

MWK-MPR-2P

RESEARCH AND DEVELOPMENT DEPARTMENT



DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

CONTRACT NO. 14-01-0001-380

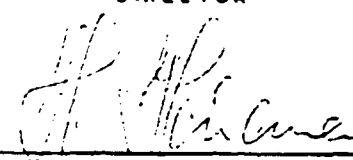
November 30, 1966

Progress Report No. 28

APPROVED:

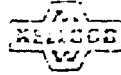

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THE M. W. KELLOGG COMPANY
A DIVISION OF PULLMAN INCORPORATED



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I. SUMMARY

This progress report is the twenty-eighth 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 with bituminous coke to determine the effect of particle size on combustion rate. For size ranges below 4/8 mesh there appears to be an exponential dependence of rate on surface/volume ratio.

One run was made at about 1800°F in an effort to better define the Arrhenius plot of the combustion rate of bituminous coke.

Six new combustion runs were made to determine the constituent in lignite ash which was responsible for the previously observed high rates of combustion of anthracite and bituminous coals. Neither the addition of calcium nor magnesia was seen to improve combustion rate. However, addition of two percent calcium sulfate increased the combustion rate of bituminous coke by a factor of about two at both 1824°F and 1640°F. Addition of two percent sodium sulfate to the melt gave identical results as with calcium sulfate.

Some experiments have been made to determine the tendency of ash to settle out from a melt. The preliminary results indicate that an appreciable degree of settling does occur in a relatively short period of time. Efforts to further precipitate out ash by the addition of calcium carbonate were not successful.

A study of one of the laboratory combustion runs on char has indicated that, on the average, all of the heat liberated by combustion could be accounted for in terms of heat losses and sensible heat increases of the gas and the melt. However, heat losses in this equipment are large (~75% of the heat of reaction) and the validity of this conclusion is therefore somewhat limited. Consideration is being given to better determine these heat losses, thereby permitting more accurate heat balance calculations to be made.



Flowsheet calculations have continued for the hydrogen plant, and similar work on a synthesis gas flowsheet has been begun.

Preliminary results of cross flow contamination experiments with ethylene glycol indicate a lower level of contamination than for water when there is no bed aeration. The effect of bed aeration appears greater, however, and at high degrees of aeration the observed contamination is about the same as for water.

Attempts to determine the split between entrained and dissolved gas carried over in cross flow experiments indicated that for the unaerated cases, dissolved gas accounted for 75 to 95 percent of the contamination.

A comparison of the actual and predicted flows in the cross flow apparatus resulted in an agreement to within about 20 percent, thus confirming the method at least for water.



II. PROCESS RESEARCH

A. Accomplishments

Studies have been made to determine the effect of particle size on combustion rate and to determine the constituent in lignite ash which gave the high rates of combustion for anthracite and oxidized bituminous coal which were reported in Progress Report No. 26. The combustion runs are summarized in Table I. Some preliminary investigations have also been made of the rate of settling of ash present in a melt.

1. Effect of Particle Size of Coke on Combustion Rate

Particle size of bituminous coke was varied by screening narrow size ranges as shown in the following table. Tests of these particles have been corrected to a nominal 1740° F average combustion temperature. Further, to allow better comparison of the effect of particle size, the surface to volume ratio of a sphere has been calculated based on the arithmetic average of the sieve openings (6/diameter). The results are tabulated below and plotted in Figure 1. After an initial rapid rise in combustion rate a linear response was obtained on the semi-logarithmic plot of rate versus the surface/volume ratio.

<u>Mesh Size</u>	<u>Avg. Size</u> <u>mm</u>	<u>Surface/Volume</u> <u>mm⁻¹</u>	<u>Comb. Rate 1740° F</u> <u>lbs. C/hr./CF</u>
4/8	3.57	1.68	8.85
12/20	1.26	4.76	10.8
40/60	0.335	17.9	14.0
80/100	0.163	36.8	18.9

2. Effect of Temperature on Combustion Rate of Bituminous Coke

Curvature in the Arrhenius plot of combustion rate against reciprocal temperature indicated further testing should be done. Run H-134 was made at 1798° F and is plotted in Figure 2. It now appears as if the rate determined at 1740° F may be low. Further testing will have to be made to clarify this situation.



3. Search for Component in Lignite Ash Which Increases Combustion Rate

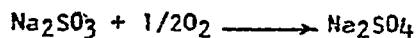
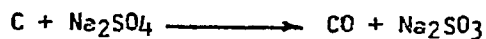
The remaining runs in Table 1, H-135 to 140, were made to define the constituent in lignite ash which enhanced the rate of combustion of anthracite and oxidized bituminous coal (Progress Report No. 26). However, bituminous coke was used in the present series of runs. Lignite ash in the melt at the two percent level increased the combustion rate of bituminous coke by a factor of 1.63 over the normal run (Figure 2).

<u>Melt Contained</u>	<u>Avg. Temp. °F</u>	<u>Comb. Rate</u>
2% Bitum. Ash	1761	14.5
2% Lignite Ash	1761	23.6

Addition of calcia and magnesia to the melt, at the two percent level, failed to have any effect on rate. However, when calcium sulfate was added to the melt, at the same two percent level, an exceptional rate of 46 lbs. C burned/hr./CF was obtained for an average temperature of 1824° F with an initial temperature of 1740° F. This is more than double the rate at 1824° F shown in Figure 2. Further verification was achieved by a second test at 1640° F initial which gave a rate almost double that in Figure 2 at the equivalent temperature.

Lignite ash can be considered to contain 42.7% calcium sulfate based upon the total sulfur composition. This leaves a slight excess of calcia. Therefore, the increase in rate appears to increase with the amount of calcium sulfate. In the last run sodium sulfate was used in place of the calcium sulfate. The amount was adjusted to contain the same amount of sulfate as in the first calcium sulfate run. The combustion rate on this run agreed identically with the calcium sulfate run. However, average temperature was a little higher.

Sulfate appears to be the catalytic agent which enhances combustion of carbon in the molten salt system. Available evidence indicates that sulfate ion increases rate by direct reaction with carbon followed by a re-oxidation of the sulfite back to sulfate by air. The reactions involved are:



Although an attempt was made to determine if calcium and sodium sulfates are soluble in molten sodium carbonate through freezing point depression, results qualitatively indicate calcium sulfate is not very soluble and sodium sulfate may be soluble. Further work is required in this area.



4. Ash Settling Studies

Preliminary experiments on the tendency of ash to settle to the bottom of a melt have been made. Six-inch high melts containing 6.84% bituminous coal ash were held one hour at 1740°F with 0.25-0.5 ft./sec. superficial gas velocity of CO₂ mixing the melt. The CO₂ inlet was located above the melt, and the melt allowed to remain quiescent for 10 minutes before sampling five inches off the bottom. Analyses showed 3.85% and 2.65% of ash in the samples in two experiments. This was encouraging and indicated ash does settle at an appreciable rate.

An 8% bituminous ash melt of 6" bed height was treated similarly and samples taken at the bottom and 5" from the bottom after 10, 20 and 30 minutes of settling. Results tabulated below show that a rapid settling occurs in 10 minutes and not much thereafter. However, thermal currents may confound these results in the small 2" ID reactor.

<u>Settling Time</u> <u>min.</u>	<u>Wt. % Ash</u>	
	<u>5" off btm.</u>	<u>Btm.</u>
0	8.0	8.0
10	3.09	9.24
20	2.75	12.1
30	3.74	10.6

The above results very definitely established that appreciable ash settling occurs in a reasonable time. It may be possible to recycle a significant amount of melt with 3-4% ash in it without having to go through the sodium carbonate recovery section. High recovery of sodium and not too high a viscosity in the bottom part of the melt will be necessary.

A further attempt was made to knock out the ash by adding calcium carbonate and allowing the mixture to settle for 10 minutes. The initial melt composition was 7.7% ash and 3.87% calcium carbonate.

<u>Settling Time</u> <u>min.</u>	<u>Wt. % Ash</u>	
	<u>5" off Btm.</u>	<u>Btm.</u>
0	11.57	11.57
10	7.64	16.35
10	6.48	12.98

The CaCO₃ behaved like ash and it appears not to have increased the settling rate.

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B. Projections

Evaluation of the effect of sulfate on gasification rate will be determined. Further investigation of ash settling will continue. Some combustion work will also be continued.

TABLE I

SUMMARY OF COMBUSTION RUNS IN MOLTEN SODIUM CARBONATE^{1/}

Run No. H- Date - 1966	131 10/28	132 10/31	133 11/2	134 11/3	135 11/7	136 11/9	137 11/11	138 11/15	139 11/16	140 11/18
Feed	← Bituminous Coke →									
% Fixed Carbon	-									
% Total Carbon	93.7									
% Vol. Matter	0.6									
% Ash	6.2									
Gms. charge	18.5									
Mesh size	4/8	80/100	40/60	← 12/20 →						
% C in melt - initial	4									
Melt										
Gms. Na ₂ CO ₃	/3/	/3/	405.7	/3/	405.7	405.7	405.7	405.7	/3/	405.7
Gms. Ash or Cmpd.	6.1	-	8.3	-	8.3	8.3	8.3	8.3	-	8.63
Compound Added	-	-	-	-	CaO	MgO	Lignite Ash	CaSO ₄	CaSO ₄	Na ₂ SO ₄
% Ash or Cmpd. in Melt	2.0	2.27	2.0	2.27	2.0	2.0	2.0	2.0	2.27	2.08
Height - inches	4	4	4	4	4	4	4	4	4	4
Conditions										
Temp. °F - initial	1735	1740	1740	1794	1740	1740	1740	1740	1640	1745
- average/2/	1740	1770	1750	1798	1740	1740	1761	1824	1649	1839
- maximum	1760	1791	1770	1814	1750	1751	1785	1851	1685	1870
Pressure - psia	44.9	44.7	44.7	45.0	45.1	45.0	44.7	44.9	44.7	44.8
Sup. Gas Vel. - ft/sec	0.90	0.95	0.98	1.0 ²	0.94	1.00	0.98	0.96	0.94	0.96
Run Time - min	70	25	35	35	85	90	30	20	45	25
Air Rate - liters/min	25.0	25.0	25.8	25.7	24.8	26.5	25.9	25.5	26.0	25.5
Results - Product Gas										
% CO ₂ - 5 min	2.7	-	4.6	5.4	2.0	1.9	6.8	11.5	4.0	11.0
- 35 min	1.8	-	1.9	1.7	1.3	1.0	-	-	1.2	-
- end	0.6	1.5	1.9	1.7	0.9	0.7	1.0	0.95	0.5	0.3
% O ₂ - 5 min	17.5	-	17.0	16.5	18.0	18.5	14.5	10.5	17.0	9.0
- 35 min	18.0	-	19.0	20.0	19.0	19.0	-	-	19.0	-
- end	20.3	19.8	19.0	20.0	20.0	20.0	18.5	20.5	20.0	19.0
Combustion Rate Constant	0.75	2.07	1.33	1.49	0.43	0.38	2.00	3.87	1.16	3.83
% Fixed Carbon Consumed	101	104	99	99	83	82	100	100	93	95
Rate - lbs C/hr/CF	8.9	24.4	15.7	17.6	5.1	4.5	23.6	45.7	13.7	45.2
% Total Carbon - devolatilized	4.5	7.2	6.0	5.8	3.0	5.4	7.2	10.9	5.5	10.8
- combusted	96.2	96.3	93.0	93.2	80.1	77.5	92.9	88.8	88.3	85.1
- left + loss	-	-	1.0	1.0	16.9	17.1	-	1.3	6.2	4.1

^{1/} Used 2-inch I.D. Inconel reactor. Coke chg. in N₂ at 0.1 ft/sec SGV, .5 min. devol. period before air in.

^{2/} Average temperature in 50% carbon consumed period.

^{3/} Reused melt from previous run.

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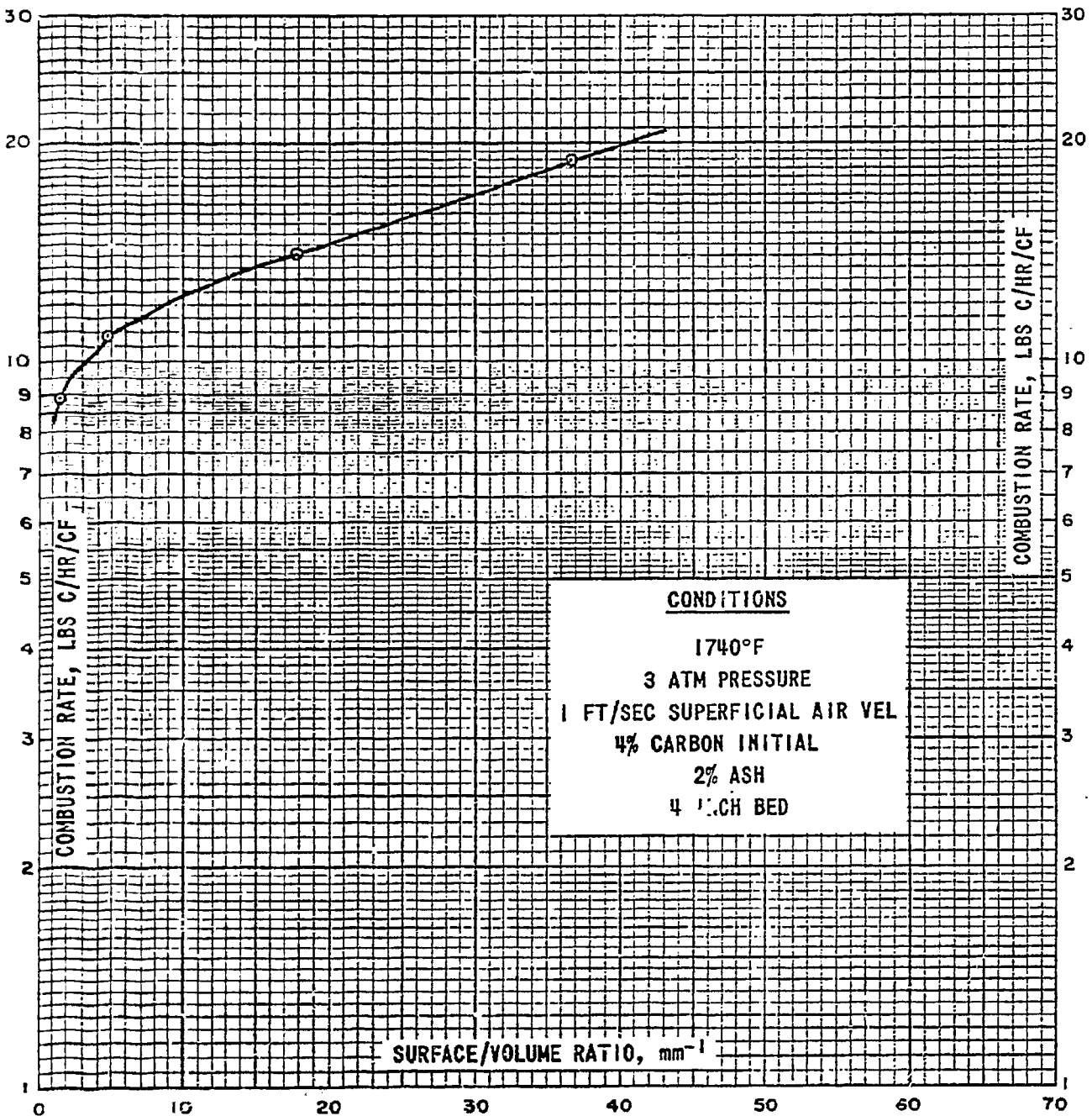


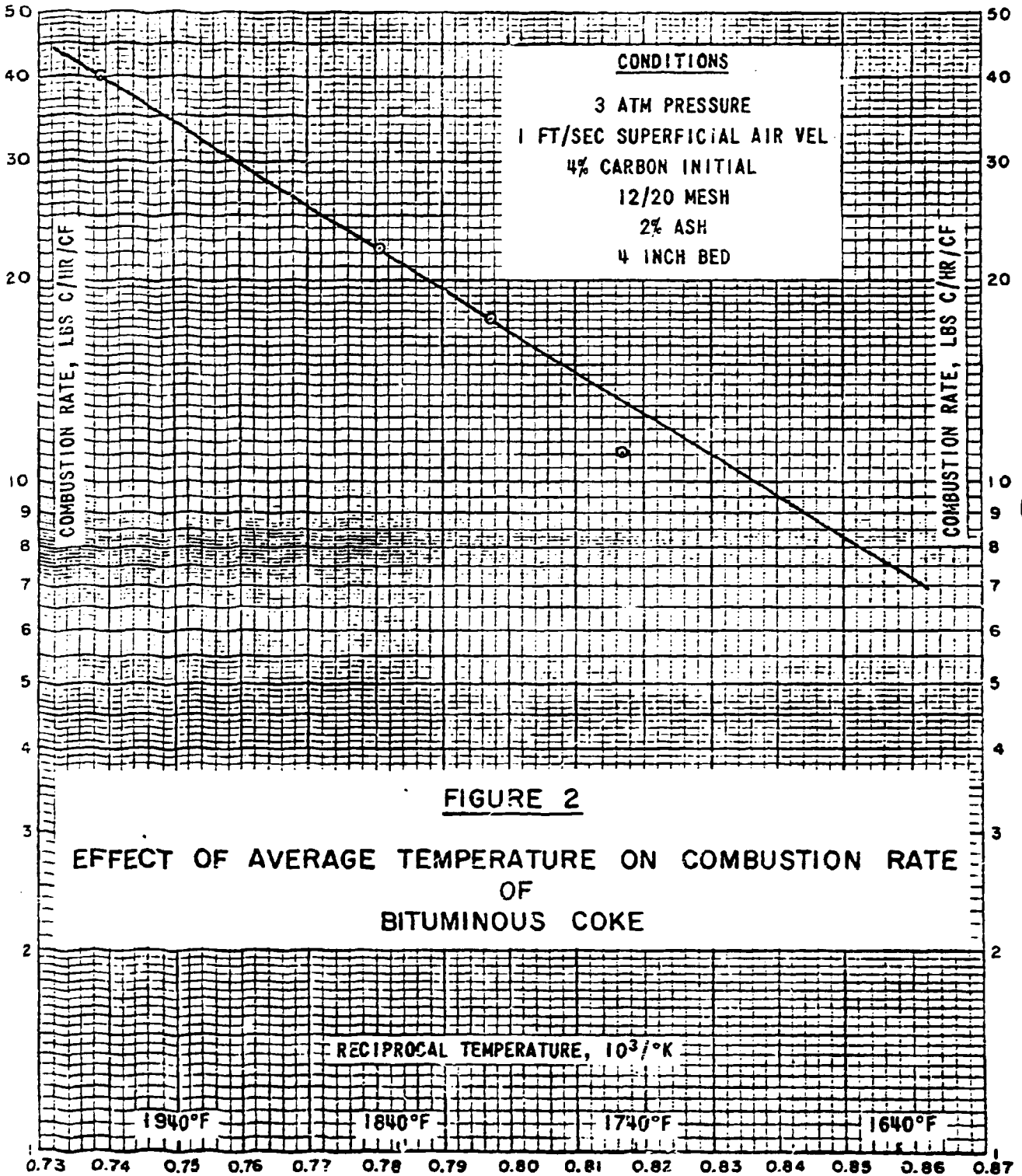
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FIGURE 1
EFFECT OF PARTICLE SIZE ON GASIFICATION RATE
OF
BITUMINOUS COKE







III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

1. Combustion Efficiency

An analysis of one of the combustion runs (H-77) made in the 2-inch bench-scale apparatus has indicated that, on the average, all of the heat liberated by combustion could be accounted for in terms of heat losses and sensible heat increases of the gas and the melt. However, it appears as though the heat losses were increasing throughout the run, and since this accounts for about 75% of the heat liberated, heat balance checks at the beginning and end of the run were somewhat off. It is quite possible that the magnitude of the heat losses (relative to the heat liberated) incurred on this small scale will make it impossible to determine the efficiency of combustion in the bench-scale unit. Nevertheless, consideration is being given to possible methods of running combustion experiments with a more accurate and continuous measurement of reactor heat losses.

2. Flowsheet Studies

Work has been continued on the preparation of a flowsheet for a hydrogen-from-coal-plant. In addition, efforts have been begun to work up a conceptual flowsheet for the production of 250,000,000 SCFD of synthesis gas from bituminous coal.

B. Projections

1. Combustion Efficiency

As has been stated, attempts will be made to determine whether the method of running combustion experiments can be modified to provide better information on the magnitude of the heat losses incurred in a given run to provide a good basis for heat balance calculations.

2. Flowsheet Studies

Work will continue on the preparation of both the hydrogen and synthesis gas flowsheets.



IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High Temperature Materials

Corrosion Test #10 will resume as soon as furnace repairs can be completed or a substitute furnace obtained. Repair has been halted by a delay in receiving necessary furnace elements from the manufacturer.

2. Mechanical Characteristics Testing

Furnace modifications have been completed and melt bed expansion tests will resume shortly.

3. Melt Circulation

Tests on cross flow contamination similar to those conducted for water have been completed for ethylene glycol (viscosity = 15.7 cp). Preliminary results indicate a lower level of cross flow contamination is obtained for the ethylene glycol where there is no bed aeration. However, the effect of bed aeration is greater and for the highest rate of aeration (1.5 feet per second superficial velocity) the contamination is approximately that obtained with water. A complete presentation of this data will be made in a later report.

Some additional work has been done on determining the actual split between entrained gas and dissolved gas carried over as cross flow contamination. From this work, which primarily involved the comparison of cross flow contamination on the two sides of the cross flow model, it was determined that for the no bed aeration cases, dissolved gas accounted for 75 to 95 percent of the total cross flow contamination. It is obvious that solubility of the contaminating gases in the melt will be significant in determining the minimum level of contamination possible. Additional work is required in this area to determine the level and rate of solubility of the contaminating gases in the melt.

A check of the actual versus the predicted flow in the cross flow model confirms our prediction method for water, in that the predicted flow was only 19 percent higher than the actual flow. The check was conducted with a superficial velocity of five feet per second in the air lift.



At a corresponding velocity in the nine-foot air lift, which was used in the development of the prediction method, the predicted value was about seven percent higher than the experimental results. But here the several inches necessary to develop the predicted two phase flow is a smaller percentage of the total length and may explain the small differences in observed and predicted results for the two cases.

B. Projections

1. Environmental Testing of High-Temperature Materials

Corrosion Test #10 will continue as soon as furnace repairs have been completed.

2. Mechanical Characteristics Testing

Bed expansion tests will be conducted shortly on the sodium carbonate melt at 1840 F.

3. Melt Circulation

The data taken for cross flow contamination using ethylene glycol as the transfer liquid will be evaluated further for effect of viscosity. Other liquids such as glycerin may be used if additional data is required. An attempt should be made to establish the amount and rate of contaminating gas that can be dissolved in the melt. Also, a better feeling for the melt viscosity will be developed from the bed expansion tests or other tests, as required.

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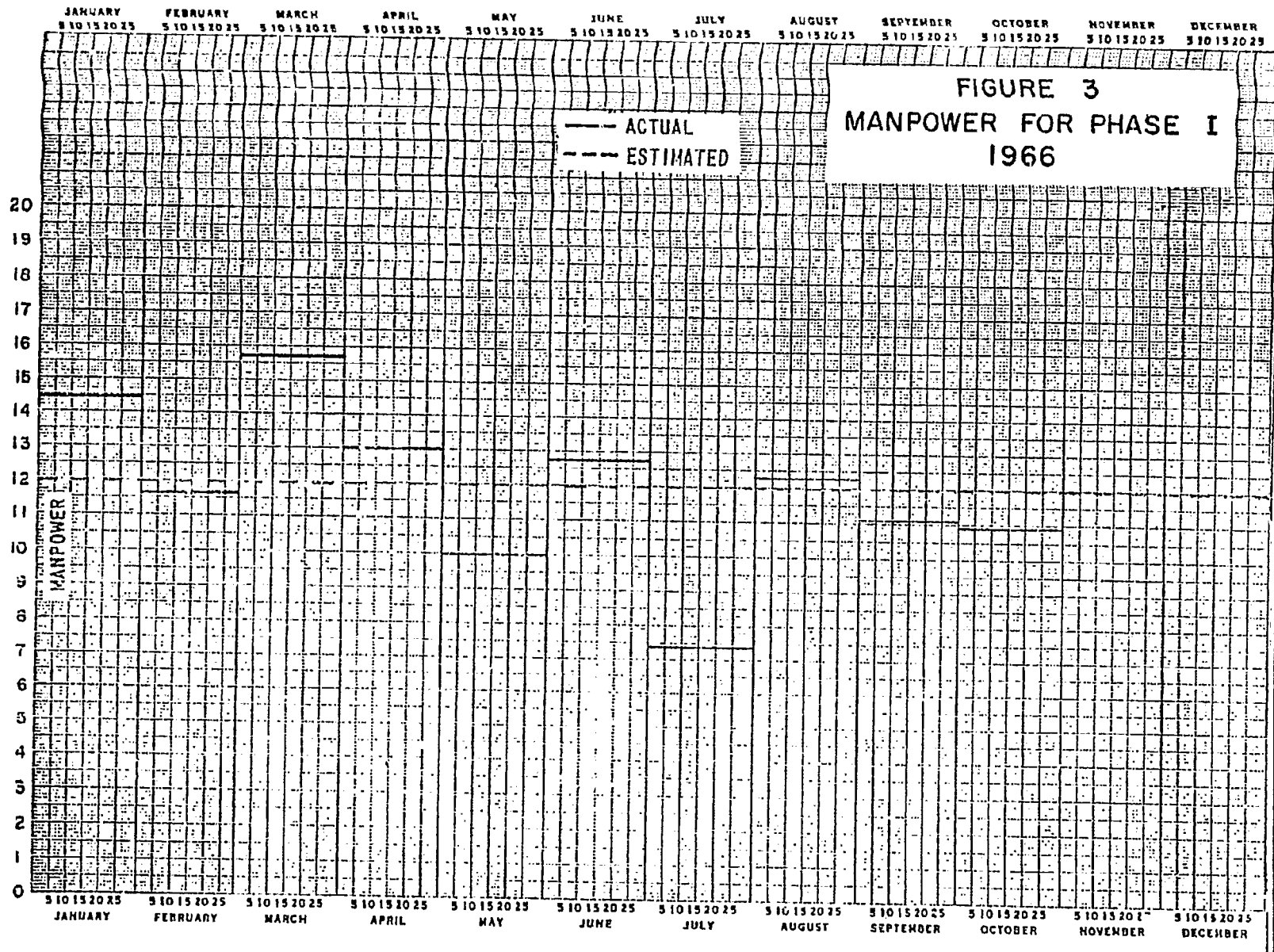
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V. MANPOWER AND COST ESTIMATES

Figure 3 shows the projected breakdown for Phase I for 1966 as well as the actual effort that was made. It can be seen that a 9.5 man-effort was made during November.

Figure 4 shows the expenditures during November. For the month, \$17,719 was expended, not including fee and G & A. The total expenditures through November were \$544,712. Including fee and G & A the total expenditures were \$622,516. This is 57% of the encumbered funds.



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