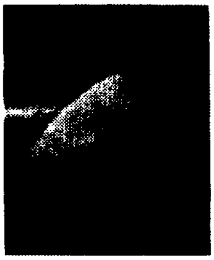

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DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Monthly Progress Reports for the
Period August 31 - December 31, 1964

The M. W. Kellogg Company
Research and Development Department
Houston, Texas

Prepared for

Office of Coal Research
U. S. Department of the Interior

OCR Contract No. 14-01-0001-380

FE--380-T-1

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Monthly Progress Reports 1 through 4 for each month
September through December 1964

MWK-MPR-1

RESEARCH AND DEVELOPMENT DEPARTMENT — M KELLOGG W

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

August 31, 1964

Progress Report No. 1

APPROVED: George T. Skaperdas
Project Manager

L. W. Friend
Director

Manager

CONTENTS

I. INTRODUCTION

The work to be performed to meet the objectives of the contract (14-01-0001-380) has been divided into three sections. These include: Process Development, Process Research and Mechanical Development. The work completed up to August 31 and the work planned for September are reported for each of the three sections of the project.

II. PROCESS DEVELOPMENT

A. Objectives

The objectives of the Process Development portion of the project are the following:

1. To coordinate flowsheet development and evaluation with experimental work conducted by the Chemical Research and Mechanical Engineering Development groups and with pilot plant design work to assure that all are proceeding in concert.

2. To provide maximum possible guidance for the experimental work by investigating a range of operating conditions and processing combinations to:

   a. determine those areas critical to economic success, and

   b. delineate the range of each variable in which experimentation will be most beneficial to the overall program.

3. To create conceptual designs, including estimated investment and economics, for commercial-scale plants to produce:

   a. pipeline gas

   b. hydrogen

   c. synthesis gas

   d. pipeline gas, hydrogen, and synthesis gas

   e. a fuel gas suitable for use as a transport vehicle.

B. Accomplishments

1. Selection of Raw Materials

Four coals -- an anthracite, a high-volatile bituminous, a sub-bituminous, and a lignite -- were chosen as the basis for all experimental and process evaluation work. Characteristics of these coals and typical ashes are summarized in Tables I and II. Major criteria used in the selection were:

a. Availability, as indicated by current production statistics.

b. Reserves sufficient to supply a large-scale coal gasification effort.

A coal char to be specified by OCR and supplied by another OCR contractor will also be considered.

2. Product Gas Specifications

Product gas specifications that we have established as reasonable goals are summarized in Table III.

Specifications for pipeline gas are subject to a review of the state of methane synthesis technology and may have to be revised at a later time.

Specifications for hydrogen will permit its use for chemical synthesis, hydrogen processing of petroleum fractions, or in the hydrogenation step of Office of Coal Research Project Gasoline.

Synthesis gas specifications have been set so that it may be used to produce gasoline (and other liquid fuels and chemicals as co-products). This is a potential large-scale consumer of coal, since 250 MM SCFD of synthesis gas is equivalent to about 6,000 barrels per day of gasoline, or about 0.15% of present U. S. refining capacity. It should be noted that this synthesis gas quantity is equivalent to about 10% of existing U. S. synthetic ammonia capacity or about 60% of present methanol production; pointing up the fact that chemicals production can never be a very big consumer of coal. Large-scale markets must be in the energy field.

3. Preliminary Screening of Ash Removal Methods

Several methods have been proposed for removing coal ash from the melt (mixture of molten salt catalyst and molten ash) of the Kellogg Gasification Process:

a. Purging (discard a portion of the melt and make up for catalyst losses by fresh additions of salt).

TABLE I

COAL CHARACTERISTICS

Rank	Anthracite	High-Volatile Bituminous	Sub-Bituminous	Lignite
Source:				
State	Pennsylvania	W. Virginia	Wyoming	North Dakota
County	Schuylkill	Logan	Lincoln	Bowman
Seam	Southern Coal Field, Panther Creek Dist.	Cedar Grove	Elkol	-
Proximate Analysis, wt. %:				
Moisture	6.3	2.5	21.7	42.4
Volatile matter	3.7	39.0	33.5	24.4
Fixed carbon	81.7	53.4	41.8	26.9
Ash	8.3	5.1	3.0	6.3
Total	100.0	100.0	100.0	100.0
Ultimate Analysis (dry Basis), wt.%:				
C	83.9	79.4	73.0	62.5
H	2.6	5.2	5.1	4.3
O	2.9	7.5	16.0	19.5
N	1.0	1.4	1.4	1.1
S	0.7	1.3	0.7	1.6
Ash	8.9	5.2	3.8	11.0
Total	100.0	100.0	100.0	100.0
Gross Heating Value, Btu/#				
As received	12,620	13,990	9,960	6,230
Dry	13,470	14,350	12,720	10,820

TABLE II

ASH CHARACTERISTICS

Coal	Anthracite	High-Volatile Bituminous	Sub-bituminous	Lignite
% Ash in Coal (dry)	8.9	5.2	3.8	11.0
Softening Temp., °F	2,980	2,750	2,060	2,180
Compositions, wt. %:				
SiO_2	56.5	51.6	30.7	33.0
Al_2O_3	36.0	33.3	19.6	13.5
Fe_2O_3	3.8	8.1	18.9	7.3
TiO_2	1.2	1.4	1.1	0.6
CaO	0.8	1.4	11.3	14.5
MgO	0.3	0.8	3.7	4.4
Na_2O	-	-	1.9	12.1
K_2O	-	-	0.5	1.0
SO_3	-	0.7	12.2	13.6
Total	98.6	97.3	99.9	100.0

TABLE III

PRODUCT GAS SPECIFICATIONS

Product Gas Type	Pipeline Gas	Hydrogen	Synthesis Gas	Transport Gas
Quantity, SCFD	← 250,000,000 →			
Temperature, °F	100	100	100	100
Pressure, psig	1000	500	400	1000
Composition, mol %:				*
H_2		98.5	$H_2/CO = 2.3$	
CO		10 ppm max		
CO_2			5 max	
CH_4	85-90	1.5	5 max	
N_2			-	
S Compounds		1 ppm max	1 ppm max	
Gross heating value, Btu/SCF	900 min.	-	-	300-400

* Raw gasifier effluent after cooling and, if necessary, CO_2 removal.

b. Prior de-ashing of the coal so that an ash-free fraction may be gasified.

c. Quenching a portion of the melt with water to dissolve the salt catalyst, filtering to separate the salt solution from undissolved ash components, and evaporating to recover the salt.

d. Precipitating ash components with carbon dioxide.

e. Settling, centrifuging, or filtering.

f. Flotation.

Preliminary screening work on these alternatives is discussed briefly.

a. Purging

The cost of salt makeup was calculated as a function of salt price, ash content of coal feed, and ash content of the gasifier melt. The results are presented in Figure 1. We have concluded that purging alone is not likely to be the solution to the ash removal problem because: (a) most coals contain more than 5% ash, (b) the salt will probably cost more than 1 cent a pound, and (c) the gasifier is not likely to operate as desired with upwards of 50% ash in the melt.

b. Prior De-Ashing

Solvent de-ashing, such as the process being developed by Spencer Chemical Company for OCR, will be considered when cost data become available.

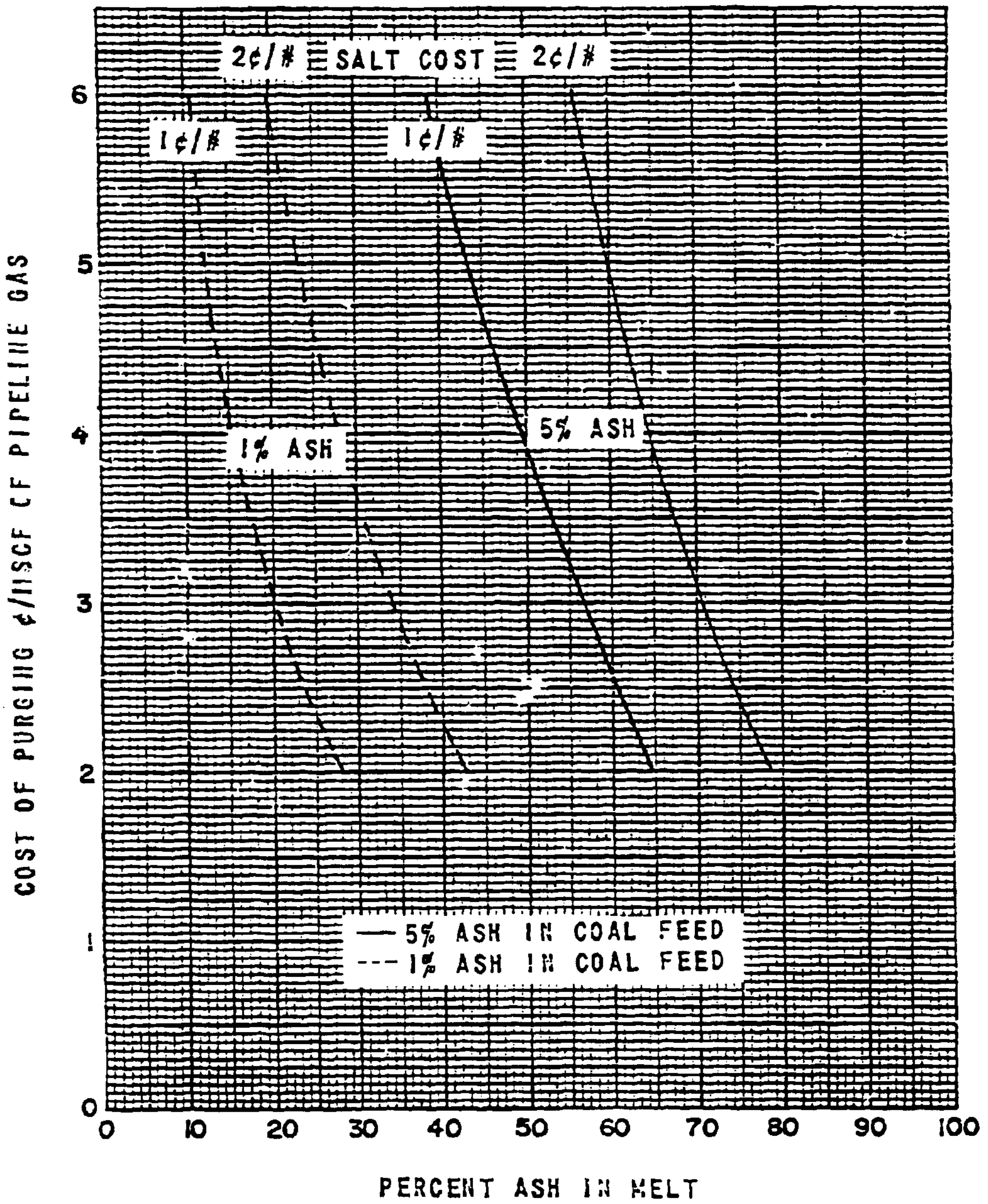
Low temperature carbonization of coal feed to produce an ash-free fraction to the gasifier was studied. This could be a solution only if a low-cost carbonization process were developed that converted at least 30% of the coal feed to ash-free liquid and if the resultant char product could be sold to a power plant as fuel at the same price per Btu as the coal costs. Even then the cost of ash removal would be equivalent to more than 5¢/MSCF of pipeline gas, and the adjacent power plant would be larger than any thermal power plant in the United States.

c. Quenching

This alternative appears feasible, although there are technical problems to be solved, for a total ash removal cost in the range of 2-5¢/MSCF of pipeline gas. More detailed designs and cost estimates will be made.

FIG 1

EFFECT OF ASH CONTENT AND SALT COST ON THE COST OF PURGING



d. Others

Investigation of the feasibility of precipitation, settling, filtering, etc. must await the results of experimental work.

4. Optimization of Methods of Heat Supply

Various methods were studied for supplying to the gasifier the endothermic heat of the gasification reactions:

a. Indirect heating (through tubular surface):

1). Gas medium
    (a) Superheated steam
    (b) Flue gas
    (c) Recycled Synthesis gas

2). Liquid medium
    (a) Liquid metal
    (b) Gasifier melt
        (1) Circulation of melt through external fired heater
        (2) Combustion inside tubes immersed in the gasifier melt

b. Direct heating (no tubular surface):

1). Combustion of fuel in the melt
    (a) Combination gasifier and melt heater
    (b) Gasification and melt heating in separate vessels

2). Electrical heating

Cases a2(b)(1) and b1(a) & (b) were judged to be most attractive and nearly equal in cost considering the precision of the figures developed. These three cases will be studied in more detail.

5. Preliminary Evaluation of Alternative Methane Removal Schemes

When hydrogen or synthesis gas are the desired end products, methane is an undesirable constituent of the gasifier effluent stream. This methane concentration can be reduced by altering gasifier operating conditions or by subjecting the gasifier effluent to catalytic reforming or partial combustion. Preliminary calculations have shown that the costs associated with reforming and partial combustion are very nearly the same and that choice of the best method is dependent on specific gasification conditions. High steam/coal ratio in the gasifier and high methane concentration in the effluent gas favor reforming. Whether either reforming or partial combustion is superior to changing gasifier conditions is not known. Further design and cost estimating work will be carried out.

6. Process Flowsheet Studies

A series of flowsheet studies has been started for the purpose of further narrowing the range of operating conditions and the variety of processing alternatives that must be investigated experimentally. These studies will include preliminary equipment design, cost estimating, and economic calculation and will serve as the first step in the creation of conceptual designs for commercial-scale plants, which is a major objective of the program. All combinations of raw materials and end products will be considered.

C. Projections - September

1. Process Flowsheet Studies

These studies will be continued.

2. Methane Synthesis

The state of the technology of methane synthesis will be reviewed, specifically the work conducted by the Bureau of Mines and the Institute of Gas Technology, with the objective of choosing the optimum methanation scheme for all future flowsheets. The choice will be based on stage of development, economic attractiveness as determined by detailed process designs and cost estimates, and potential for future improvements.

3. Gas Purification

A review will be started of the many gas purification schemes (for removal of carbon monoxide, carbon dioxide, and sulfur compounds) that might be considered in the production of pipeline gas, hydrogen, synthesis gas, and transport gas. The objective will be to find the optimum processing scheme for each end product, which will then be used in all future flowsheets.

III. PROCESS RESEARCH

The reactor to study the rate of gasification of various coals has been designed. This is shown on Figure 2. This is essentially a 2" diameter Inconel pipe reactor 24" high with a coal feeding section. The coal will be dropped into the molten salt reactor by means of quick opening valves. Parameters that will be investigated will be pressure, temperature, ash content of molten salt, particle size, steam rate, contact times, bed height and others. Batch tests are planned for primary evaluation of gasification rates. In addition, design of bench-scale continuous gasification is being studied to evaluate the possibility of making continuous feed runs on the bench scale.

Concurrently with the kinetic study, investigation on the physical properties of Na_2CO_3-ash and Na_2CO_3-NaCl-ash systems will be performed.

Specifically during the next period work will be performed along two lines:

a. Solubility of ash components in molten sodium carbonate as a function of temperature and ash composition. Melting point curves will also be developed.

b. Studies will be made to determine the gas velocities required to mix molten salt and coal. This will be simulated by using wood charcoal and water.

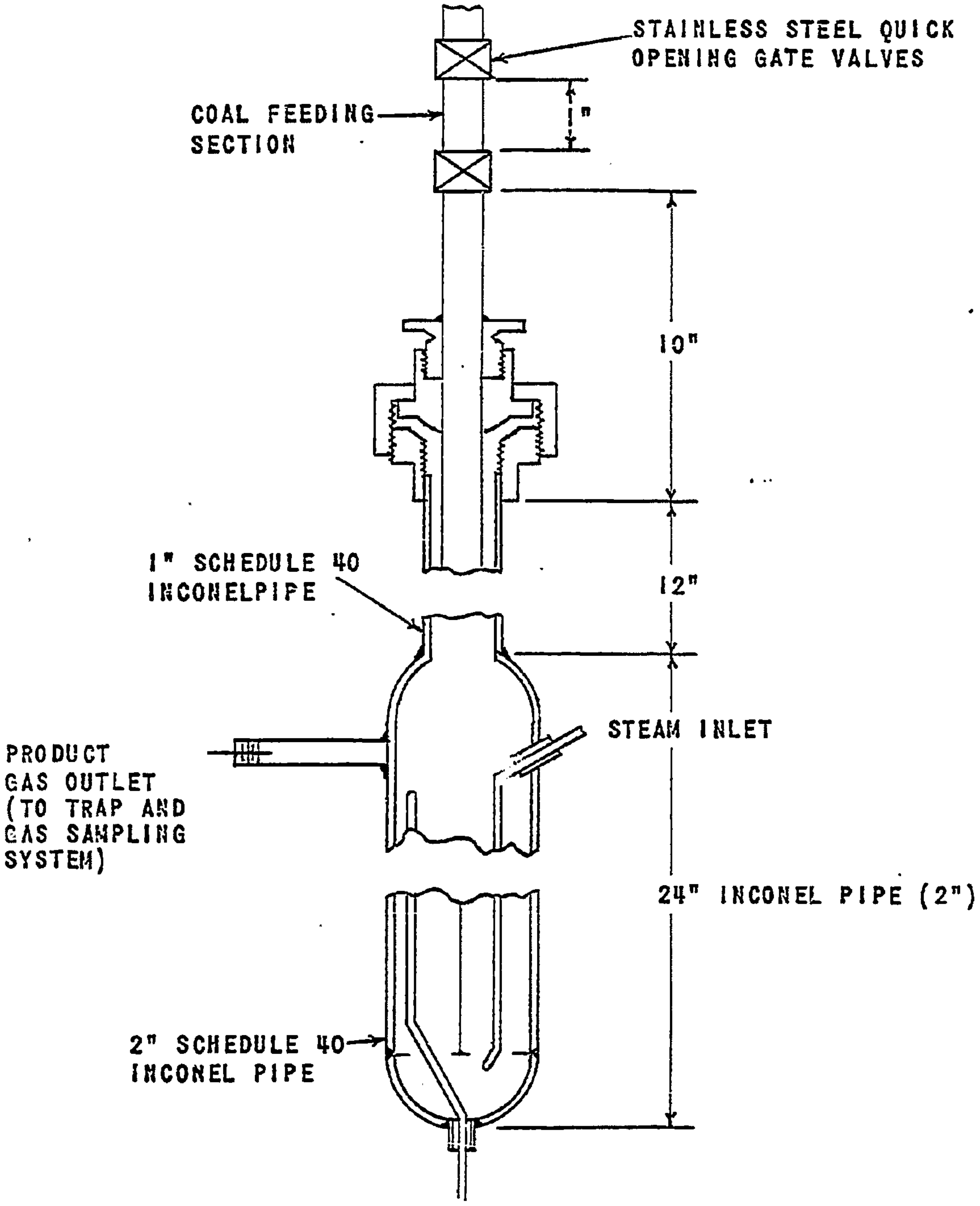


FIG 2
MOLTEN SALT COAL
GASIFICATION REACTOR

IV. MECHANICAL DEVELOPMENT

A. Environmental Testing of High-Temperature Alloys

An environmental test program has been initiated having as its objective the selection of construction materials to be used for plant components. The test apparatus is shown in Figure 3 and is designed to fit inside an 8" ID X 25" long electric furnace. The apparatus will have DSD temperature - compensating quick-disconnect type connections at each end to facilitate loading, unloading and internal inspection.

While it is recognized that corrosion may be accelerated by high fluid velocities, it is considered premature at this time to propose a pumped circulating loop. However, the test apparatus is designed to cause a general circulation of the melt and thus the test coupons will not be in a completely stagnant environment. Since contamination of the molten salt by ash, sulfur and other constituents of the coal may significantly affect the corrosivity of the melt, it will be necessary to conduct tests with contaminated, as well as pure, melts. The types and extent of the contaminants will have to be determined from further process studies.

Corrosion data from prior pilot plant work with molten salt yielded promising results on some alloys, as follows (231 hours of exposure):

Material	Composition	Inches/Year
Incoloy 800	20 Cr - 33 Ni	0.00
AISI 310	25 Cr - 20 Ni	0.01
50/50 Alloy	50 Cr - 50 Ni	0.01
AISI 309	25 Cr - 12 Ni	0.02

On the basis of these results, the above test apparatus is being constructed from Incoloy 800. The above listed alloys, and other corrosion-resistant, high-temperature alloys will be checked out for suitability with this environmental test apparatus.

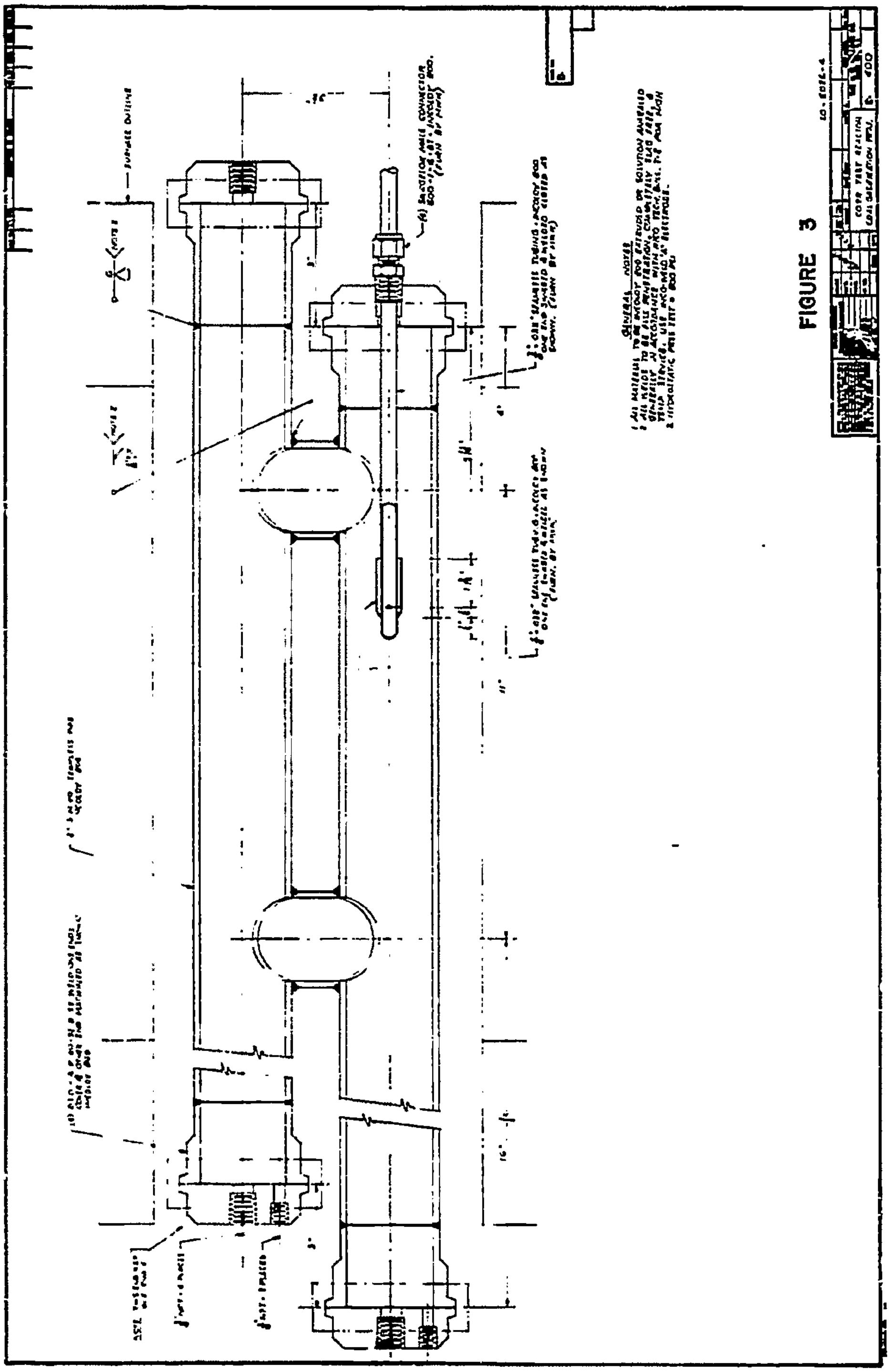


FIGURE 3

In considering material suitable for industrial plant application, it is necessary to give attention to welded joints, since the weld metal may not be equal in corrosion resistance to the parent metal. For example, Incoloy 800 is generally welded with Inco-weld "A" electrodes, but in some environments better corrosion resistance is obtained if AISI type 312 or 310 electrodes are used. Accordingly, in addition to testing plain coupons, test samples made by welding two half-coupons together will be used. Another practical problem worthy of attention is the determination of the type of joint connection suitable for molten salt service. The test apparatus will permit an appraisal of the DSD, metallic O-ring joint, in this environment.

In addition to metal alloys, refractory materials for vessel linings are also being investigated. Major refractory manufacturers have been contacted and test samples of commercially available refractories considered suitable for this service will be obtained and evaluated.

B. Coal Feeding Mechanism for Bench Scale Experimental Work

Methods of controlling the very low flow of coal into a bench scale set-up are being studied. Two schemes are being pursued, both relying on intermittent, rather than continuous, feed. Figure 4 shows a device which intermittently feeds spherical slugs by action of a perforated rotating plate. Figure 5 shows a design utilizing an intermediate chamber between the storage hopper and the reactor feed tube. This chamber alternately communicates between the hopper and the feed tube by proper sequencing of the pinch-type valves. By this action discrete quantities of coal are periodically fed to the hopper. For tests performed at pressures from atmospheric to about 120 psig, the valves and hopper will be maintained at a temperature above the dew point so that the pulverized coal should flow freely. For tests run above 120 psig, special elastomers for the valve elements will have to be considered or a condensate removing device will have to be placed between the reactor and the lower valve.

Conventional feeding devices such as the star feeder and the screw conveyor have been considered, but past experience at Kellogg with these devices have shown them to be unsuitable and unreliable for very low feed rates.

FIG. 4 PLATE-TYPE FEEDER

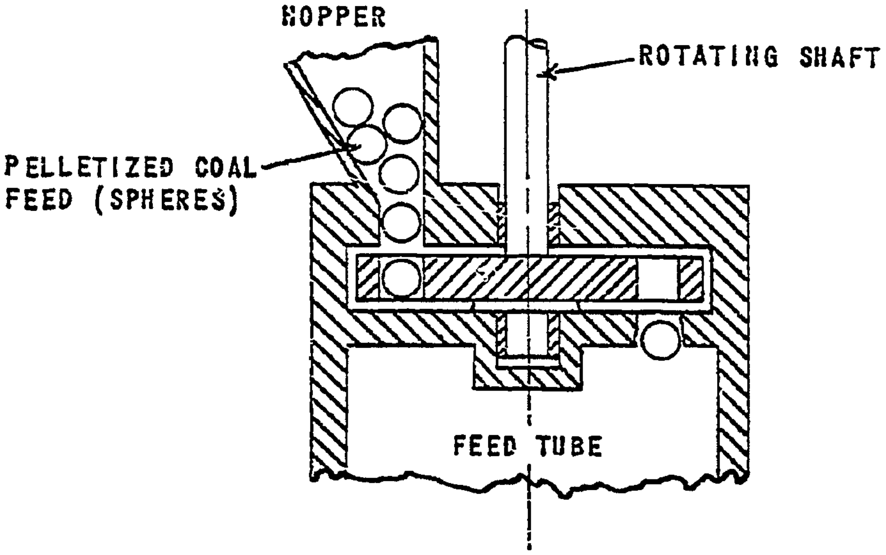
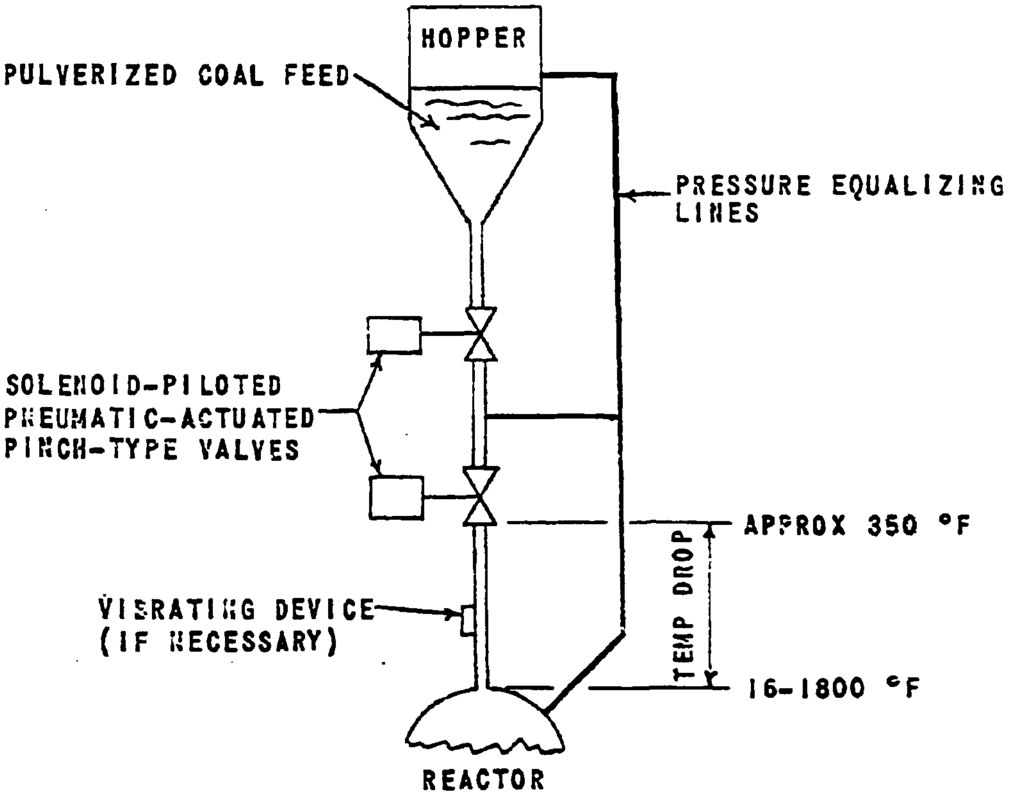


FIG. 5 GRAVITY TYPE FEEDER



V. MANPOWER AND COST ESTIMATE

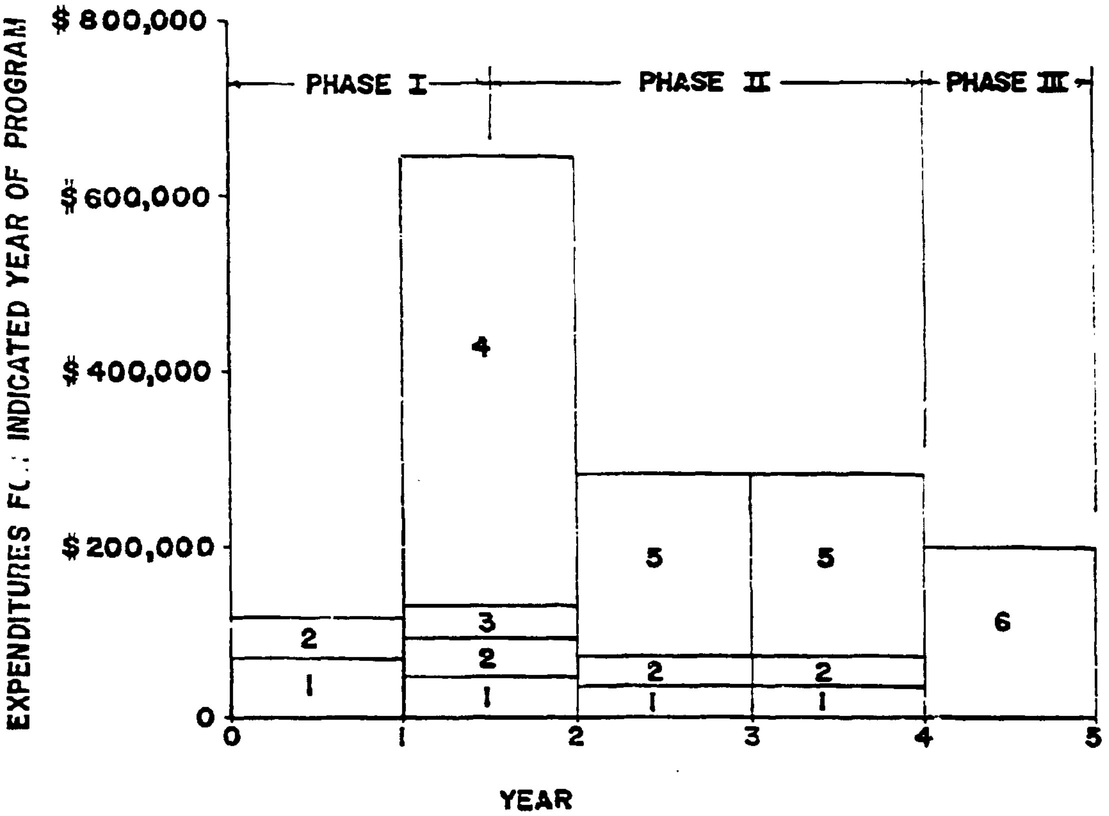
Figure 6 shows a breakdown of development costs excluding fee and G & A. The three phases will cover a period of five years. Phase I will be completed in 18 months. The second half of the second year pilot plant construction will increase cost to over $600,000. The third and fourth years will be primarily concerned with pilot plant operations. The fifth year will be devoted to commercial projection studies.

Figures 7 and 8 show the projected manpower breakdown for Phase I. It can be seen that a six-man effort has been reached in August. A seven-man effort will be attained in September and will continue until the end of Phase I.

Figures 9 and 10 show expenditures and cost estimates for Phase I. Through August the expenditure was $21,597.41 not including fee and G & A. This represents 10% of the estimated development cost for Phase I. It is estimated that about $14,000 will be spent during September. By the end of 1964 it is estimated that $67,000 will be spent. This represents approximately 31% of Phase I.

FIGURE 6
KELLOGG GASIFICATION PROCESS
ESTIMATED ANNUAL DEVELOPMENT COSTS

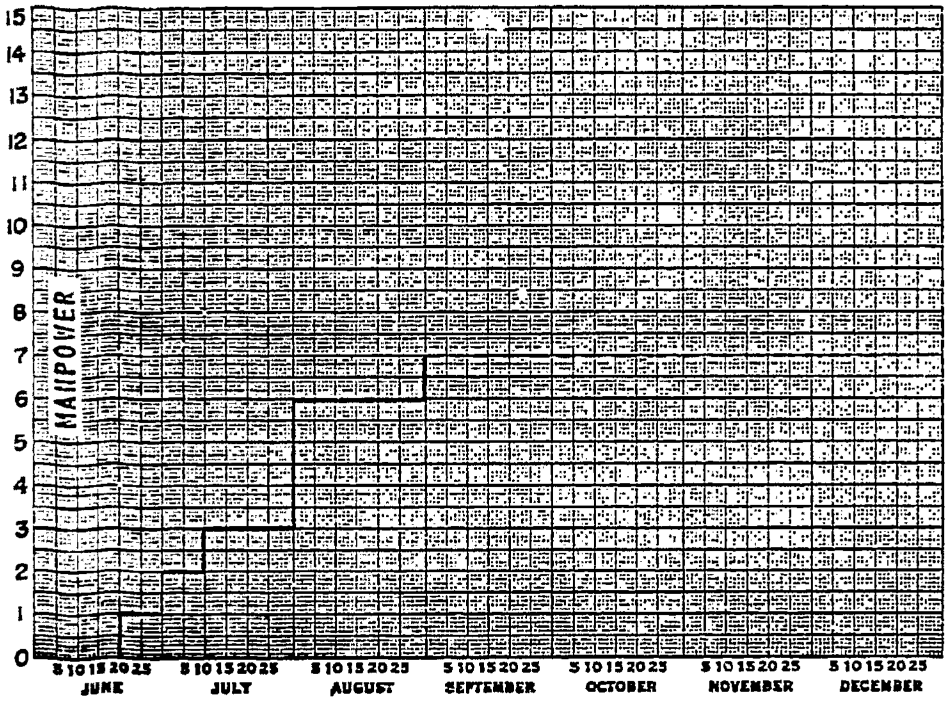
(EXCLUDING FEE AND G & A)



KEY

1 CHEMICAL ENGINEERING DEVELOPMENT
2 EXPERIMENTAL WORK
3 PILOT PLANT DESIGN
4 PILOT PLANT CONSTRUCTION
5 PILOT PLANT OPERATION AND MAINTENANCE
6 COMMERCIAL PROJECTION STUDIES

FIGURE 7
MANPOWER FOR PHASE I
1964



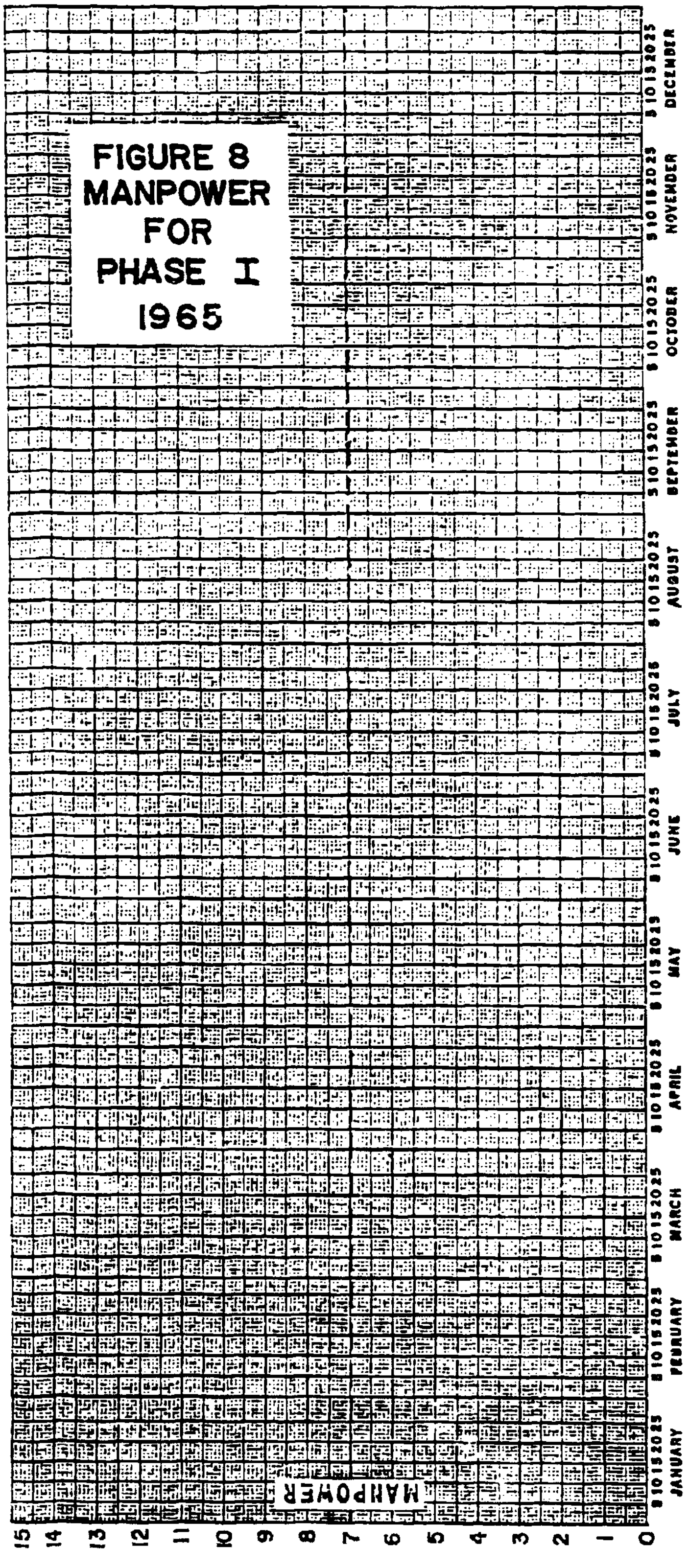
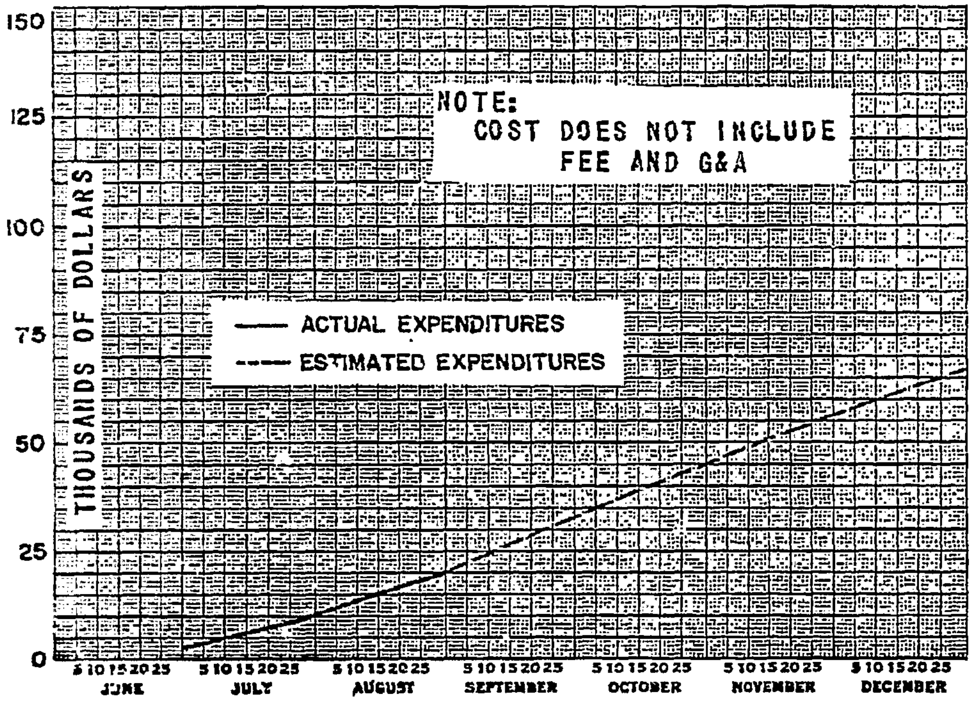


FIGURE 8
MANPOWER
FOR
PHASE I
1965

FIGURE 9
COST ESTIMATE FOR PHASE I
1964



NOTE:
COST DOES NOT INCLUDE
FEE AND G&A

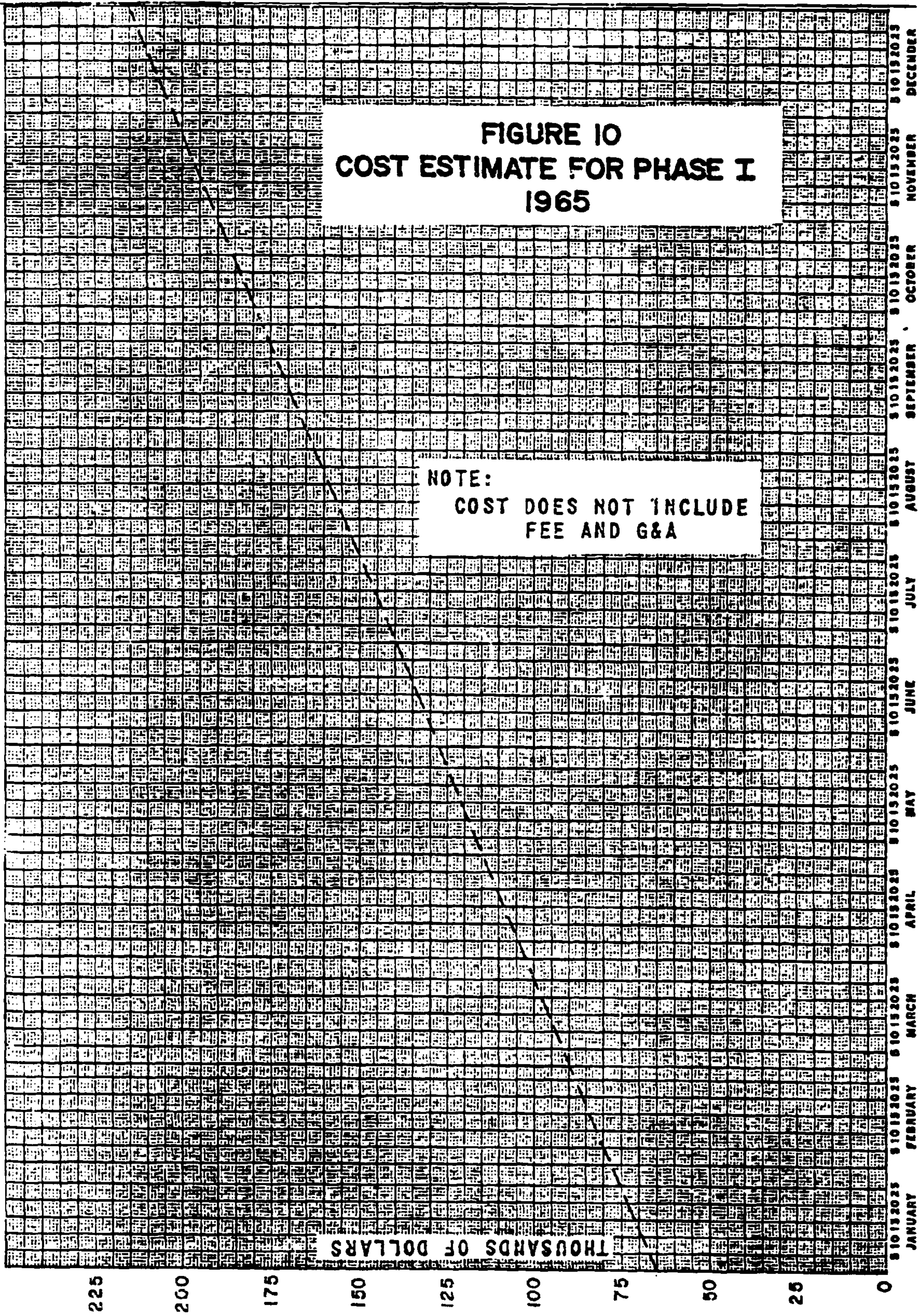


FIGURE 10
COST ESTIMATE FOR PHASE I
1965

NOTE:
COST DOES NOT INCLUDE
FEE AND G&A

MWK-MPR-2

RESEARCH AND DEVELOPMENT DEPARTMENT

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

September 30, 1964

Progress Report No. 2

APPROVED:

Project Manager

Director

Manager
Research and Development

CONTENTS

I. INTRODUCTION

Equipment for the gasification rate and material of construction tests designed during the previous month was placed on order. It is hoped that this equipment will be in operation next month.

Pending arrival and commissioning of this equipment, work has continued on process development studies, bench-scale experimentation on physical property determinations and on procurement of corrosion test coupons. Each of these areas are discussed below.

II. PROCESS DEVELOPMENT

A. Accomplishments

1. Process Flowsheet Study

The study of alternative process flowsheets for the gasification section of the pipeline gas plant is proceeding. The purpose of the study is to further narrow the range of operating conditions and processing alternatives that must be investigated experimentally. The following variables are being considered:

a. type of coal

b. temperature

c. steam/carbon ratio

d. pressure

e. superficial gas velocity

f. method of heat supply

g. methane content of gas

The study will include preliminary process design and equipment sizing for each alternative flowsheet, followed by an approximate estimate of investment and operating costs. Selection of the most attractive schemes will be based on economic potential and a consideration of possible operating difficulties.

2. Methane Synthesis

The technology of catalytic methane synthesis has been reviewed for the purpose of choosing the optimum methanation scheme for all future flowsheets. The final selection will be made from among the following systems:

a. Kellogg transport reactor

b. Fixed fluidized-bed reactor (1, 2)

c. Dual-reactor, hot-gas-recycle system (3, 4)

d. Tube-wall reactor (5)

Process designs have been completed for the four systems and cost estimates are now in progress. The final choice will be based on stage of development, economic attractiveness, and potential for future improvements.

3. Gas Purification

A study is now underway to evaluate various gas purification schemes for the purpose of selecting the optimum system for each of the end products under consideration (pipeline gas, hydrogen, synthesis gas, and transport gas). The following regenerable solvent processes are being considered:

a. Hot potassium carbonate

b. Monoethanolamine

c. Fluor (propylene carbonate)

d. Vetrocoke (arsenic-promoted K_2CO_3)

e. Catacarb (organic-promoted K_2CO_3)

f. Sulfinol (sulfolane)

g. Rectisol (refrigerated methanol)

These solvent processes will be combined with iron oxide and activated carbon contacting steps as required to reduce concentrations of carbon dioxide and sulfur compounds to acceptable levels.

It is expected that preliminary evaluations coupled with literature information will permit reduction of the number of possible combinations to a manageable level. Estimated investment and operating costs obtained from process proprietors or calculated on the basis of Kellogg designs will facilitate selection of the optimum systems.

B. Projections

1. Process Flowsheet Studies

These studies will be continued. As soon as it becomes apparent which one or two of the many schemes being considered appears most promising, that system will be subjected to more detailed design and estimating work.

2. Methane Synthesis

The comparison of alternative methane synthesis processes will be completed and the optimum one will be chosen for inclusion in all future flowsheets producing pipeline gas. The work carried out under a NASA contract (6), and brought to our attention by the OCR Contract Officer, will be investigated.

3. Gas Purification

The evaluation of gas purification processes will continue, with emphasis on the production of pipeline gas. Information will be solicited from several process proprietors (Fluor, Shell, Lurgi) for the specific gas compositions and flow rates encountered. Hopefully, the initial screening will simplify the subsequent task of choosing the best purification train for producing hydrogen and synthesis gas.

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6. Rosenberg, S. D., G. A. Guter, F. E. Miller, and G. R. Jameson, "Catalytic Reduction of Carbon Monoxide with Hydrogen", NASA Contractor Report CR-57.

[illegible]

The [illegible] of ash-Na$_2$CO$_3$ mixtures has been studied. [illegible] anthracite ash-Na$_2$CO$_3$ mixture [illegible] The pouring point decreased [illegible] from [illegible]°F for pure soda [illegible] 60 parts of ash per 100 parts [illegible] mixtures, however, [illegible] At 1800°F a mixture of [illegible] parts of [illegible] parts of Na$_2$CO$_3$ is so viscous that it will not pour from a crucible.

Pouring point determinations were also made on various bituminous coal ash-Na$_2$CO$_3$ mixtures. The results are shown in Figure 2. The viscosity of these mixtures qualitatively increased more rapidly with increase in ash content than did the anthracite ash mixtures. At 1800°F the viscosity of a 40 parts bituminous coal ash mixture is approximately the same as a 60 parts anthracite ash mixture.

A number of water leaching tests have been made to determine the ease of sodium recovery from various ash containing melts. The procedure used consisted of placing 10 grams of pulverized melt in a 400 ml beaker and adding 200 ml of distilled water. The mixture was then boiled on a hot plate for times varying from 5 to 120 minutes with water makeup as needed. After boiling the mixture was vacuum filtered and the filtrate, residue and a sample of the original melt were sent to the analytical laboratory for sodium analyses. Results of the analyses have not yet been received. A preliminary idea of the recovery can be obtained, however, from the quantities of residue obtained. Plots of residues versus extraction time are given in Figures 3 through 8. It will be seen that the water soluble portions are very quickly (within 5 minutes) leached out of even coarsely ground melt and that the quantity of residue tends to be just slightly more than the quantity of ash added. When complete analyses are obtained, sodium weight balances will be made for each test. Nevertheless, the preliminary data indicate that recovery of sodium carbonate by leaching it from ash is probably feasible.

A portable viscosimeter is on order and ash-carbonate viscosity tests will be made as soon as it is received.

Samples of two North Dakota lignites have been received. A quantity of lignite ash is now being accumulated for future tests.

Melting points of lignite ash/Na_2CO_3 and subbituminous ash/Na_2CO_3 will be obtained.

The 2-inch Inconel gasification reactor has been received. Coal gasification work will begin shortly.

FIGURE I
MELTING POINT OF ANTHRACITE ASH IN SODIUM CARBONATE

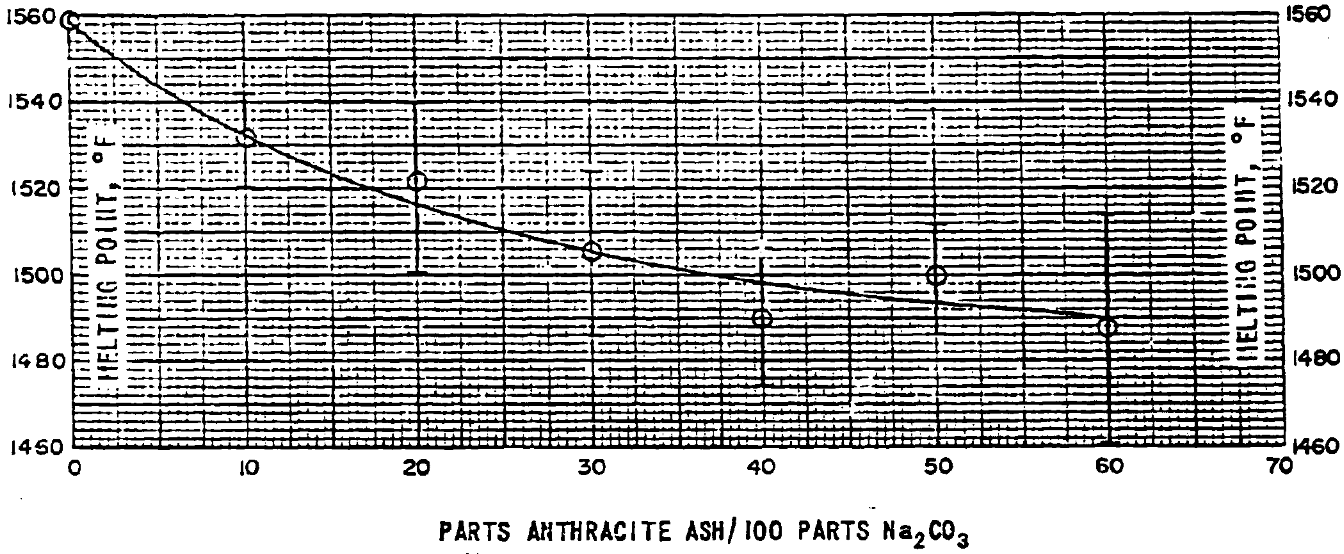


FIGURE 2
MELTING POINT OF BITUMINOUS ASH IN SODIUM CARBONATE

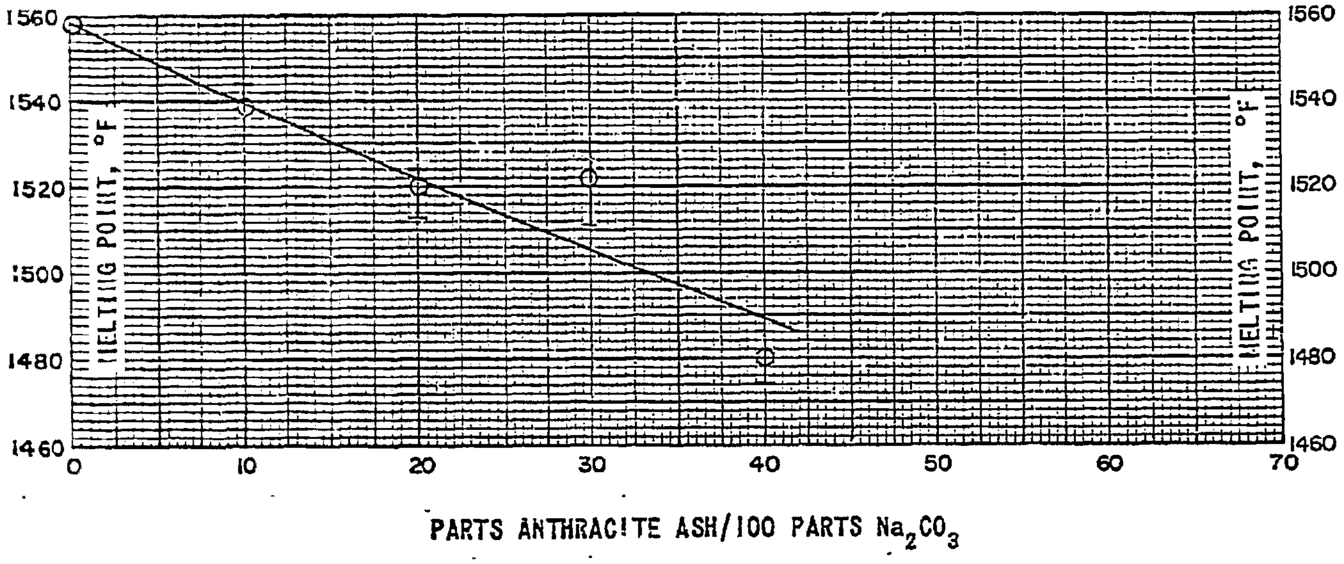
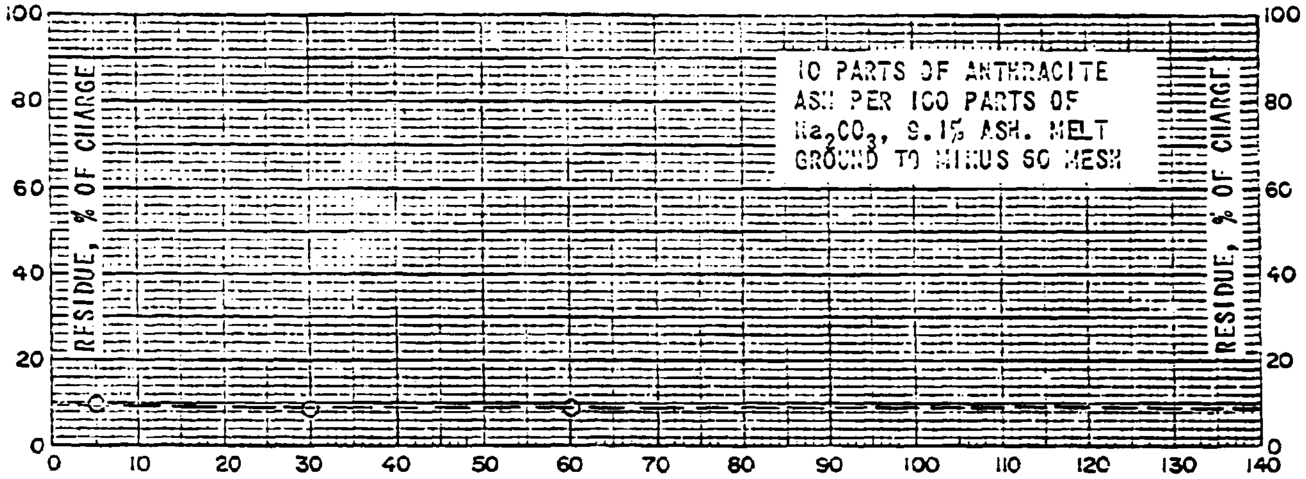


FIGURE 3
WATER EXTRACTION OF ASH-CARBONATE AT 100 °C



EXTRACTION TIME, MINUTES

FIGURE 4
WATER EXTRACTION OF ASH-CARBONATE AT 100 °C

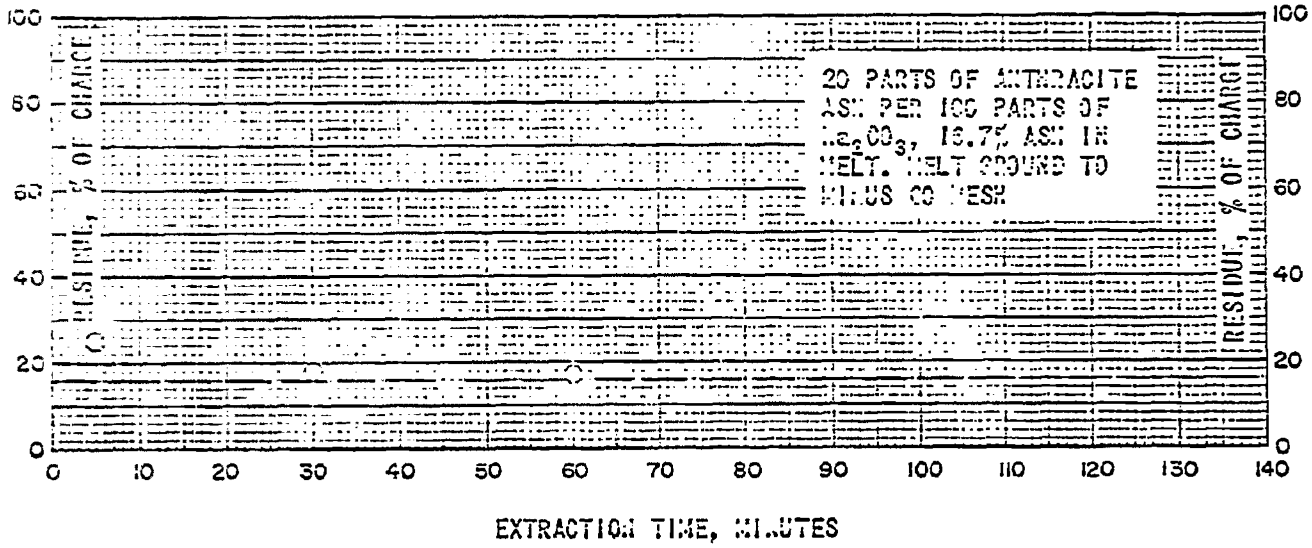


FIGURE 5
WATER EXTRACTION OF ASH-CARBONATE AT 100 °C

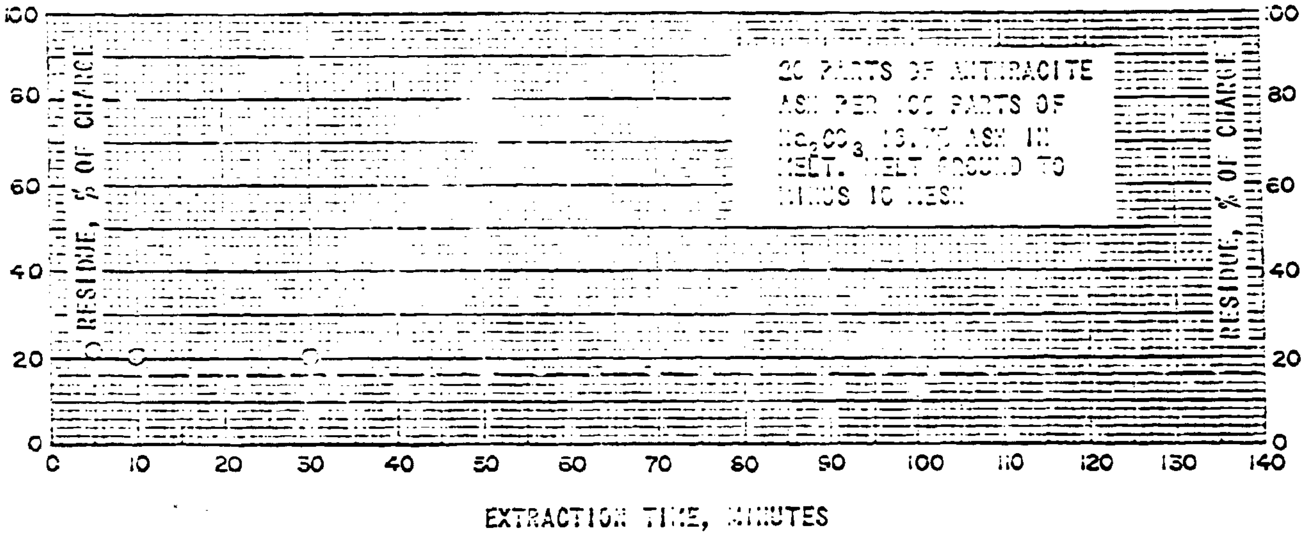


FIGURE 6
WATER EXTRACTION OF ASH-CARBONATE AT 100 °C

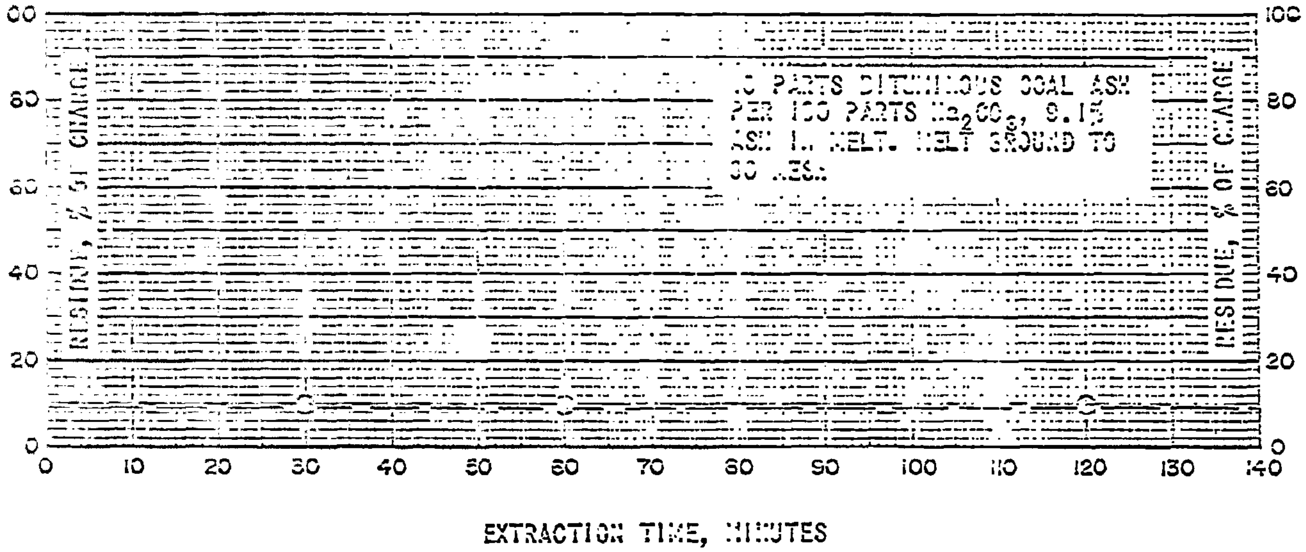


FIGURE 7
WATER EXTRACTION OF ASH - CARBONATE AT 100 °C

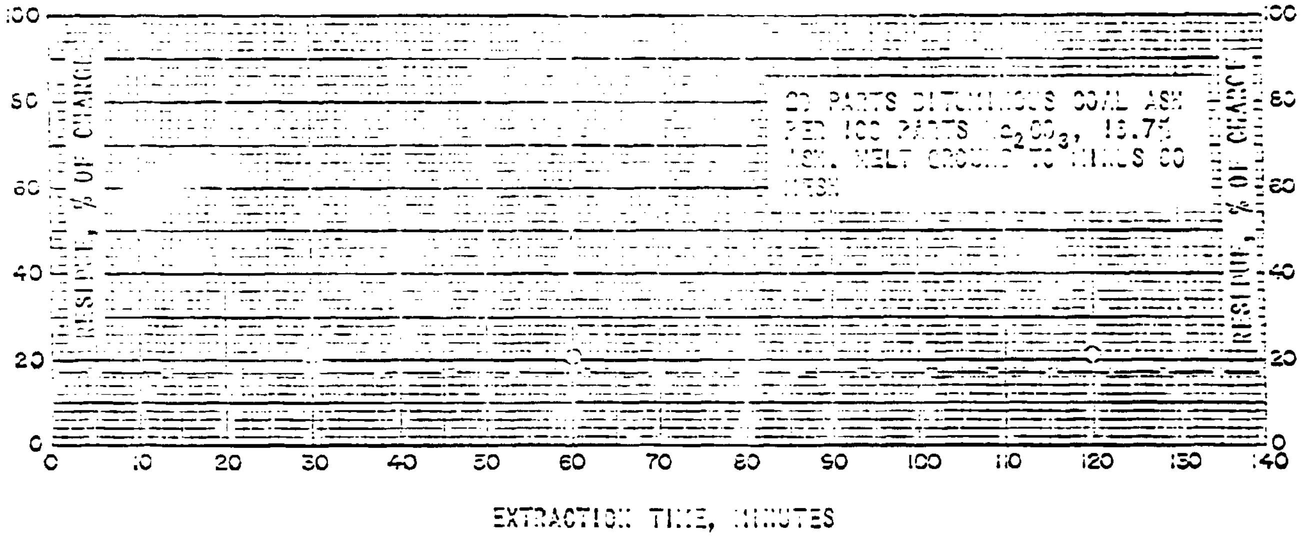
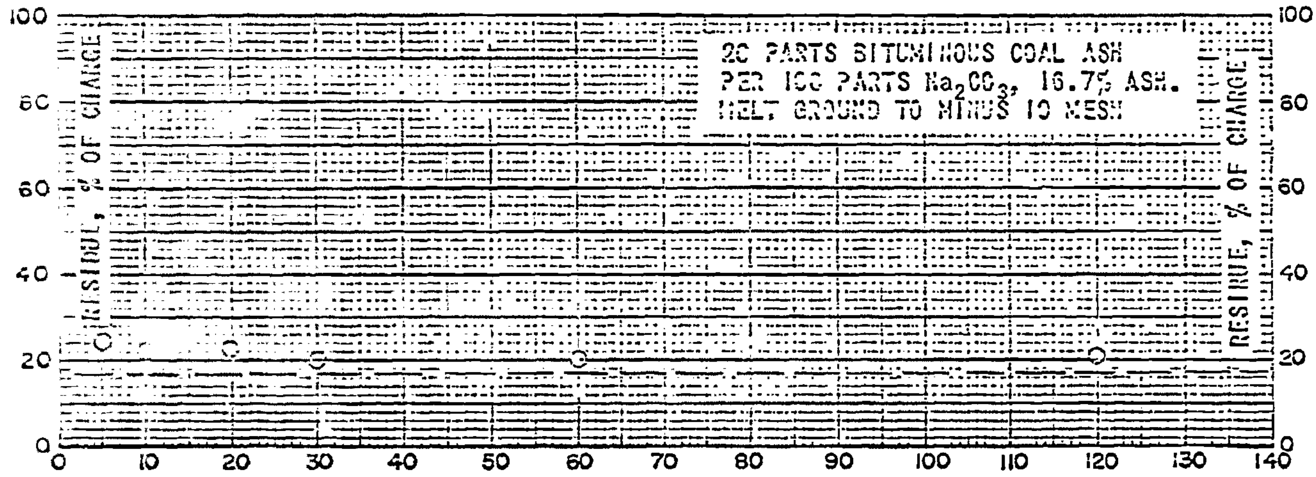


FIGURE 8
WATER EXTRACTION OF ASH-CARBONATE AT 100 °C



EXTRACTION TIME, MINUTES

IV. MECHANICAL DEVELOPMENT

A. Environmental Testing of High-Temperature Materials

Test samples of high-temperature, corrosion resistant alloys have been procured from three independent sources and will be subjected to our corrosion resistance test. The alloys are as follows:

International Nickel Company

Inconel 600
Inconel 702
Incoloy 800
Incoloy 804
AISI Type 309
AISI Type 310
50-50 Alloy (50% Nickel - 50% Chrome)

Stellite Division - Union Carbide

Hastelloy B
Hastelloy C
Multimet
Haynes Alloy 25

Rolled Alloys, Inc.

RA 309 (Rolled Alloy's equivalent of AISI Type Stainless Steel)
RA 310
RA 330
RA 333
Rayonel 600 (RA's equivalent of Inconel 600)

In addition to plain coupons all of these alloys will be tested with welds made in accordance with the suppliers' recommended procedure for high-temperature corrosion resistance.

Test samples of refractory materials are being supplied by three major manufacturers. The refractories are as follows:

Carborundum Company

Mullfrax W - fused mullite grain
Mullfrax H
Zircofrax 0 - zirconium oxide
Magnafrax
KT Silicon Carbide

Harbison-Walker Refractories Company

Chromex B
Harklase
Harbide
Korundal XD
Varnon BF

General Refractories

Chrome Magnesite
Magnesite Chrome

Figure 9 is a schematic diagram of the test set-up. The specimens will be immersed in the salt bath, maintained at 1800°F, and remain there for a total of 500 hours. The test will be interrupted at the end of 250 hours so that the corrosion rate at the intermediate point can also be determined. Thus, having two corrosion rate points, the corrosion rate change with time can be noted.

The corrosion rate will be determined on the basis of two observations -- weight change and linear dimension change. The corrosion rate based on weight loss will be calculated by the use of the following formula:

$$\text{Corrosion Rate} = \frac{\Delta W}{S \times t} \times \frac{1}{\gamma}$$

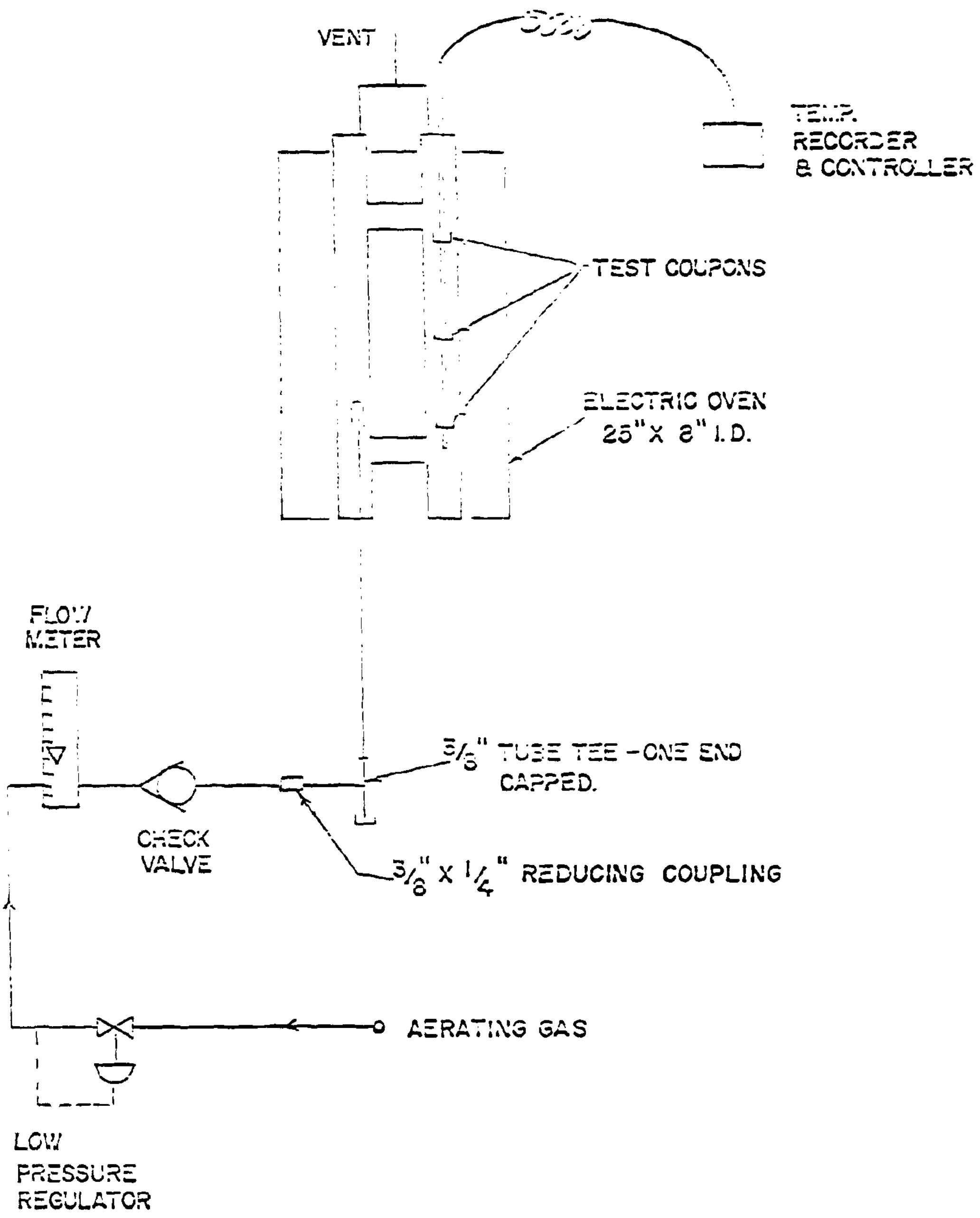
ΔW = loss of weight

S = surface area

t = time of test

γ = density of material

FIGURE 9
CORROSION TEST EQUIPMENT
(SCHEMATIC)



The corrosion rate based on change in linear dimension will be determined by the reduction of pregauged thicknesses on the specimen as measured with a micrometer. To supplement this change-of-dimension determination, it is intended to microscopically examine sections through the specimens to observe if any intergranular corrosion has taken place.

B. Coal Feeding Mechanism for Experimental Work

Of the two schemes described in the last report, the gravity type feeder system is to be investigated first. Two 1/4-inch Tube-O-Matic valves (Airmatic Valve, Inc.) have been placed on order and will be checked out for operability and reproducibility in handling and controlling a low flow rate of pulverized coal. It is planned to set the valving system up with a motorized switching arrangement and to calibrate the powder feed rate for various cycling frequencies.

V. MANPOWER AND COST ESTIMATES

Figure 10 shows the projected manpower breakdown for Phase I for 1964 as well as the actual effort that was attained. It can be seen that a six-man effort was maintained during September. It is hoped that a seven-man effort can be attained in October when the gasification rate and corrosion test equipment is placed on stream.

Figure 11 shows the expenditures during September as well as the cost estimates for Phase I for 1964. For the month of September, $11,000 was expended not including fee and G. & A. The total expenditures through September were $32,600. This represents approximately 15.2% of Phase I.

FIGURE 10
MANPOWER FOR PHASE II
1954

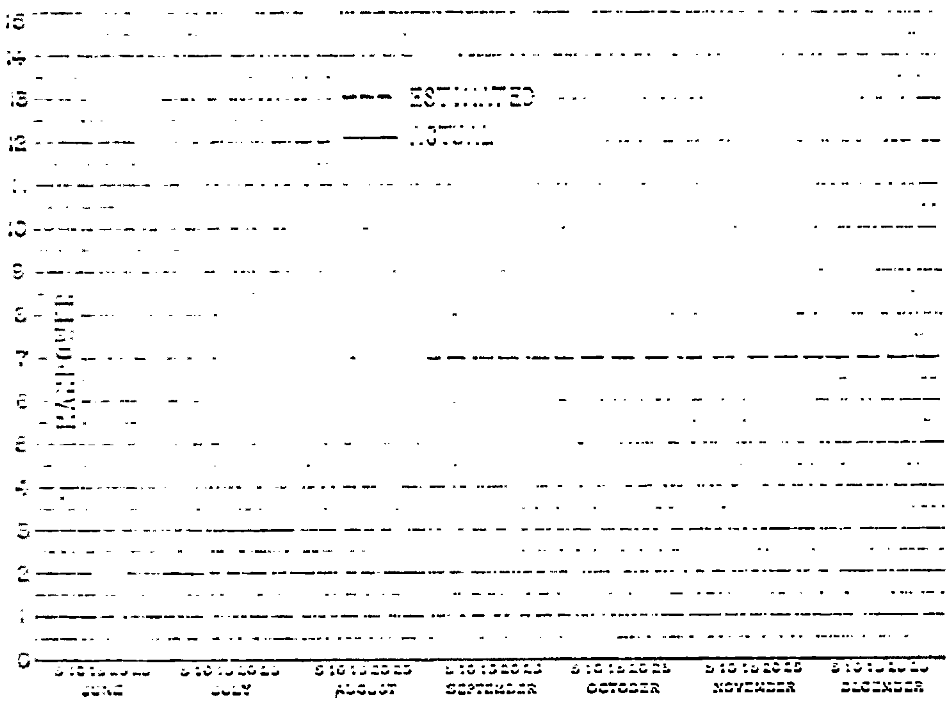
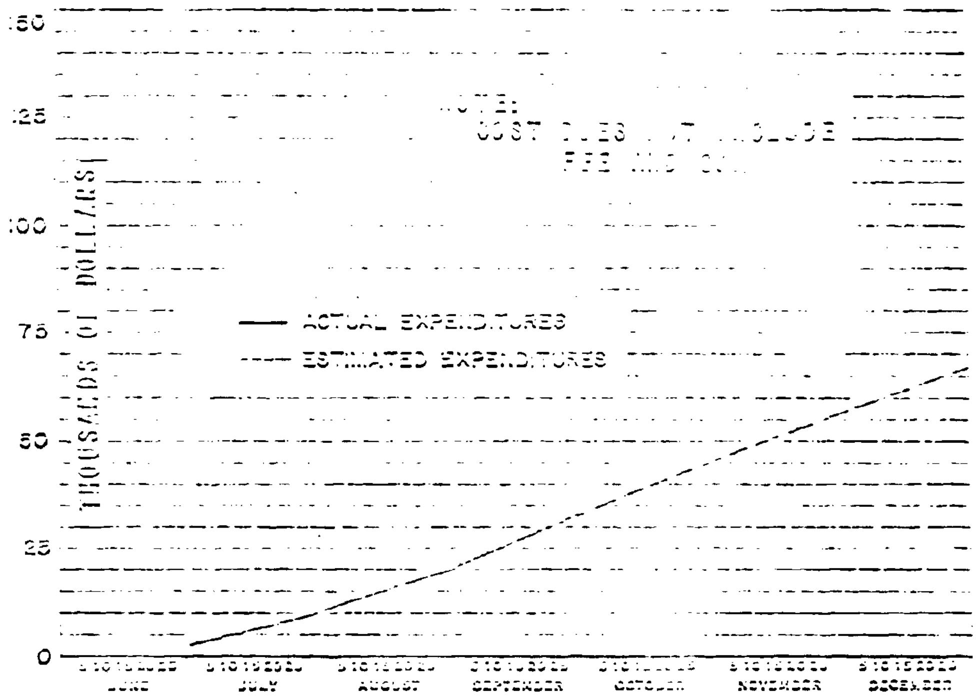


FIGURE II
COST ESTIMATE FOR PHASE II
1964



MWK-MPR-3

RESEARCH AND DEVELOPMENT DEPARTMENT — M KELLOGG W

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

October 31, 1964

Progress Report No. 3

APPROVED:

Project Manager

Directer
Chemical Engineering Development

Manager
Research and Development

CONTENTS

I. INTRODUCTION

The equipment for the gasification rate tests has been received and is now being commissioned.

Work was continued on process development studies, bench-scale experimentation on physical property determinations, and the coal feeding mechanism for bench-scale experimental work. Each of these areas are discussed below.

II. PROCESS DEVELOPMENT

A. Accomplishments

1. Process Flowsheet Studies

The continuing study of alternative process flowsheets for the gasification section of the pipeline gas plant has the objective of narrowing the range of operating conditions and processing alternatives that must be investigated experimentally. Some recent results of these studies are presented in Table I. These results are based on preliminary process designs of the gasification section, reasonably complete material and energy balances, and very approximate estimates of plant cost.

Several features of Table I merit elaboration:

a. Coal ash is allowed to accumulate in the molten salt catalyst to the level of 20% by weight. The ash is removed by quenching a slipstream of melt with water to dissolve the Na_2CO_3, filtering out the ash particles, and recovering Na_2CO_3 from solution by one of several schemes to be mentioned below. Recovery of Na_2CO_3 is assumed to be 95%. Experimental results to date have indicated that a 20% mixture of ash in melt will probably have acceptable fluid properties and that water quenching of melt is a promising method of separation.

b. Contact time of gas with melt in the gasifier has been set at 10 seconds. This is presently expected to be more than adequate, but the actual requirement must await experimental measurement of gasification rates. Although the rate will vary with different gasifier operating conditions, the contact time has been held constant for all cases in Table I.

c. A range of superficial gas velocities in the gasifier has been considered. Permissible velocity will depend on quality of gas-melt contacting and entrainment of melt experienced; these factors will have to be determined experimentally.

TABLE 1

EVALUATION OF ALTERNATIVE COAL GASIFICATION FLOWSHEETS

Basis: Raw Material: Bituminous coal
Product: Raw synthesis gas equivalent to 250 MM SCFD of pipeline gas
Melt Composition: Na_2CO_3 - 20% coal ash
Method of Contacting in Gasifier: Sparging
Gas-Melt Contact Time: 10 seconds
Method of Na_2CO_3-Ash Separation: Water quench
Operations Included: Coal feeding, gasification, combustion
heat supply, Na_2CO_3-ash separation, gas cooling
(plus compression of synthesis gas to 400 psia in Flowsheet No. 1-E)

Flowsheet Number	Gasifier Operating Conditions				Method of Heat Supply	Gasifier Diameter, ft.	Number of Gasifiers On Stream	Approximate Investment, MM $	Raw Synthesis Gas Production Cost, ¢/MSCF of Pipeline Gas							Flowsheet Number
	Temperature F	Pressure, psia	Steam/Carbon, lb./lb.	Superficial Gas Velocity, ft/sec					Coal at $4/ton	Steam and Cooling Water	Power at 0.7¢/kwh	Labor & Overhead	Na_2CO_3 losses	Maintenance and Fixed Charges at 13% of Investment	Total	
1-A-1	1600	400	2	0.5	Direct Combustion at High Pressure	12	39	50	18.2	5.0	0.9	3.0	1.4	6.6	35.1	1-A-1
1-A-2	↓	↓	↓	1.0	↓	↓	20	46	↓	↓	↓	1.6	↓	6.1	33.2	1-A-2
1-A-3	↓	↓	↓	2.0	↓	↓	10	42	↓	↓	↓	0.9	↓	5.5	31.9	1-A-3
1-B-1	1800	↓	↓	1.0	↓	↓	23	54	18.7	3.3	1.2	1.9	1.5	7.1	33.7	1-B-1
1-B-2	↓	↓	↓	↓	↓	↓	23	55	↓	1.8	1.2	1.9	↓	7.2	32.3	1-B-2
1-B-3	↓	↓	↓	↓	↓	25	5	47	↓	3.3	1.2	0.5	↓	6.2	31.4	1-B-3
1-C	↓	↓	↓	↓	Direct Combustion at Low Pressure	8.5	30	52	↓	(-1.6)	3.8	2.3	↓	6.5	31.6	1-C
1-D	↓	↓	↓	↓	Fired-Tube Heater	12	14	62	↓	(-2.6)	1.3	1.2	1.2	8.1	27.9	1-D
1-E	↓	45	↓	3.0	Direct Combustion at Low Pressure	↓	67	83	↓	(-1.4)	21.6	5.1	1.5	10.9	56.4	1-E
1-F	↓	400	3	1.0	Direct Combustion at High Pressure	↓	30	56	19.0	4.6	1.2	2.3	1.5	7.4	36.0	1-F

d. Three methods of heat supply that were found to be most promising in previous screening studies(1) were evaluated:

(1) Direct combustion of coal in the melt at high pressure (gasifier operating pressure). In this case the melt can be circulated between gasifier and combustion chamber by utilizing a gas lift or the kinetic energy of the entering gas streams. Thus no melt pump is needed. However, it is necessary to compress combustion air to the high pressure and later to expand the flue gas to recover as much energy as possible. The scheme requires, therefore, a large and rather costly compressor-expander (in effect, a gas turbine) and an efficient means of removing entrained melt from the flue gas to protect the expander.

(2) Direct combustion of coal in the melt at low pressure. This scheme avoids air compression, except as required to get through the combustion chamber and heat recovery equipment, but requires a high-head pump for circulating the melt between gasification pressure and combustion pressure.

(3) Circulation of melt through fired-tube heater. While requiring a minimum of air compression, this method needs a melt circulation pump and a metal heat transfer surface capable of withstanding corrosion by the melt at a temperature somewhat higher than that prevailing in the gasifier. Finding a satisfactory material of construction for these heater tubes will pose a major problem.

e. Gasifier diameters of 12 feet, about the largest that can be shop-fabricated and shipped to the site, and 25 feet were considered. Even larger diameters may be feasible, the major limitation probably being the maximum metal wall thickness that can be fabricated in the field. The larger-diameter units are expected to offer economics in both first cost and operating cost.

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(1) Progress Report No. 1, August 31, 1964, page 10.

f. Flowsheets I-C, D, and E show steam credits because the flue gas from combustion need not be expanded to recover power. The energy is used instead to generate steam, and it is assumed in calculating this credit that the steam can be used to advantage elsewhere in the plant. This can be verified only by a complete plant design and overall energy balance.

Some conclusions may be drawn from Table I:

a. The gasifier must operate at high pressure, in the range of 400 psia. Case I-E shows that the cost of compressing synthesis gas generated at low pressure up to a level satisfactory for synthesis of methane is prohibitive.

b. If satisfactory materials of construction can be found, the best method of supplying heat is the fired-tube heater. Case I-D offers the lowest gas production cost, which may be further reduced by almost 2¢/MSCF by using fewer, large-diameter gasifiers.

c. The second-best method of heat supply is direct combustion in the melt at low pressure. Case I-C will be better than I-B-3 if given the advantage of larger gasifiers.

d. Severe investment penalties will be incurred if allowable superficial gas velocity in the gasifier falls below about 0.5 feet per second.

e. Increasing steam/carbon ratio from 2 to 3 increases product gas cost significantly (Case I-F vs. Case I-A-2). The lowest ratio consistent with satisfactory gasification rates should be employed.

f. Increasing temperature of gasification has little effect on gas cost (Case I-B-1 vs. I-A-2), neglecting the fact that materials of construction will be more severely tested at the higher temperature. If rate of gasification is markedly improved by an increase in temperature or if melt handling becomes much easier, such a change may be advantageous.

g. Efficient utilization of heat by overall integration of the process is important, as indicated by the significant steam credits in cases I-C, D, & E.

Utilizing the figures for Case 1-D of Table I and the results of previous Kellogg designs for converting coal into pipeline gas, the total production cost of pipeline gas can be estimated. These figures are presented in Table II. Even though costs may be expected to change as more precise plant designs are developed, it is evident that the target gas production cost, 50¢/MSCF, is within reach.

2. Methane Synthesis

The status of the methane synthesis evaluation is virtually unchanged. Choice of the optimum methanation system is awaiting cost estimates for the four alternatives that have been designed.

3. Gas Purification

Evaluation of gas purification processes is continuing. Process designs have been completed for monoethanolamine and Vetrocoke preparatory to estimating plant costs. Design and cost information have been requested from Fluor, Shell, and Lurgi to permit a comparison with their purification processes (Fluor Solvent CO_2 Removal, Sulfinol, and Rectisol, respectively).

4. Na_2CO_3 Recovery

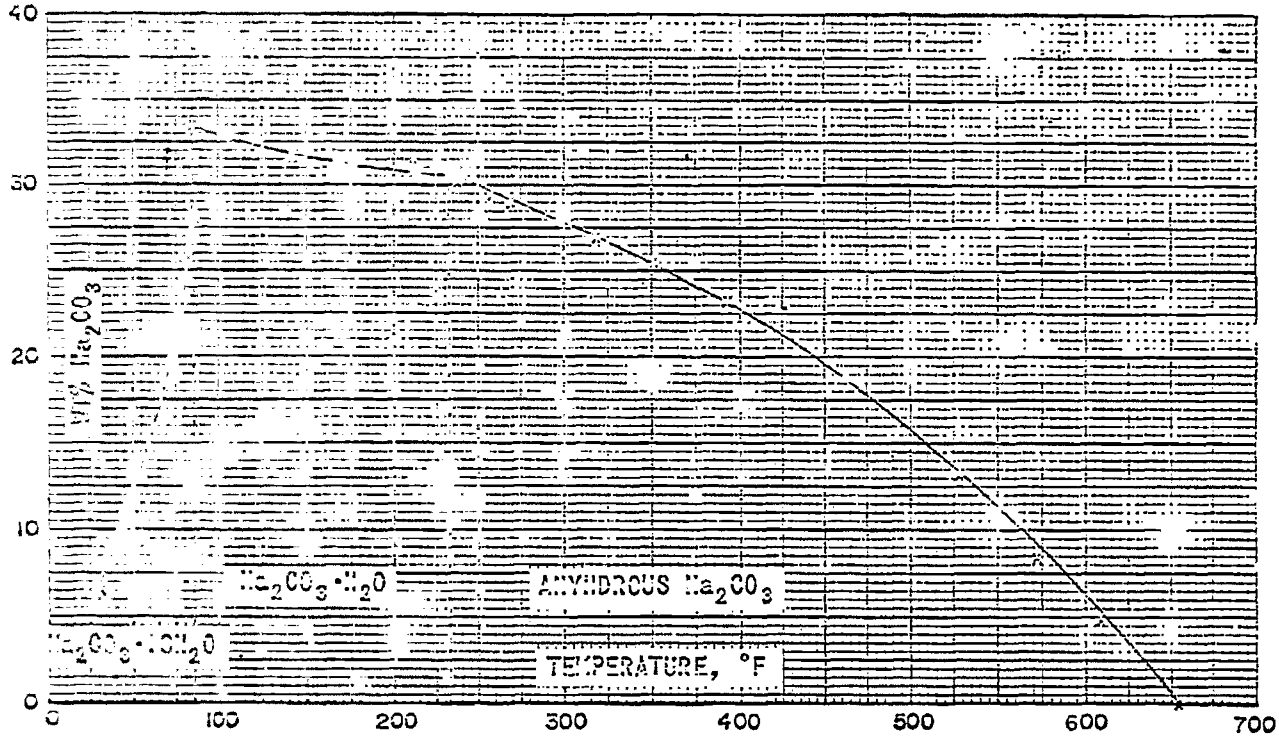
The currently-favored scheme for separating coal ash from molten sodium carbonate catalyst is to quench a slipstream of melt from the gasifier with water to dissolve the Na_2CO_3, then filter off the ash constituents, and finally recover the Na_2CO_3 from solution. The best method of recovering the salt from aqueous solution is not obvious, although the solubility curve for Na_2CO_3 presented in Figure I suggests two possibilities:

a. Cooling to temperatures below about 80°F to crystallize the decahydrate.

b. Heating to high temperatures (at high pressures) to crystallize anhydrous Na_2CO_3.

These two routes, along with evaporative crystallization, are being investigated to determine likely operating problems associated with each and to estimate costs. The most attractive Na_2CO_3 recovery scheme will then be incorporated into the flowsheet studies previously discussed.

FIGURE I
SOLUBILITY OF SODIUM CARBONATE
IN WATER



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1. *"Handbook of Chemistry and Physics"*, 40th Ed., p. 1701, Chemical Rubber Publishing Co., (1958-1959).
2. Waldeck, W.F., Lynn, G., and Hill, A.E., *J. Am. Chem. Soc.*, 54. 928 (1932).

TABLE II

PROJECTED PIPELINE GAS PRODUCTION COST

Basis:
Bituminous coal at $4/ton
250 MM SCFD of pipeline gas
Flowsheet No. 1-D
Maintenance and fixed charges at 12% of investment

Operation	Pipeline Gas Production Cost ¢/MSCF
Coal storage & preparation	2*
Gasification (Table I)	28
Water - gas shift & gas purification	10*
Methanation & product gas compression	2*
Total	42

---

*Figures based on prior Kellogg plant designs.

B. Projections

1. Flowsheet Studies

The evaluation of alternative process flowsheets will be continued, utilizing the conclusions of screening studies made to date. Specifically, future flowsheets will incorporate gasification at high pressure, heat supply by either fired-tube heater or direct combustion at low pressure, and ash removal by water quenching. Within this context the effect of coal gasification rate, of methane content of raw gas, and of degree to which ash is permitted to accumulate in the melt will be studied. By means of more complete design, more precise material and energy balances, and more detailed cost estimates, plus a careful evaluation of experimental data as it becomes available, the optimum combination of operating conditions for the gasification section will be more clearly delineated.

2. Methane Synthesis

The comparison of alternative methane synthesis processes will be completed, and the optimum one will be chosen for inclusion in all future flowsheets producing pipeline gas.

3. Gas Purification

The evaluation of gas purification processes will be continued as information requested on the several proprietary processes is received. Plant costs will be estimated for those processes designed by Kellogg.

4. Na_2CO_3 Recovery

Costs will be estimated for recovering sodium carbonate from aqueous solution using the several methods proposed. The best scheme, considering both operability and cost, will be incorporated into the flowsheet studies.

III. PROCESS RESEARCH

A. Accomplishments

Melting point determinations of ash-sodium carbonate mixtures were continued.

Melting point determinations were made on South Beulah lignite-sodium carbonate mixtures. The mixtures were melted at 1600°F, raised from 1600°F to 1800°F over a two-hour period (to reduce foaming due to gas evolution) and held at 1800°F for 15 minutes. The freezing temperature was then recorded. The results are shown in Figure 2. The results using Elkol subbituminous coal ash-sodium carbonate mixtures are given in Figure 3. With both types of ash, viscosity increased rapidly so that mixtures of 40 parts of ash and 100 parts of carbonate would not pour from the crucible at 1800°F.

At the time that the data reported in Figures 2 and 3 were collected, it was felt that high solubilization of ash was achieved at the heating time and temperature employed since the literature indicates that the reaction rate between the major ash component, SiO_2, and sodium carbonate is very rapid. A few minutes at 1800°F should be sufficient. Initial attempts at exploring the effect of longer reaction time at 1800°F are proceeding. Preliminary results show that further reaction does occur. A sample of Island Creek #27 Bituminous coal ash (9% in carbonate) yielded a 1540°F melting point after 15 minutes reaction time. After 6 hours at 1800°F the melting point is depressed to about 1450°F. Reaction time, melting point relationships are now being developed for several ash-carbonate mixtures.

Proximate and sulfur analyses of a bituminous coal and two lignite samples to be used in bench scale work are shown in Table 3.

Sodium recoveries for the boiling water leach tests initially reported in last month's summary (as weight loss) are shown in Table 4.

Initial attempts have been made to separate the ash from the carbonate by settling. The results are shown in Table 5. While some separation has been achieved, the results have not been particularly successful. It appears that settling might be easy to achieve were it not for the fact that gas, probably CO_2, is continually being liberated in the melt and keeps it agitated.

FIGURE 2
MELTING POINT OF LIGNITE ASH
-
SODIUM CARBONATE

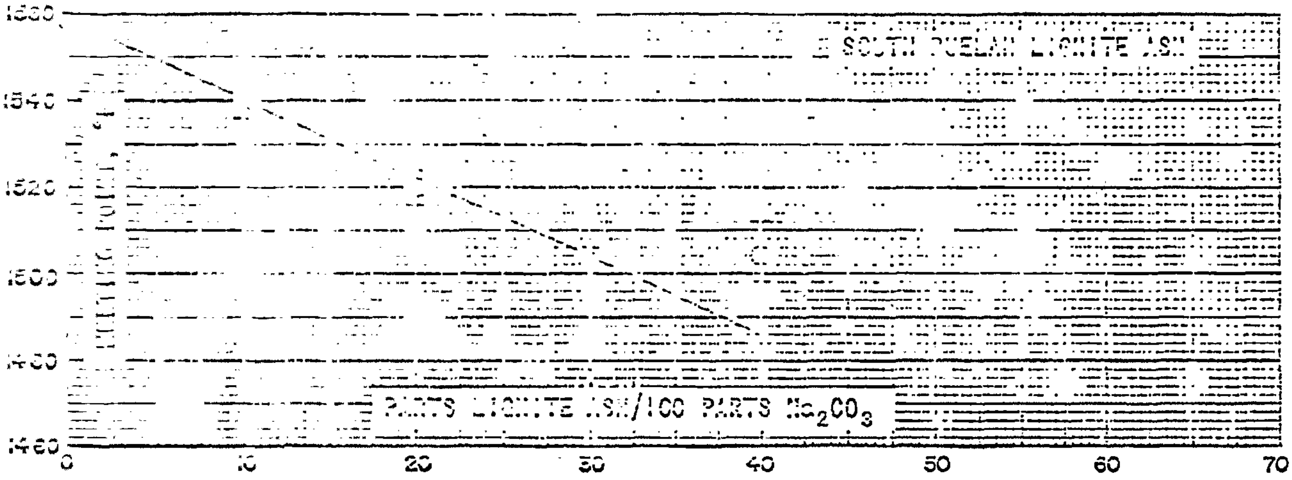


FIGURE 6
MELTING POINT OF SUBBITUMINOUS ASH
IN
SODIUM CARBONATE

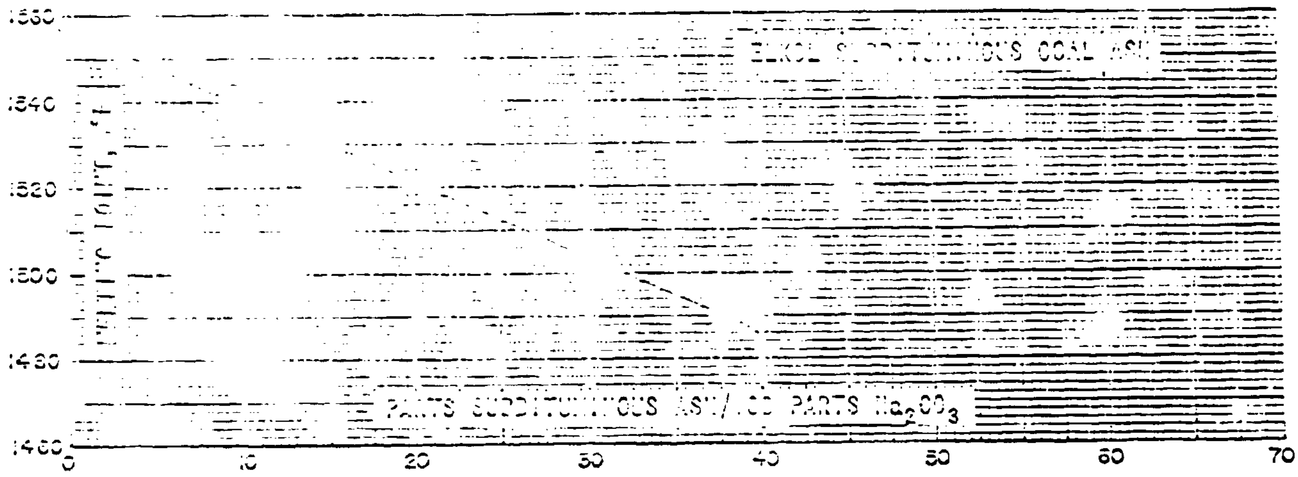


Table 3
PROXIMATE AND SULFUR ANALYSES OF SAMPLES OF BITUMINOUS COAL AND LIGNITE

	Island Creek No. 27 Bituminous Coal	North Beulah Lignite	South Beulah Lignite
Moisture	1.3%	31.7%	31.2%
Volatile Matter	37.3	29.8	30.3
Ash	3.8	6.5	9.0
Fixed Carbon	57.6	32.0	29.5
	100.0	100.0	100.0
Sulfur, as received	0.65%	0.75%	1.17%

TABLE -
RESULTS OF TESTS ON
BOILING WATER LEACHING OF
SODIUM FROM ASH CARBONATE MELTS

Run No.	Source of Ash	Parts of Ash Per 100 Parts of Na_2CO_3	Melt Ground to	Boiling Water Leach Time, minutes	Percent of Sodium Leached From Melt*
4A	Island Creek No. 27 Bituminous Coal	30	-60 mesh	30	88.0
4B	"	"	"	60	93.9
4C	"	"	"	120	93.0
5A	"	10	"	30	97.1
5B	"	"	"	60	97.5
5C	"	"	"	120	97.3
6A	"	20	"	30	94.5
6B	"	"	"	60	93.9
6C	"	"	"	120	93.8
7A	Greenwood Anthracite	10	"	5	98.2
7B	"	"	"	30	96.7
7C	"		"	60	95.7
8A	"	20	"	5	91.0
8B	"	"	"	30	92.7
8C	"	"	"	60	92.1
9A	Island Creek No. 27 Bituminous Coal	20	-10 mesh	30	92.7
9B	"	"	"	60	93.7
9C	"	"	"	120	90.2
10A	"	"	"	5	90.4
10B	"	"	"	10	91.0
10C	"	"	"	20	92.0
11A	Greenwood Anthracite	"	"	5	89.8
11B	"	"	"	10	91.0
11C	"	"	"	30	90.2

* Based on analyses of filtrate and residue. Test consisted of boiling 10 g of pulverized melt for noted time in 200 cc's of water and then vacuum filtering to remove residue.

[illegible]

Test No.	[illegible]	[illegible]	[illegible]	[illegible]
1	20	1 hr	[illegible]	[illegible]
2	10	"	[illegible]	[illegible]
3	10	"	3[illegible]	[illegible] 1/3
4	10	"	3[illegible]	[illegible] 1/3

Note: Test consists of [illegible] at 1000°C, [illegible] to 100°C, filtering, holding at 1150 [illegible], cooling, cutting the metal [illegible] to obtain samples (100°C), [illegible] to -10 [illegible] for 10 minutes, filtering and [illegible] of [illegible].

[illegible]

1. The reactor system for the measurement of gasification rate is essentially completed and work on this phase will begin shortly.

2. An Inconel spindle is being fabricated for the viscosimeter. Viscosity measurements will be made on various melts.

3. The study of the relationship between reaction time and melting point will be continued.

[illegible] TECHNICAL PROGRESS

A. [illegible]

1. [illegible] Materials

Samples of metal alloys and refractories, as listed in the last report, have been prepared for the first run of the corrosion resistance test. The test area is being prepared and the test vessel will be installed when it is received from the fabricator.

2. Coal Feeding Mechanism for Bench-Scale Experimental Work

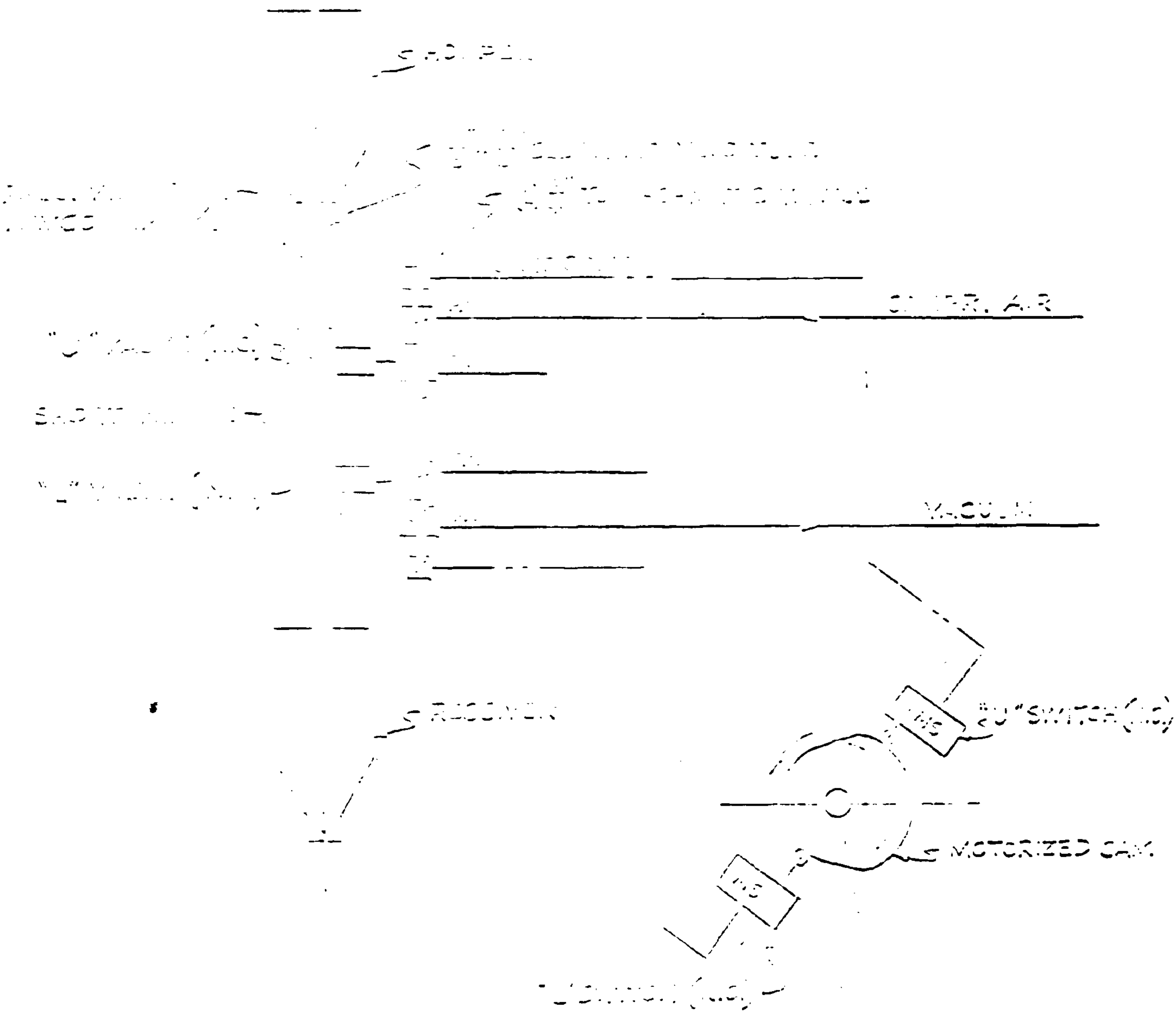
Two Pneu-Matic valves have been procured, set up as shown schematically in Figure 4, and tested for operability and reproducibility in handling and controlling the flow of pulverized coal. As can be seen from Figure 4, the valves arranged in tandem are representative of a gravity flow, lock-chamber-type feeder system. The valves are of the pinch tube type, using Nylon sleeves for the active valve elements. They are pneumatically energized and are controlled by solenoid actuated three-way pilot valves. By properly sequencing the action of the valves, the compartment between the valves functions as a lock-chamber. Since this lock-chamber has a fixed volume, the rate of feeding can be controlled by varying the speed of the motorized cam. Figure 5 shows the valve sequencing and cam details.

The initial test on the feeding system was performed with glass beads (Superbrite 070-5005; 70% -20/+40, 30% -40/+60) as the working medium. This was followed by a test using finely pulverized anthracite coal. The coal powder was analyzed and found to have the following size distribution:

3%	+60
6%	-60/+100
[illegible]	-100/+200
[illegible]	-200/+325
22%	-325

After loading the hopper the material displayed a bridging action and it became evident that the powder could not be made to flow without assistance. After installing a pneumatic vibrator on the system, the powder flowed uniformly down the feeder tube. Figures 6 and 7 are the

[illegible] MECHANISM



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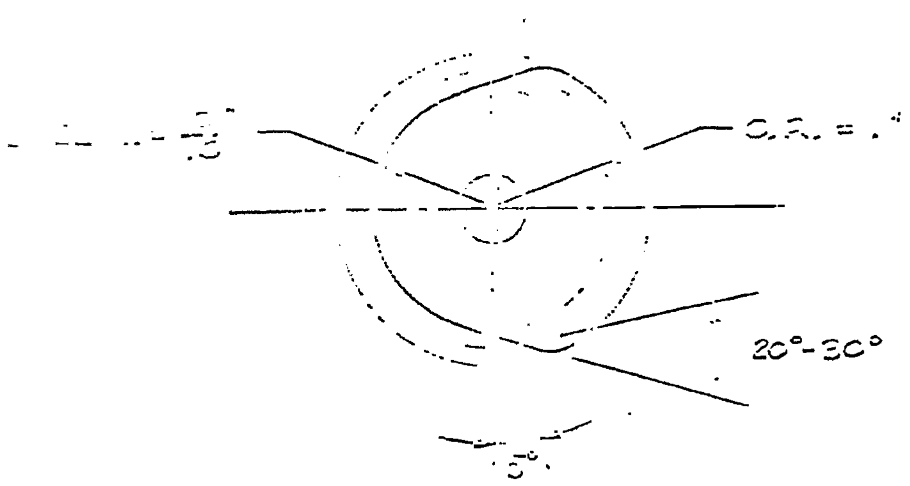
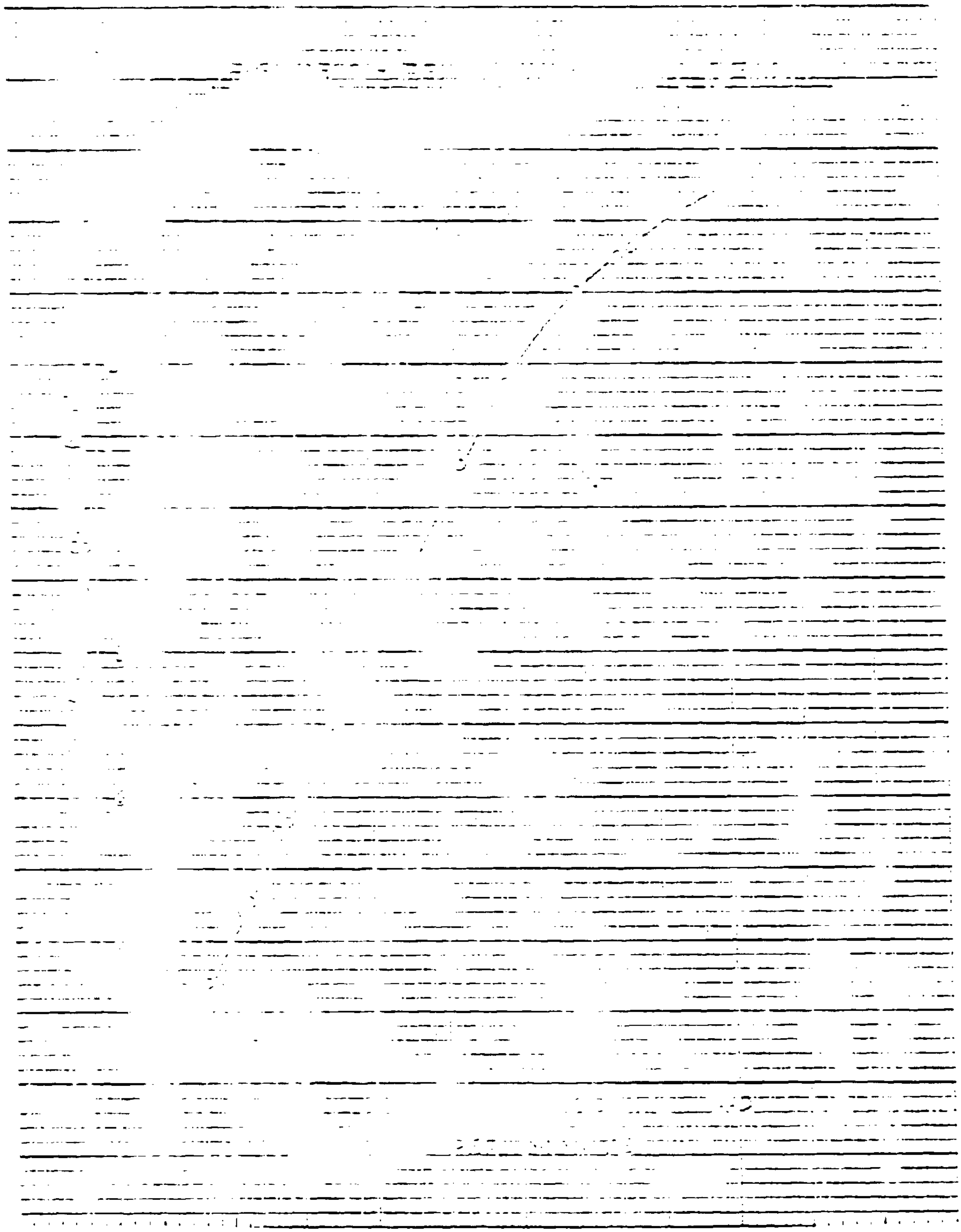
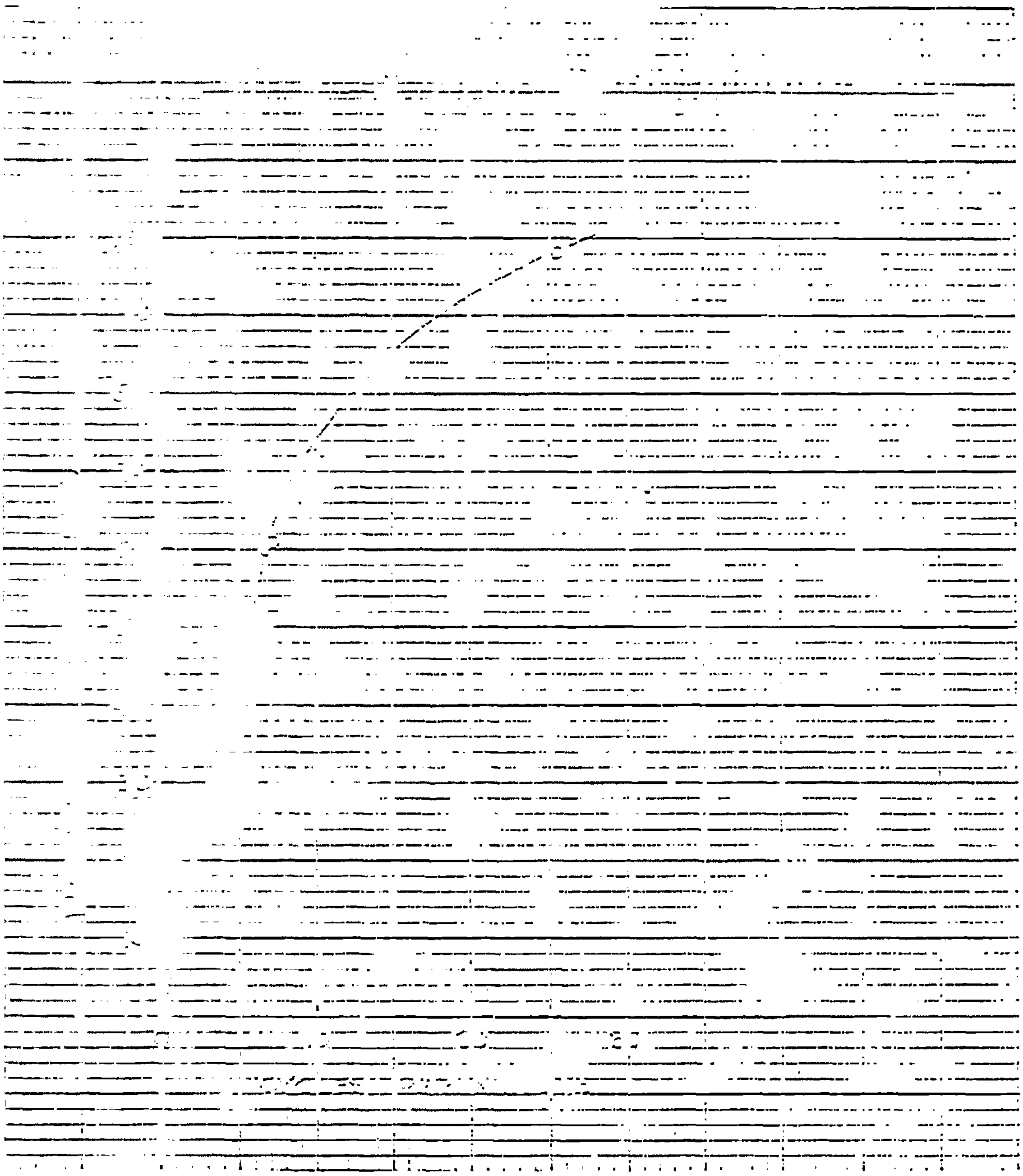
OPE[illegible]

"J" VALVE "L" VALVE







[illegible] of these [illegible] each [illegible] performance characteristic was [illegible] critical cycling frequency and then showed a progressive [illegible] as the frequency was increased. This critical frequency represents the condition of the upper valve remaining open just long enough for the lock chamber to completely fill. Any cycle frequency higher than this will result in the "open" period of the upper valve being shortened and therefore the lock chamber will only partially fill during the cycle. This action will result in the feed rate losing its proportionality with the cycle frequency as is demonstrated by the test results.

E. [illegible]

1. [illegible]

During the next [illegible] it is expected that the test vessel will be received from the fabricator and installed in the test area. After this, the setup will be completed, checked out, and made ready for test.

The exact compositions of the melt and the circulation gas to be used have not as yet been established. These will be chosen to simulate as closely as possible the most adverse corrosion condition anticipated in the plant.

2. [illegible] Bench-Scale Experimental Work

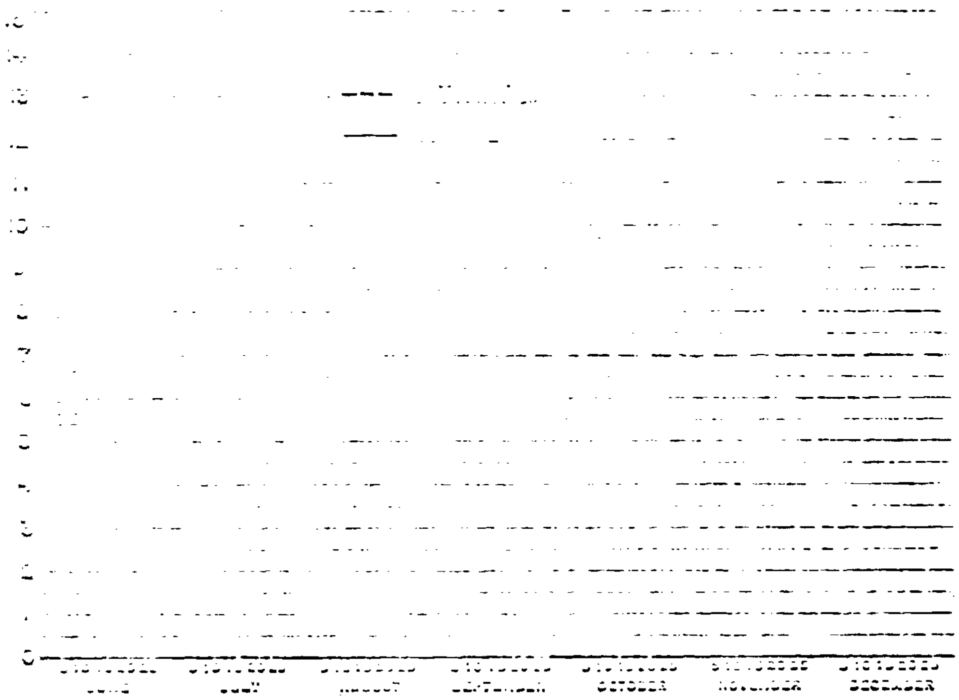
Further tests using coarser coal powders are planned with the objective of eliminating the vibrator. Based on the test data, a flow rate predictability curve will be constructed and the device will be made ready for installation in an experimental process system.

[illegible]

Figure 6 shows the projected manpower breakdown for Phase I for 1964 as well as the actual effort [illegible] attained. It can be seen that an eighteen man effort was [illegible] during October. It is anticipated that manpower will increase in November due to the start up of test equipment.

Figure 5 shows the expenditures during October as well as the cost estimates for Phase I for 1964. For the month of October, $ 5,100 was expended not including Fee and G. & A. The total expenditures through October were $47,700. This represents approximately 25% of Phase I.

[illegible]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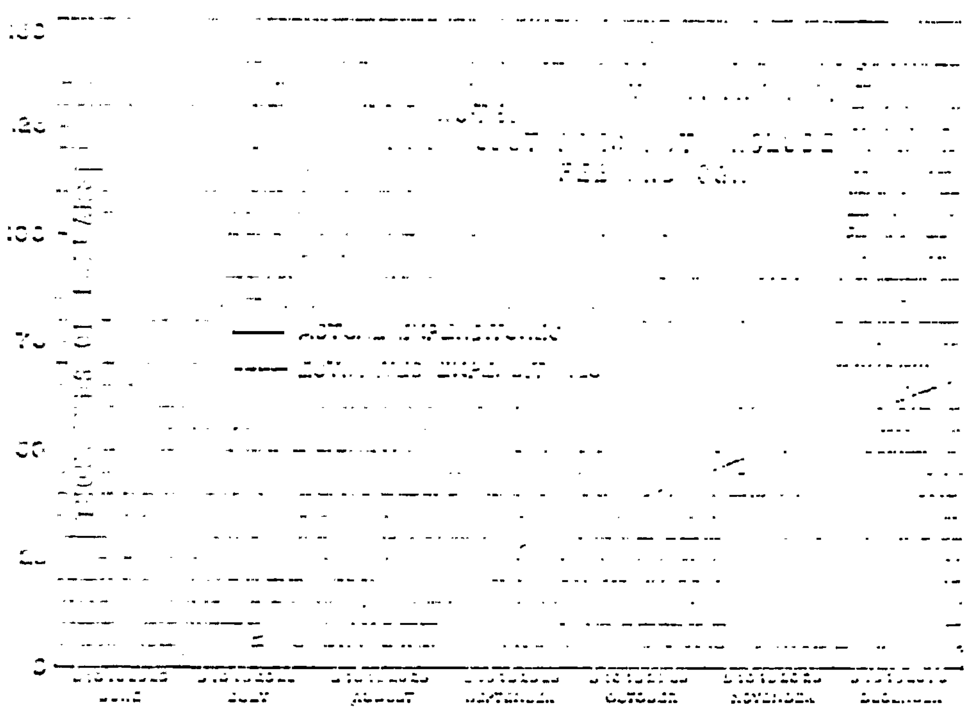
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SEPTEMBER
OCTOBER
NOVEMBER
DECEMBER

MWK-MPR-4

RESEARCH AND DEVELOPMENT DEPARTMENT

M KELLOGG W

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

November 30, 1964

Progress Report No. 4

APPROVED: Geo. T. Skaperdas
Project Manager

Leo Friend
Director
Chemical Engineering Development

Manager
Research and Development

CONTENTS

I. INTRODUCTION

Two gasification runs were made with anthracite in molten sodium carbonate at 1700°F. With 1.2% anthracite and a steam rate of 50 lbs./hr./100 lbs. of carbon, an initial gasification rate of 23 lbs. carbon gasified/hr./100 lbs. carbon was obtained; with 0.7% anthracite and 174 lbs. steam/hr./100 lbs. of carbon, the gasification rate was 125 lbs. carbon gasified/hr./100 lbs.

Work was continued on process development studies and bench-scale experimentation on physical property determinations. The test vessel for environmental testing of various materials has been received and is being set up for operation.

II. PROCESS DEVELOPMENT

A. Accomplishments

1. Process Flowsheet Studies

The effect of methane concentration in the raw synthesis gas on the economics of producing pipeline gas from bituminous coal was investigated. This methane can be produced by two mechanisms:

a. Decomposition of hydrocarbon materials present in the coal

b. Synthesis reactions, such as:

$$CO + 3\,H_2 \longrightarrow CH_4 + H_2O \qquad (1)$$

$$C + 2\,H_2 \longrightarrow CH_4 \qquad (2)$$

Two methane concentration levels were considered.

a. Assuming that all hydrogen in the coal feed appears as methane (the maximum that could be produced by decomposition reactions), yielding about 8% CH_4 in the wet synthesis gas.

b. Assuming that reaction (1) is at equilibrium, which yields about 3.5% methane at 1800°F and 400 psia.

The major change from case a to case b is that the gasification reaction is more highly endothermic so that more combustion coal must be burned and the cost of raw synthesis gas increases by about 0.5¢/MSCF of pipeline gas product. Most of this increase will be recovered during the methane synthesis step because more heat will be liberated.

It was concluded that the maximum probable variation in methane content of raw synthesis gas will have an insignificant effect on the cost of pipeline gas product. For other product gases (hydrogen, synthesis gas, transport gas) the effect must still be investigated.

2. Gas Purification

A purification system employing acetone as solvent is being designed for the comparative evaluation of gas purification processes. Design and cost information are being awaited on the Fluor Solvent CO_2 Removal, Sulfinol, and Rectisol processes.

3. Na_2CO_3 Recovery

Another scheme is being studied, in addition to the four discussed in the previous progress report, for recovering sodium carbonate from the aqueous solution produced by quenching the gasifier melt. This scheme involves precipitation of the bicarbonate according to the reaction:

$$Na_2\,CO_3\ (aq.) + H_2O + CO_2\ (g) \longrightarrow 2NaHCO_3\ (c) \qquad (3)$$

There is plenty of carbon dioxide available from the gas purification step; the sodium bicarbonate will be returned to the gasifier, where reaction (3) will be reversed. The quantities of steam and CO_2 thus produced are small when compared with the quantities of these gases taking part in the gasification reactions. One big advantage of the scheme is the absence of major heat effects; lower operating costs are expected for this reason.

B. Projections

1. Flowsheet Studies

The economic effect of adding potassium and lithium carbonates to the gasifier to lower the catalyst melting point will be investigated. This could be an important factor in the search for satisfactory materials of construction.

The effect of gasification rates in the molten salt system will be studied more thoroughly. To date, in the absence of experimental data, approximate gasifier sizes have been estimated by selecting a superficial gas velocity and a gas-melt contact time that seemed reasonable, though no allowance could be made for the effect of these factors on coal utilization or equilibrium concentration of carbon in the melt during gasification. As appropriate experimental data become available, these factors will be studied to assist in guiding both the process designs and experimental programs.

2. Methane Synthesis

The comparison of alternative methane synthesis processes will be completed.

3. Gas Purification

Evaluation of gas purification processes will continue.

4. Na_2CO_3 Recovery

The comparison of alternative sodium carbonate recovery schemes will be completed, except for estimates of capital investment, and the most attractive scheme from the standpoint of both operability and economics will be chosen. Capital cost is not expected to be a major factor in this choice, so it will probably not be necessary to wait until such cost estimates are obtained. Experimental work will be recommended, if necessary, to support the chosen carbonate recovery flowsheet.

III. PROCESS RESEARCH

A. Accomplishments

Coal Gasification Kinetics

Experimentation on the gasification of coal in the bench-scale reactor has begun. The apparatus, previously shown, is a two-inch I. D. Inconel tube supported in a two foot, high temperature Kanthal furnace. Steam and nitrogen are bottom fed and pellets of coal prepared from various mesh sizes top fed through two quick opening gate valves. Initial experiments are being performed on a batch basis with continuous coal and steam addition planned for the future.

Results of the first tests are tabulated in Tables I and II and production of CO, CO_2, H_2 and unreacted water given in Figures 1-5. The initial rate of carbon gasification is taken as the slope of initial linear portion of the CO + H_2 curves in Figures 1 and 3 for runs J-9650 and J-9651 respectively. Neglecting the small correction involving the initial hydrogen content of the anthracite the rate of CO + H_2 evolution (total reducing power of the gas) is equal to the rate at which carbon in the bed is gasified. In both runs J-9650 and J-9651, the steam consumption during these linear sections was high, although error may be involved during this time period due to equilibration of the following reaction which is a steam consumer:

$$Na_2CO_3 + H_2O \rightleftharpoons 2NaOH + CO_2$$

This equilibrium, however, does not influence the total reducing power (CO + H_2) of the gas.

Using this calculation procedure the rate of coal gasification at different steam rates has been computed and the results of runs J-9650 and J-9651 plotted in Figure 5.

Physical Properties

Melting point time relationships for mixtures of bituminous coal ash and molten carbonate have been developed. The change in melting point of pure carbonate with time was also studied. The decrease in the melting point of these mixtures is shown in Figures 6 and 7. The

TABLE I
COAL GASIFICATION - TEST UNIT RESULTS

Run No. ---- J-9650 ----
Date ---- 11/23-24/64 ----
Run Time, mins. ---- 390 ----
Salt Charge ---- 414 gms Na_2CO_3 ----
Carbon Source ---- 5.0 gms Anthracite (minus 60 mesh) ----

Operating Conditions

Temperature, °F ---- 1700 ----
N_2 Rate, cc/min. ---- 49 ----
H_2O Rate, cc/min ---- 2 ----
Pressure, psig ---- 0 ----

Sample Time, Mins.	10	20	35	55	80	95	120' (1)	120	190	240	300	360	390
Gas Composition, mole %													
N_2	22.0	45.0	66.0	60.8	56.5	69.0	70.0	52.0	66.0	74.8	78.0	75.0	70.5
CO	33.5	17.0	21.5	25.0	23.5	14.5	16.5	15.5	4.8	3.0	3.0	1.8	2.0
CO_2	31.7	14.5	8.0	10.8	11.8	6.0	5.3	9.5	13.2	12.5	11.5	10.6	12.5
H_2	12.8	23.5	4.5	3.4	8.2	11.5	8.2	23.0	16.0	9.7	7.5	12.6	7.0

(1) Run interrupted and continued next day.

TABLE II
COAL GASIFICATION - TEST UNIT RESULTS

Run No.	J-9651
Date	12/1/64
Run Time, mins.	240
Salt Charge	414 gms Na_2CO_3
Carbon Source	2.9 gms Anthracite (minus 60 mesh)
Operating Conditions	
Temperature, °F	1700
N_2 Rate, cc/min.	111
H_2O Rate, cc/min.	4
Pressure, psig	0

Sample Time, Mins.	10	20	40	50	60	80	95	135	155	175	195	215	235
Gas Composition, mole %													
N_2	44.0	39.0	47.5	68.5	75.0	68.5	79.0	76.0	79.0	82.5	77.5	86.5	82.0
CO	11.3	11.5	9.8	5.0	2.0	4.7	3.2	2.0	1.4	1.0	1.4	0.3	0.7
CO_2	3.2	3.0	3.7	2.0	6.6	6.6	5.0	8.2	6.0	6.6	10.5	5.6	9.7
H_2	41.5	46.5	39.0	24.5	16.4	20.2	12.0	13.8	12.8	9.9	10.6	7.6	7.6

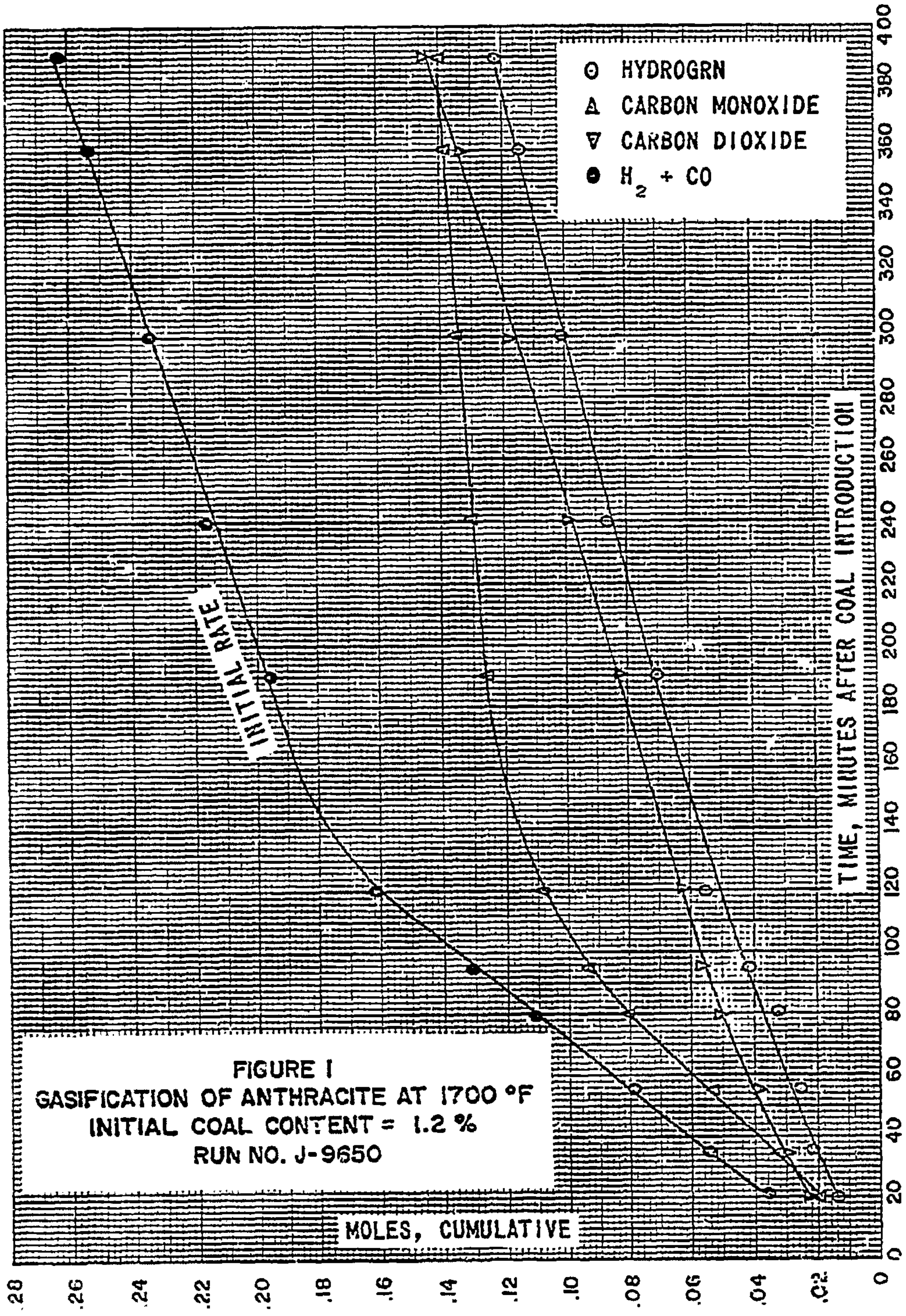


FIGURE I
GASIFICATION OF ANTHRACITE AT 1700 °F
INITIAL COAL CONTENT = 1.2 %
RUN NO. J-9650

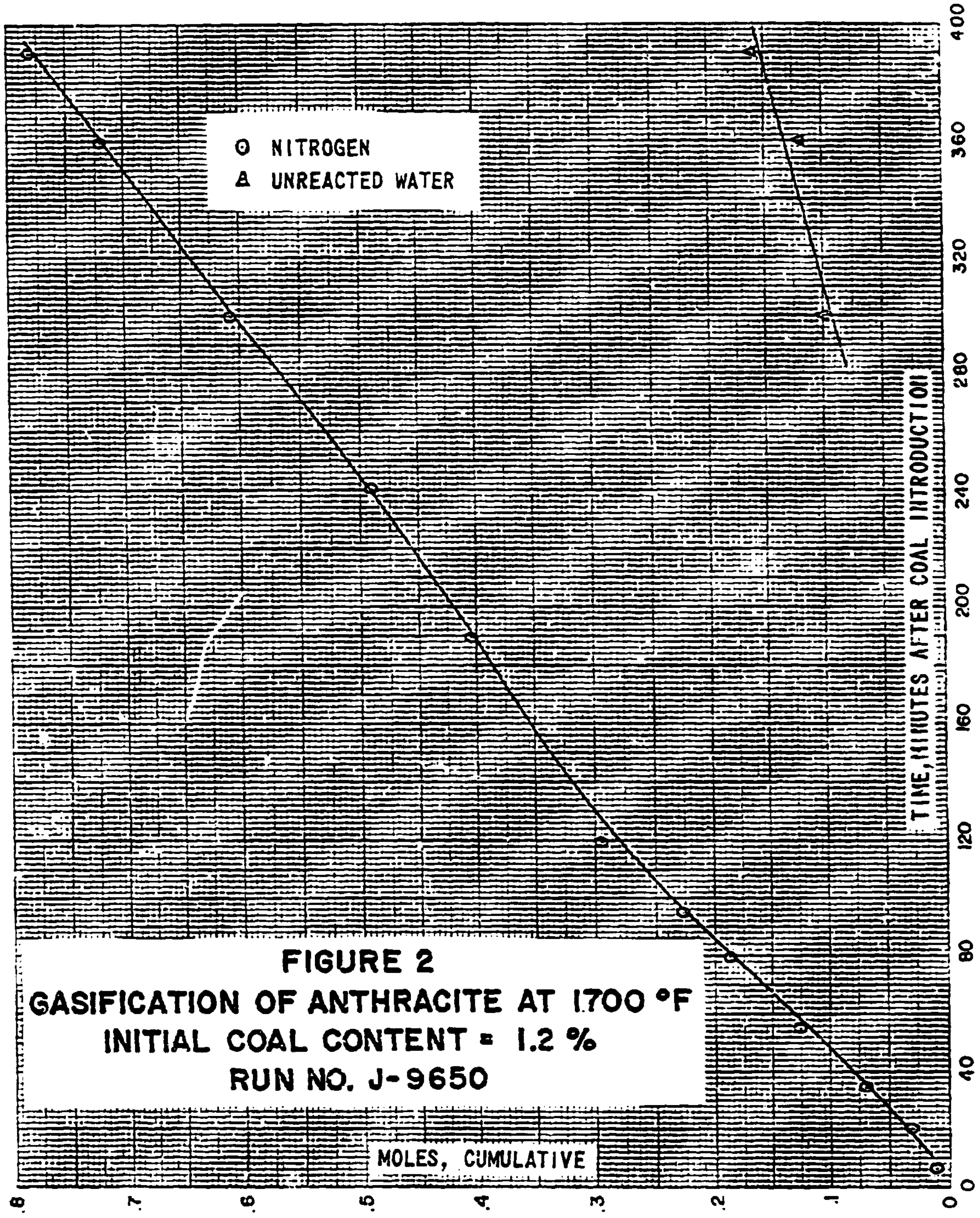


FIGURE 2
GASIFICATION OF ANTHRACITE AT 1700 °F
INITIAL COAL CONTENT = 1.2 %
RUN NO. J-9650

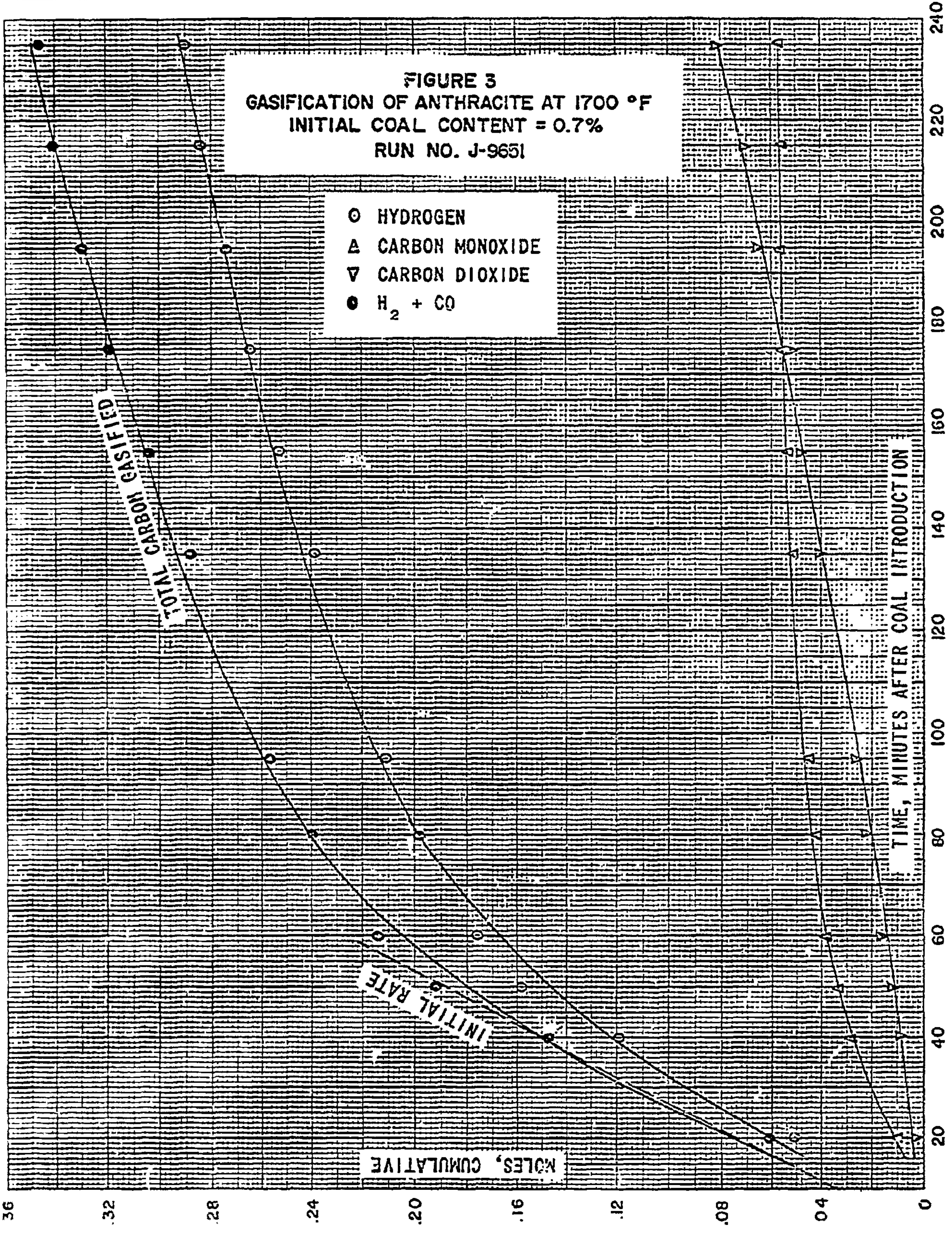


FIGURE 3
GASIFICATION OF ANTHRACITE AT 1700 °F
INITIAL COAL CONTENT = 0.7%
RUN NO. J-9651

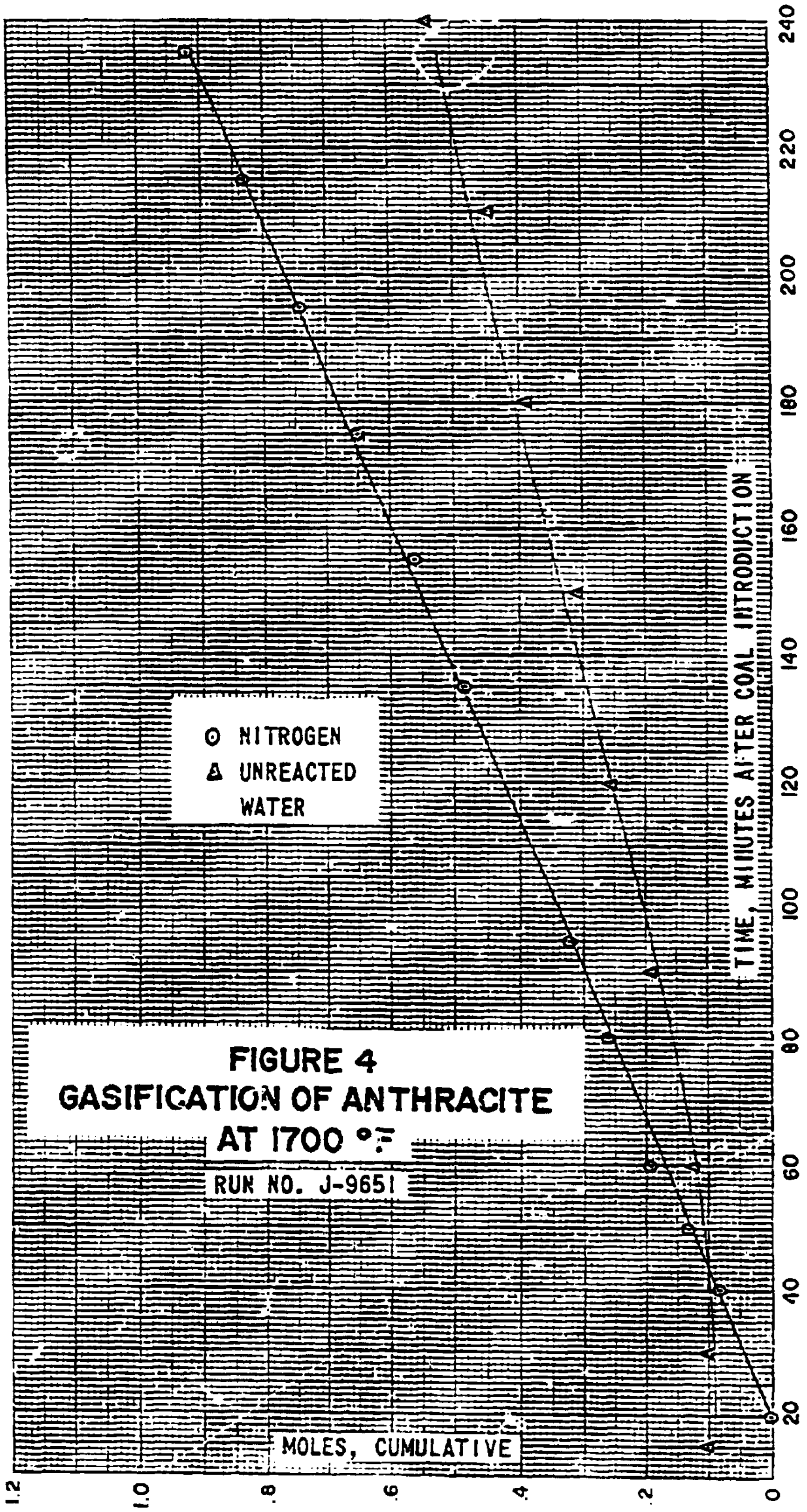


FIGURE 4
GASIFICATION OF ANTHRACITE
AT 1700 °F
RUN NO. J-9651

FIGURE 5
COAL (ANTHRACITE) GASIFICATION
1700 °F MOLTEN Na_2CO_3
2" I.D. REACTOR, 4" BED HEIGHT
MINUS 60 MESH COAL

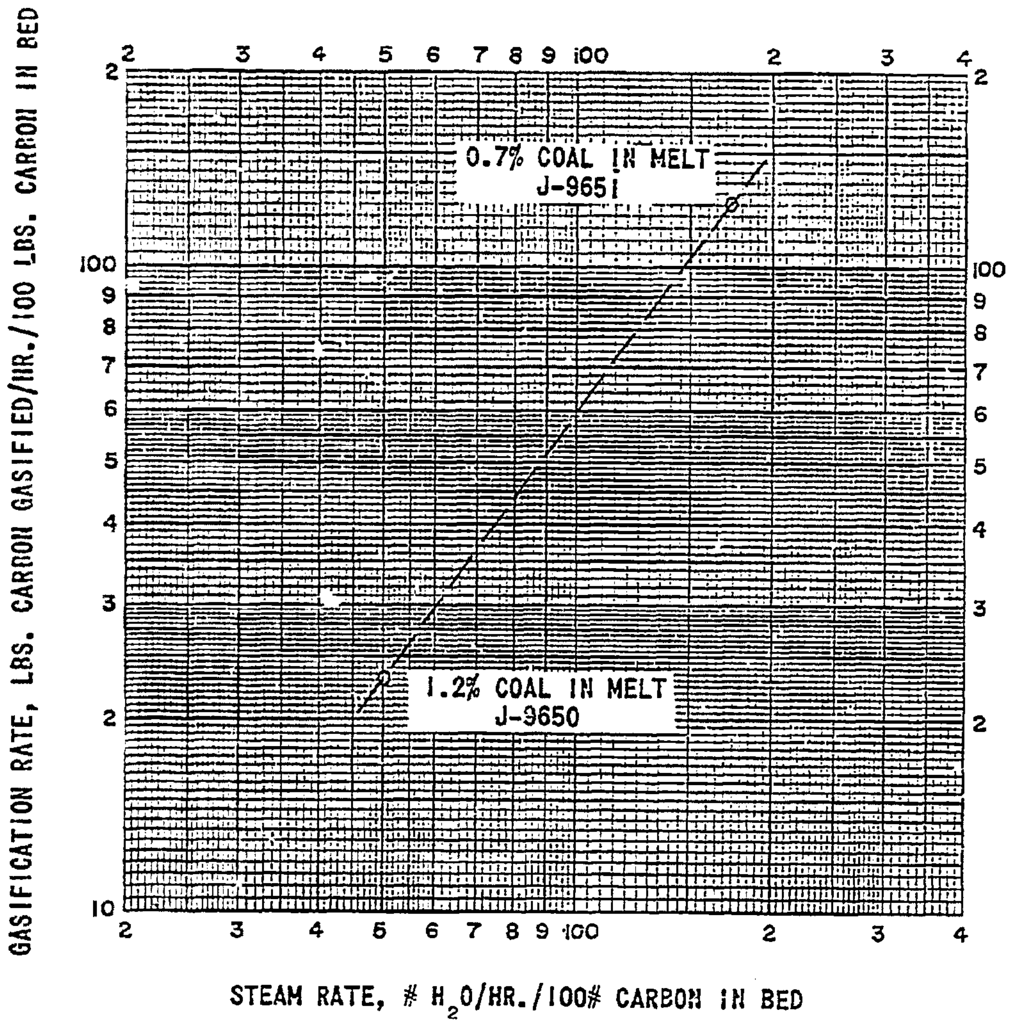


FIGURE 6
MELTING POINT OF BITUMINOUS ASH
IN
SODIUM CARBONATE
WITH TIME

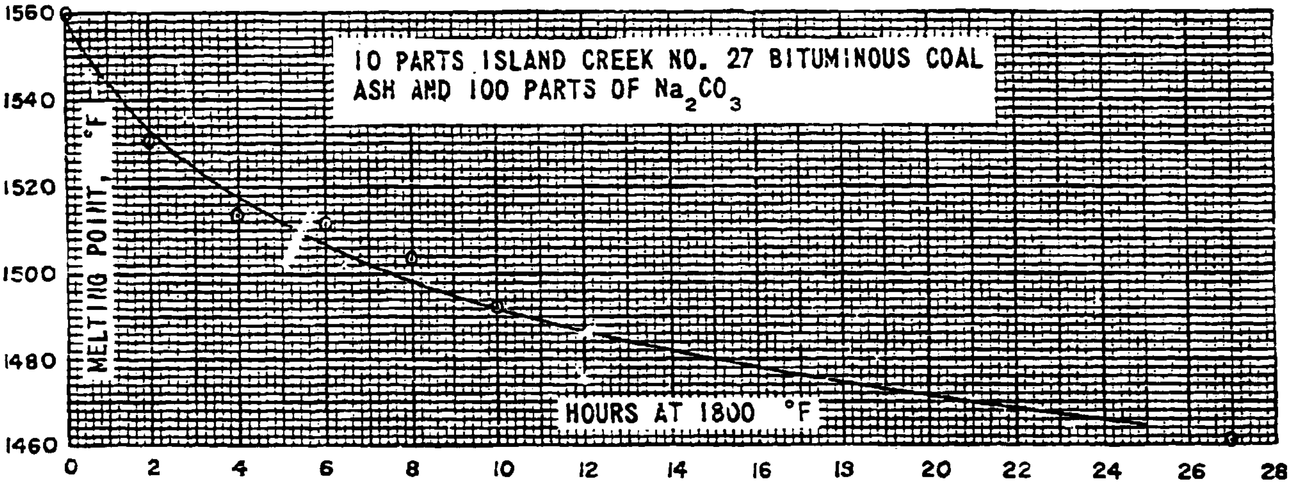
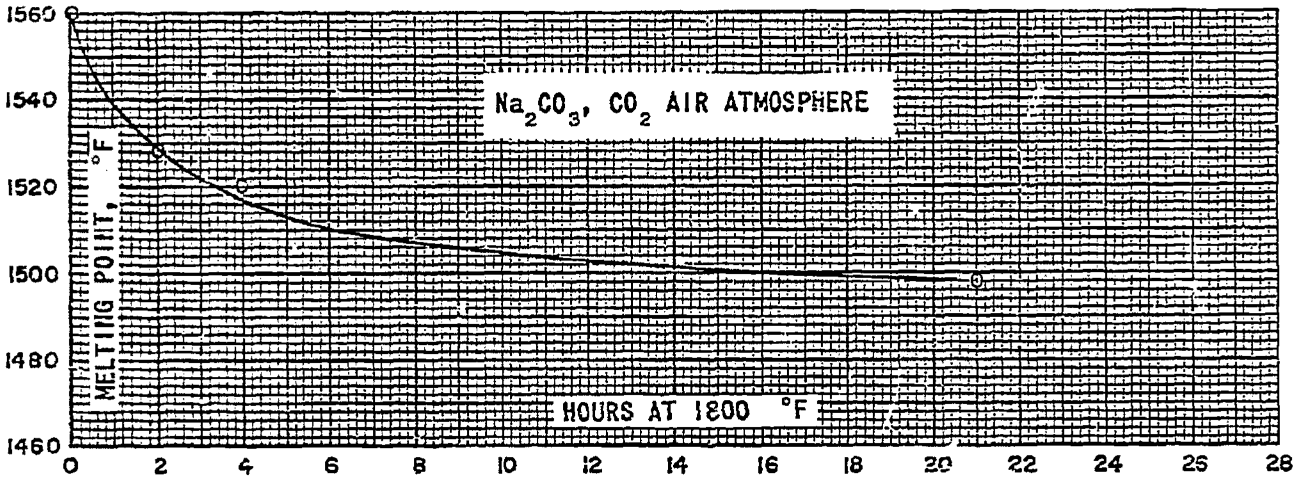


FIGURE 7
MELTING POINT OF SODIUM CARBONATE
IN AIR WITH TIME



behavior of the melting point of these mixtures under one atmosphere CO_2 pressure is shown in Figures 8 and 9. The dissociation of Na_2CO_3 and the solubilization of SiO_2 and/or Al_2O_3 in the coal ash is apparently completely supressed by the imposition of a CO_2 atmosphere.

Corrosion Tests

Preliminary corrosion tests have been carried out using new 310 stainless steel crucibles for each run. In each test the crucible was held at 1800°F for four hours, dumped, cooled, cleaned and inspected.

Previous qualitative information indicated that lignite ash was the more severe corrosive agent. The high content of sulfur in the lignite ash was suspected. Tests were therefore performed using lignite ash in molten carbonate in 310 ss crucibles. Test specimen A, (Figure 10) showed very severe corrosion. The presence of graphite, B, (as reducing agent) greatly reduced the corrosion and the presence of graphite and steam dramatically reduced corrosion as shown in test specimen C. Tests using Na_2SO_4, Na_2S or Na_2SO_3 in molten salt also showed serious corrosion, which could also be reduced by the addition of graphite and steam.

Thermodynamics

Compilation of pertinent thermodynamic data from the literature has begun. The first data compiled involving the reduction of sulfur compounds has shown rather large negative free energy changes. The reactions tabulated to date are given in Table III. The high corrosive effect of sulfur compounds coupled with the large effect of carbon and steam appear to indicate a sulfate or sulfide corrosion mechanism.

B. Projections

Future work will continue in the area of gasification kinetics, measurement of viscosity of ash/carbonate mixtures, investigation of possible SiO_2 and Al_2O_3 corrosion mechanisms and further compilation of thermodynamic data especially oxidation-reduction reactions involving iron, chromium and nickel.

FIGURE 8
MELTING POINT OF SODIUM CARBONATE IN CARBON DIOXIDE WITH TIME

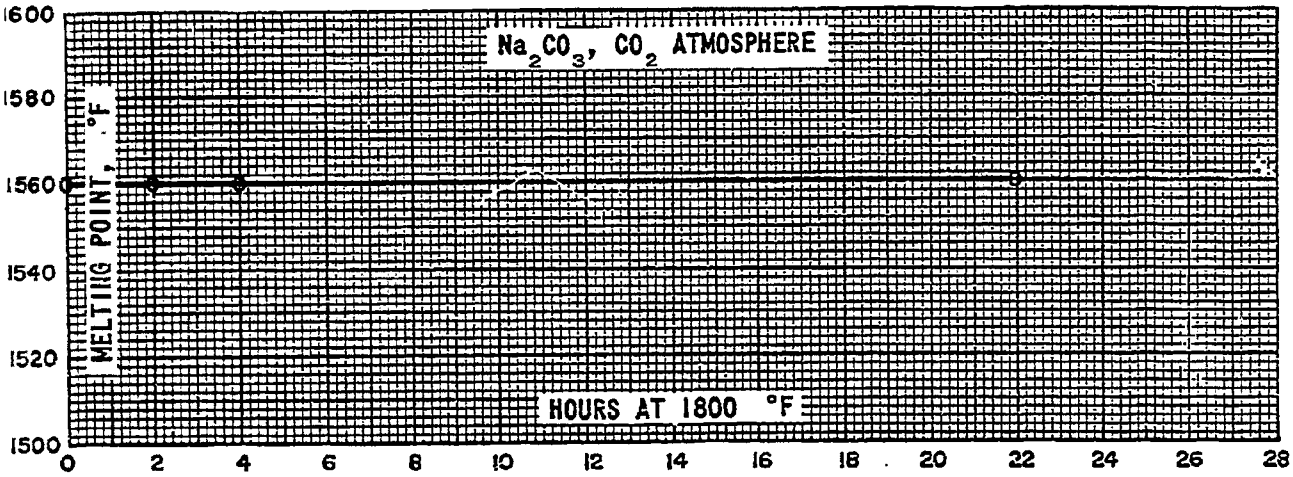


FIGURE 9
MELTING POINT OF BITUMINOUS ASH
IN SODIUM CARBONATE WITH CARBON DIOXIDE
WITH TIME

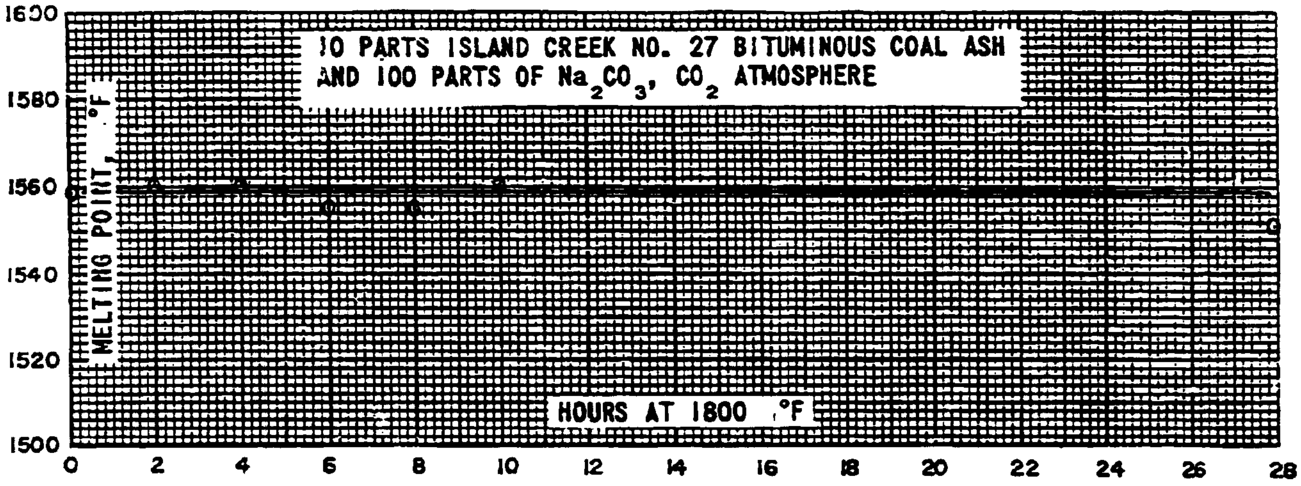
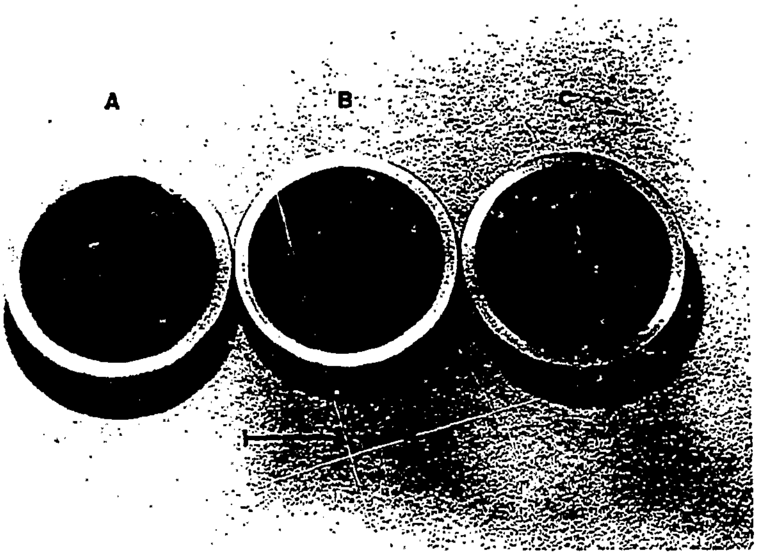


FIGURE 10

CORROSION OF 310 STAINLESS STEEL

Molten Sodium Carbonate - Lignite Ash

1800°F, Four Hours



Sample /1/	A	B	C
Melt Composition	----10% Lignite Ash in Molten Na_2CO_3----		
% Graphite	0	10%	10%
CO_2 Atmosphere	760 mm.	760 mm.	735 mm.
Steam Atmosphere	0	0	25 mm.

/1/ Not shown: pure Na_2CO_3, which resulted in little, if any, corrosion

TABLE III
FREE ENERGY CHANGES ASSOCIATED WITH SELECTED REACTIONS

		ΔF @ 1300°K - Kcal/mole
1.	$Na_2SO_4 + 2C \longrightarrow Na_2S + CO_2$	-39.7
2.	$Na_2SO_4 + 2C \longrightarrow 2NaOH + \frac{1}{2}CO_2 + CO + \frac{1}{2}CS_2$	-35.0
3.	$Na_2SO_4 + C + H_2O \longrightarrow Na_2CO_3 + CO_2 + H_2S$	-31.0
4.	$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$	-16.2
5.	$CO + H_2O \longrightarrow CO_2 + H_2$	+ 1.45
6.	$CO + S \longrightarrow COS$	+ 2.54
7.	$CO + H_2S \longrightarrow COS + H_2$	+ 8.8
8.	$Na_2S + 2H_2O \longrightarrow 2NaOH + H_2S$	+24.9
9.	$CO + 3H_2 \longrightarrow CH_4 + H_2O$	+25.6
10.	$Na_2CO_3 \longrightarrow Na_2O + CO_2$	+34.2
11.	$Na_2S + H_2O \longrightarrow Na_2O + H_2S$	+42.9

All data except Na_2SO_4 from JANAF thermochemical data; all compounds in the liquid or gaseous states.

Data for Na_2SO_4 averaged from:

a) K. K. Kelley, Bur. Mines Bul. 584, p. 174
b) D. M. Ginzburg, J. Gen. Ch. USSR, 26, 968-70, (1956)
c) A. A. Fotviev, Zh. Prikl. Khimii, 35, 2402-2409 (1962)

IV. MECHANICAL DEVELOPMENT

A. Work Accomplished

1. Environmental Testing of High Temperature Materials

The test vessel and all other special components have been received and are being set up for operation. A tentative plan for the initial test has been established which will closely simulate anticipated process conditions (other than pressure) and thereby yield pertinent data. Figure 11 schematically shows the arrangement and test operating conditions. The appropriate gas composition and flow rate and graphite feed rate are presently under study and will be based on maintaining a stable composition of the melt during the test period. Although the temperature on the figure is indicated at 1800°F, the temperature of the test may be reduced to 1700°F if results of current process experimental work warrant this reduction.

2. Coal Feeding Mechanism for Bench-Scale Experimental Work

The coal feeding mechanism, described in the previous report, is being set up for operation in conjunction with the corrosion test as shown in Figure 11. In this application a controlled rate of graphite will be fed into the test vessel in a continuous automatic fashion.

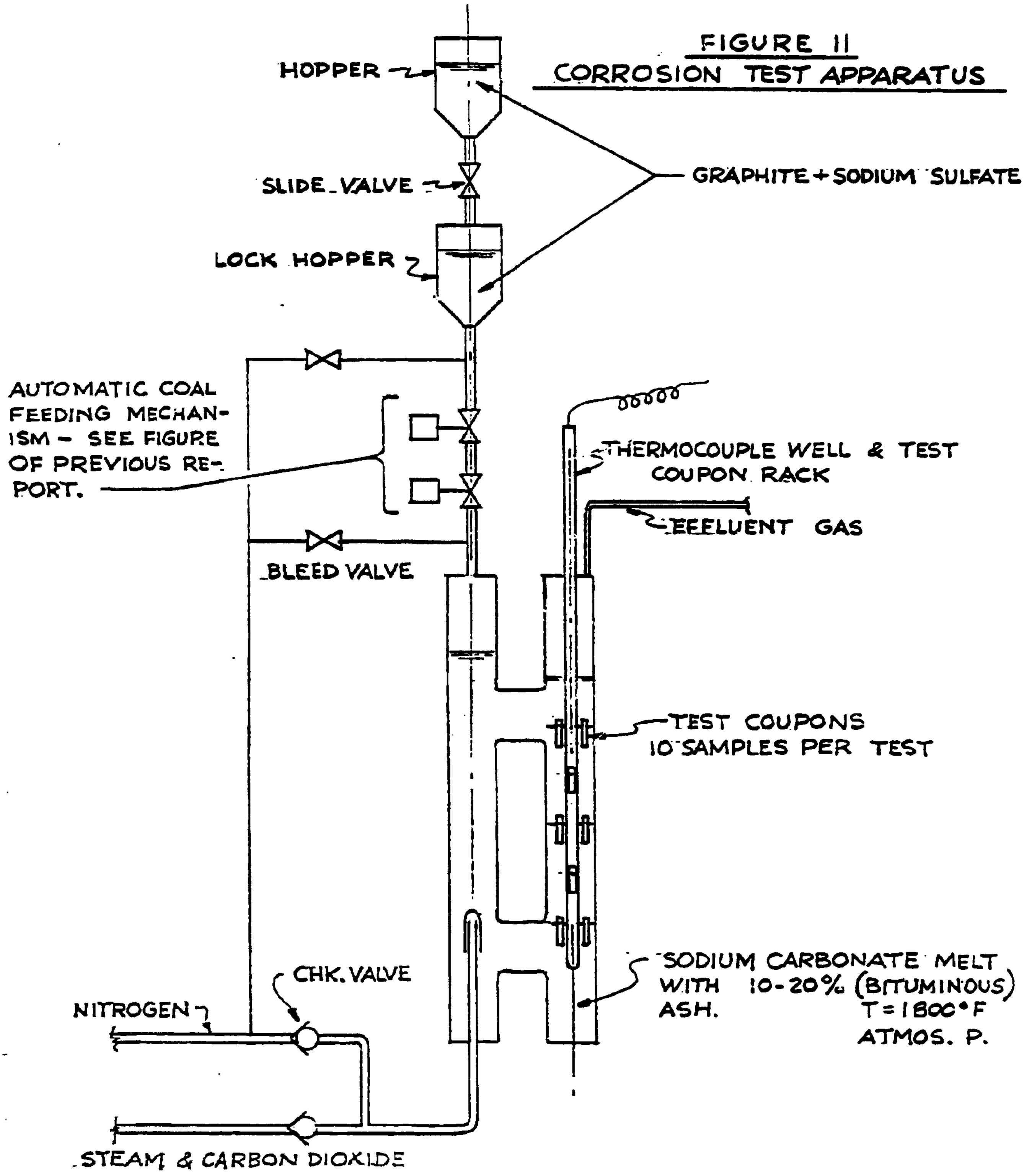
B. Work Projected

1. Environmental Testing of High Temperature Materials

Upon completion of the test setup, the first test will be initiated. The materials to be tested first are:

- Inconel 600
- Inconel 702
- Incoloy 800
- Incoloy 804
- AISI Type 309
- AISI Type 310
- 50 - 50 Alloy
- Hastelloy B
- Hastelloy C
- Rayonel 600

FIGURE 11
CORROSION TEST APPARATUS



2. Coal Feeding Mechanism for Bench-Scale Experimental Work

The coal feeding mechanism, operating in conjunction with the corrosion test, will be subjected to an endurance test permitting an assessment of the ability of the device to maintain a constant feed rate over an extended period of operation. In addition, the mechanism will be tested under conditions closely resembling a continuous feed bench scale coal gasification operation.

V. MANPOWER AND COST ESTIMATES

Figure 12 shows the projected manpower breakdown for Phase I for 1964 as well as the actual effort that was attained. It can be seen that a seven and one half-man effort was sustained during November. This is a slight decrease from the eight-man effort in October. Due to the holiday shut-down in December, the average man hour effort for the month will be much lower.

Figure 13 shows the expenditures during November as well as the cost estimates for Phase I for 1964. For the month of November $12,200 was expended not including fee and G. & A. The total expenditures through November were $60,400. This represents approximately 29% of Phase I.

FIGURE 12
MANPOWER FOR PHASE I
1964

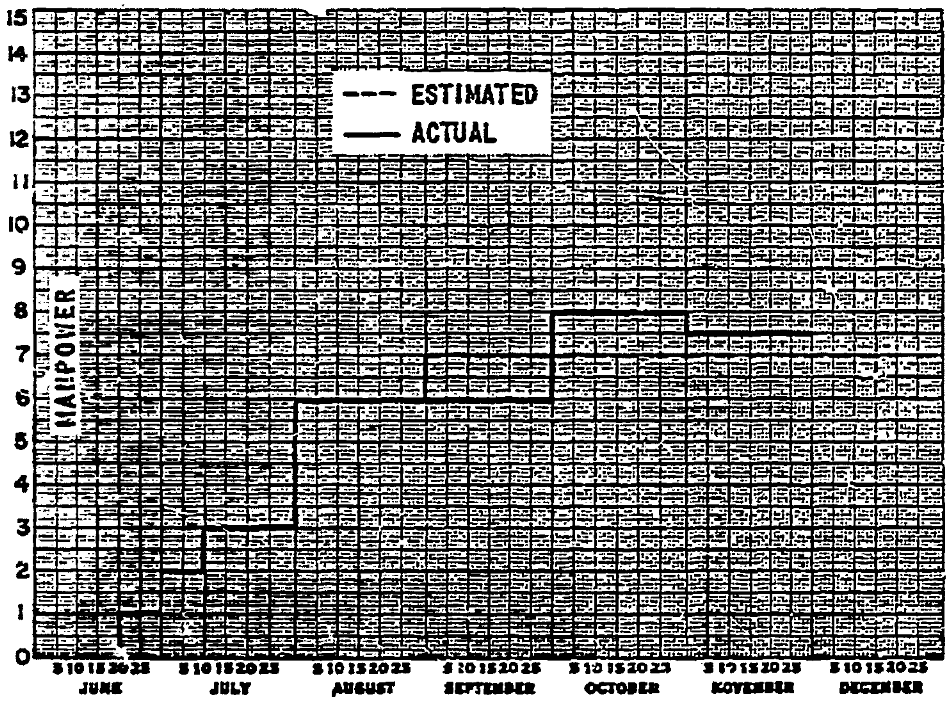
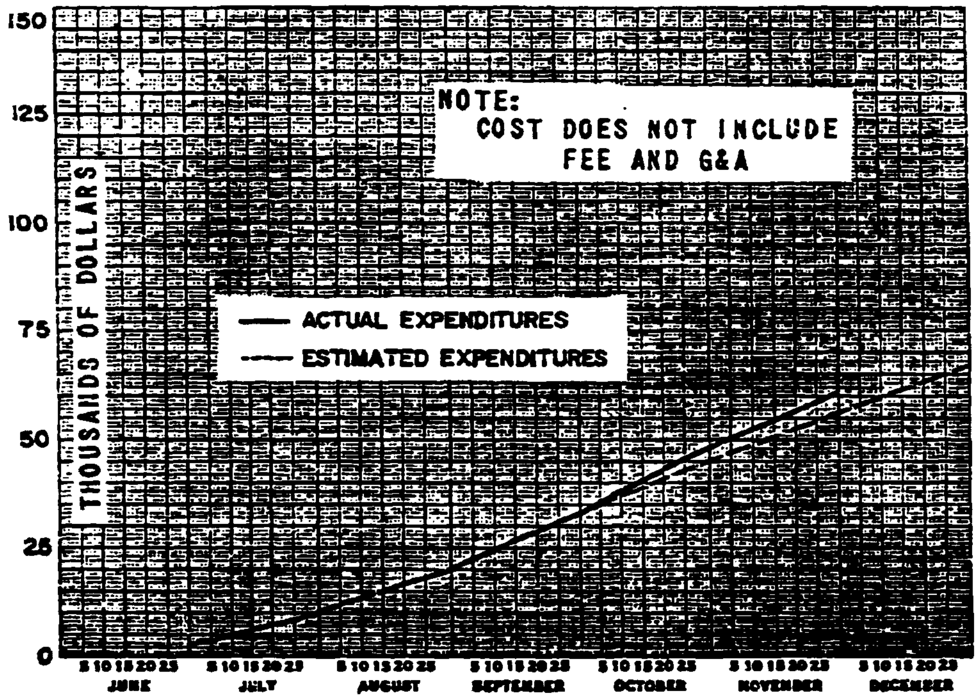


FIGURE 13
COST ESTIMATE FOR PHASE I
1964



NOTE:
COST DOES NOT INCLUDE
FEE AND G&A

MWK-MPR-5

RESEARCH AND DEVELOPMENT DEPARTMENT KELLOGG

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

December 31, 1964

Progress Report No. 5

APPROVED:

Project Manager

Le Friend

Director
Chemical Engineering Development

Manager
Research and Development

CONTENTS

I. INTRODUCTION

The viscosity of a 30% anthracite ash-70% sodium carbonate at 1800°F decreases rapidly with time; from 40,000 centipoise intially to 7,000 in four to six hours. Tests of the rate of gasification of anthracite coal at contact times of 4.5 seconds indicate that the steam conversion to synthesis gas is directly proportional to the concentration of coal in the molten suspension.

Work was continued on process development. The recovery of Na_2CO_3 by precipitation with CO_2 and water to form insoluble bicarbonate seems to be the most attractive.

The environment test facilities have been set up and the metering devices were calibrated.

II. PROCESS DEVELOPMENT

A. Accomplishments

1. Na_2CO_3 Recovery

Five methods have been evaluated for recovering sodium carbonate catalyst from the aqueous solution produced by quenching gasifier melt with water. It has been assumed in making the evaluation that bituminous coal is gasified at 1800°F and 400 psia, that heat is provided for the gasification by means of a fired-tube melt heater, and that ash is permitted to build up in the circulating melt to a level of 20% by weight. These conditions correspond to flowsheet No. I-D (Progress Report No. 3, page 4), which offers the lowest gasification costs if the associated technical problems can be solved.

The five salt recovery methods studied are the following:

a. High Pressure Evaporative Crystallization (Case I-D2)

As in all the schemes, hot melt from the gasifier is quenched with cooling water at atmospheric pressure to dissolve most of the sodium carbonate catalyst and leave the insoluble coal ash constituents in suspension, so that they may be removed by filtering. Five percent of the carbonate is assumed to be lost with the ash. The filtrate is heated at 400 psia to precipitate anhydrous Na_2CO_3, which is separated and returned to the gasifier. The major advantage of this scheme is that the large heat requirement for evaporating quench water is not wasted, but is used to produce steam at 400 psia for gasification. The major problem would probably be the fouling of heat exchanger surfaces by precipitated salts. Because of the inverse solubility curve of sodium carbonate in this temperature range (Progress Report No. 3, page 8) it will precipitate at (or on) the heat exchanger surface, where temperature is highest.

b. Low Temperature Crystallization (Case I-D3)

After the melt is quenched and insoluble ash constituents filtered off, the Na_2CO_3 solution is cooled to 40°F by evaporating water at sub-atmospheric pressure in a steam-jet chiller. The decahydrate of sodium carbonate is precipitated and separated from the solution by centrifuging, and the water of hydration is then driven off in a rotary dryer using hot flue gas from the gasification section. Dried Na_2CO_3 is returned to the gasifier.

The large heat requirement for removing water of hydration is the major disadvantage, because this energy is then largely unavailable for further work. Also, fouling of exchanger surfaces is a possible problem, although this could be avoided at some increase in operating cost by treating the refrigeration less frugally.

c. Low Pressure Evaporative Crystallization (Case I-D4)

The heat exchanger fouling problem associated with Case I-D2 is avoided here by direct contact of aqueous solution with hot flue gas to evaporate water. However, the heat consumed is degraded to a level where it can no longer be used, so the operating costs are significantly higher than those for Case I-D2.

d. High Temperature Precipitation (Case I-D7)

This scheme makes use of the inverse solubility of sodium carbonate at high temperatures. After quenching and filtration of ash components, the Na_2CO_3 solution is heated in a series of exchangers to precipitate anhydrous Na_2CO_3. The crystals are separated by centrifuging, while the mother liquor is cooled and recirculated to the quench drum. Heat costs are minimized by recuperative heat exchange, but the problem of surface fouling will probably be severe.

e. Precipitation of Bicarbonate (Case I-D10)

After quenching and filtering of ash components, the 20% sodium carbonate solution is contacted with carbon dioxide at about 25 psia. Insoluble sodium bicarbonate is formed according to reaction (1) and, after separation by centrifuging,

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3\downarrow \qquad (1)$$

is returned to the gasifier. There reaction (1) is reversed, producing CO_2 and H_2O, but the quantities are small and have little effect on gas composition. The bicarbonate decomposition is endothermic, so gasifier duty is increased slightly in this case and a little more coal must be burned in the fired-tube heater. This salt recovery process yields a low operating cost because no heat is required. Further, operating difficulties should be minimized because the flowsheet is simple and there are no exchanger surfaces to foul.

The estimated cost of ash removal and catalyst recovery according to the five flowsheets just discussed is summarized in Table I. The incremental coal cost for Case I-D10 represents that heat required to decompose sodium bicarbonate. Total operating costs in Table I do not include fixed charges because capital investment has not yet been estimated. However, this is not expected to affect the relative position of the several cases.

Cases I-D3 and I-D4 yield high costs because of their wasteful use of heat, as already discussed. These have been given no further study. For the remaining three cases it is of interest whether their relative position will be affected by changes in the underlying assumptions. For this reason the effect of 10% ash in the entering melt (instead of 20%) and of 10% Na_2CO_3 losses (rather than 5%) were investigated. The results are also presented in Table I. It is found that salt recovery costs do increase significantly under these conditions, but the relative positions of Cases I-D2, I-D7, and I-D10 do not change.

It is concluded that Case I-D10 is the most attractive of the salt recovery methods considered because it is simple, its estimated costs are among the lowest, and a minimum of operating difficulties is expected.

2. Methane Synthesis

The comparison of alternative methane synthesis processes has been substantially completed. This study was interrupted so that maximum effort could be devoted to making a preliminary estimate of hydrogen costs. Results of the methane synthesis comparison will be reported next month.

TABLE I

COST OF ASH REMOVAL AND CATALYST RECOVERY

Basis: Raw Material: Bituminous Coal
Product: Raw synthesis gas equivalent to 250 MM SCFD of pipeline gas
Na_2CO_3 Losses: 5% per pass through recovery system
Method of heat supply: Fired-tube heater
Entering melt composition: 20% ash, 80% Na_2CO_3

Case No.	1-D2	1-D3	1-D4	1-D7	1-D10
Cost of Ash Removal and Catalyst Recovery, ¢/MSCF of Pipeline Gas					
Incremental coal	-	-	-	-	0.3
Heat at 40¢/MM BTU	-	2.0	2.3	0.1	-
Cooling water	-	0.4	-	-	-
Power at 0.7¢/kwh	0.2	-	-	0.1	0.2
$NaCo_3$ losses at 1.55¢/#	1.2	1.2	1.2	1.2	1.2
Labor and overhead	0.2	0.2	0.1	0.1	0.1
Total, excl. fixed charges*	1.6	3.8	3.6	1.5	1.8
Total Cost, ¢/MSCF, with 10% ash in entering melt	3.4	-	-	3.2	3.9
Total Cost, ¢/MSCF, with 10% ash in melt and 10% Na_2CO_3 loss per pass	6.1	-	-	5.9	6.6

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*NOTE: One million dollars of investment adds 0.13¢/MSCF of pipeline gas.

3. Gas Purification

Information has been received from Fluor Corporation and from Shell Development Company concerning the application of their respective gas purification processes to the removal of CO_2 and H_2S for this study. In addition, cost estimates have been completed for our own designs of monoethanolamine, Vetrocoke, and acetone wash systems. When data on Rectisol are received from Lurgi, this study to choose the optimum gas purification sequence for each product gas of interest will be concluded.

4. Hydrogen Production Costs

In response to a request from the Office of Coal Research, a study is in progress to make preliminary estimates of the cost of producing 250 MM SCFD of hydrogen from bituminous coal via molten salt gasification. The result will be a table of costs similar to that presented previously for pipeline gas (Progress Report No. 3, page 4). The effect of the following variables will be investigated.

a. Gasifier operating conditions
b. Product hydrogen purity
c. Extent of methane production in gasifier
d. Method of methane removal
    (1) Catalytic reforming
    (2) Partial oxidation

5. Effect of Coal Gasification Rate on Choice of Heat Supply Method

Several methods have been suggested (Progress Report No. 1, page 10) for supplying heat for the endothermic gasification reactions. The most promising of these were found to be: (1) circulation of melt through an external fired-tube heater, and (2) combustion of coal in direct contact with the melt. It has become apparent that the second alternative may not be a feasible one unless carbon gasification rates are extremely high. The reasoning behind this statement is reproduced below.

Melt is circulated between heater and gasifier at a rather substantial rate to supply the required heat of reaction as sensible heat of melt.

Quantity of coal burned in the heater to liberate this heat is only about 0.4% of the melt circulation rate. Now considering the direct combustion case, if the melt entering the heater contains more than 0.4% carbon, combustion will be incomplete and excess carbon will be present in the melt. In fact, if equilibrium for reaction (3) is achieved, the carbon will be burned predominantly to CO, not to CO_2.

$$CO_2 + C \rightleftharpoons 2CO \qquad (3)$$

Because combustion to CO liberates only about 30% as much heat as combustion to CO_2 at 1800°F, more combustion air must be supplied and more coal must be burned to provide the required heat. The CO-containing flue gas is a rather poor fuel and besides is produced in such large quantity that it can not be utilized by the plant. The net result is that the increased coal consumption will add about 9¢/MSCF to the cost of pipeline gas, which is clearly unacceptable.

In order to have less than 0.4% carbon in the melt entering the heater and still retain a gasifier of reasonable dimensions, coal gasification rates must be higher than corresponding uncatalyzed rates by several orders of magnitude.

This problem caused by excess carbon in the melt disappears in the case where heat is supplied via a fired-tube heater because the flue gas is not in contact with the melt.

6. Pumping of Melt

A number of gasifier configurations of interest require pumping the "melt", the mixture of molten sodium carbonate, coal ash, and ungasified carbon. In the most severe case, that of gasification at high pressure and direct-contact heating of melt at low pressure, the melt would have to be pumped against a head of several hundred pounds per square inch. It has been assumed that a pump can be developed for this service. It is conceivable that a material of construction can be found that is resistant to corrosion by the melt, but which is not satisfactory for pump fabrication because of the high stresses and close tolerances involved. In that case melt could be transferred against a 400-psi head by a series of lock hoppers lined with the corrosion-resistant material and pressurized with carbon dioxide. Incremental cost for this operation over the cost of pumping the melt is estimated to be about 1-2¢/MSCF of pipeline gas. If depressuring of melt cannot be accomplished with a valve but must also be done via lock hoppers, then total cost for melt transfer would be about 2-3¢/MSCF of pipeline gas, or 0.6-1¢/MSCF of hydrogen. This method of melt transfer requires a multitude of lock hoppers and an elaborate, expensive piping system, however, so simple pumping is much to be preferred if it is technically feasible.

B. Projections

1. Hydrogen Production Costs

The preliminary estimates of the cost of producing hydrogen from bituminous coal as a function of the several variables listed will be completed.

2. Methane Synthesis

The results of the evaluation of alternative methane synthesis processes will be reported.

3. Flowsheet Studies

Studies of economic effect of adding potassium and/or lithium carbonate to the melt and of the effect of varying rates of gasification on the process were interrupted by the interest in hydrogen costs. These studies will be resumed.

4. Gas Purification

The evaluation of gas purification processes will continue.

III. PROCESS RESEARCH

A. Accomplishments

1. Physical Property Data

Viscosity tests have begun on molten sodium carbonate-ash mixtures in the 1700°F region. Viscosities are measured using a standard Brookfield model RVT Viscometer. A special Inconel Viscometer spindle was constructed for use in the determinations. A 1.7 inch I. D. x 16 inch Inconel tube was used as a container for the melts. The tube was supported in a high temperature Kanthal furnace.

The viscosity of 30% Greenwood anthracite ash-70% sodium carbonate was measured at 1600°F in a carbon dioxide atmosphere. The viscosity decreases rapidly with time. The initial viscosity of about 40,000 centipoises equilibrates in four to six hours at about 7,000 centipoises. The presence of steam in the imposed CO_2 atmosphere may slightly affect the rate of equilibration of the viscosity. After 23 hours the melting point of this mixture was determined to be about 1470°F. This is 30°F below the equilibrated melting point of this mixture when the data are obtained in a platinum crucible. This is probably due to the influence of corrosion products on the melting point. Corrosion products probably do not influence the viscosity to any great extent since the viscosity was relatively stable at 7000 centipoise from 5 hours to 23 hours.

Melting Point Data on 30% Greenwood anthracite ash-70% sodium carbonate in the presence of a CO_2 atmosphere have been compiled. A platinum crucible was used as container. The 30% anthracite ash-carbonate mixture rapidly equilibrates to a 1500°F melting point. The melting point data taken with CO_2 and with steam and CO_2 in an Inconel tube equilibrated at 1470°F. This indicated (1) the possible effect of corrosion products on lowering the melting point and (2) that the presence of steam in the CO_2 atmosphere apparently did not reduce the melting point further. Pure Na_2SiO_3 (10%) reduces the melting point only about 20°F below that of pure Na_2CO_3 and SiO_2 in molten carbonate appears to dissolve quite slowly or 10% SiO_2 (20% Na_2SiO_3) is past a low meeting eutectic. In any event, the decrease in melting point from pure Na_2CO_3 for 10% SiO_2 or 10% Na_2SiO_3 under one atmosphere CO_2 pressure is small.

2. Kinetics of Coal Gasification

Two experiments on the rate of gasification of anthracite (Greenwood) coal in molten sodium carbonate have been completed. Higher steam feed rates than previously reported were employed, therefore lower steam conversions to synthesis gas were obtained. In the previous runs considerable steam was consumed via the reaction to form sodium hydroxide ($Na_2CO_3 + H_2O \rightleftarrows 2NaOH + CO_2$). Less than 100% steam conversion was achieved in the latest runs using a higher steam rate. These data listed in the table below indicate that the amount of coal in the bed (availability of coal) is the limiting factor in the gasification rate under these conditions.

GASIFICATION OF ANTHRACITE COAL AT 1700°F
2 Inch I. D. Inconel Reactor
Minus 60 Mesh 414 g. Na_2CO_3, P_{H_2O} = 0.5 ATM

Run No.	% Coal in Melt	Initial Gasification Rate (Moles carbon gasified/hr)	Steam Rate, Moles/Hr.
J-9652	2.4%	0.18	0.88
J-9654	4.8%	0.4	0.88

3. Projections

Future work will involve continuation of viscosity measurements of ash/salt mixtures and the effect of operating parameters on the kinetics of gasification of anthracite coal. Other coals will be studied in the future.

IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High Temperature Materials

The test facility has been set up and the input metering devices (overhead solids feeder, gas flow meter, and water pump) are presently undergoing calibration. Except for this preliminary work, the equipment is ready for the test procedure.

B. Projections

1. Environmental Testing of High Temperature Materials

Upon completion of the calibration of the metering devices and the check-out of the components, the materials corrosion test will commence. The conditions of the test will be as follows:

Reactor

Inventory: Na_2CO_3 - 3440 g.
Ash - 400 g.
Graphite - 160 g.

Temperature: 1650°F

Pressure: Atmospheric

Feed

Steam - 103 g/hr.

Nitrogen - 5.51 SCFH

Graphite (pulverized) - 18.28 g/hr.

Na_2SO_4 (pulverized) - 1.7 g/hr.

Effluent

CO	0.603 SCFH
CO_2	0.534 SCFH
H_2S	0.0095 SCFH
H_2	1.77 SCFH
H_2O (g)	2.968 SCFH (67.5 g/hr.)
N_2	5.51 SCFH

Preliminary observations during bench-scale process studies have indicated that the corrosion rate of nickel alloys, such as Inconel and Incoloy, is inhibited by the presence of carbon in the melt. In order to monitor the carbon contents of the melt, there will be periodic carbon balance checks made on the process.

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