

MWK-MPR-10

RESEARCH AND DEVELOPMENT DEPARTMENT



DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

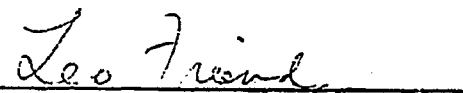
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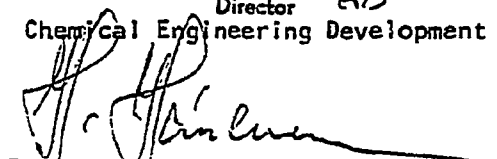
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Progress Report No. 10

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I. INTRODUCTION

About forty runs were made on the coal feeding equipment using +20/-10 mesh sand as the solid material and air as the transporting medium.

A paper entitled "Preliminary Evaluation of the Kellogg Coal Gasification Process" was presented at the American Gas Association Production Conference at Buffalo, New York.

Detailed design work was initiated for a test unit to examine the effects of variables at pressure levels to 400 psig. A reactor size of 3-inches I. D. by 5 feet high has been selected as a convenient size for bench-scale batch experiments to provide a reasonable scale up for design of a continuous pilot plant.

The effect of steam partial pressure at 90% and 30% levels under 1 atm. total pressure with nitrogen and at 0.5 ft./sec. superficial gas velocity in the reactor was determined. There was no effect on gasification rate.

A two to three fold increase in specific gasification rate was obtained by a change of mesh size from (12/20) to -200.

Analytical work was completed on the study of the effects of variables on the recovery of sodium carbonate from melts. From the results it is concluded that with 10% ash in the melt the loss of sodium carbonate is 3% of the amount charged to the recovery unit.



II. PROCESS DEVELOPMENT

A. Accomplishments

A paper entitled "Preliminary Evaluation of the Kellogg Coal Gasification Process" was presented at the American Gas Association Production Conference at Buffalo, New York.

Evaluation of gas purification processes was continued, with the objective of selecting the optimum scheme for pipeline gas and for hydrogen. The following regenerable solvent processes are being studied:

- a. Hot potassium carbonate
- b. Monoethanolamine
- c. Fluor (propylene carbonate)
- d. Vetrocoke (arsenic-promoted K_2CO_3)
- e. Sulfinol (di-isopropanolamine in tetramethylene sulfone)
- f. Acetone
- g. Rectisol (refrigerated methanol)

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

For pipeline gas the CO_2 level must be reduced to about 1% and the sulfur compounds, to less than 0.1 ppm prior to synthesis. In producing hydrogen the CO_2 should be less than 10 ppm, while a sulfur concentration of 1 ppm is acceptable.

The Fluor and Shell Sulfinol processes appear to have an edge over the others for several reasons:



- a. good solvent capacity
- b. non-corrosive solvent
- c. sulfur compounds removed reversibly
- d. low utilities consumption
- e. low investment

It seems quite possible that the same process combination will be chosen for pipeline gas and hydrogen although specifications for purified gas differ somewhat. Information requested from Lurgi on the Rectisol process has still not been received.

B. Projections

Evaluation of gas purification schemes will be continued and, hopefully, concluded. Process flowsheets will be prepared for the complete pipeline gas plant so that overall thermal efficiency can be studied and a better estimate of plant investment can be made.



III. PROCESS RESEARCH

A. Accomplishments

1. Gasification Kinetics

A reproducibility run was made using Coke I, the 850°C coked bituminous coal (Island Creek #27), followed by seven runs using the same coal coked to 600°C (Coke II). These runs are summarized in Table I and discussed below. Rate based on the production of oxides of carbon is considered the most reliable for discussion below.

A number of runs on Coke I can be averaged showing that reasonably good reproducibility has been obtained by the method employed for studying gasification. These runs are tabulated below.

<u>Run No. J-</u>	<u>% C Gasified</u>	<u>Gasification Rate k</u>	
		<u>Input</u>	<u>Output</u>
9777	90.6	0.16	0.19
9778	100.2	0.26	0.26
9779	97.7	0.20	0.21
9781	82.2	0.17	0.17
9782	86.1	<u>0.19</u>	<u>0.27</u>
	Average	0.20	0.22

Run J-9782 was a duplicate run of J-9777. Runs J-9778 and 9779 used Na₂CO₃ preimpregnated coke and run J-9781 employed 20/40 mesh coke instead of 12/20 mesh used in all the other runs. Thus the results indicate no effect of preimpregnation or mesh size in the range mentioned.

TABLE I
GASIFICATION OF BITUMINOUS COKE IN MOLTEN Na₂CO₃ (1)

Run No. -J-	9782	9783	9784	9785	9786	9787	9788	9789
Feed(2)	Coke I			Coke II				
% Volatile Matter	1.6			7.6				
% Fixed Carbon	90.7			86.6				
Ash	7.7			5.8				
gms. charged	38.3	35.8	35.1	35.6	35.0	35.0	26.9	20.0
mesh size				12/20			-200	12/20
% Steam in N ₂ Inlet	90	90	0	90	0	30	90	0
Total Run Time - min.	305	270	65	275	45	220	175	30
% C Gasified - basis C oxides(6)	86.1	72.0	21.9	106.5	3.9	122.3	121.0	10.4
Reducing Power - 1/2 (H ₂ +CO)	70.4	84.5	17.3	81.3	-	92.4	72.8	-
Ratio H/O in Dry Gas	1.6	2.4	-	1.5	-	1.4	1.1	1.3
Specific Gasification Rate(3)								
Input C - basis C oxides	0.19	0.15	0.1	0.32	-	0.39	0.90	-
Output C - basis C oxides	0.27	0.29	-	0.29	-	0.29	0.53	-
Input C - basis 1/2 (H ₂ +CO)	0.13	0.22	-	0.22	-	0.29	0.55	-
Output C - basis 1/2 (H ₂ +CO)	0.26	0.30	-	0.32	-	0.31	0.78	-
Notes		(4)	(5)		(4)	(7)		(7)

- (1) Normal run conditions: 1700-1770°F, atm. pres., steam partial pressure 13.3-13.6 psia, 0.51 superficial gas velocity, 4" glescent bed height, 414 grams Na₂CO₃.
- (2) Island Creek #27 bituminous coal coked to 850°C (Coke I) or to 600°C (Coke II).
- (3) k in hr⁻¹ from $k = -\frac{1}{t} \log \frac{c}{c_0}$, assuming first order carbon reaction.
- (4) Possibility of some gas unrecorded.
- (5) Possibility of small amount of water vapor in nitrogen at 0.5 ft./sec. super. gas velocity
- (6) Includes CO and CO₂ from volatile matter, probably about 2% from Coke II.
- (7) No nitrogen sweep gas.





Two runs were made to evaluate the new coke and to establish its reactivity versus Coke I. Run J-9783 was questioned because of the possible loss of some product gas before the meter, consequently the run was repeated in J-9785. As seen in the following comparison of gasification rates on the two cokes, Coke II is about 30% more reactive than Coke I.

		Gasification Rate k <u>Input</u>	<u>Output</u>
Coke I	Ave. 5	0.20	0.22
Coke II	J-9783	0.15	0.29
	J-9785	0.32	0.29

The effect of steam partial pressure at the 90% and 30% levels under 1 atmosphere total pressure with nitrogen and at 0.5 ft./sec. superficial gas velocity in the reactor was determined. The results show no effect on gasification rate as is seen in the following tabulation. This is in agreement with earlier results on anthracite coal.

<u>Run J-</u>	<u>% Steam</u>	Gasification Rate k <u>Input</u>	<u>Output</u>
9787	30	0.39	0.29
9785	90	0.32	0.29

The effect of a gross change in particle size was achieved by grinding a charge of 12/20 mesh coke II down to -200 mesh, then mixing it with an equal weight of sodium carbonate, pelleting it and regrinding to give 12/60 mesh particles which could be charged to the reactor in the normal way. A 20 mesh sieve retains particles larger than 0.84 mm., while -200 mesh passes particles smaller than 0.074 mm., hence at least a factor of eleven in particle size was obtained. Another way of looking at the difference in particle size as represented by surface area is to consider the 12/20 mesh as 1 mm cubes, of 6 sq. mm surface area, which when cut to 0.05 mm cubes now represents

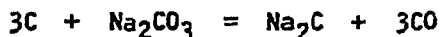


120 sq. mm., a 20 fold change in surface area. This change in surface area produced a two to three fold difference in specific gasification rate.

<u>Run J-</u>	<u>Mesh Size</u>	<u>Gasification Rate k</u> <u>Input</u>	<u>Output</u>
9788	-200	0.90	0.53
9785	12/20	0.32	0.29

The non-response of previously studied variables on gasification rate suggested that the possibility of direct reaction of carbon and sodium carbonate might explain the data. In order to determine this, two types of runs were made; in J-9784 nitrogen gas was used without the addition of steam to give agitation of the melt by a superficial gas velocity of 0.5 ft./sec. and in J-9786 and 9789, neither steam nor nitrogen was added. In 9784, a very small but undetermined amount of water vapor entered the reactor (the nitrogen gas passed by the water inlet tube which was not blocked off). In 9786, a leak developed during the run at a union in the feed system, thus the run was repeated in 9789.

In the first case, with agitation from the nitrogen, about 20 percent of the carbon was gasified at a k of roughly 0.1 hr^{-1} before total dropoff of carbon monoxide production. While without any agitation, about 10 percent of the carbon was gasified before the reaction stopped. In both cases carbon monoxide production was high initially. Thus although some direct reaction of carbon and carbonate is evident, the reaction stops fairly quickly. No direct evidence can be presented to explain the mechanism although it is obvious steam is necessary for the normal reaction rates observed. A possible mechanism can be proposed as follows.



The Na_2C prevents further reaction of the carbon. If steam is present it reacts with the sodium carbide:



The Na_2O does not exist very long in the presence of steam and carbon dioxide formed from the water gas shift. This reaction must be rate controlling.



In the -200 mesh feed run, it was notable that carryover of salt was not observed since the reactor exit tube did not require the usual reaming out procedure. Explanation of this, as well as evidence for the above mechanism, must await a concerted attack on the problem.

During the month, the second gasification unit was put into commission. The original reactor had to be retired because of corrosion which was exhibited by breakoffs of the 1/4 inch inconel tubing used for the thermowell and inlet tubes.

2. Sodium Carbonate Recovery

Analytical work was completed on the quantitative experiments reported last month studying the effect of certain variables on the recovery of sodium carbonate from bituminous coal (Island Creek #27) ash-sodium carbonate melts. The details of the recovery scheme were described in the last summary. The results are shown in Table 2.

The results are presented as the percent of silica, of combined R_2O_3 oxides of aluminum and iron, and of sodium which was in the original charge that remains in the residue after leaching. Since this residue will be discarded in the process, it is desired that the silica and combined oxide results be high and the sodium result be low. Leach conditions at the two levels of solution to solid and for the two times indicate no major effect. Even particle size at the two levels leads to similar results and no effect. The only major effect appears to be due to the ash content of the melt, the higher ash content leading to higher sodium loss, which is undesirable. In the following, the results have been averaged for the runs shown.

Runs	Ash Melt		Average Residue i Results		
	% Ash	Mesh Size	% of SiO_2	% of R_2O_3	% of Na
1-4	10	12/20	68	90	3.7
5-8	10	40/100	58	86	3.0
9-12	20	12/20	78	99	11
13-16	20	40/100	82	97	12
1-8	10	-	63	88	3.3
9-16	20	-	80	98	11

TABLE 2

SODIUM RECOVERY FROM BITUMINOUS COAL ASH- Na_2CO_3 MELTS

Run No.	Composition of Ash Melt					Leach Conditions		Results		
	% Ash	% SiO_2	% R_2O_3	% Na	Mesh Size	gms. Sol'n per gm Solid	Time min.	% of Charge in Residue 1		
								SiO_2	R_2O_3	Na
1	} 10	3.92	2.69	40.0	12/20	12	20	69.7	95.4	3.61
2						12	10	74.7	100.3	3.94
3						6	20	66.8	83.7	3.81
4						6	10	60.6	79.7	3.44
5	} 10	3.65	2.37	40.4	40/100	12	10	52.8	81.3	3.10
6						12	20	62.5	88.0	2.93
7						6	10	63.1	90.3	3.12
8						6	20	54.0	83.2	2.75
9	} 20	8.02	8.22	37.8	12/20	12	20	84.2	93.2	10.7
10						12	10	81.1	98.8	10.8
11						6	20	68.2	105.1	10.5
12						6	10	78.9	99.4	11.3
13	} 20	8.60	7.80	36.0	40/100	12	10	81.4	102.3	12.2
14						12	20	81.8	97.0	11.7
15						6	10	82.8	94.0	10.7
16						6	20	83.2	95.0	13.1

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It appears that besides the higher sodium retention, higher silica and combined oxides are also retained by the residue from the higher ash content melt. Thus it is concluded that 10% ash in the melt appears much more desirable than 20% and leads to a reasonable 3% sodium carbonate loss. About 35% of the silica was dissolved and probably gets recycled in the NaHCO_3 solution. Some spot analyses will be made to confirm this and to also try to locate the 12% dissolution of the combined R_2O_3 oxides. The effect of these substituents upon recycling may be ascertained at a later date.

3. Pressure Test Unit

Detailed design work was initiated for a test unit to examine the effects of other variables at pressure levels to 400 psig. A reactor size of 3-inches I. D. by 5 feet high has been selected as a convenient size for bench-scale batch experiments to provide a reasonable scaleup for design of a continuous pilot plant.

A pressure shell, lined with corrosion resistant ceramic, will be used to contain the molten salt bed. Endothermic heat of reaction will be supplied by passing an electric current through the molten salt between two immersed electrodes. Steam and coal will be fed and product gas removed continuously.

To aid in the design of the steam plus coal feed system, a 3-inch glass model has been set up to study bubble behavior and solid-liquid mixing using various designs of feed tubes. Glycerin-water and glycerin-cabosil mixtures have been used to study the effect of viscosity on contacting, and bits of cork have been used to simulate the density difference of coal and molten salt to observe the extent of mixing.

B. Projections

Gasification work will concentrate on establishing reproducibility of the new second unit with the older unit, on determining, if possible, the reactivity of bituminous coal directly and the effect of changing parameters. Very little work is contemplated on further sodium recovery experimentation. Introduction of additives to the melt for possible gasification improvement will be tried with finely divided ferric

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oxide, and possibly nickel supported on magnesia. Consideration must also be given to a study of combustion of the melt containing carbon.

Final design of the pressure test unit will be completed during the coming month so that materials can be ordered and equipment built for use during August.



IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High Temperature Materials

Since the experimental results of Test #2 showed zirconia to be a highly promising refractory material for this application, the Zirconium Corporation of America, a pioneer in the zirconium products business, was contacted. (The Carborundum product, Zircofrax 0, is produced and distributed on a developmental basis) Four different test samples of their products, listed below, are being procured.

1. Code W1247 - A standard compound used in manufacture of refractory plates and bricks.
2. Code 1027 - A special compound used in manufacture of refractory plates and bricks.
3. RMF-5F - A phosphate bond, air set, refractory grade ram mix of 98% stabilized zirconia.
4. Zircoa-Cast 600 - A dense, 60-mesh, self-setting 99% zirconia (lime stabilized) castable which hardens hydraulically in a confined mold.

2. Coal Feeding Studies

The experimental test setup outlined previously has been run and several minor modifications made. To date some forty runs have been made using +20/-10 mesh sand as the solid material and air as the transporting medium.



The tests were run at the following conditions:

Pressure in the transport tube: 1, 10 & 20 psig

Velocity in the transport tube: 30, 35, 40 & 50 fps

Solids loading approximately: 0.2 to 1.0 lb. sand/ft³ of air

The results of these test runs are being analyzed currently and the results will determine what the next test step should be.

B. Projections

1. Environmental Testing of High Temperature Materials

All the materials and fabricated products required for the construction of the equipment for Test #3 have been ordered. The test area is being made ready and the test equipment will be set up upon receipt of the new reactor.

2. Coal Feeding Studies

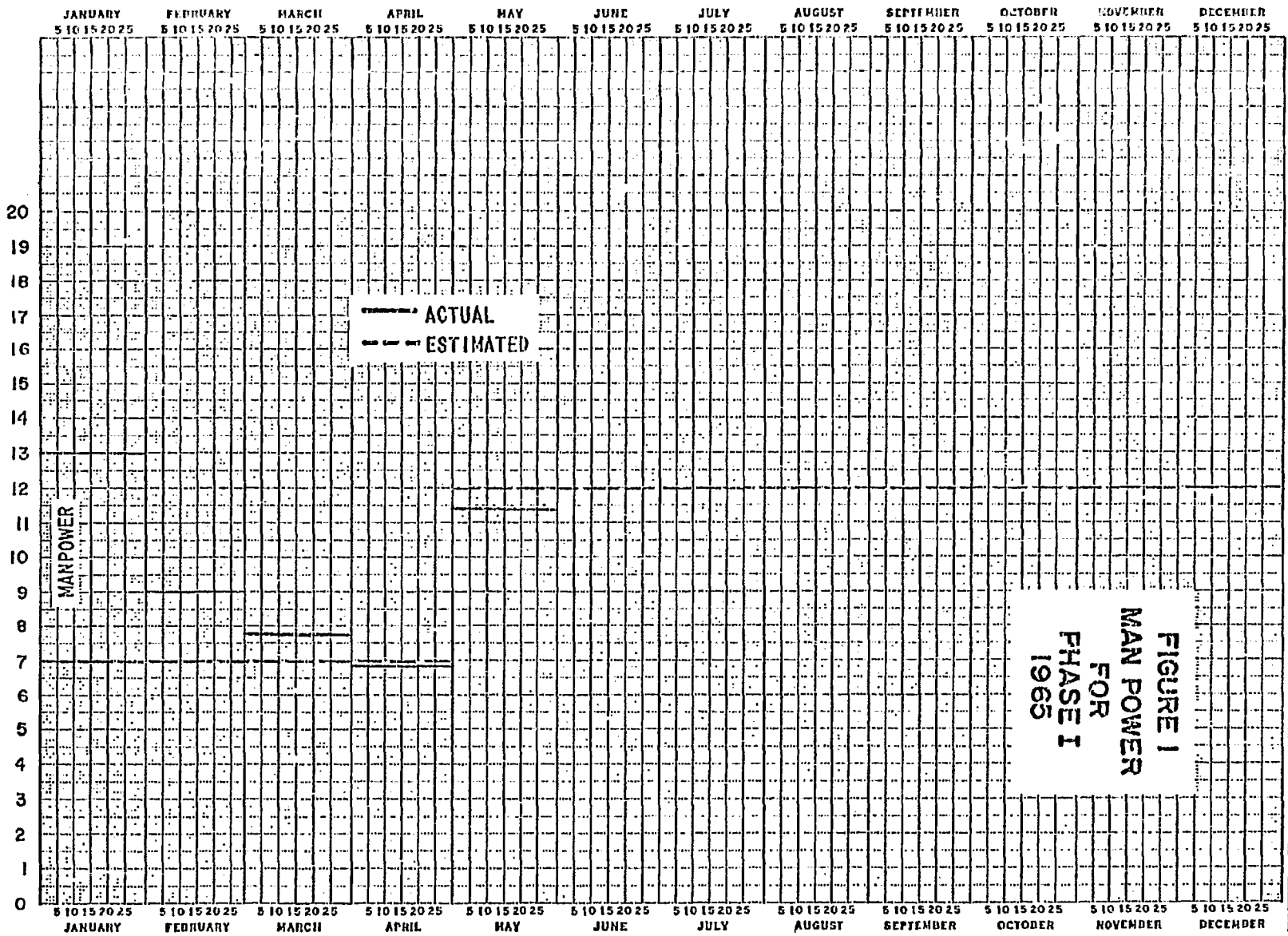
Some further testing with sand and air may be required, based on the results of current tests. Ultimately, coal and an inert carrier gas will be tested.



V. 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 an 11.4 man effort was made during May.

Figure 2 shows the expenditures during May. For the month \$20,177 was expended not including fee and G & A. The total expenditures through May were \$159,000. Including fee and G & A the total expenditures were \$186,944. This is 47 percent of the encumbered funds.



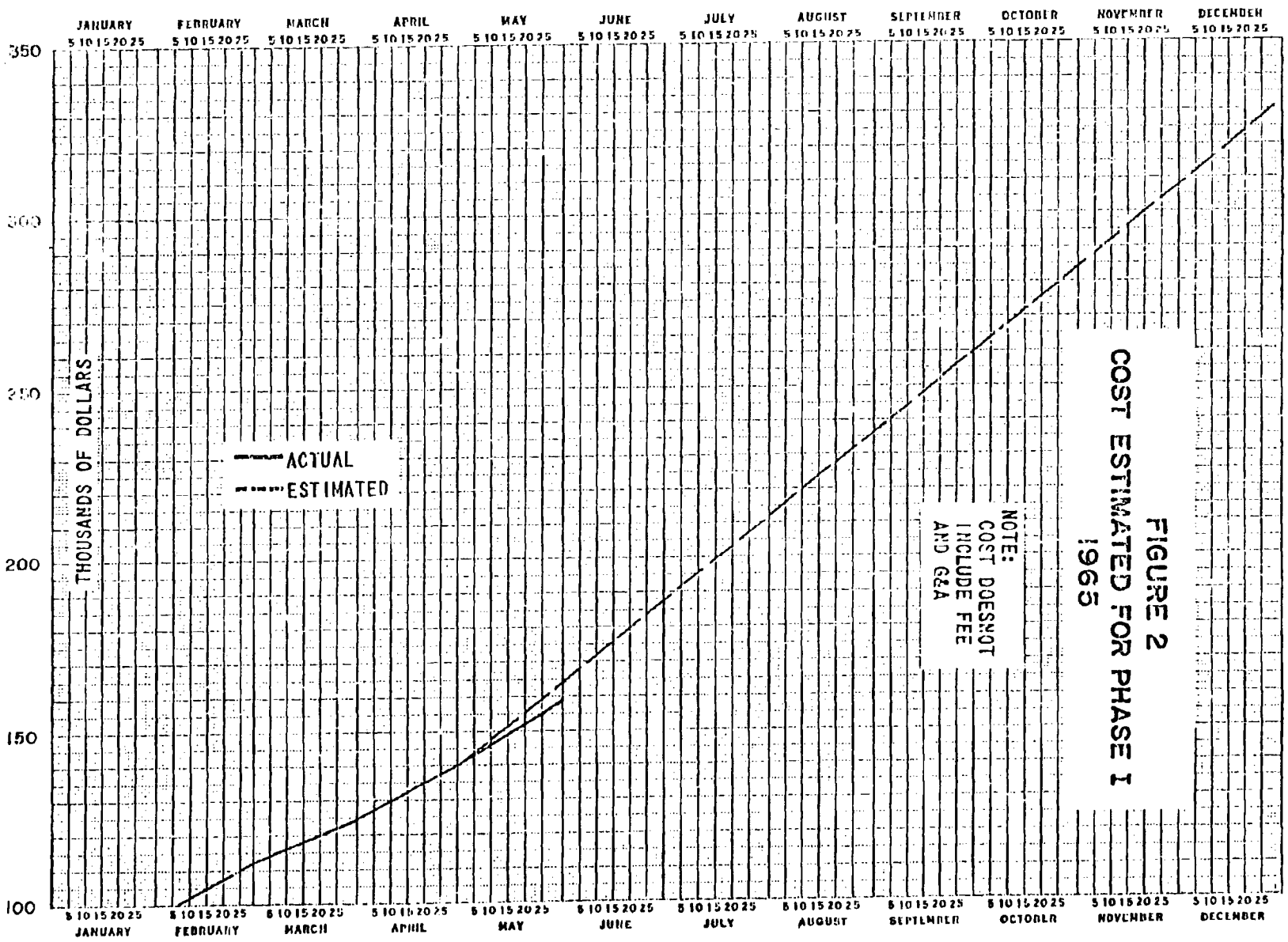


FIGURE 2
 COST ESTIMATED FOR PHASE I
 1965

NOTE:
 COST DOES NOT
 INCLUDE FEE
 AND G&A