MWK- MPR-9

RESEARCH AND DEVELOPMENT DEPARTMENT — KELLOGG M W

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

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Progress Report No. 9

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I. INTRODUCTION

Evaluation of alternate gas purification schemes continues. Work is also being done on the conversion of raw synthesis gas from the gasifier into high purity hydrogen.

Planning was started for the high-pressure molten salt test unit.

Observation of all the gasification runs to date appear to indicate type of feed, steam rate, bed height, preimpregnation, and particle size have little effect on the specific reaction rate.

Quantitative experiments on the recovery of sodium values from coal ash-sodium carbonate melts have been started.

Three of the four refractory samples recovered from corrosion test #2 appear acceptable for this service. These are Chromex B, Zircofrax O and Ritex CB.

II. PROCESS DEVELOPMENT

A. Accomplishments

Evaluation of alternate gas purification schemes was resumed; current emphasis is on the conversion of raw synthesis gas from the gasifier into high-purity hydrogen.

A meeting was attended at the Institute of Gas Technology to discuss:

1. Adoption by all OCR contractors of a uniform method of calculating pipeline gas economics.

2. A set of minimum standards for pipeline gas produced from coal.

It was decided to use the method first proposed by the American Gas Association General Accounting Committee on May 1, 1961, perhaps with minor revisions. A draft of the suggested method will be circulated to the OCR contractors involved for their comments. Concensus of the meeting with respect to pipeline gas standards was that these should remain fairly flexible and not be considered "specifications". A list of the suggested standards will also be circulated for comment.

Planning was started for the high-pressure molten salt test unit. The following general characteristics were established:

1. There will be no melt circulation outside the reactor.

2. The unit must serve for both gasification and combustion tests at high pressure, though not simultaneously.

3. A suitable refractory material, such as fused zirconia, will be used to avoid contact between metal vessel walls and the molten salt.

4. Heat for gasification will be supplied electrically.

5. Coal will be fed semi-continuously; i.e. batches at frequent intervals.

A tentative test program has been outlined, and process design of a unit capable of carrying out the program is now underway.

A draft of a paper entitled "Preliminary Evaluation of the Kellogg Coal Gasification Process" was prepared for presentation at the American Gas Association Production Conference at Buffalo, New York, on May 24-25.

B. Projections

Evaluation of gas purification schemes and secondary product recovery will be continued. Process flowsheets will be prepared for the complete pipeline gas plant so that overall thermal efficiency can be studied.

III. PROCESS RESEARCH

A. Accomplishments

1. Gasification Kinetics

All the runs to date in which bituminous coke (Island Creek #27 coal coked at 800°C overnight and 2 hours at 850°C) was charged to the 2-inch ID atmospheric bench scale reactor are presented in Table 1.

In Table 1 the specific gasification rate has been obtained based upon the carbon charged (inlet C) for carbon to oxides and to 1/2 ($CO + H_2$), the reducing power. The gasification rates have been obtained also on an outlet carbon basis (assumed 100% at end of run). The main purpose of this was to try to find a common basis for comparison of results because of the highly variable % input carbon gasified and the high variation in the hydrogen to oxygen atomic ratio indicating reactor-product gas reactions.

Based upon the oxides of carbon produced, the specific gasification rate on an input basis indicates a higher gasification rate for the finer material of 40/60 mesh over the 12/20 and 20/40 sizes but weight balances were poor perhaps due to the smaller size and loss by elutriation before reaction in the reactor. In addition, impregnation appears to give only a slight improvement. Until reproducibility is evaluated, none of these statements can be considered definitive. Notably on an outlet basis, the rate for the finer material shows a marked threefold improvement over the others.

Comparison of the rates using the less exact reducing power as a basis shows all three sizes to be equal on a inlet carbon basis and impregnation to be slightly, if any, inferior. However, on an outlet basis a trend toward higher reactivity for the finer size is evident and impregnation helps slightly.

TABLE I

GASIFICATION OF BITUMINOUS COKE IN MOLTEN Na_2CO_3 (1)

Run No. -J-	Coke gms.	Coke mesh size	Coke gms. carbon	gms. Na_2CO_3 Impreg. on coke	Run Time Min.	% Input Carbon Gasified Basis Carbon Oxides	% Input Carbon Gasified Basis 1/2 $(CO + H_2)$
9777 (2)	38.6	12/20	35.0	-	365	90.6	129
9781	33.5	20/40	30.4	-	330	82.2	90.8
9780	38.0	40/60	34.5	-	180	75.7	64.2
9778	34.3	12/20	31.1	3.8	290	100.2	70.6
9779	37.6	12/20	34.1	8.2	340	97.7	93.6

(1) Bituminous coke from coking Island Creek #27 coal up to 850°C., leaving 1.6% volatiles and 90.7% carbon. Conditions of runs: 1700-1770°F, atm. pres., steam partial pressure 13.3-13.6 psia in nitrogen, 0.51 superficial gas velocity, 4" qiescent bed height, 414 gms. Na_2CO_3.

(2) Melt from previous run was used.

TABLE 1 (Continued)

GASIFICATION OF BITUMINOUS COKE IN MOLTEN Na_2CO_3 (1)

Run No. -J-	H/O in Dry Gas	Specific Gasification Rate - k in hr^{-1} (3): Basis Carbon Oxides, Inlet C	Basis Carbon Oxides, Outlet C	Basis 1/2 ($CO + H_2$), Inlet C	Basis 1/2 ($CO + H_2$), Outlet C
9777 (2)	3.0	0.16	0.19	0.21	0.16
9781	2.3	0.17	0.17	0.23	0.23
9780	1.6	0.29	0.62	0.20	0.30
9778	1.4	0.26	0.26	0.12	0.22
9779	1.9	0.20	0.21	0.18	0.20

(1) Bituminous coke from coking Island Creek #27 coal up to 850°C., leaving 1.6% volatiles and 90.7% carbon. Conditions of runs: 1700-1770°F, atm. pres., steam partial pressure 13.3-13.6 psia in nitrogen, 0.51 superficial gas velocity, 4" qiescent bed height, 414 gms. Na_2CO_3.

(2) Melt from previous run was used.

(3) For $k = -\frac{1}{t} \log \frac{c}{c_o}$, first order carbon reaction.

Overall, the effects observed above appear to be minor and more of a ten-fold increase in rate is what is desired. Observation of all the runs to date appears to indicate that type of feed, whether anthracite coal, lignite or coke from Mexican or bituminous coal, and variations in steam rate, bed height, preimpregnation, and particle size have little effect on the specific reaction rate which appears to average about 0.3 The two high results on Mexican coke are unexplainable especially in view of two other runs which gave normal values.

2. Sodium Carbonate Recovery

Quantitative experiments on the recovery of sodium values from coal ash-sodium carbonate melts have been started. Although the work on coal ash from bituminous coal (Island Creek #27) has been completed, none of the chemical analyses are available. Upon receipt of these analyses and successful evaluation of the results, other ash-sodium carbonate melts will be treated similarly.

Bituminous coal ash-sodium carbonate melts at two levels of ash content, ten and twenty percent, were prepared as follows. The ash-sodium carbonate mixture was melted in an Inconel tube while bubbling moist CO_2 (5 to 1 ratio of CO_2 to H_2O vapor) through the melt at 0.25 ft./sec. superficial velocity in order to keep the ash well dispersed. After six hours, the melt was quickly solidified by pouring into a graphite box. The solidified mass was then ground with mortar and pestle to give maximum recovery of 12/20 mesh and 40/100 mesh for the recovery tests.

The recovery scheme consists of:

1. Leaching 20 gms. of the 12/20 or 40/100 mesh melt with 9% $NaHCO_3$ solution at the boiling point. Two levels of solution to solids ratio are used -- 6 to 1 and 12 to 1. Two levels of leaching time are 10 minutes and 20 minutes.

2. Filtration on a 25 micron stainless steel crucible with vacuum separates Residue No. 1 (undissolved ash) and a filtrate. The residue after drying and weighing will be analyzed for Na, SiO_2, Al_2O_3 and Fe_2O_3. The original melt will be analyzed similarly.

3. The filtrate is saturated with CO_2 using a graduate and a coarse fritted glass bubbler. The CO_2 is bubbled in at 140 cc/min for 1.25 hours which gives maximum precipitation (at 70°F). The precipitated $NaHCO_3$ is separated on a Buchner funnel using #1 Whatman paper and vacuum. This residue is air dried, weighed and submitted for Na analysis. The filtrate is measured and also submitted to Na analysis. If, after receiving the above analyses, it appears desirable to analyze further for SiO_2 and Al_2O_3 balances, the samples will be resubmitted.

B. Projections

Gasification work will concentrate on determining reproducibility with the 12/20 mesh bituminous coke previously used. A new bituminous coke prepared at 600°C with 7.6% volatiles will be tested in order to ascertain reactivity on gasification rate and also to determine ability to analyze the data. If this is satisfactory, the direct approach with the coal instead of coke will be tried and evaluated. Preparation for additive study to increase reaction rate will be started.

Further experimentation of sodium recovery scheme with other ash-carbonate melts must await chemical analysis. Melts of the various ashes and sodium carbonate will be prepared.

IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High Temperature Materials

The four refractory samples recovered after Test #2 and described in the last report were positively identified as follows:

Sample #1 - Chromex B. A chrome-magnesite composition manufactured by Harbison-Walker.

Sample #2 - Zircofrax O. A zirconia product manufactured by Carborundum.

Sample #3 - Ritex CB. A chrome-magnesite composition manufactured by General Refractories.

Sample #4 - Harklase. A magnesite composition manufactured by Harbison-Walker.

Of these four specimens, the first three appear acceptable for this service. Samples #1 and #2 can be considered on an equal status for first choice with #3 as the second choice. In order to arrive at a more critical evaluation, further tests on the acceptable refractories are planned. In addition to these refractory materials it is contemplated to test some high-density fused cast refractories recommended by Harbison-Carborundum and sold under the tradename of Monofrax. These refractories have relatively high coefficients of heat transfer (35-45 Btu in./hr. SF°F) and might be used where higher thermal conductivity properties are desirable.

Since all of the high nickel wrought alloys of Test #1 indicated unsatisfactory corrosion resistance alloys lower in nickel will be tried in Test #3.

Table 2 is a summary of metal alloys recommended by leading manufacturers as their best contenders for this process. This table also indicates the initial test results and future test planning. Table 3 is a similar summary for refractory materials.

2. Coal Feeding Studies

An experimental test set-up for measuring the pressure drop in dilute phase solids-gas flow in horizontal pipes has been completed. This test apparatus consists of a length of horizontal tube, a solids feed and recovery system, and appropriate instrumentation for measuring gas and solids flows as well as the differential pressure along the tube. From these differential pressure measurements, it is theoretically possible to correlate the weight per unit time of solids being carried by the gas.

B. Projections

1. Environmental Testing of High Temperature Materials

Drawings have been completed for the new test reactor and the fabrication order will be let out within a few days.

Plans are in progress for Test #3 and Figure 1 is a schematic flow diagram of the process. Specimens for this next test are being prepared and the tentative list is as follows:

Metal Alloys

	Cr - Ni
RA 446	27 - 3 (max)
Thermalloy (centrifugally cast) 38	28 - 11
Thermalloy 28	29 - 0.50
Thermalloy 47	26 - 20

TABLE 2

METAL ALLOYS

Organization & Recommendation	Test	Results	Remarks
International Nickel Company			
Inconel 600	1	U*	
Inconel 702	1	U	
Incoloy 800	1	U	
Incoloy 804	1	U	
Type 309			
Type 310	1	U	
Stellite Div., Union Carbide			
Hastelloy B	1	U	Hastelloy X has been tested in an earlier program and found to be unsatisfactory.
Hastelloy C	1	U	
Rolled Alloys, Inc.			
RA 600	1	U	
RA 330			Similar to Incoloy
RA 333	1	U	
RA 446	3		
RA 430			
Titanuim Metals Corp. of America			Titar [illegible] not recommended. It has no corrosion resistance at temperatures above 1000°F.
Zirconium Metals Corp. of America			Corrosion resistance mechanism of zirconium (and other reactive metals) depends on the formation of an oxide protective layer. It is not recommended as a corrosion resistant material at temperatures above 750°F.

TABLE 2 (Continued)

METAL ALLOYS

Organization & Recommendation	Test	Results	Remarks
Fansteel Metallurgical Corp.			Literature received indicates that tantalum is effected by Na_2CO_3 at high concentrations and temperatures. A tantalum alloy (10% tungsten) is to be checked out in a crucible test.
Universal - Cyclops Steel Corp.			
50 Cr - 50 Ni	1	U	
Eledio-Alloys Div., Am. Brake Shoe			
Thermalloy 72			13 Cr - 60 Ni
Thermalloy 47	3		25 Cr - 30 Ni
Thermalloy 38	3		38 Cr - 11 Ni
Thermalloy 28	3		29 Cr - Fe
Climax-Molybdenum			Literature received indicates that molybdenum and molybdenum based alloys have poor corrosion resistance to fused (molten) Na_2CO_3.
Carpenter Steel Company			No recommendations

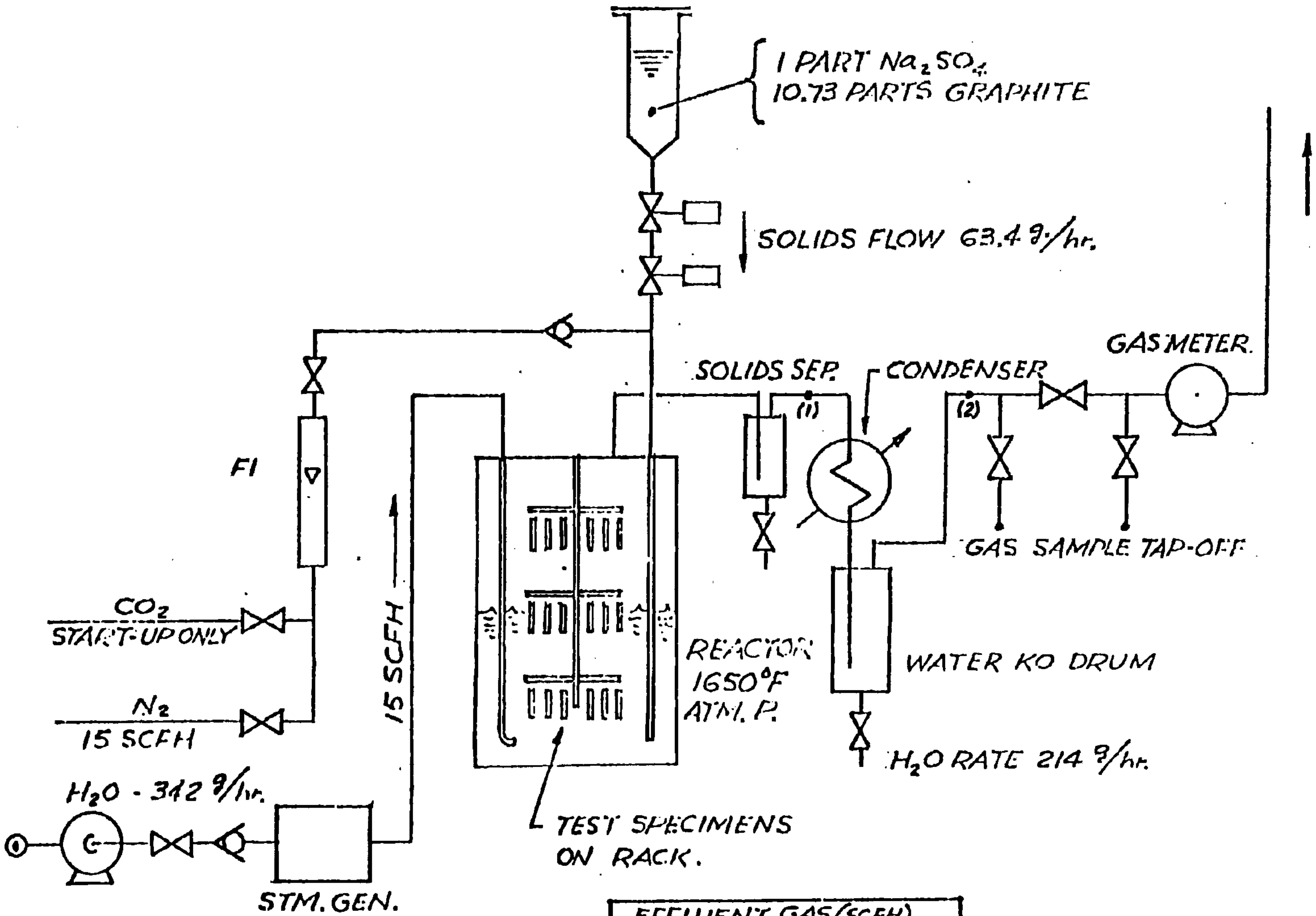
*Unsatisfactory

TABLE 3

REFRACTORY MATERIALS

Manufacturer & Recommendation	Composition								Test	Result
	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3	MgO	SiC	SiO_2	ZrO_2		
Carborundum Co.										
Zircofrax O	0.5	4.2	-	0.2	-	-	0.5	94.4	1, 3	S
Mullfrax H	90.71	0.07	-	0.15	0.01	-	8.63	-	1	U
Mullfrax W	78.66	-	-	0.38	-	-	20.59	-	1	U
Magnafrax	64.3	.05	-	0.05	30.4	-	0.06	4.9		
KT Silicon Carbide	-	-	-	-	-	Approx 100	-	-	1	U
Harbison-Walker Refractories Co.										
Harbide	2.1	-	-	1.1	-	89.2	7.3	-	1	U
Chromex B	21.7	0.7	25.9	12.5	34.2	-	5.0	-	1, 3	S
Varnon BF	41.8	0.3	-	1.3	0.3	-	53.1	-	1	U
Korundal XD	89.3	0.1	-	0.2	0.05	-	10.2	-	1	U
Harklase	0.2	0.9	-	0.3	97.5	-	0.8	-	1	U
General Refractories Company										
Ritex C			50		Approx 32					
Ritex CB ("B" for burned)			50		Approx 32				1, 3	S
Harbison-Carborundum Corporation										
Monofrax A	99.3	-	-	-	-	-	0.1	-	3	
Monofrax K-3	60.4	-	27.3	-	-	-	1.8	-	3	
Monofrax M	94.8	-	-	-	-	-	1.1	-		
Monofrax S-3	49.9	-	-	-	-	-	15.3	33.2		

FIGURE 1 - SCHEMATIC FLOW DIAGRAM OF CORROSION TEST PROCESS



EFFLUENT GAS (SCFH)	(1)	(2)
CO	1.906	1.908
CO_2	1.878	1.878
H_2S	.030	.030
H_2	5.61	5.61
$H_2O(g)$	9.4	–
N_2	15	15
TOT.	33.826	24.426

Refractory Materials

Zircofrax O	ZrO_2 - 94%
Ritex CB	Cr_2O_3 50%, MgO approx 32%
Chromex B	Cr_2O_3 - 25.9%, MgO - 34.2%, Al_2O_3 - 21.7%
Monofrax K-3	Cr_2O_3 - 27.3%, Al_2O_3 - 60.4%
Monofrax A	Al_2O_3 - 99.3%

Coated Metal Alloys

Hard Chrome Plated RA 330
Plasma Zirconia Sprayer on RA 330

2. Coal Feeding Studies

Testing of the above described apparatus will be undertaken in an effort to accurately correlate the solids flowing in the tube to the measured pressure drop along the tube.

V. MANPOWER AND COST ESTIMATES

A review was made of the objectives of the development program in the light of recent experimental findings.

Manpower requirements based on the estimate that Phase I would be completed in June, 1966, will average 12 over this period. Figure 1 shows the estimate of manpower for 1965 as well as the actual manpower used. It can be seen that at the beginning of the year it was estimated that an average 7 man effort would be made. For April a 7 man effort was made. Starting May 1 it is estimated that this will be increased to 12 and will continue at this level until Phase I is completed.

Figure 2 shows the expenditures through April. For the month $13,663 was expended not including fee and G & A. The total expenditure through April was $138,824. Including fee and G & A the total expenditures were $164,064. Figure 2 also shows the estimated expenditures through 1965. It can be seen that monthly expenditures will increase to about $25,000 per month starting May 1, 1965. This reflects the increased manpower that will be used in order to complete Phase I as of June, 1966.

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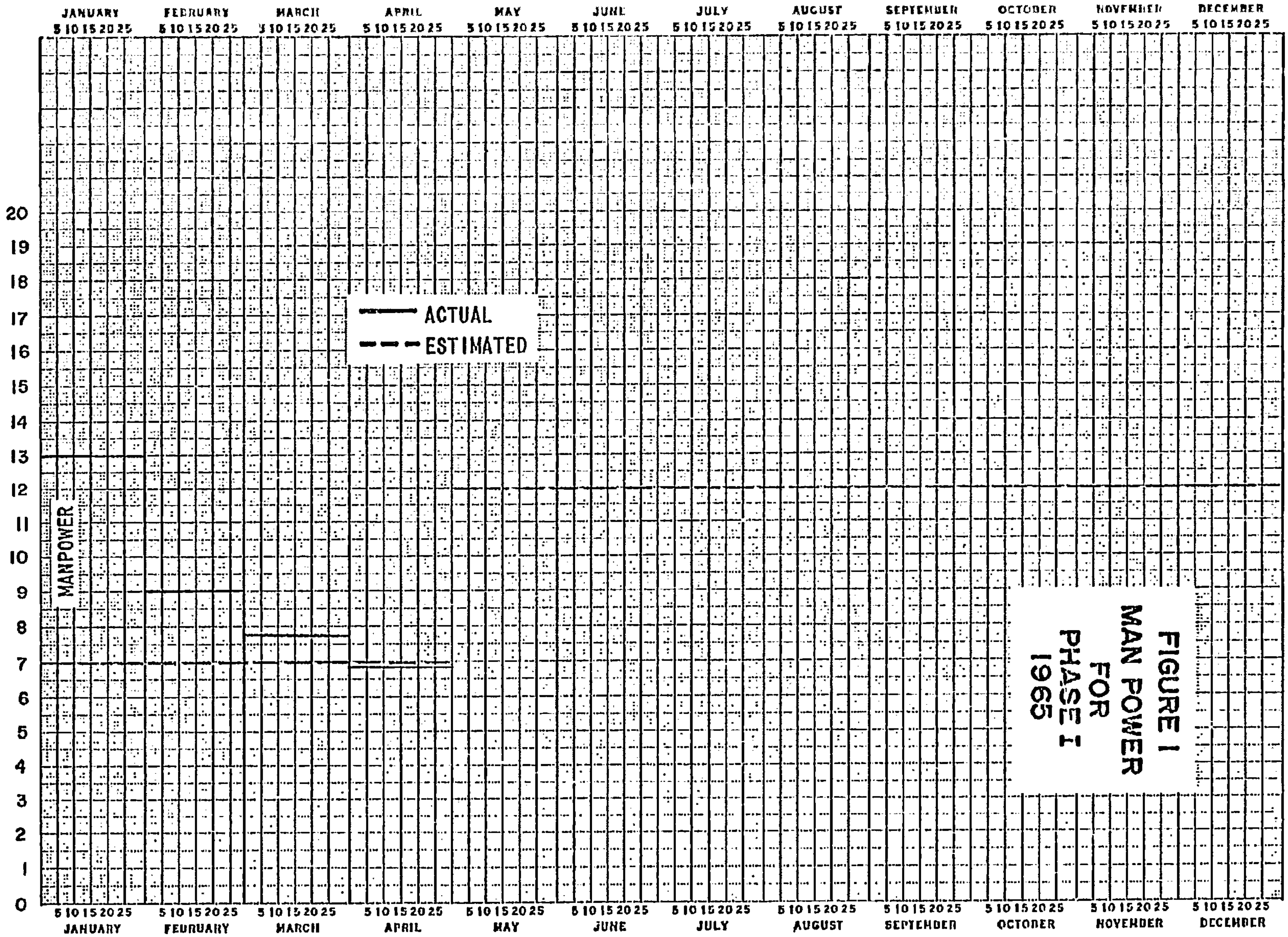

FIGURE I
MAN POWER
FOR
PHASE I
1965

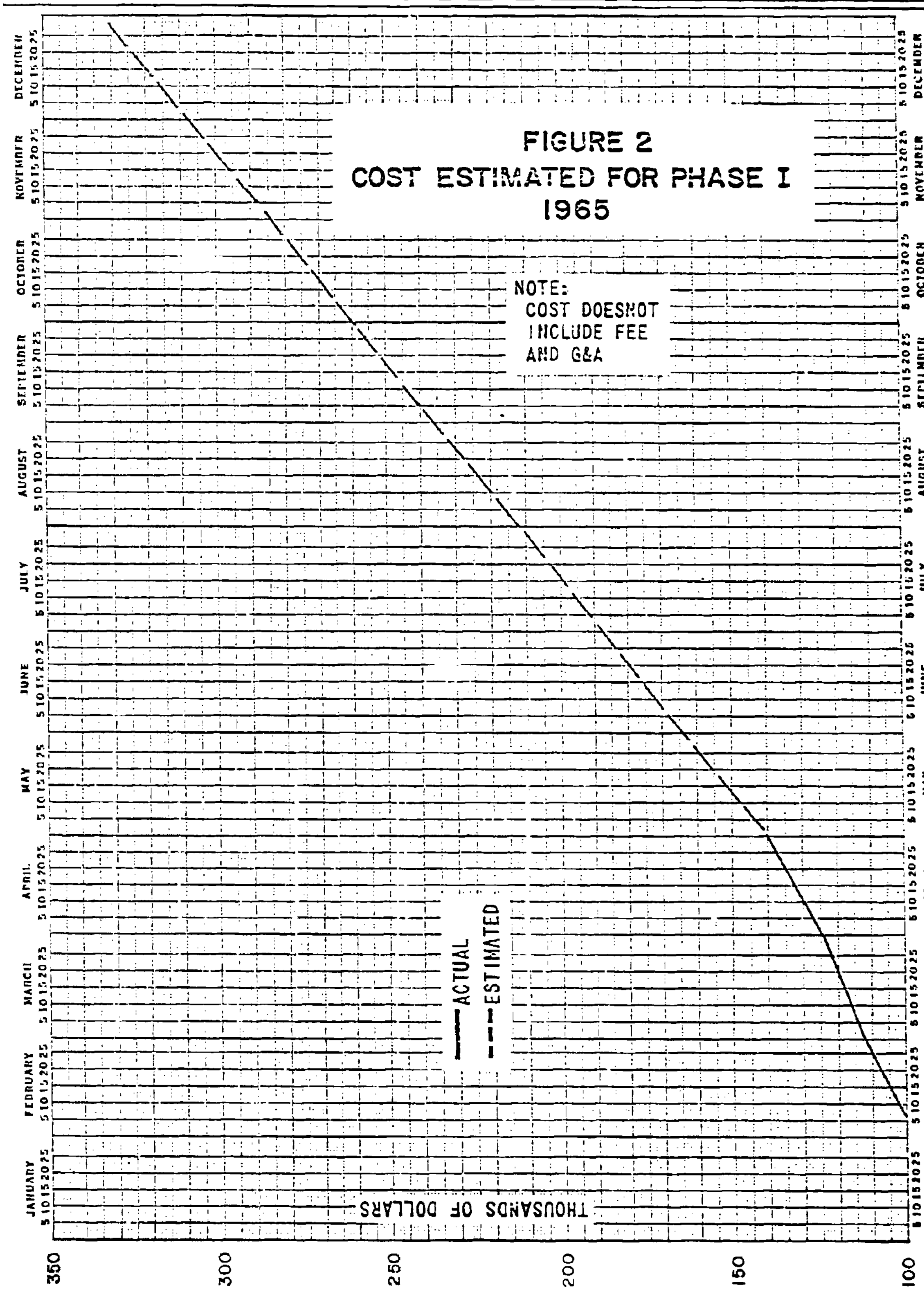

FIGURE 2
COST ESTIMATED FOR PHASE I
1965