

RESEARCH AND DEVELOPMENT DEPARTMENT



MWR-MPR-17

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

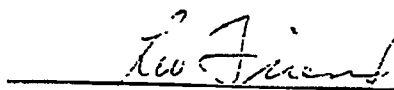
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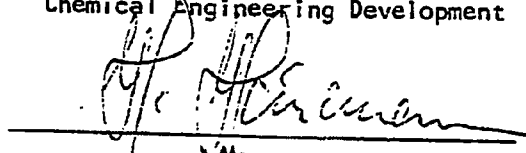
December 31, 1965

Progress Report No. 17

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THE M. W. KELLOGG COMPANY  
A DIVISION OF PULLMAN INCORPORATED



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RESEARCH & DEVELOPMENT DEPARTMENT

REPORT NO. 17

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## I. INTRODUCTION

The objective of this contract with the Office of Coal Research is to develop the Kellogg Gasification Process to the point where it will be able, on a commercial scale, to convert coal into pipeline gas at a cost of 50¢/MSCF or hydrogen at 25¢/MSCF. Five raw materials are to be studied -- an anthracite, a high-volatile bituminous coal, a sub-bituminous coal, a lignite, and a char. Although Kellogg's experimental work will not extend beyond the production of raw synthesis gas, the overall project must make engineering evaluations for four ultimate end products -- pipeline gas, hydrogen, synthesis gas, and transport gas.

Basis for the Kellogg Gasification Process is the reaction between steam and fine coal in a molten salt bath to form synthesis gas, a mixture of hydrogen and carbon monoxide, according to the reaction:



The necessary heat of reaction is supplied by circulating a heated molten salt stream. In addition, the molten salt mixture is chosen to catalyze the gasification reaction so that it may be carried out at a relatively low temperature.

The program is divided into three phases of study extending over a five-year period. Phase I, which is now in progress, involves several concurrent efforts:

1. Bench-scale process research -- to investigate melt properties, reaction kinetics, and the effect of process variables.
2. Chemical engineering studies and development -- to determine the optimum process flowsheet and operating conditions and to coordinate experimental work with overall project objectives.
3. Mechanical development -- to find acceptable materials of construction and develop techniques for handling the molten salt and powdered coal.



Phase I will be concluded by the design of a pilot plant to gasify 24 tons of coal per day, if it is found that a pilot plant program is justified by the bench-scale experimentation and economic studies.

Phase II will be devoted largely to the construction and operation of a pilot plant to convert a variety of raw materials into raw synthesis gas. The effect of operating variables found to be significant in Phase I will be investigated to obtain data for design of a commercial plant.

Phase III will involve the detailed process design of a commercial plant to produce 250 million standard cubic feet a day of product gas, including cost estimates and projected economics for those areas of the country that appear to offer commercial possibilities.



## II. SUMMARY

This progress report is the seventeenth since the awarding of the contract. It is concerned with the first phase of the contract and summarizes the progress that has been made in the three principal areas now being studied: process research, chemical engineering studies, and mechanical development.

The effect of increased superficial velocity on rate of gasification was investigated in the 2-inch-diameter Inconel reactor. With no coal ash present in the melt, gasification rate increased by a factor of 1.6-2.0 as superficial velocity was doubled, from 0.5 to 1.0 feet per second. With a melt containing 8% ash initially, which in itself increases gasification rate significantly, doubling the superficial velocity leads to a much smaller increase in the rate constant. It appears that both higher superficial velocity and ash content are important factors in increasing gasification rate, probably because of better steam-carbon contacting. Present flowsheet designs employ superficial velocities of 0.5-1.5 ft/sec and rates consistent with those determined in experiments at 0.5 ft/sec with ash present; if indicated trends persist for combustion as well as gasification, calculated reactor volumes may be high by 10-20%.

Changes were made in accessory equipment in an effort to try even higher gas velocities, say 2 ft/sec. However, salt carryover was too great and the unit plugged. It was concluded that design of the reactor itself and the off-gas-handling equipment would have to be modified to permit study of higher velocities.

The effect of carbon monoxide on gasification rate was investigated by using a mixture of 30% steam-70% CO as gasifying medium. Unfortunately, most of the steam reacted with CO to yield water-gas shift equilibrium, and little coal was gasified. No conclusion was possible as to the effect of carbon monoxide on the kinetics of the steam-carbon reaction.



The effect of higher reactor pressure on gasification rate was also investigated. At 1850 F, 0.5 ft/sec, with no ash present initially in the melt, specific rate constant for gasification of bituminous coke increased by a factor of 2.4 as steam partial pressure tripled, from 13.5 to 41 psia. Further study of the effect of pressure is under way. The observed increase in gasification rate with increased pressure offers the possibility of decreasing reactor size and capital cost or of lowering the operating temperature to ease the burden on materials of construction.

Process designs and economic studies of plants for producing pipeline gas from subbituminous coal and bituminous coal are continuing. Studying the effect of varying assumptions on estimated costs will continue to serve the purpose of guiding experimental effort into the most sensitive process areas.

A 400-hour corrosion test of samples of high-purity, high-density alumina obtained from four manufacturers was completed under gasification conditions. Samples of Monofrax A, the product of Harbison-Carborundum Corporation, again survived the test in good condition, showing an average corrosion rate of about 0.2 inches per year. All the other samples disappeared. Although all samples tested were high-purity, high-density alumina, only Monofrax A is melted and cast to shape; the others are all cast from particles and then fused at high temperature. This appears to be the key to the much better performance of Monofrax A.

A 300-hour test of two of the other aluminas (not Monofrax A) under oxidizing conditions, to simulate the combustor conditions of a commercial flowsheet, showed much better corrosion resistance than under gasifier (reducing) conditions. This confirms that the bulk of the corrosion test work to date has in fact been conducted under the most stringent conditions expected to be encountered, i.e., those in the gasifier.

Another corrosion test run will begin soon on still other high-purity aluminas, on yttria-stabilized zirconia, and on Haynes Alloy 150 (28 Cr, 50 Co, 20 Fe).



### III. PROCESS RESEARCH

#### A. Accomplishments

##### 1. Gasification Studies

All the gasification runs conducted during the month are presented in Table I. The effect of higher superficial gas velocity at several temperatures was studied, the effect of carbon monoxide overpressure was looked at, and runs at higher steam pressures were started.

The effect of higher gas velocity, as represented by 1 ft/sec superficial velocity of 90% steam in nitrogen, has been determined at two additional temperatures and also in the presence of 8% bituminous coal ash in the molten salt. The reaction rate constants for these runs are compared in the following tabulation with those from an Arrhenius plot of runs using 0.5 ft/sec superficial gas velocity.

<u>Run</u>	<u>Temp. °F</u>	<u>% Ash</u>	<u>Rate Constant -k at</u>	
			<u>1 ft/sec</u>	<u>0.5 ft/sec</u>
9917	1650	-	0.95	0.23
9918	1740	-	1.09	0.55
9916	1845	-	2.25	1.37
9920	1845	8	2.57	2.3



Table I

Gasification of Bituminous Coal and Coke in Molten  $\text{Na}_2\text{CO}_3$  /1/

Run No. J-	9917	9918	9919	9920	9921	9922	9923
Date - 1965	11/30	12/3	12/6	12/8	12/14	12/20	12/22
Feed	←----- Coal -----→			←---Coke IV ---→			
% Total Carbon	←----- 81.3 -----→			←---93.2 ---→			
% Volatiles	←----- 37.2 -----→			←--- 0.6 ---→			
% Ash	←----- 3.9 -----→			←--- 6.2 ---→			
gms. charged	←----- 20.0 -----→			←---19 ---→			
mesh size	←----- 12/20 -----→						
$\text{Na}_2\text{CO}_3$ - gms.	←----- 414 -----→		381	←-----414 -----→			
bed ht.-inches	←----- 0 -----→		4	←----- 0 -----→			
Ash - gms.	←----- 0 -----→		33	←----- 0 -----→			
% in melt	←----- 0 -----→		8	←----- 0 -----→			
% C in melt init.	←----- 0 -----→		3.8	←----- 0 -----→			

Conditions

Temp-°F	1650	1740	1840	1845	1840	1850	1850
Pressure-psia	15	15	15	15	15	15	46
% Steam	91	91.5	30	91.2	90	92.7	90.2
Gas in Steam	$\text{N}_2$	$\text{N}_2$	$\text{CO}$	$\text{N}_2$	$\text{N}_2$	$\text{N}_2$	$\text{N}_2$
Ft./Sec. strm & Gas	1.0	1.0	0.5	1.0	2.0	0.5	0.5
Min. to 0 % CO	65	(55)	-	35	-	75	25
Total Run-min.	65	65	55	35	-	85	35

Results

% C to $\text{CO}$ & $\text{CO}_2$	88.4	87.2	22	88.5	-	84.8	79.2
% C to $\text{C}_{1-3}$	4.1	5.8		3.8	-	-	0.1
% C to tar, etc.	5.5	5.5	5.5	5.5	-	-	-
Total % C	98	99	28	98	-	85	79

Spec. Gasif. Rate Const.

Basis Input	0.95	1.09	-	2.57	-	(0.67)	(1.20)
Basis Output	0.95	1.09	-	2.57	-	0.82	2.0

Rate-lbs.C/hr/CF

at 10% C in bed	30	34	-	80	-	26	62
at 4% C in bed	11	13	-	30	-	10	24

Salt Carryover-gms.

	18.2	17.1	11.4	-	-	10.0	8.5
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Notes

- /1/ Island Creek #27 Bituminous coal used and coked at 950°C to give coke IV; 2 inch I.D. Inconel reactor, steam preheated to 700-750°F.
- /2/ From 5 to 55 min. when a plug developed, the conversion of C to  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{C}_{1-3}$  was constant at 18-24%, average 22%.
- /3/ High salt carryover at 2 ft/sec; when coal added high gasification rate and salt carryover caused immediate plugging of unit.
- /4/ Some of coke charge hung up in the inlet system.





The significant improvement in rate at the higher velocity is well exhibited by the results on the non-ash runs. The  $k$  value of 0.95 for run 9917 appears high and may be due to an erroneous temperature record (less significance is placed on this value). It does appear that a factor of about 1.6-2.0 in rate was achieved by doubling the velocity of steam-nitrogen through the molten salt. However, when one compares the results for the melts containing 8% ash, only a small difference exists between the two runs at 0.5 and 1 ft/sec velocity. Addition of 8% ash improves  $k$  as much as increasing the velocity from 0.5 to 1 ft/sec does, and it appears that combining both the 8% ash and the higher velocity gives an added boost in rate.

The improvement noted above appears to be due to better contact of steam and coke. The increased agitation by the higher velocity of steam through the liquid most probably improves contact. The effect of ash is quite obscure although, as was conjectured earlier, it perhaps improves the wettability of the coke and thus its distribution in the liquid or it helps to produce a larger number of small steam bubbles, thus obtaining better contact of the reacting species.

In addition, part of the ash constituents may function catalytically to increase the rate of the steam-carbon reaction.

In run 9920 at 1840°F, 1 ft/sec, 8% ash in melt and only 0.9 atmosphere steam pressure, the rate of 30 pounds of carbon gasified per hour per cubic foot of melt at 4% carbon level meets the desired commercial design rate.



An unsuccessful attempt to obtain 2 ft/sec superficial gas velocity was made in run 9921. This required a new steam generator and a Lapp pump for the water system to generate 2 ft/sec through the 2 inch I.D. Inconel reactor. At this velocity, salt carryover was very high, requiring frequent reaming of the outlet lines. When the coal was charged, the gas make was too high for the 20 CF meter to handle, and the salt and coal carryover caused a plug to develop in just one minute. The plug could not be relieved, and the unit had to be shut down. This reactor system cannot be operated at this high velocity level.

The presence of carbon monoxide in the steam was investigated in run 9919 where 30% steam in carbon monoxide was passed into the reactor at 0.5 ft/sec. A reaction rate constant could not be obtained because the conversion remained approximately constant from 5 minutes to 55 minutes, when a plug in the outlet required shutdown. Apparently, after the first five minutes none of the carbon from the coal reacted. Only the carbon monoxide fed in was reacting with steam to give a water-gas equilibrium constant of 1.05, which represents equilibrium at 1500-1520°F. This value, in agreement with some previous runs, indicates equilibrium is being obtained at this temperature. Practically all the water fed in was utilized in the water-gas reaction as only a cc or two was condensed in the outlet. Thus, very little steam was available for the carbon-steam reaction. Consequently, the effect of carbon monoxide on the kinetics of the carbon-steam reaction cannot be ascertained from this experiment.

Investigation of the effect of steam pressure up to the maximum permitted for the Inconel reactor presently in use required some modifications to the inlet and outlet sections. First it was established that the reactor could take up to 60 psia for about 200 hours at 1840°F. A new



reactor was commissioned after attaching a 75 psia relief valve and knockout drum to the top of the reactor for safety. A relief valve was also added to the water system ahead of the steam generator. An 80 CF meter was placed in service. Modifications were made to the gas chromatographic equipment to improve stability. This was ultimately achieved when a 50°C constant temperature oven was attached to the partitioner. To prevent tars from interfering with the pressure controller, a Grove back-pressure regulator, and to insure operability the bituminous coal was coked at 1740°F to give Coke IV. This material will be used for the pressure runs.

The first run with Coke IV (Run 9922) was made at atmospheric pressure, 1850°F, 0.5 ft/sec superficial velocity, 3.8% carbon in melt initially. The specific gasification rate constant was 0.82, based on output because some coke hung up in the inlet system. Coal under these conditions would have shown a k of 1.37; thus Coke IV shows lower reactivity than the coal.

In the first run above atmospheric pressure, namely 46 psia in run 9923, suitable adjustments in steam and nitrogen flow rates were made to maintain the 0.5 ft/sec superficial velocity in the reactor at 1850°F and 3.8% carbon in melt initially. The rate constant was 2.0, again based upon output because of coke loss in the inlet system. This rate constant represents an exceptional increase in rate due to the increase in steam pressure from approximately 13.5 psia to 41.4 psia. Further work on the effect of steam pressure is continuing.

#### B. Projections

The effect of steam pressures up to 55 psia on the kinetics of gasification are presently being studied and will probably take most of January.



#### IV. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

##### A. Accomplishments

Assessment of the economic potential for producing pipeline gas from subbituminous coal was continued during December. Flowsheet changes were made to incorporate improvements resulting from recent experimental work, as discussed last month, and to improve energy utilization throughout the plant. Material balances and utilities requirements are being revised to reflect the changes made. Capital investment required for supplying steam, power, cooling water, etc. and for other offsite facilities is now being estimated.

Process design of the plant for producing pipeline gas from bituminous coal was also continued. Equipment is now being sized so that an estimate of capital cost can be made.

A technical paper, "Development of the Kellogg Coal Gasification Process", was presented before the Symposium on Processing of Coal and Its By-Products at the Philadelphia Meeting of the American Institute of Chemical Engineers.

##### B. Projections

Process designs and cost estimates for producing pipeline gas from subbituminous and bituminous coals will be continued so that an economic appraisal of the process at this stage of development can be presented and the sensitive areas in the design, where further experimentation is necessary if the process is to realize its full potential, can be pointed out.



V. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High-Temperature Materials

Test #7 has been completed during this report period. This test, conducted in a reducing atmosphere, was of approximately 400 hours duration, and included samples of the following materials (all high-purity, high-density aluminas):

1. McDanel AP-35 (Both reactor liner and test coupons.)
2. Coors AD-99
3. Norton 4995
4. Monofrax A

Upon examination at the end of this test, the following results were obtained:

1. McDanel AP-35 - liner cracked, test coupons completely missing.
2. Coors AD-99 - completely missing.
3. Norton 4995 - completely missing.
4. Monofrax A - all three samples recovered.

The walls of the reactor liner (McDanel AP-35) had become thinner and had cracked, probably due to thermal shock or mechanical crushing during the rapid cool-down at the end of the test period. The Monofrax A samples were in very good condition and exhibited only slight evidence of corrosion. Corrosion rates calculated from these samples averaged about 0.2 inches per year.

Of interest is the fact that the Monofrax A withstood the test while other high-purity aluminas did not. One possible explanation for this is in the manufacture of the Monofrax. Monofrax A is the only material in this test that is melted and cast to shape; the other specimens are all "slip-cast," i.e., cast then fused at high temperature.



The other test described in the last report, that of environmental testing in an oxidizing atmosphere, has also been completed. The McDanel AP-35 liner in this test was not affected, but the same material used as the gas inlet tube was eroded away to failure at the liquid-gas interface. This erosion seemed to be uniform and caused the inlet tube to have a resultant taper. Duration of this test was approximately 300 hours. A specimen of Norton 5995 included in this test lost no weight and appeared in good condition.

## 2. Coal Feeding Studies

The coal feeder has been incorporated into the corrosion test facility and will be used in all further environmental testing as a replacement for the previously-used lock-hopper.

### B. Projections

#### 1. Environmental Testing of High-Temperature Materials

As soon as the test facility can be readied, Test #8 will begin. Samples scheduled for this test include:

Lucca Lox                    - High-Purity Alumina  
Norton 5995                    "                    "                    "  
Zirconia Y-1027)  
Zirconia Y-1485) - Yttria-stabilized Zirconia  
Zirconia Y-1484)  
Zirconia Y-1225)  
Haynes Alloy 150 - 28 Cr, 50 Co, 20 Fe.

This test is scheduled for 400 to 500 hours duration.

A second oxidation test will also be run, testing at least the Monofrax A and possibly some of the Zirconia materials.

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2. Coal Feeding Studies

The coal feeder previously discussed will be used in further environmental testing. Work is continuing on designing a coal feeder for the high-pressure reactor.

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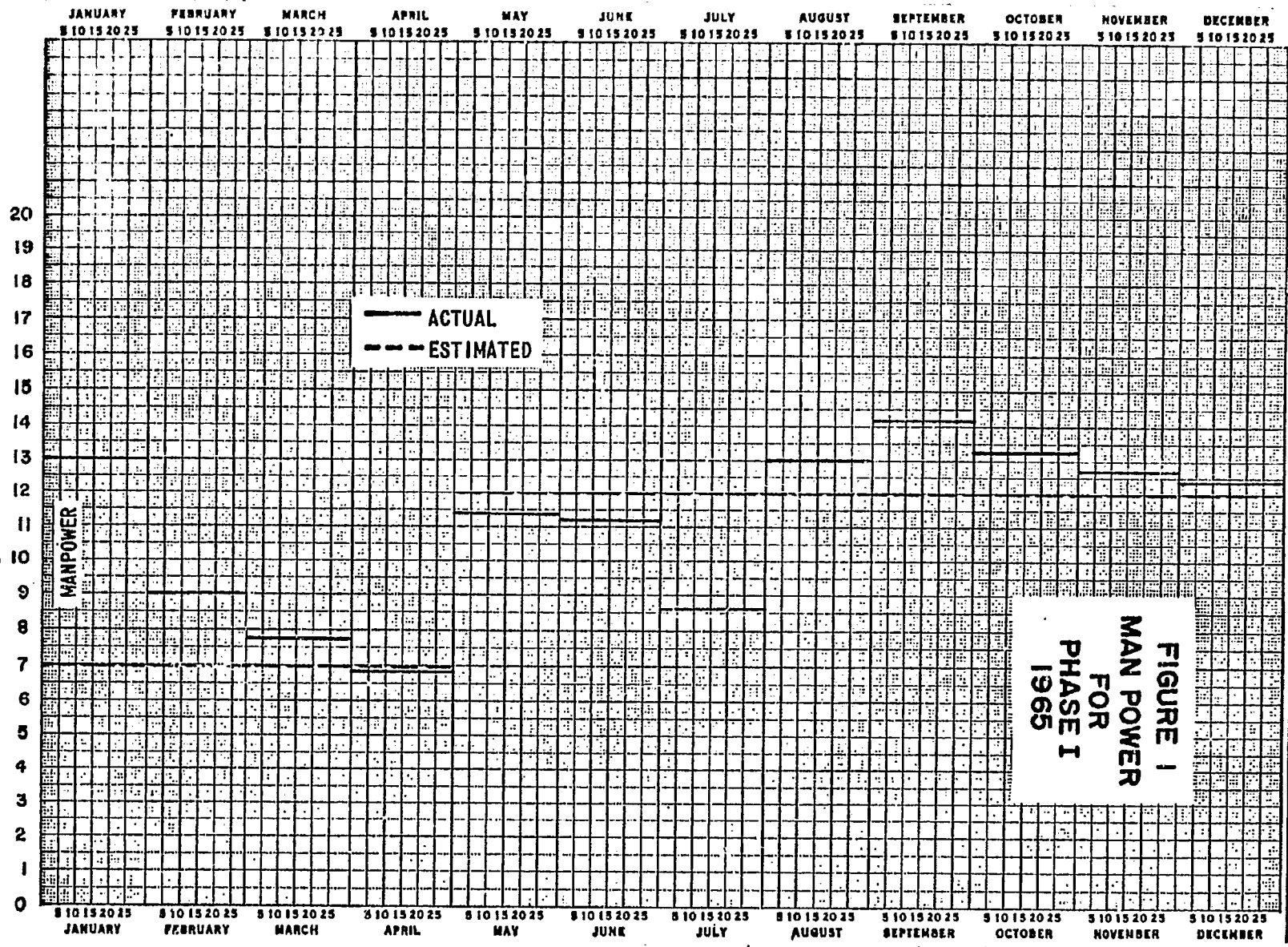
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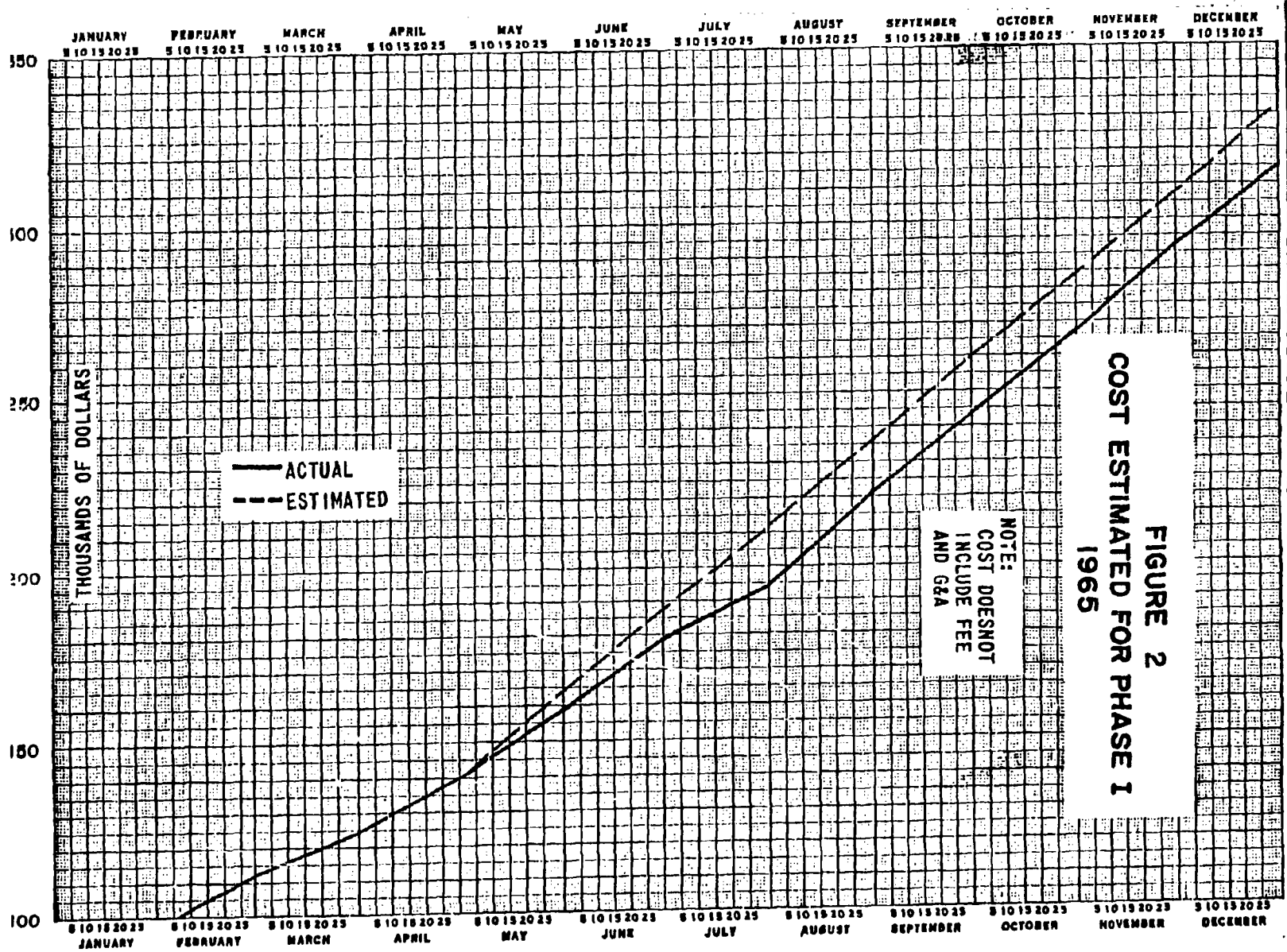
### VI. MANPOWER AND COST ESTIMATES

Figure 1 shows the projected manpower breakdown for Phase I for 1965 as well as the actual effort that was made. It can be seen that a 12.4 man-effort was made during December.

Figure 2 shows the expenditures during December. For the month \$23,203 was expended, not including fee and G & A. The total expenditures through December were \$315,496. Including fee and G & A the total expenditures were \$363,183. This is 60.5% of the encumbered funds.







**FIGURE 2**  
**COST ESTIMATED FOR PHASE I**  
**1965**

NOTE:  
 COST DOES NOT  
 INCLUDE FEE  
 AND G&A

— ACTUAL  
 - - - ESTIMATED

THOUSANDS OF DOLLARS

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