MWK-MPR-25

RESEARCH AND DEVELOPMENT DEPARTMENT

KELLOGG

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

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APPROVED:

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CONTENTS

I. SUMMARY

This progress report is the twenty-fifth 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 gasification runs were made at ten atmospheres pressure and one at three atmospheres in order to better define the curve of rate versus pressure which was previously presented. Temperatures of 1640, 1700 and 1815°F were investigated, and the results obtained indicate that the relationship originally shown is still a perfectly good one.

Two runs were made at 1690°F to check the slopes of previously obtained Arrhenius plots for anthracite and FMC char drawn with the aid of data obtained at 1640 and 1740°F. The rates obtained fell exactly on the lines drawn through the original data confirming the validity of these plots.

Five new combustion runs have been made at three atmospheres total pressure with a bituminous coke and the FMC char. Combustion rates for the bituminous coke were greater than those used for design at temperatures of 1840°F and above. The combustion of the FMC char was so rapid that during the first few minutes of each run all the oxygen fed was consumed.

One run was made to determine the reactivity of the FMC char with molten salt according to the reaction:

$$C + Na_2CO_3 \rightleftharpoons 2CO + Na_2O$$

About 38 percent of the carbon reacted with a rate of about 3 lbs./hr./CF.

Preparation of a flowsheet for the production of pipeline gas from lignite continued. Preliminary cost calculations have indicated that the increased ash quantity handled in this case has led to higher gas costs, and new processing schemes are currently being devised to minimize this problem.

In an effort to gain a better understanding of the effect of ash on melt viscosity, experiments were made to determine the time required for known quantities of various fluids to flow through an open tube, thus obtaining a relative measure of viscosity. The results of these tests indicated that under conditions of reasonable turbulence, the viscosity of a 12 percent ash-Na_2CO_3 mixture might be closer to that of water than was previously believed.

Simulated melt circulation experiments using air-water and air-glycerine-water systems have been carried out in an attempt to determine important design parameters and to develop an analytical method for designing such an "air lift" flow system. Efforts to predict the flow rates for the air-water system have been encouraging with calculated values agreeing with experimental values within about 20 percent. Results with the higher viscosity glycerine-water system have not been as good most probably because the analytical expression used to calculate the circulation rate may not be valid for the range of liquid flows encountered in the experiments with the high viscosity fluid.

II. PROCESS RESEARCH

A. Accomplishments

Gasification runs with coke from bituminous coal were made at 10 atmospheres total pressure and 1640, 1700 and 1815°F to complement the earlier results on the effect of steam pressure on rate. Two gasification runs were made at 1690°F with the most and least reactive feedstocks, namely FMC char and anthracite, to check the slopes of the previously obtained Arrhenius plots. Six combustion runs were made, three utilizing coke from bituminous coal and three with FMC char as feed.

1. Effect of Steam Pressure on Rate of Gasification of Bituminous Coke

In the work presented some time ago on the effect of steam pressure on the gasification rate, only one run was obtained at 10 atmospheres pressure. Obviously, considerable weight had to be given to this run in order to define a curve for rate versus pressure. In order to firm up this curve, three new runs were made at 10 atmospheres pressure and one at 3 atmospheres using coke derived from bituminous coal. The results of these runs are presented in Table 1 and in Figure 1. As can be seen from this figure, these new data do confirm the relationship which was originally presented.

2. Feedstock Evaluation

At the Contractors' Meeting in July at [illegible], the question was raised as to the validity of the slopes drawn for the Arrhenius plots of the various feedstocks, since the lines were each drawn with only two data points available. Therefore, in order to firm up these plots, the most reactive and least reactive feedstocks (FMC char and anthracite, respectively) were tested at 1690°F, the mid-point in the plot of rate versus reciprocal temperature. Runs H-45 and 46 resulted in the two points shown in Figure 2 at 1690°F and indicate excellent agreement with the slopes originally drawn. This completes the experimental work on gasification at this time.

TABLE [illegible]

GASIFICATION RUNS IN MOLTEN SODIUM CARBONATE(1)

Run No. H-	43	44	45	[illegible]	47	48
Date - 1966	8/2	8/3	8/5	[illegible]	[illegible]/11	8/12
Feed	Bit. Coke VI		Anthracite	FMC Char	Bit. Coke VI	
% C - Fixed	-			76.4	-	
% C - Total	93.2		80.8	76.8	93.2	
% Vol. Matter	0.6		5.9	3.5	0.6	
% Ash	6.2		11.7	20.1	6.2	
gms. Charged	18.5		21.35	22.57	18.5	
mesh size	12/20		12/20	12/20	12/20	
Gms. Na_2CO_3	414	(2)	405.7	405.7	414	
Gms. Ash	0	0	8.3	8.[illegible]	0	
% Ash in Na_2CO_3	0	0.27	2	2	0	
% C in Melt - Init.	4	4	4	4	4	
Bed Ht. - inches	4	4	4	4	4	
Conditions						
Temp. - °F avg.	1640	1644	1690	1691	165[illegible]	1815
Pres. - psia	148.7	45.4	44.7	44.7	149.9	149.7
% Steam in N_2	89.9	89.6	90.7	91.7	90.1	90.4
Stm. Pres. - psia	133.7	40.7	40.5	41.0	135.1	135.3
Sup. Gas Vel. - ft/sec	0.46	0.48	1.00	0.99	0.47	0.50
Run Time - min.	45	65	35	20	30	25
cc H_2O in/hr	1860	570	1197	[illegible]	1850	1651
cc N_2 in/min	4412	1368	2550	[illegible]42	4215	4085
Results - basis feed						
% C in Devol. gas	1.8	2.8	2.9	16.1	2.9	4.2
% C in Prod. gas	101.8	98.6	94.6	[illegible].6	100.2	97.5
% C to tar - loss	-	-	-		-	-
Total % C	103.6	101.4	97.5	[illegible]	103.1	101.7
Gasif. Rate Constant - hr^{-1}						
k_1 - input	1.02	0.75	[illegible]	[illegible].19	1.83	3.27
k_2 - output	0.97	0.73	[illegible]	4.09	1.76	3.21
Rate - at 4% C in bed						
lbs C/hr/CF melt	11.4	8.6	17.7	[illegible]	20.8	37.9
Salt Carryover - gms	3.4	8.4	11.4	[illegible]	4.7	3.2

(1) Used 2-inch I.D. Inconel reactor. Bit. Coke VI m[illegible] at 950°C.

(2) Reused melt from previous run.

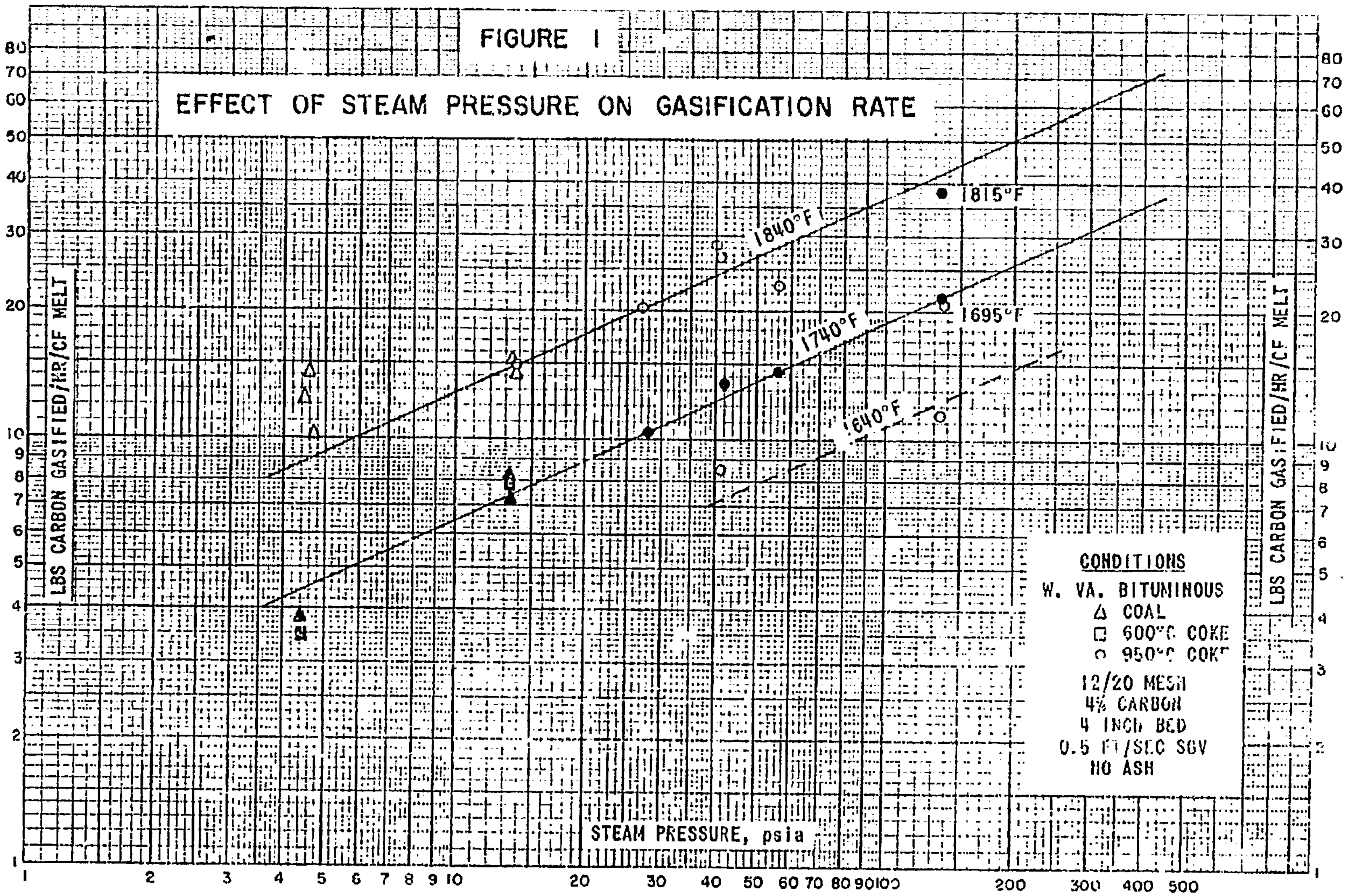
FIGURE 1
EFFECT OF STEAM PRESSURE ON GASIFICATION RATE
LBS CARBON GASIFIED/HR/CF MELT
STEAM PRESSURE, psia
1840°F
1815°F
1740°F
1695°F
1640°F
CONDITIONS
W. VA. BITUMINOUS
Δ COAL
□ 600°C COKE
○ 950°C COKE
12/20 MESH
4% CARBON
4 INCH BED
0.5 FT/SEC SGV
NO ASH

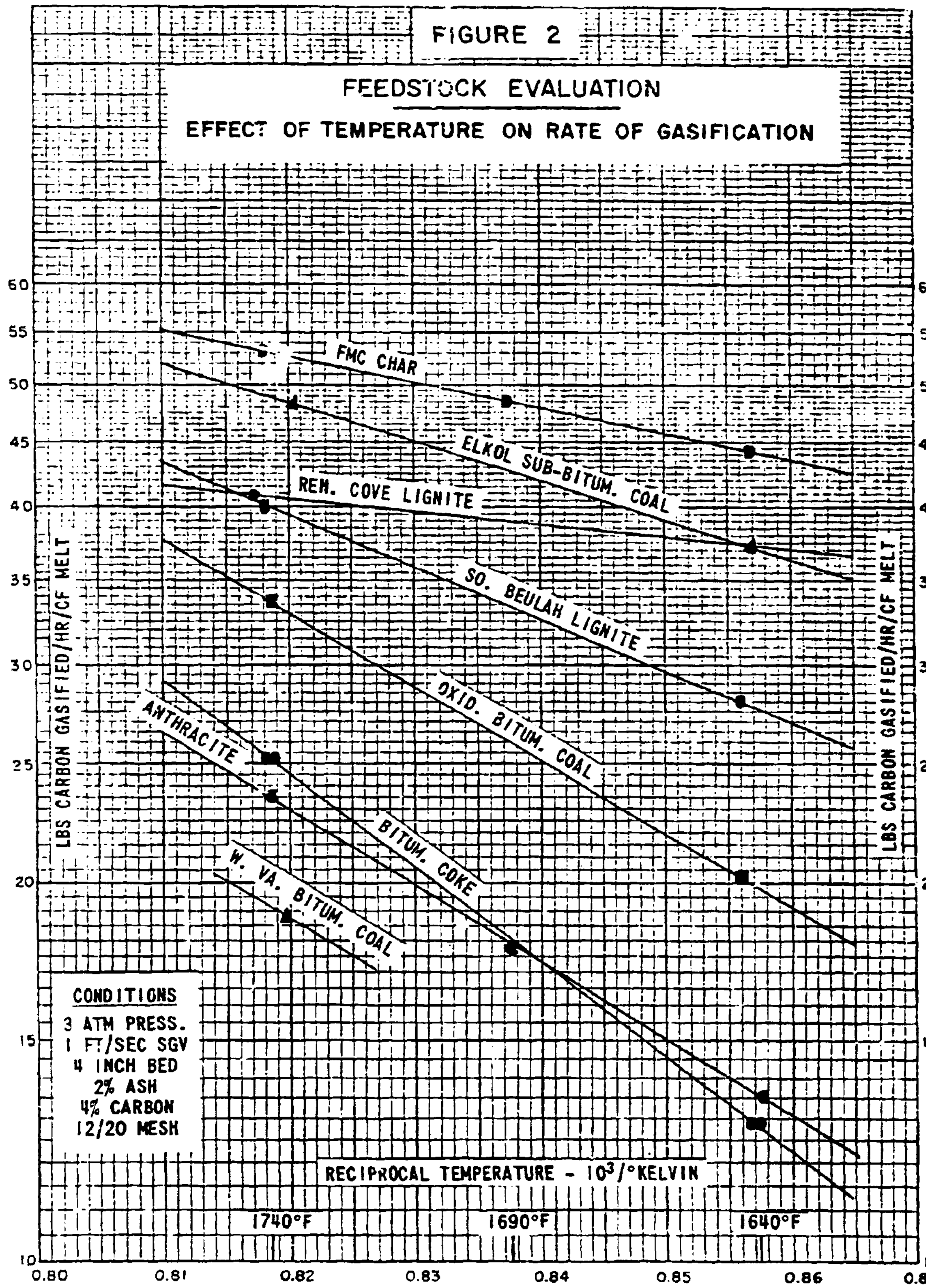
FIGURE 2
FEEDSTOCK EVALUATION
EFFECT OF TEMPERATURE ON RATE OF GASIFICATION
FMC CHAR
ELKOL SUB-BITUM. COAL
REN. COVE LIGNITE
SO. BEULAH LIGNITE
OXID. BITUM. COAL
ANTHRACITE
BITUM. COKE
W. VA. BITUM. COAL
CONDITIONS
3 ATM PRESS.
1 FT/SEC SGV
4 INCH BED
2% ASH
4% CARBON
12/20 MESH
LBS CARBON GASIFIED/HR/CF MELT
RECIPROCAL TEMPERATURE - 10³/°KELVIN
1740°F
1690°F
1640°F
10
15
20
25
30
35
40
45
50
55
60
0.80
0.81
0.82
0.83
0.84
0.85
0.86
0.87

3. Combustion Studies

The following conditions, which are based upon those used in most of the recent gasification studies, were fixed for the preliminary studies on combustion under pressure:

(a) 3 atmospheres absolute pressure
(b) 1 ft./sec. superficial gas velocity
(c) 4 inch quiescent bed height
(d) 2% ash in melt, ash derived from feedstock employed
(e) 4% carbon initially, based on fixed carbon in feedstock
(f) 5 minute devolatilization period in N_2 before air introduced

It is the intent of this study to generate combustion data at two or more temperature levels on the same feedstocks that were used in gasification. The summary of the runs on bituminous coke and FMC char are presented in Table II.

Although first order kinetics are not strictly obeyed beyond 50% carbon consumption, such a kinetic model has been used as a satisfactory means for comparison and to permit the combustion results to be compared with those for gasification.

Combustion of bituminous coke under 3 atmospheres of air pressure proceeds reasonably well especially above 1840°F where the rate exceeds 20 pounds of carbon burned per hour per cubic foot of melt at 4% carbon in the melt. A 45°F increase in temperature of the molten salt was observed due to the combustion of the coke at an initial temperature of 1940°F.

The very reactive FMC char made from an Illinois coal burned so fast that during the first few minutes of the run all the oxygen fed was consumed indicating a combustion rate somewhat in excess of 70 lbs./hr./CF. This occurred at initial bed temperatures of 1640 and 1740°F in which runs almost 90% of the carbon was consumed within 5 minutes.

The high reactivity of FMC char suggested that it should be charged to the molten salt at 1640°F and its reactivity with Na_2CO_3 be ascertained. This was done in run H-79 where only nitrogen at 0.1 ft./sec. was passed through the unit. About 16% of the carbon charged showed up in the product gas in the first five minutes. The rate then slowed and in 30 minutes, when the run was terminated, only 38% of the carbon had reacted. Thus the overall rate was only 3 lbs./hr./CF. The very high carbon monoxide content in the product gas indicates the following reactions take place:

$$C + Na_2CO_3 = 2\ CO + Na_2O$$

$$CO + \text{Oxidized Inconel} = CO_2 + \text{Inconel}$$

Although a reaction can be written,

$$C + 2Na_2CO_3 = 2\ CO + CO_2 + 2Na_2O$$

the high CO/CO_2 ratios observed in the product gases (2.6 to 5) suggest that this latter reaction is a rather unlikely one.

B. Projections

Work will continue on combustion to establish the effect of the variables.

TABLE II

SUMMARY OF COMBUSTION RUNS IN MOLTEN SODIUM CARBONATE[1]

Run No. H-	49	50	76	77	78	79
Date - 1966	8/16	8/17	8/18	8/30	8/31	8/31
Feed	← Bit. Coke VI →			← FMC Char →		
% Fixed Carbon		-			76.4	
% Total Carbon		93.2			76.8	
% Vol. Matter		0.6			3.5	
% Ash		6.2			20.1	
gms. charge		18.5			22.57	
mesh size		12/20			12/20	
% C in melt - init.		4			4	
Na_2CO_3 - gms.	405.7	(2)	(2) + 25	405.7	(2)	(2)
Ash - gms.	8.3	-	-	8.3	-	-
% Ash in bed	2	2	2	2	2	2
Bed Height - inches	4	4	4	4	4	4
Conditions						(3)
Temp. °F - initial	1740	1840	1940	1740	1640	1640
Temp. - °F ave.	1743	1841	1974	1870	1762	1643
Temp. - °F max.	1754	1863	1985	1940	1847	-
Pressure - psia	44.7	45.3	45.2	45.0	44.5	44.3
Sup. Gas Vel. - ft/sec	0.87	0.88	0.90	0.87	0.79	0.1
Run Time - min.	50	30	15	5+	5+	30
Air Rate - l/min.	23.1	22.3	21.7	22.9	22.8	2.5 - N_2
Results - Prod. Gas						
% CO_2 - 5 min.	4.0	7.0	11.5	18.0	18.0	7.5
- 35 min.	2.4	-	-	-	-	-
- end[4]	1.3	1.4	3.6	0.4 (15)	1.5 (10)	0.6
% O_2 - 5 min.	18.0	15.0	11.5	2.0	2.3	0
- 35 min.	18.5	-	-	-	-	-
- end	20.9	18.5	19.0	20.5	18.0	0
% CO - 5 min	0.1	0.1	0	0.9	1.0	20.0
Combustion Rate Constant (5)	0.99	1.82	3.43	>6	>6	0.26
Total % C Consumed (4)	102	102	101	88 (5)	89 (5)	38
Rate - lbs C/hr/CF	11.7	21.5	40.5	>70	>70	3.1

(1) Used 2-inch I.D. Inconel reactor. Bitum. coke VI made at 950°C.

(2) Reused melt from previous run.

(3) No air, only 0.1 ft/sec N_2.

(4) Minutes in parenthesis.

(5) Same kinetic basis as gasification runs.

III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

1. Lignite Flowsheet

Calculations have continued for the preparation of a flowsheet for a plant capable of producing 250,000,000 SCFD of pipeline gas from lignite. The general processing sequence chosen is essentially the same as that used for the bituminous, subbituminous and anthracite cases and therefore will not be repeated here. Preliminary calculations have indicated that the cost of pipeline gas will be quite a bit higher than that for the bituminous case. Fixed investment is estimated to be approximately \$190,000,000 and gas selling price with lignite at \$1.50 per ton is about 63¢/MSCF. However, when these numbers were obtained it became evident that the increased ash quantity handled in the lignite case was adding significantly to the cost and that the processing scheme probably should be modified to compensate for it. As was pointed out in the anthracite study, one way of reducing the problems associated with high-ash coals (increased gasifier heat load to decompose $NaHCO_3$, increased gasifier and combustor sizes, increased CO_2 removal, etc.) would be to decompose the recycle $NaHCO_3$ before feeding it to the gasifiers. This alternative is being investigated and preliminary indications are that the investments for gasification, gas purification (CO_2 removal), and offsite facilities (power generation from waste heat) will be substantially reduced while the cost of ash removal will be increased by the addition of the $NaHCO_3$ decomposition step. Overall, it is anticipated that both the investment and gas selling price will be reduced by this scheme.

2. Hydrogen Flowsheet

Flowsheet calculations continued for the hydrogen-from-coal plant. Equipment sizing has been completed for most of the major items except for the heat exchangers. These exchangers will be sized as soon as the overall plant energy requirements are calculated.

B. Projections

1. Pipeline Gas

The flowsheet and economics for producing pipeline gas from lignite will be completed.

2. Hydrogen

Work will continue on the preparation of the "process package" for the hydrogen-from-coal plant.

IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High Temperature Materials

The new samples for Corrosion Test #10 have been prepared and the test apparatus is completely ready. There has been a delay in receiving the pre-mixed gas cylinders, but these should be received very shortly, with testing beginning immediately thereafter.

2. Mechanical Characteristics Testing

The 5-3/4" reactor test facility is complete in major detail, with the furnace ready for initial drying. All wiring is in and complete and all instrumentation is finished.

In choosing a material to simulate the Na_2CO_3 melt, a question has been raised as to the actual melt viscosity. This in the past has been measured by a Brookfield Viscosimeter, and was found to be approximately 100-120 cp at 1840°F and 8% ash. However visual observation of the melt indicated the viscosity might be lower, perhaps more like that of water.

In order to investigate the viscosity problem further, the device in Figure 3 was constructed. This device was filled to a depth of 8-1/2" with a liquid of known viscosity, then the time required for the liquid to flow through the outlet tube was measured. This test was repeated for several liquids including molten Na_2CO_3 + 12% ash; the results being given in Figure 4. From these results it would appear that under conditions of turbulence the viscosity of the molten Na_2CO_3-ash mixture might be closer to that of water than previously believed. Certainly further investigation of this point is warranted.

3. Melt Circulation

An "air lift" type flow system is being studied as a possible means of melt circulation in the reaction system. Studies to date have concentrated on establishing design parameters and development of analytical tools for designing the flow system. Both air-water and air-glycerine-water systems have been explored.

Encouraging results have been obtained for the air-water system in that pump rates have been predicted to within +16 to -24 per cent over a wide range of air rates and submergence for a 1-3/8" I.D. tube 9 feet long.

Figure 5 shows the test set up used to determine experimental flow rates. Flow rates were predicted using the Martinelli-Lockhart pressure drop correlation for two-phase, two-component flow in pipes. The expression is:

Driving Head = Friction Loss + Velocity Loss (Gas & Liquid)

$$\frac{h_s}{R_l} - (h_s + h_d) = \frac{\left(\frac{\Delta P}{\Delta L}\right)_{tph} \cdot L}{p_l R_l} + \frac{p_g V_g^2}{p_l R_l 2g} + \frac{V_l^2}{R_l 2g}$$

Entrance losses are assumed negligible.

$\left(\frac{\Delta P}{\Delta L}\right)_{tph}$	= Pressure Drop Per Unit Length Two Phase Flow (LBS/FT^2-FT)
g	= Gravitational Constant (32.2 FT/SEC^2)
h_s	= Submergence of Air Lift Tube (FT)
h_d	= Lift Height (FT)
L	= Length of Air Lift Tube (h_s+ h_d) (FT)
R_l	= Liquid volume Fraction In Tube
p_g	= Density of Gas (LBS/FT^3)
p_l	= Density of Liquid (LBS/FT^3)

V_g = Superficial Air Velocity (Exit Conditions) (FT/SEC)

V_l = Superficial Liquid Velocity (Exit Conditions) (FT/SEC)

Figure 6 shows the comparison of experimental and predicted results.

Less encouraging results were obtained for a 100 centipoise glycerine-water mixture in that predicted rates of flow were considerably below experimental data. A preliminary review indicates that the Martinelli-Lockhart correlation may not accurately predict the liquid volume fraction (R_l) and perhaps pressure drop, for laminar liquid flow which characterized the 100 centipoise glycerine-water system.

The significance of this apparent failure for laminar flow is being investigated in light of the outflow test which indicates the flowing melt viscosity may be close to that of water.

B. Projections

1. Environmental Testing of High Temperature Materials

Corrosion Test #10 will begin as soon as the pre-mixed gases arrive.

2. Mechanical Characteristics Testing

The 5-3/4" reactor furnace will be dried out immediately, then bed expansion studies will begin using beds deeper than previously possible.

Work will also continue in an effort to better understand the melt viscosity at elevated temperatures.

3. Melt Circulation

Work will continue on the prediction of melt circulation with an air-lift type system. An attempt will be made to establish the limit of applicability of the Martinelli-Lockhart correlation and extend results to a design procedure for melt circulation.

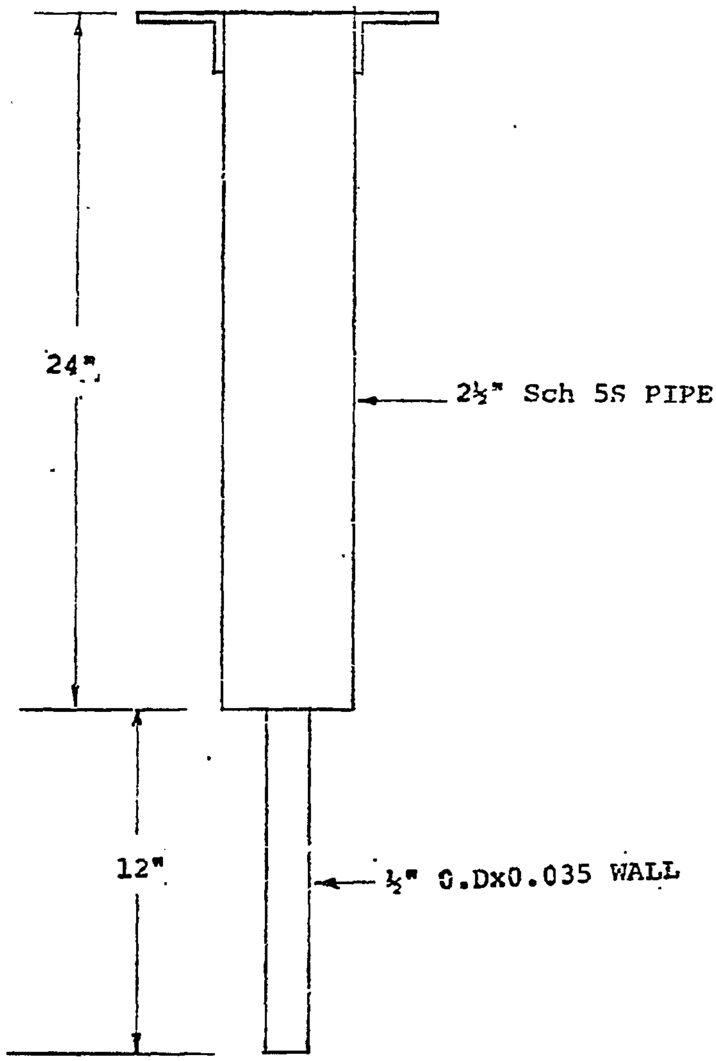

FIGURE 3
MELT OUTFLOW VESSEL

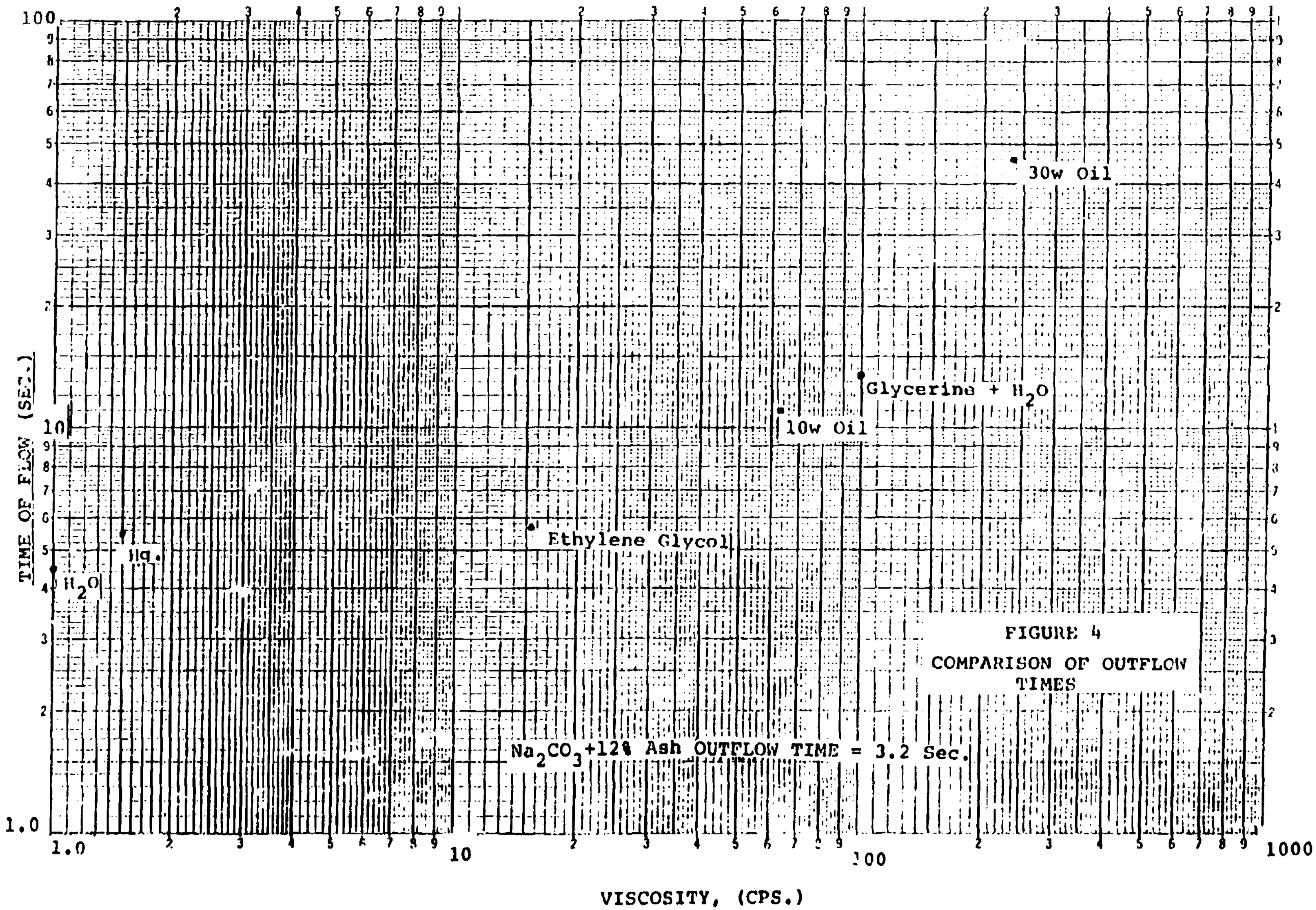

FIGURE 4
COMPARISON OF OUTFLOW TIMES

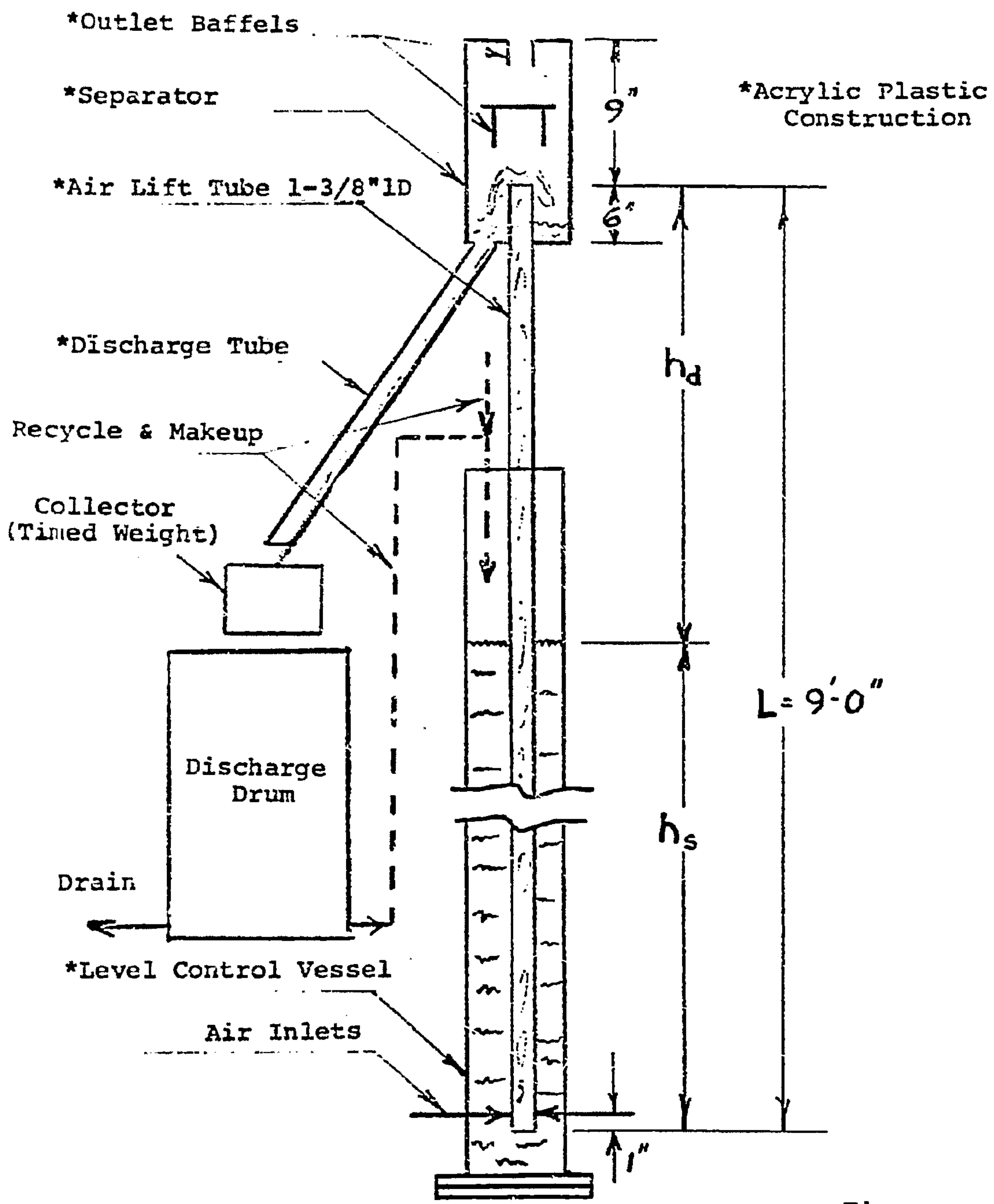

Figure 5

Air Lift Flow Test
Apparatus

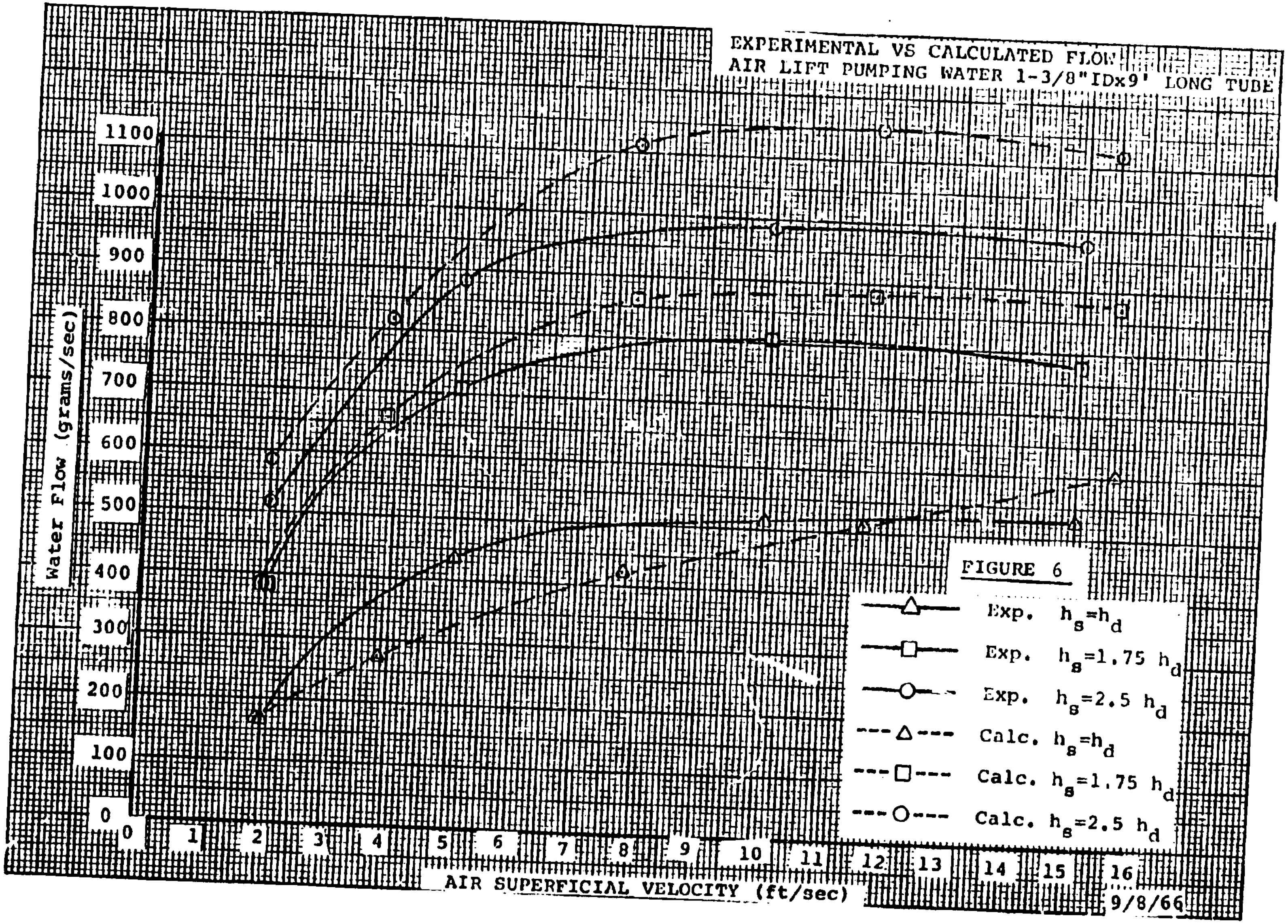
EXPERIMENTAL VS CALCULATED FLOW
AIR LIFT PUMPING WATER 1-3/8"IDx9' LONG TUBE
Water Flow (grams/sec)
0
100
200
300
400
500
600
700
800
900
1000
1100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
AIR SUPERFICIAL VELOCITY (ft/sec)
Exp. $h_s=h_d$
Exp. $h_s=1.75\ h_d$
Exp. $h_s=2.5\ h_d$
Calc. $h_s=h_d$
Calc. $h_s=1.75\ h_d$
Calc. $h_s=2.5\ h_d$
9/8/66

FIGURE 6

V. MANPOWER AND COST ESTIMATES

Figure 7 shows the projected breakdown for Phase I for 1966 as well as the actual effort that was made. It can be seen that a 12.3 man-effort was made during August.

Figure 8 shows the expenditures during August. For the month $21,209 was expended, not including fee and G&A. The total expenditures through August were $488,072. Including fee and G&A the total expenditures were $557,979. This is 51% of the encumbered funds.

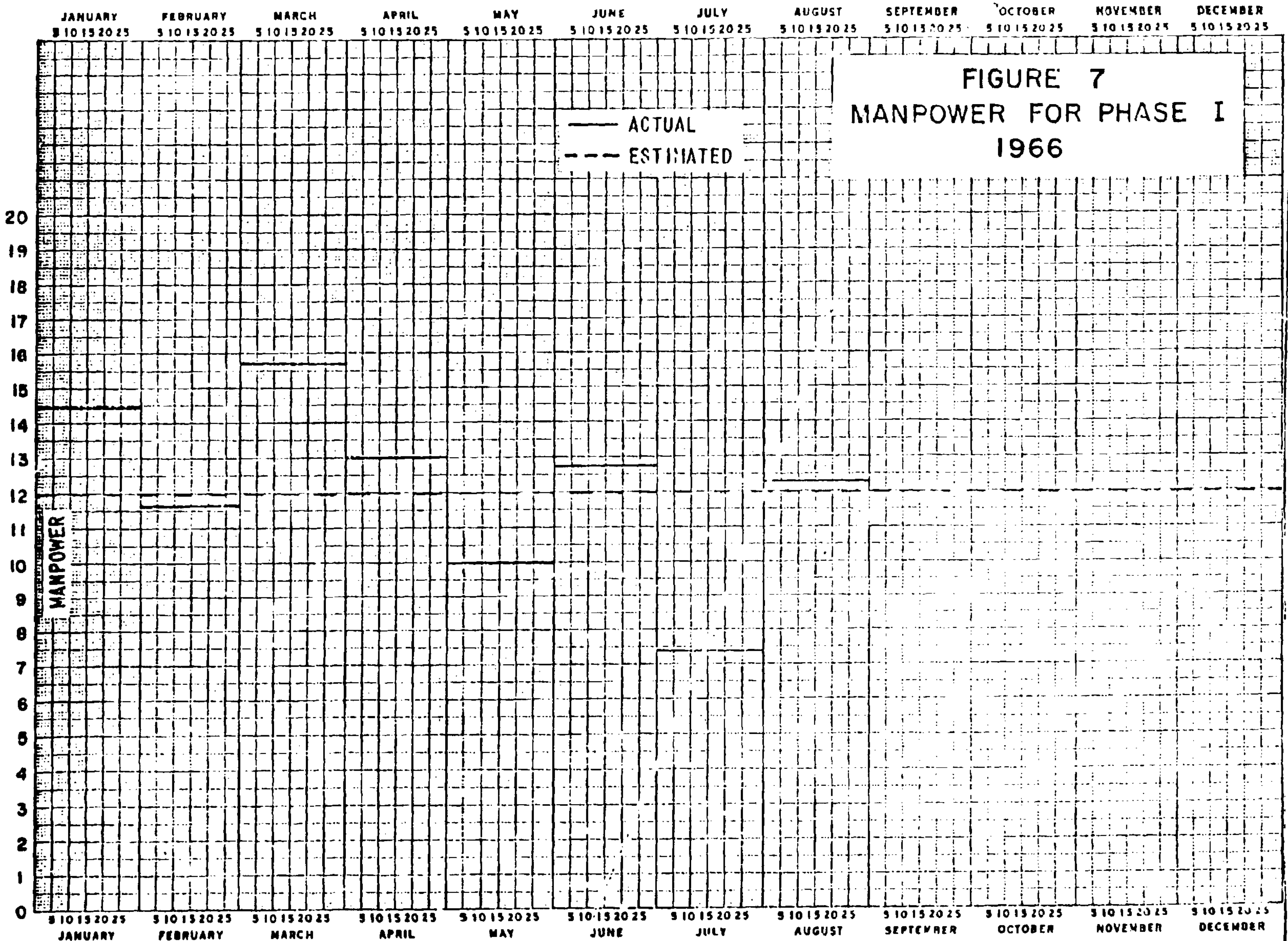

FIGURE 7
MANPOWER FOR PHASE I
1966

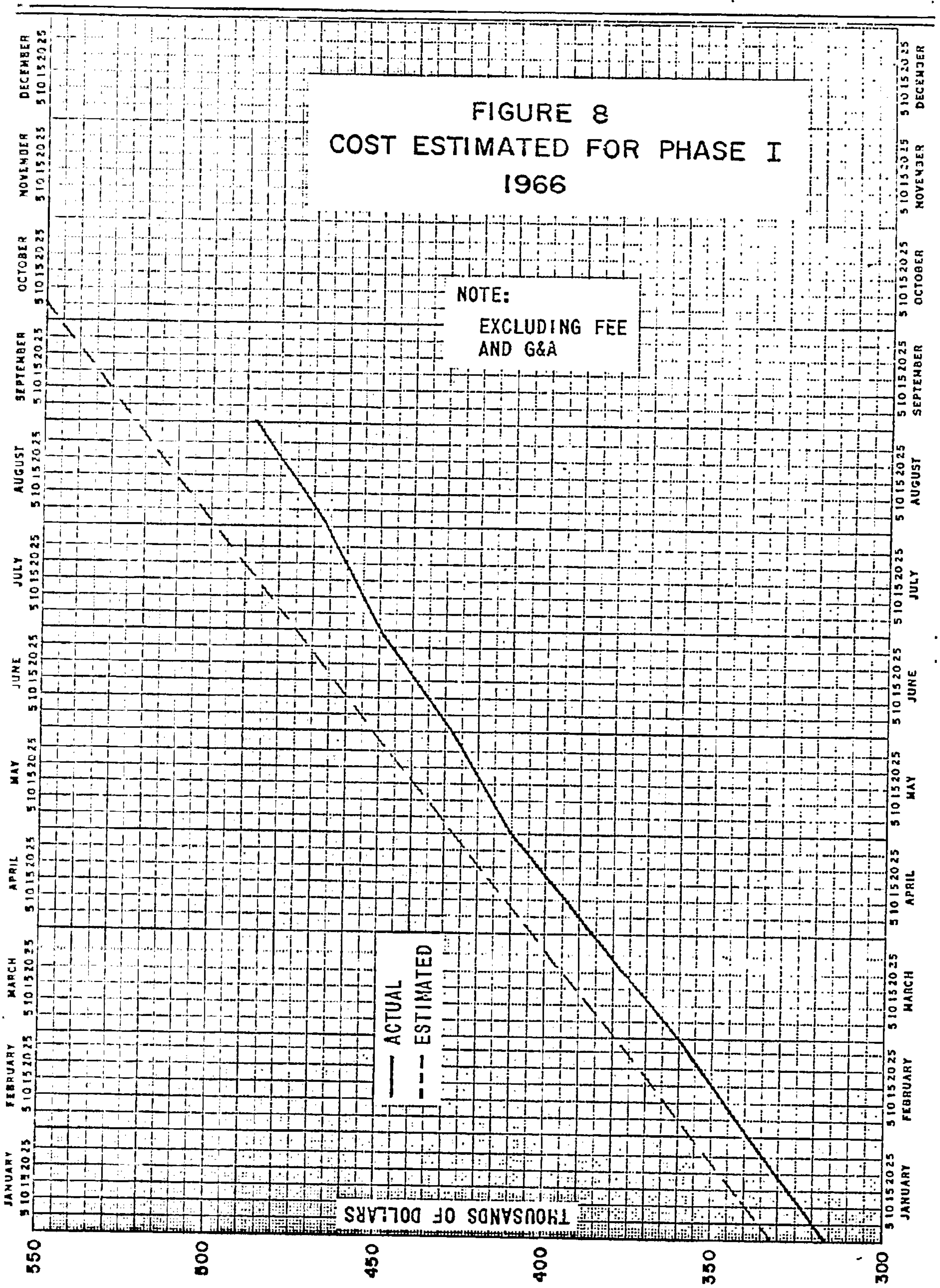

FIGURE 8
COST ESTIMATED FOR PHASE I
1966