MWK-MPR-32

RESEARCH AND DEVELOPMENT DEPARTMENT

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

March 31, 1967

Progress Report No. 32

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CONTENTS

1. SUMMARY

This progress report is the thirty-second 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.

Three new combustion runs were made to determine the effect of carbon dioxide on the burning rate of anthracite and to better define the effect of sodium sulfate content of the melt on the combustion rate of bituminous coke. The presence of 20 percent carbon dioxide in air was found to increase the combustion rate of anthracite by about 50 percent over an otherwise identical run using 20 percent nitrogen in air. The addition of 0.5 percent sodium sulfate to the melt was found to increase the combustion rate of bituminous coke by a factor of more than two over a similar run with no sulfate added, thereby substantiating a previously proposed dependence.

Seven new runs were made in an attempt to find means of increasing the gasification rate of anthracite. Decreasing the particle size from the usual 12/20 mesh to 80/100 mesh was found to increase gasification rate by a factor of about 2.2. Similarly, increasing the anthracite gasification temperature from 1740 to 1840°F resulted in an increase in rate by a factor of 1.6. Thermal pretreatment of anthracite decreased its gasification reactivity by about 30 percent. Other ashes, such as those of char, sub-bituminous and lignite, used in place of anthracite ash did not enhance the gasification rate. Similarly, the presence of sodium sulfate in the melt had no effect on the anthracite gasification rate.

One run was made to dete mine the effects of omitting presteaming of the melt before gasification. The gasification rate of anthracite was found to be unaffected, although there was evidence of a gas-melt reaction resulting in carbon dioxide emanating from the melt.

A gasification run at three atmospheres total pressure with a steam partial pressure of one atmosphere resulted in a rate completely consistent with the predicted rate obtained using the original curve for the effect of steam pressure on the gasification rate of coke. The steam conversion in this run was about 32 percent (compared with less than 10 percent in most previous runs) indicating a lack of rate dependence on steam conversion in this range.

Work has continued in an effort to fix the process design of the one-ton-per-hour gasification pilot plant. Review of the preliminary flowsheet by the Process Research and Mechanical Development groups continued.

A literature search to find information on the solubility of flue gas in the molten salt indicated that this solubility may be high enough to contaminate the pipeline gas beyond the acceptable level of inerts. However, a probable solution to the problem was devised consisting of a steam stripping section for the melt being transferred to the gasifier. Provisions to test this will be included in the pilot plant.

Capital cost estimation of the hydrogen plant neared completion as did the process design of the plant capable of producing synthesis gas from bituminous coal.

Tests have been carried out to determine the extent of entrainment in the aeration gas leaving a sodium carbonate melt containing eight percent ash. Gas velocities of 0.5 and 1.5 feet per second have been investigated. Volatility and/or entrainment rates of from 2 to 3 grams per hour have been observed. However, a complete analysis of these data has not as yet been made since analyses of the deposits is not yet available.

A computer program was completed for the sizing of melt transfer lines and flow predictions. It will be used to size the melt transfer lines for the proposed pilot plant.

II. PROCESS RESEARCH

A. Accomplishments

1. Combustion Studies

a. Effect of Carbon Dioxide in Air on Combustion of Anthracite

The results of three new combustion runs are presented in Table 1. The first run studied the effect of having 20% carbon dioxide in air on the rate of combustion of anthracite. The second run, where nitrogen replaced the carbon dioxide, served as the basis for comparison. The results tabulated below show that carbon dioxide enhanced the gasification rate by about 50% over the nitrogen run. The reaction of CO_2 with C to form CO accounts for the increased activity.

Run	Combustion Rate lbs./hr./cu. ft.
174 - 20% CO_2 in Air	14.3
175 - 20% N_2 in Air	9.7

b. Effect of Na_2SO_4 in Melt on Combustion of Coke

Run 173 was a repeat of an earlier run (148) in which it was suspected that incomplete removal of the sulfate from the prior run led to an abnormally high combustion rate. This was substantiated in this new run which allows a curve to be drawn for the combustion rate of bituminous coke as a function of sodium sulfate content. Correction of the rates to 1740°F was required and the results are shown in Figure 1. The results show an almost linear relationship on the arithmetic plot. Although a previous run at 4% Na_2SO_4 was made, the combustion rate exceeded full use of air, 70 lbs./hr./cu. ft., and this point could not be used.

2. Gasification Studies

The results of the gasification runs are presented in Table 2.

FIGURE 1

EFFECT OF Na_2SO_4 IN MELT ON COMBUSTION RATE OF BITUMINOUS COKE

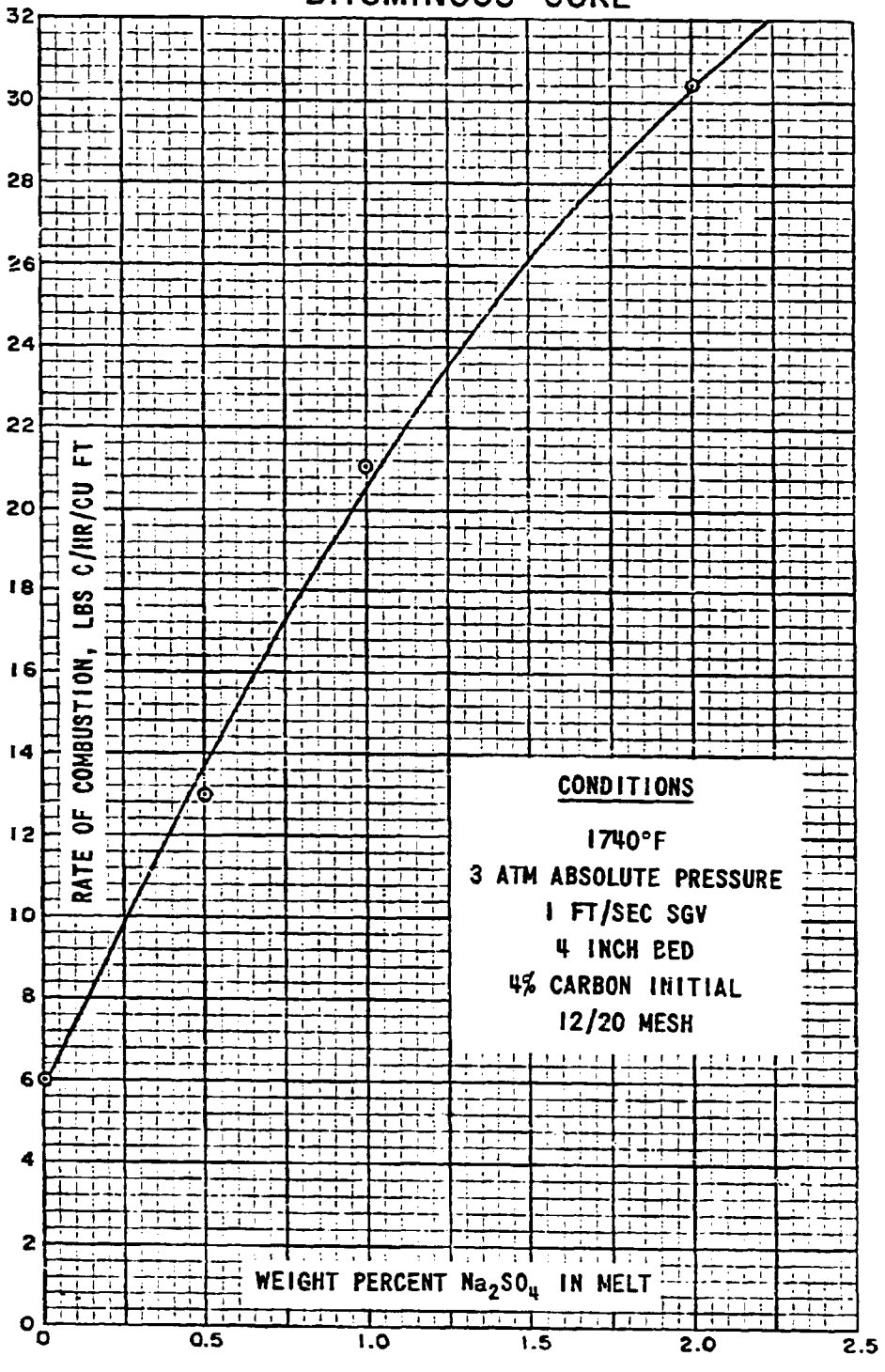

TABLE I

SUMMARY OF COMBUSTION RUNS IN MOLTEN SODIUM CARBONATE(1)

Run No. H-	174	175	179
Date - 1967	2/24	2/27	3/2
Feed	--- Anthracite ----		Coke VI
% Total Carbon	80.8		93.2
% Vol. Matter	5.9		0.6
% Ash	11.7		6.2
Gms. Charge	21.35		18.5
Mesh Size	12/20		12/20
% C in Melt - Initial	4		4
Melt			
Gms. Na_2CO_3	397.4	397.4	411.4
Gms. Ash	16.6	16.6	2.1(5)
% Ash in Melt	4.0	4.0	0.5(5)
Height - Inches	4	4	4
Conditions	(3)	(4)	
Temp. °F - Initial	1840	1840	1736
- Average(2)	1840	1840	1740
- Maximum	1858	1860	1770
Pressure - psia	17.7	17.7	44.7
Sup. Gas Vel. - ft/sec	1.02	0.97	1.02
Run Time - min	70	75	50
Air Rate - liters/min	8.1	7.7	27.1
Product Gas Analyses			
% CO_2 - 5 min	26.0	6.6	3.5
- 35 min	22.0	3.6	1.3
- end	19.9	0.9	0.4
% O_2 - 5 min	8.5	10.5	17.0
- 35 min	14.5	13.0	19.0
- end	15.7	15.0	19.0
Results			
Combustion Rate Constant	1.21	0.82	1.10
Rate - lbs C/hr/cu ft at 4% carbon	14.3	9.7	13.0
% Carbon - Devolatilized	19.2	18.4	7.2
- Combusted	80.7	80.3	92.5

(1) Used 2-inch I. D. Inconel reactor. Feed charged in N_2 at 0.1 ft/sec SGV, 5 minute devolatilization before air in.

(2) Average temperature in 50% carbon consumed period

(3) 20% CO_2 in air used.

(4) 20% N_2 in air used.

(5) Na_2SO_4 instead of coal ash.

TABLE II

SUMMARY OF GASIFICATION RUNS IN MOLTEN SODIUM CARBONATE(1)

Run No. H-	180	181	182	183	184	185	186	187	188
Date - 1967	3/6	3/8	3/10	3/14	3/16	3/20	3/22	3/24	3/28
Feed	Tr Anth.(2)	← Anthracite →							Coke VI
% Total Carbon	85.4				80.8				93.2
% Vol. Matter	0.5				5.9				0.6
% Ash	12.5				13.7				6.2
Gms. Charge	20.22	21.35	21.35	21.19	21.35	20.94	21.30	21.35	18.5
Mesh Size	12/20	12/20	80/100	←		12/20			→
% C in Melt - Initial	←				4				→
Melt									
Gms. Na_2CO_3	405.7	397.4	405.7	405.7	405.7	405.7	405.7	405.7	414
Gms. Ash	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	-
Gms. Na_2SO_4 or Type Ash	Anth.	8.3	Anth.	Anth.	Char	Elkol	Beulah	Lignite	-
% Ash in Melt	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	-
% Na_2SO_4 in Melt	-	2.0	-	-	-	-	-	-	-
Bed Height - Inches	4	4	4	4	4	4	4	4	4
Conditions									
Temperature - °F	1740	1740	1740	1840	1740	1740	1740	1740	1740
Pressure - psia	44.7	44.7	44.7	44.7	44.7	44.7	44.7	44.7	44.6
% Steam in N_2	91.0	91.1	91.2	91.1	90.7	91.0	90.8	90.3	39.1
Steam Press - psia	40.7	40.7	40.8	40.7	40.5	40.7	40.6	40.4	17.4
Sup. Gas Velo. - ft/sec	1.03	1.03	1.02	1.07	1.05	1.03	1.03	1.04	0.46
Run Time - min	50	35	30	25	35	40	40	45	70
cc H_2O in/hr	1200	1197	1194	1188	1199	1197	1199	1196	230
cc N_2 in/min	2468	2429	2385	2419	2912	2460	2528	2651	7428
Results									
% C in Devol. Gas	2.9	3.5	8.1	3.3	2.2	2.1	2.3	10.8	2.5
% C in Prod. Gas	91.5	96.3	89.3	93.7	99.0	93.7	99.4	133.6	96.7
% C Loss	5.6	-	2.6	3.0	-	4.2	-	-	0.8
Gasif. Rate Constant - hr^{-1}									
k_I - input	0.95	1.57	3.05	2.40	1.64	1.32	1.59	(2.69)	0.66
k_O - output	1.05	1.57	3.27	2.54	1.64	1.44	1.59	1.37	0.66
Rate - lbs C/hr/cu ft at 4% C_f output basis	12.4	18.5	38.6	29.9	19.4	17.0	18.8	16.2	7.8
Salt Carryover - gms	10.5	6.8	4.0	7.2	10.7	8.2	11.6	9.1	9.6

(1) Used 2-inch I. D. Inconel reactor. Melt presteamed 15 minutes, N_2 only for 5 minutes, feed added and N_2 flow for 5 minutes devolatilization, then steam started.

(2) Anthracite calcined in N_2 for one hour at 1800°F.

(3) No presteaming before feed charged.

a. Results with Anthracite as Feed

The Office of Coal Research suggested that attempts be made to increase the gasification rates of anthracite. The first method attempted was a thermal treatment of anthracite by calcination at 1800°F in a stream of nitrogen for one hour. This drove out most of the volatile matter. Gasification run 180 showed that the activity of this material was decreased about 30%. Comparison is made in the following table:

Run	Pretreatment of Anthracite	Combustion Rate lbs./hr./cu.ft.
180	Thermal - 1800°F	12.4
Avg. 184-187	None	17.9

This indicates that a loss of surface area rather than a gain occurred in the thermal treatment.

In the next run, 181, the presence of two percent sodium sulfate along with 2% anthracite ash failed to show any enhancement due to the sodium sulfate. The gasification rate was 18.5 lbs. C/hr./cu.ft., in good agreement with the aforementioned 17.9.

However, by comminuting the anthracite to a lower particle size, namely 80/100 mesh in test 182, the gasification rate was increased to 39 lbs. C/hr. cu./ft. This reflects the large increase in surface area.

Also, by increasing the test temperature from 1740°F in the above runs to 1840°F in run 183, the gasification rate was increased from 18 to 30 lbs./hr./cu.ft. This is a very satisfactory rate for 12/20 mesh anthracite.

In the next four runs, use of ashes derived from three different feedstocks, namely, FMC char ash, Elkol subbituminous coal ash, and South Beulah lignite ash, all gave essentially the same gasification rate which averaged 17.9 $\pm$ 1.6.

In run 187, pre-steaming of the bed was omitted to observe the effect on carbon content in the devolatilized gas. Not only was the devolatilized gas higher in carbon but so was the overall carbon balance, thus indicative of the melt giving up a large amount of carbon dioxide. By adjusting to a 100% output basis, the gasification rate turned out to be normal. Further work is being done to study the mechanism involved in devolatilization and steaming.

b. Effect of Steam and Total Pressure on Gasification of Coke

The last run, 188 with coke from bituminous coal, was made to determine the effect of a steam pressure of about one atmosphere in a total pressure of three atmospheres using nitrogen as the diluent. The original curve for the effect of

steam pressure on gasification of coke, as presented in the ACS paper for publication in Advances in Chemistry, has been used to compare the result in the above run:

Source	Stm. Pres.-psia	Gasif. Rate-lbs/hr/cu.ft.
Run 188	17.4	7.8
Curve	17.4	8.1

The rates are in excellent agreement, and thus the dependence of rate on steam pressure, especially in the low pressure steam region, appears reliable. Consumption of steam in this run was 25, 31 and 32% at 5, 10 and 15 minutes respectively. Most of the data for the pressure curve was obtained at less than 10% steam consumption.

B. Projections

The effect of sulfate content in the melt on the rate of combustion of anthracite will be determined. Experiments and thermodynamic evaluations will be made to better understand the effects of presteaming and devolatilization on the composition of the melt and the effects on combustion and gasification rates.

Studies have been initiated to study the effect of carbon dioxide on ash removal characteristics, and distribution of silica during ash separation and recovery of sodium bicarbonate. In addition, the effect of alumina content on the characteristics of a melt and the partial pressure of carbon dioxide needed to suppress alumina solubility will be investigated.

III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

1. Pilot-Plant Design

Work has continued in cooperation with the Mechanical Development Group in an effort to fix the process design of the one-ton-per-hour gasification pilot plant. Thus far, no significant changes in the process have been necessitated as a result of the mechanical review, although this work is still in progress.

In an attempt to delineate potential problem areas which have not yet been studied experimentally, the question arose as to how much flue gas (nitrogen) from the combustion section might be soluble in the melt and subsequently transferred to the gasification section. This could be an important question since there is a rather tight specification on the quantity of inert gas in the final pipeline gas ($< 5\%$). This limit corresponds to an allowable leakage of about 3×10^{-4} moles N_2 per mole melt at the melt circulation rate used in the conceptual design (Progress Report No. 21) . Literature data[1] for a comparable system (O_2 in Li_2CO_3-Na_2CO_3 melts) indicated a solubility of 3×10^{-3} moles O_2 per mole melt at 1000°C and showed an increasing solubility with increasing temperature.

It is obvious, therefore, that solubility cannot be ignored in this system. However, the problem can probably be remedied by stripping the melt with steam as it leaves the combustor (possibly in the melt transfer line). A calculation of the minimum stripping gas rate revealed that only about 10 percent additional steam is needed above the gasifier steam requirement. Also, if some gasification occurs in this stripper, the stripping becomes easier since the total number of moles increases as gasification proceeds. The energy balance for the combustor would not be greatly affected since whatever coal is gasified would be burned in the combustor. Of course, there would be an additional coal and air requirement. A beneficial effect of this stripping would be realized since it has been shown in the laboratory that combustion rates are improved by the addition of steam.

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(1) J. Electrochem. Soc., 113, 404 (1966).

2. Flowsheet Studies

Estimation of the capital cost of the hydrogen-from-coal plant continued through March and is now nearing completion. Process calculations for the synthesis gas plant were also continued and are now essentially completed. Estimation of equipment sizes and costs remains to be done.

B. Projections

1. Pilot Plant Design

It is planned to fix the final process design by the end of April. This final design will incorporate suggestions made by both the Process Research and Mechanical Development Groups, and hence should provide the required flexibility needed to test the potential problem areas envisioned by each of these groups.

2. Flowsheet Studies

Capital cost estimation of the hydrogen-from-coal plant should be completed during April. With this figure available, gas cost will be calculated for the 250 MM SCFD plant.

IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Mechanical Characteristics Testing

Tests are being conducted to determine entrainment in the aeration gas exiting a sodium carbonate melt containing eight percent ash. Carbon Dioxide is used as the aeration gas. The tests are carried out in the 5-3/4 inch I. D. vessel shown on Figure 6 shown in Progress Report No.31. Tests have been completed for 0.5 feet per second and 1.5 feet per second superficial velocity of the aeration gas. Table 3 shows the results of tests completed to date. An analysis of the deposits found in Test #3 will be obtained and reported in a later report.

2. Melt Circulation

A computer program has been completed for the sizing of melt transfer lines and flow predictions. The program is based on the work previously reported in this area and will be used to size the melt transfer lines for the proposed pilot plant.

B. Projections

1. Mechanical Characteristics Testing

Tests of entrainment in exit aeration gas will be concluded.

2. Melt Circulation

Sizing of the melt transfer lines for the pilot plant will be completed and performance curves plotted for the gas lift system.

3. Gasification Tests

We are investigating the possibility of using the Trent Furnace and the 5-3/4 inch I. D. x 6-foot high vessel used for the entrainment and bed expansion tests to conduct gasification tests. To date, satisfactory tests have been limited to a 2-inch I. D. vessel with bed heights of less than one foot. Gasification tests in this vessel could be conducted with up to a three-foot bed and the wall effects experienced with the smaller vessel could be significantly reduced.

TABLE 3

ENTRAINMENT IN AERATION GAS EXITING A SODIUM CARBONATE MELT BED (CO_2 AERATION GAS - 8% ASH IN BED)

3" BED 5-3/4 INCH I.D. VESSEL

Test	Bed Superficial Velocity (Ft/Sec)	Time of Test (Hrs.)	Bed Temp (Avg.) °F	Exit Temp (Avg.) °F	Cooler Inlet Temp °F	Cooler Exit Temp °F	Deposit In Exit Line Wt. (Grams)	Deposit In Filter Wt. (Grams)
1	0.5	2.0	1822	715	375	70	6 gms. (White Powder)	Some Evidence Not Measurable (White Powder)
2	1.5	2.0	1783	1065	860	240	3 gms. (White Powder)	3 gms. (White Powder)
3	1.5 (2.5' Bed Height)	7.5	1795	960	790	210	Inlet 3.74 gms.* Bottom 3.62 gms.* Outlet 1.6 gms. (White Powder)	3.72 gms.* (White Powder)

*Samples sent for content analysis.

V. MANPOWER AND COST ESTIMATES

Figure 2 shows the projected breakdown for Phase I for 1967 as well as the actual effort that was made. It can be seen that a 13.5 man-effort was made during March.

Figure 3 shows the expenditures during March. For the month $23,107 was expended, not including fee and G & A. The total expenditures through March were $618,835. Including fee and G & A the total expenditures were $707,094. This is 64% of the encumbered funds.

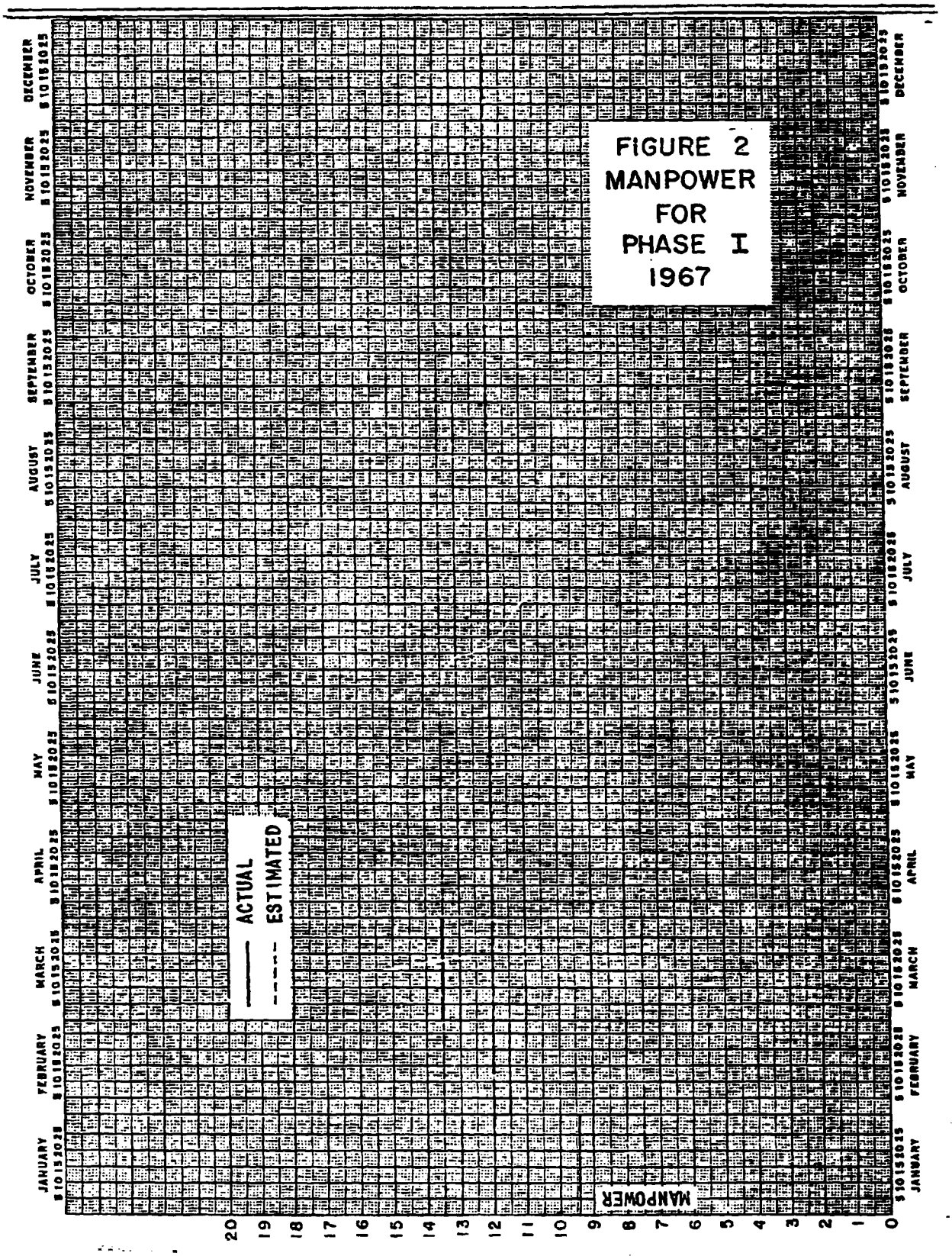
FIGURE 2
MANPOWER
FOR
PHASE I
1967
ACTUAL
ESTIMATED
MANPOWER
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
JANUARY
FEBRUARY
MARCH
APRIL
MAY
JUNE
JULY
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NOVEMBER
DECEMBER

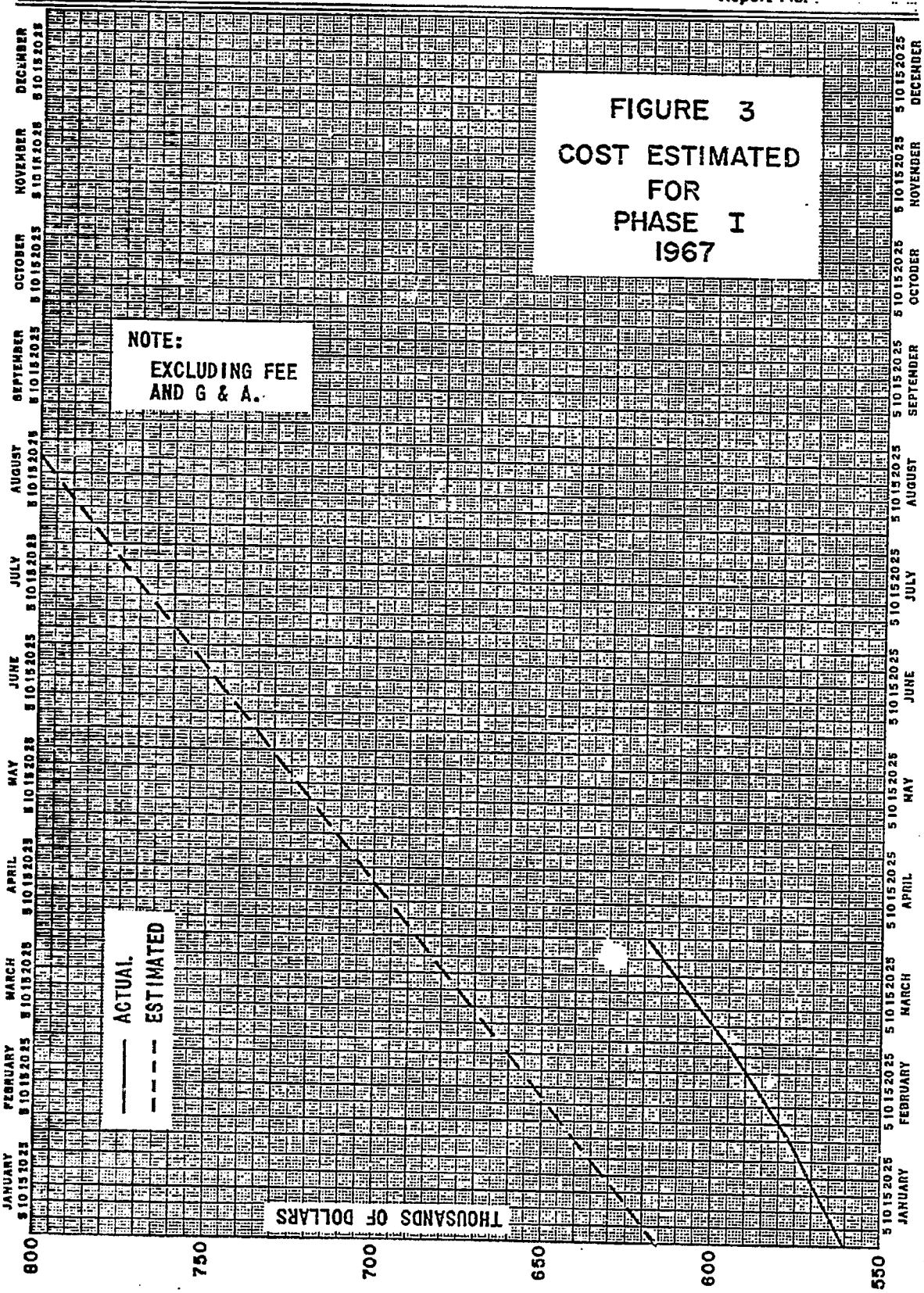
FIGURE 3
COST ESTIMATED
FOR
PHASE I
1967
NOTE:
EXCLUDING FEE
AND G & A.
ACTUAL
ESTIMATED
THOUSANDS OF DOLLARS
800
750
700
650
600
550
JANUARY
FEBRUARY
MARCH
APRIL
MAY
JUNE
JULY
AUGUST
SEPTEMBER
OCTOBER
NOVEMBER
DECEMBER