MWK-MPR-29

RESEARCH AND DEVELOPMENT DEPARTMENT

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

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Progress Report No. 29

APPROVED: _____
Project Manager

_____
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_____
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RESEARCH & DEVELOPMENT DEPARTMENT

CONTENT

I. SUMMARY

This progress report is the twenty-ninth 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 with bituminous coke defined the effect of temperature on rate with 2% ash present. This ash had been recalcined because the original material was found to be incompletely calcined. Rates obtained with the completely calcined material were about twenty percent lower than with the original material.

Four additional runs were made to better define the effect of varying amounts of sodium sulfate on the rate of combustion of bituminous coke. Addition of from 0.5-1.0% sodium sulfate produced a fourfold increase in rate over a sulfate-free run.

One gasification run was made with 2% sodium sulfate added to the melt. No significant difference in rate was noted over a similar run made without the additive. Thus, as previously postulated, sodium sulfate has no effect on gasification.

Additional ash settling experiments were carried out in order to investigate the effect of melt temperature on settling rate. The results indicate that the rate increases with temperature up to about 1,840°F beyond which it tends to fall off, most probably due to reaction of ash with melt.

Flowsheet calculations were continued for plants capable of producing hydrogen and synthesis gas from bituminous coal.

Bed expansion tests at 1,800°F using melt containing 8% ash were completed. As was the case with the other materials, (water, ethylene glycol and 100 cp. glycerine-water) there was considerably less splashing with the higher bed depths than with the lower ones. Measured bed expansion for the melt was lower than for any of the other systems studied.

Cross flow contamination tests have been completed for ethylene glycol. A lower level of contamination was obtained for glycol than for water when there was no bed aeration. However, the effect of bed aeration was greater and at the highest aeration rate the contamination was approximately that obtained for water. Contaminations with both systems are still of the order required for satisfactory commercial operation.

II. PROCESS RESEARCH

A. Accomplishments

1. Combustion Rate of Bituminous Coke

The bituminous coal ash which had been added to recent melts was found to have a 15.6% weight loss at 1,300°F. Consequently, the ash was recalcined at 1,300°F. A redetermination was made of the effect of temperature (average) on the combustion rate of bituminous coke using this recalcined ash at the level of two percent in the melt. The results are depicted in Figure 1. It does appear that the recalcination has had an effect on lowering the combustion rate by about twenty percent. It is believed that possible loss of sulfur during recalcination of the ash occurred which could account for this effect. Sulfur analyses on the ashes have been requested.

2. Effect of Sodium Sulfate Concentration in the Melt on the Combustion Rate of Bituminous Coke

The amount of sodium sulfate in the melt was varied from 0.5 to 4% and rate of combustion of bituminous coke was determined. The following tabulation shows the effect on rate and on average temperature of combustion. All the runs started at 1,740°F initially.

Run No. H-	% Na_2SO_4 in Melt	Avg. Temp. °F	Combustion Rate lbs. C/hr./CF
129	0	1740	6.0
148	0.5	1759	23.1
146	1.0	1761	24.7
143	2.0	1829	54.5
140	2.1	1839	45.2
147	4.0	1854	>70

The addition of 0.5 to 1% sodium sulfate produced a fourfold increase in combustion rate of bituminous coke over the sulfate-free run. Higher amounts of sulfate increased the rate of combustion further which caused an increase in the molten salt temperature. This complicated the results. More runs will be made to allow correlation of the data. Tentatively, an increase of 1 to 2% sodium sulfate may increase the rate from 25 to 30 lbs. C/hr./cu.ft.at 1760°F.

3. Effect of Sodium Sulfate in Melt on Rate of Gasification

In run 142, 2% sodium sulfate was added to the melt to determine if it would enhance the rate of gasification of bituminous coke. Under similar conditions but without ash, the gasification rate was 21 lbs C/hr./cu.ft. This value agrees quite well with 19 lbs C/hr./cu.ft. obtained in the above run. Thus, it is concluded that sodium sulfate has no effect on gasification. An equivalent run containing 2% ash gave 25 lbs C/hr./cu.ft. rate, further proof that sodium sulfate had no effect.

Some hydrogen sulfide was qualitatively noted in the product gas indicating that reduction of sulfate can occur under gasification conditions. The amount of sulfur lost must have been small since the same melt on reuse in a combustion test (H-143) gave a high combustion rate of about 55 lbs C combusted/ hr./cu.ft. compared to an earlier test which gave a rate of about 45 - a reasonable check in this rapid combustion region.

Measurement of freezing points of 1, 3, 5, and 10 weight percent sodium sulfate in sodium carbonate indicated that the sulfate dissolves in the melt.

	- % Na_2SO_4 in Na_2CO_3 -				
	0	1	3	5	10
Freezing Point, °F	1563	1561	1562	1557	1540

4. Ash Settling Studies

A melt composition of 88.4% Na_2CO_3, 7.7% bituminous coal ash and 3.9% $CaCO_3$ was held at 1840°F without agitation for 10 minutes before sampling the top and bottom of the melt. The following tabulation shows the ash content in these samples and in an earlier test reported last month at 1740°F. The increased settling rate with increasing temperature is most probably a function of the decreasing viscosity of the melt with increasing temperature.

Temperature °F	Wt. % Ash in Sample 4-5" off Bottom	Bottom
1740	6.5	13.0
1840	2.9	15.4

Additional settling experiments were performed at 1840° and 1940° for an 8% ash containing melt and compared in the following tabulation with a prior result at 1740°F. The loss of settling at 1940°F, along with the observation that carbon dioxide was being evolved from the quiescent melt in the 10 minute settling period, indicated that reaction of ash and melt was interfering.

Temperature °F	Wt. % Ash in Sample 4-5" off Bottom	Bottom
1740	3.1	9.2
1840	2.1	12.9
1940	5.0	10.8

The last ash settling test was performed with 4% coke (20/40 mesh) present in an 8% ash containing melt to establish the effect, if any, of coke on settling. At 1840°F and a 10 minute settling time, the top sample showed 4.7% residue and the bottom 19.2% residue. Magnetic corrosion products were observed in both residues which complicates interpretation. However, the coke does not prevent settling of the ash and it is believed that the coke had no effect on the ash settling rate. The observation was made that the coke floated on the surface of the melt in the quiescent period, in agreement with the relative densities.

B. Projections

Additional combustion tests on the effects of melt height and carbon concentration remain to be done, as well as other runs to complete the combustion work.

TABLE I

SUMMARY OF GASIFICATION AND COMBUSTION RUNS IN MOLTEN SODIUM CARBONATE /1/

Run No. H-	141	142	143	144	145	146	147	148
Date - 1966	11/22	12/8	12/9	12/13	12/14	12/16	12/19	12/20
Feed	← Bituminous Coke →							
% Total Carbon				93.2				
% Vol. Matter				0.6				
% Ash				6.2				
Gms. Charge				18.5				
Mesh Size				12/20				
% C in Melt - Initial				4				
Melt								
Gms Na_2CO_3	405.7	405.7	/3/	405.7	/3/	409.9	/3/	411.9
gms Ash or Cmpd.	8.3	8.3		8.3		4.1	+12.4	2.1
Compound Added	-	Na_2SO_4	Na_2SO_4	-		Na_2SO_4	Na_2SO_4	Na_2SO_4
% Ash or Cmpd in Melt	2.0	2.0	2	2.0	2.3	1.0	4.0	0.5
Height - inches	4	4	4	4	4	4	4	4
Conditions	Comb.	Gasif.	← Combustion →					
Temp °F - initial	1740	1740	1745	1635	1844	1741	1740	1740
- average/2/	1740	1740	1829	1640	1849	1761	1854	1759
- maximum	1753	-	1875	1645	1866	1788	1936	1785
Pressure - psia	44.7	64.9	44.7	44.7	44.7	44.8	44.0	45.0
Sup. Gas Vel. - ft/sec	0.98	1.03	0.98	0.96	1.07	0.99	0.90	0.99
% Steam in N_2	-	90.8	-	-	-	-	-	-
Steam pressure - psia	-	40.8	-	-	-	-	-	-
Run Time - min	55	40	15	95	25	30	5	25
Air Rate - liters/min	26.0	-	26.0	26.7	27.1	26.1	25.9	26.1
cc H_2O/hr	-	1196	-	-	-	-	-	-
cc N_2/min	-	2499	-	-	-	-	-	-
Results								
Combustion Gas							/4/	
% CO_2 - 5 min	3.3	-	12.5	1.6	6.1	6.8	18.0	6.7
35 min	1.3	-	-	0.9	-	-	-	-
end	0.9	-	1.2	0.4	2.0	0.7	-	1.8
% O_2 - 5 min	18.0	-	7.5	20.0	15.0	14.0	2.0	15.0
35 min	19.0	-	-	20.5	-	-	-	-
end	19.5	-	18.5	20.0	19.0	19.1	-	19.0
Gasification Rate Constant	-	1.64	-	-	-	-	-	-
Gasification Rate - lbs C/hr/CF	-	19.4	-	-	-	-	-	-
Combustion Rate Constant	0.70	-	4.62	0.36	1.61	2.09	>6	1.96
Combustion Rate - lbs C/hr/CF	8.3	-	54.5	4.3	19.0	24.7	>70	23.1
% Total Carbon								
Devolatilized	7.0	12.2	9.6	3.8	9.1	9.0	14.5	7.6
Combusted or Gasified	73.3	88.1	91.6	76.6	90.5	91.0	70.3	91.1
Remaining or Loss	19.7	-	-	19.6	0.4	-	15.2	1.3

/1/ Used 2-inch ID Inconel reactor. In combustion, coke added in N_2 at 0.1 ft/sec, 5 minute devolatilization period before air in.

/2/ Average temperature in 50% carbon consumed period.

/3/ Reused melt from previous run.

/4/ Plugged in 5 minutes, analyses are for composite gas not 5 minute sample.

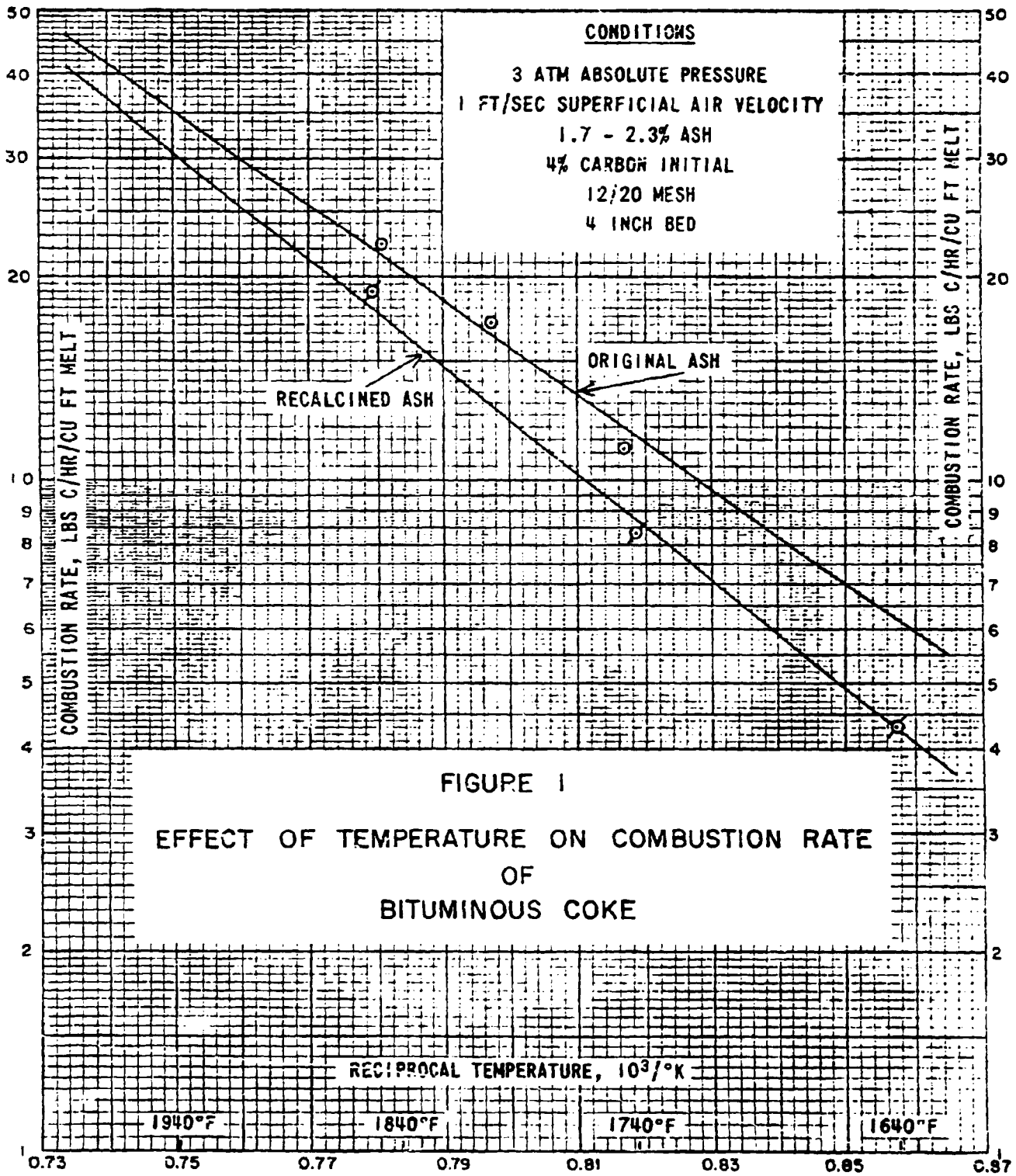


FIGURE 1

EFFECT OF TEMPERATURE ON COMBUSTION RATE OF BITUMINOUS COKE

III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

Preparation of the process flowsheets for plants capable of producing hydrogen and synthesis gas from bituminous coal continued during December. For the case of the hydrogen plant, final heat and material balances were made in accordance with our concept of preparing "process packages" for the various products under consideration.

B. Projections

Process designs will be continued for the two end products currently being studied. In addition, efforts will be continued in an attempt to define the most critical and sensitive areas of these designs, as well as those for pipeline gas, to determine what, if any, further experimentation is necessary before beginning the process design for the proposed one-ton-per-hour pilot plant.

IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High Temperature Materials

Corrosion Test #10 will resume shortly.

2. Mechanical Characteristics Testing

The melt bed expansion tests have been completed. Figures 2 through 4 show the results of this test for a one, two and three foot bed at various bed superficial velocities up to three feet per second. These tests were conducted in a 5-3/4 inch I.D. vessel approximately six feet high. The vessel was heated in an electric furnace to approximately 1840°F, producing a melt temperature of 1800°F.

Bed aeration was accomplished by a central sparger consisting of a 1/2 inch pipe inserted from the top of the vessel to within two inches of the bottom. Bed height measurements were made using the electrical dip stick method previously described. Again, the lower curve represents the point where nearly continuous contact is maintained between the dip stick and the bed, the upper curve shows where substantial initial contact is first made with the bed.

Comparing the three bed heights it will be noted that the nearly continuous contact curve does not substantially change with bed height. However, the upper or initial contact curve varies considerably with bed height. Directionally, this effect was also noted in the other materials similarly tested and previously reported (water, ethylene glycol, 100 cp. glycerine-water mixture). Corresponding to these results at the higher bed levels a significant reduction in splashing and bed loss on the vessel wall was noted.

The table following briefly summarizes the results of the bed expansion tests. The summary is limited to the results obtained with three foot beds as this is considered the most significant for future application.

BED EXPANSION (PERCENT EXPANSION)

Material	Bed Superficial Velocity 0.5 f/s	1.0 f/s	2.0 f/s
Water	18-25	32-42	56-66
Ethylene Glycol	20-25	33-41	55-65
100 cp. Glycerine-Water	15-19	27-36	45-55
Melt 1800°F 8% Ash	11-16	21-29	38-50(E)

3. Melt Circulation

Tests on cross flow contamination similar to those conducted for water have been completed for ethylene glycol. The final results of this test are reported in Figure 6. The final results of the water tests are shown in Figure 5. As previously reported, based on the preliminary data, 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 at the highest rate of aeration the contamination is approximately that obtained for water. Both show a contamination level with the inlet extentions in the order of 0.02 cubic feet of contamination gas per cubic foot of liquid transferred, for transfer rates less than 10 feet per second for water and 5 feet per second for the ethylene glycol.

As previously stated, these results are encouraging and within the order of magnitude of contamination levels currently envisioned for the actual process. Additional work is required, however, before extrapolation of this data may safely be made to a circulating melt system. The solubility of nitrogen in ethylene glycol and the contaminating gases in the melt will have to be determined.

B. Projections

1. Environmental Testing of High Temperature Materials

Corrosion Test #10 will continue to completion.

2. Mechanical Characteristics Testing

Consideration will be given to the determination of entrainment in the aeration gas exiting a sodium carbonate melt bed. Previous work in this area has been limited to shallow beds of about one foot or less and relatively small diameter vessels. With the vessel used in the bed expansion test, it should be possible to develop some useful entrainment data for two or three foot beds in a 5-3/4 inch I.D. vessel. This data will be helpful in the design of the reactor overhead equipment.

Methods of determining solubility of nitrogen or oxygen in ethylene glycol and carbon dioxide or other contaminants in sodium carbonate melt will be explored.

3. Melt Circulation

The cross flow contamination results for both ethylene glycol and water will be extended to aeration superficial velocities of 2.0 feet per second to include proposed design aeration rates.

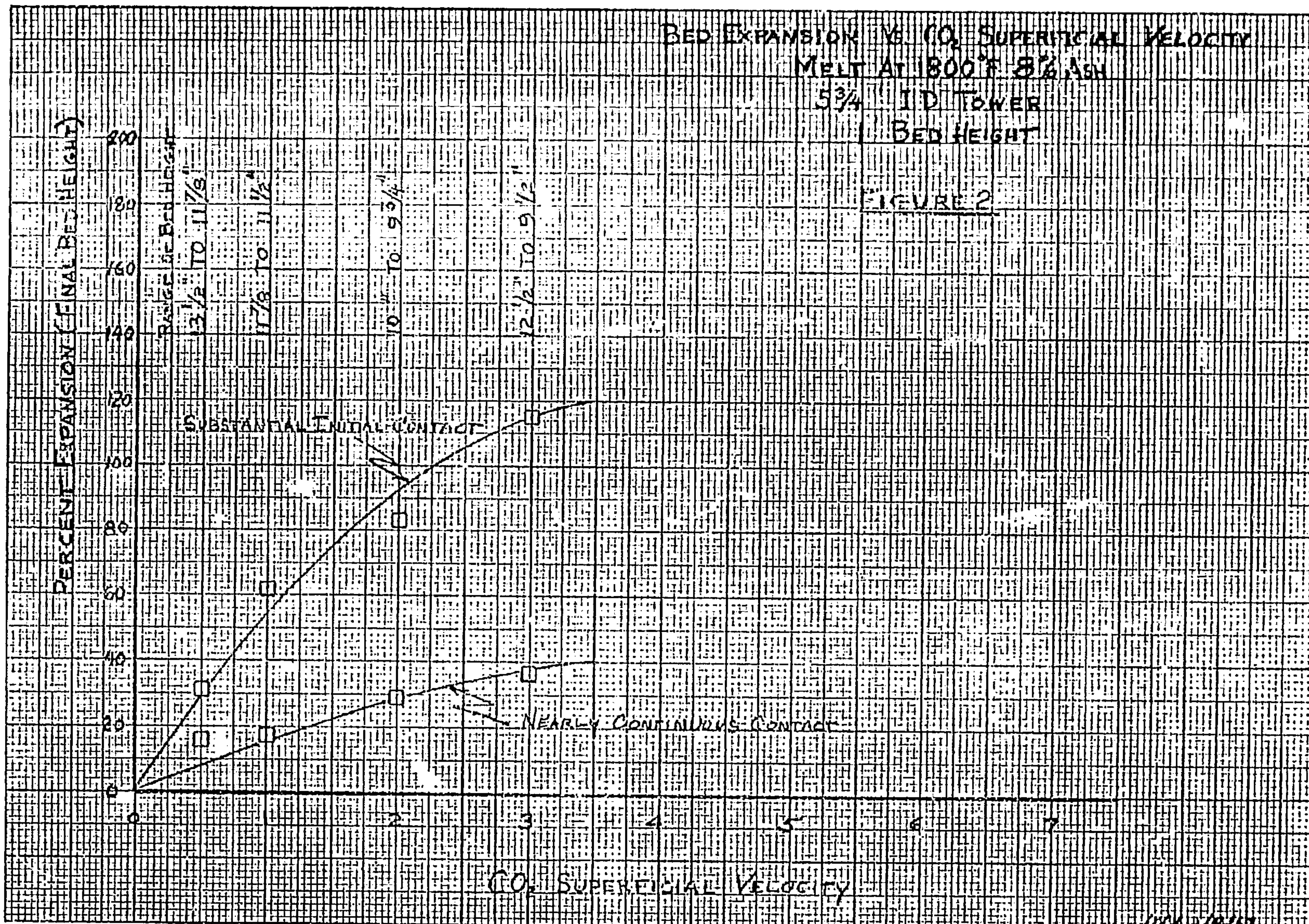
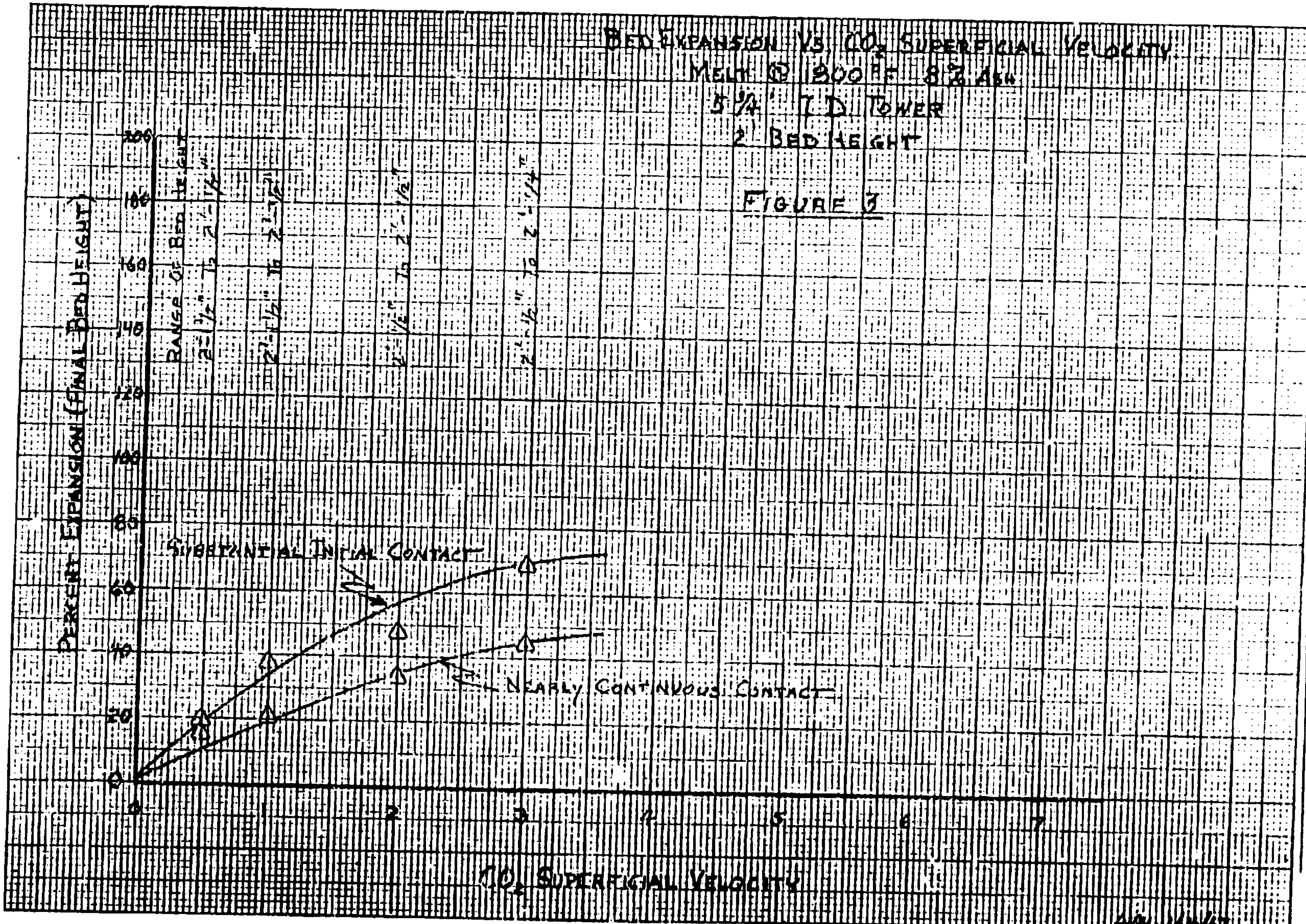

Bed Expansion Vs. CO_2 Superficial Velocity
Melt At 1800°F 8% Ash
5 3/4" I.D. Tower
Bed Height
Percent Expansion (Final Bed Height)
200
180
160
140
120
100
80
60
40
20
0
Range of Bed Height
13 1/2" to 11 7/8"
11 7/8" to 11 1/2"
10" to 9 3/4"
12 1/2" to 9 1/2"
Substantial Initial Contact
Nearly Continuous Contact
0
2
3
4
5
6
7
CO_2 Superficial Velocity

Figure 2



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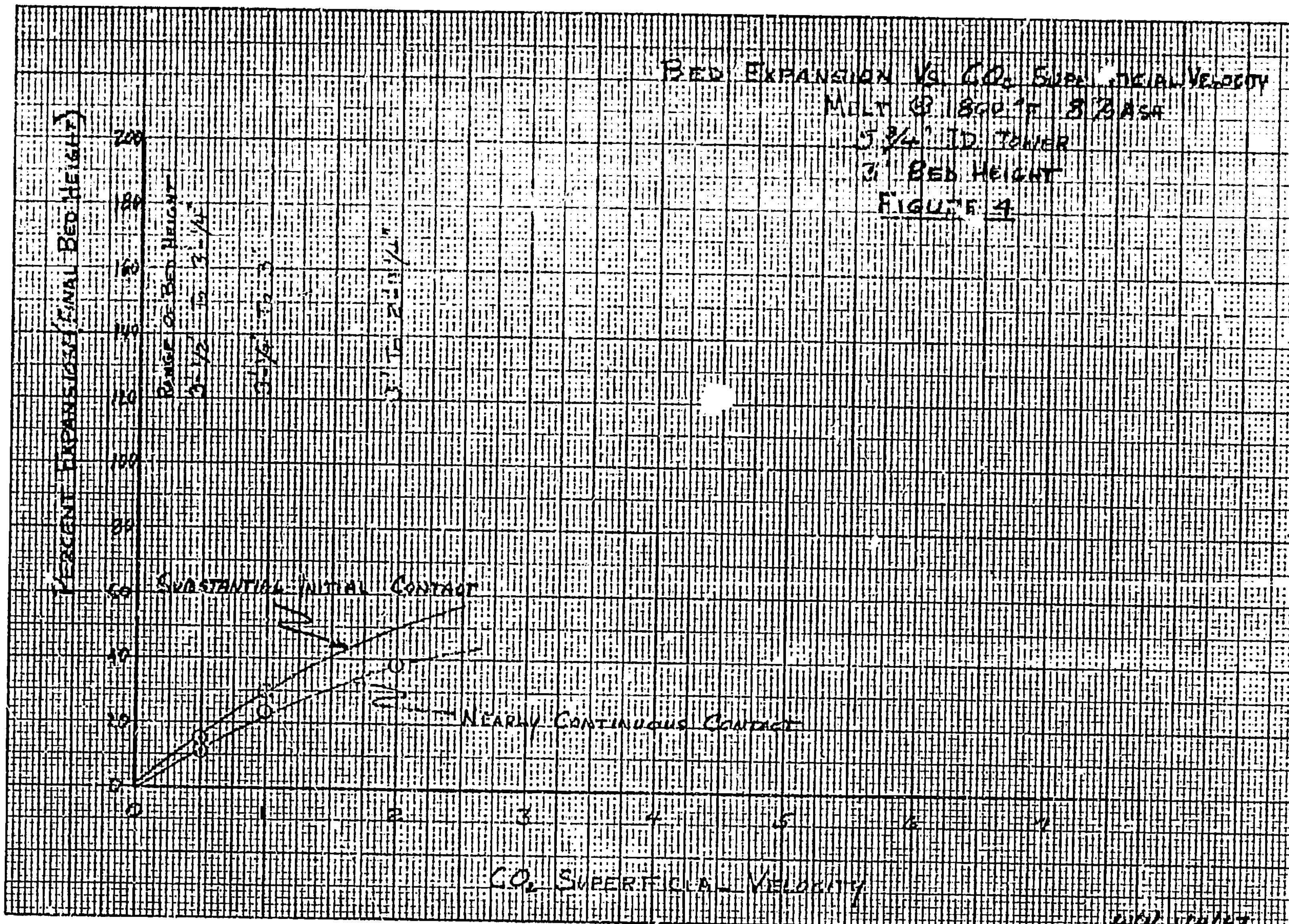
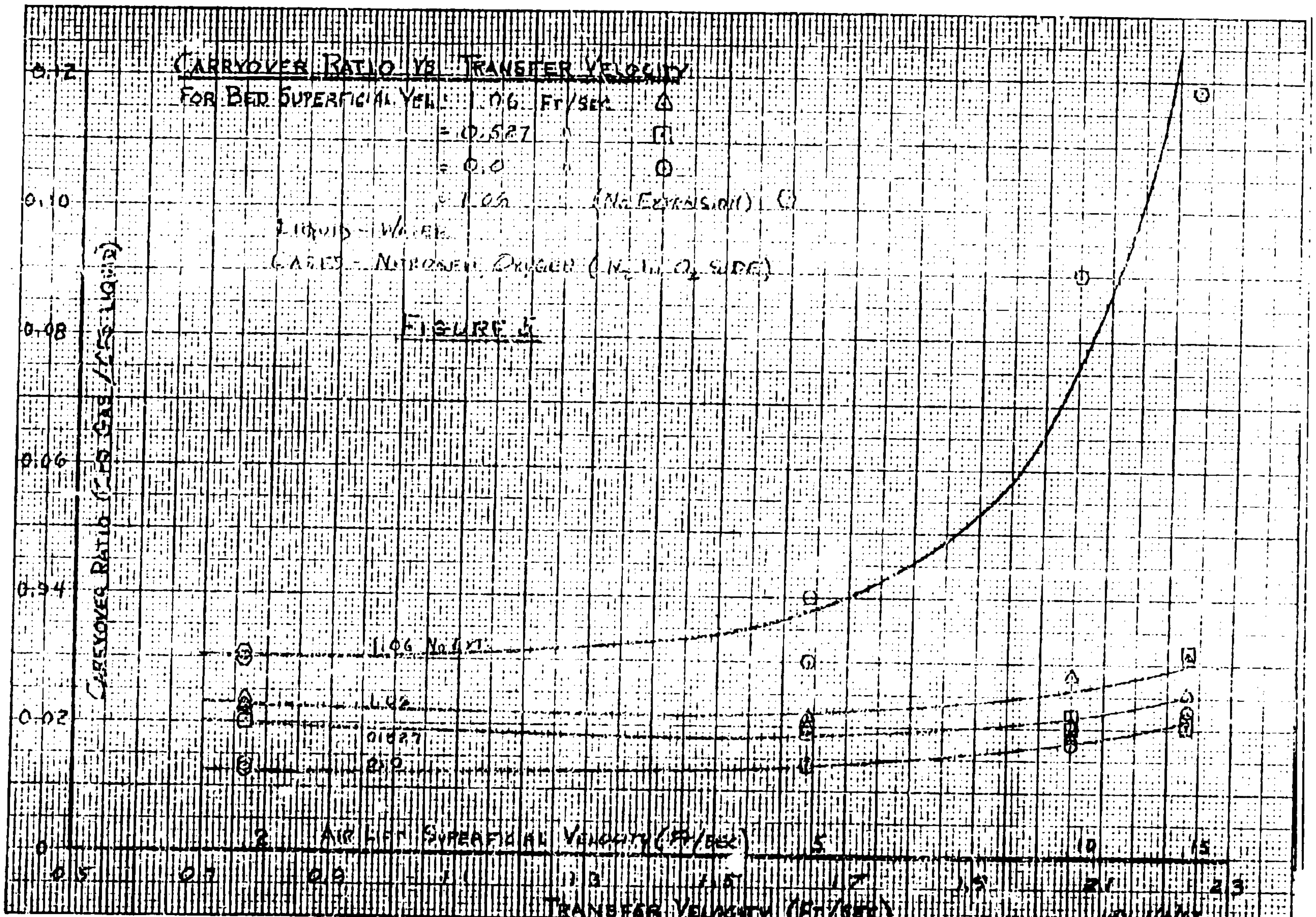
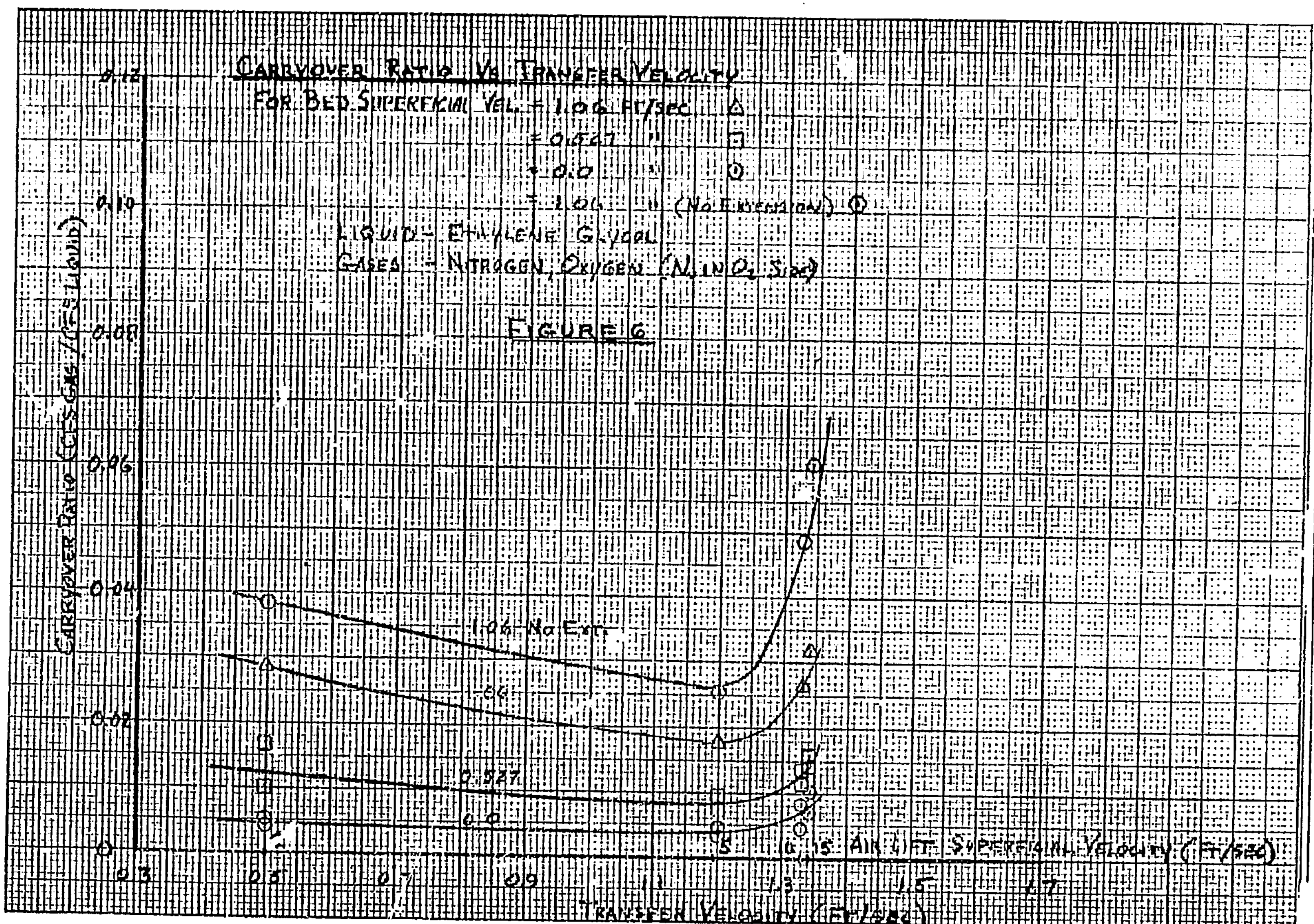

BED EXPANSION VS CO_2 SUPERFICIAL VELOCITY
3' BED HEIGHT
FIGURE 4
PERCENT EXPANSION (FINAL BED HEIGHT)
RANGE OF BED HEIGHT
SUBSTANTIAL INITIAL CONTACT
NEARLY CONTINUOUS CONTACT
0
20
40
60
80
100
120
140
160
180
200
0
1
2
3
4
5
6
7
CO_2 SUPERFICIAL VELOCITY


Carryover Ratio vs Transfer Velocity
For Bed Superficial Vel. = 1.06 Ft/Sec.
= 0.527
= 0.0
= 1.06 (No Expansion)
Liquid - Water
Gases - Nitrogen, Oxygen
Figure 5
Carryover Ratio
1.06 No Ext.
1.06
0.527
0.0
Air Lift Superficial Velocity (Ft/Sec)
Transfer Velocity (Ft/Sec)
0.12
0.10
0.08
0.06
0.04
0.02
0


CARRYOVER RATIO VS TRANSFER VELOCITY
FOR BED SUPERFICIAL VEL. = 1.06 FT/SEC
= 0.527
= 0.0
= 1.06 (NO EXTENSION)
LIQUID - ETHYLENE GLYCOL
GASES - NITROGEN, OXYGEN (N2 IN O2 SIDE)
FIGURE 6
0.12
0.10
0.08
0.06
0.04
0.02
0
1.06 No Ext.
1.06
0.527
0.0
AIR LIFT SUPERFICIAL VELOCITY (FT/SEC)
0.3
0.5
0.7
0.9
1.1
1.3
1.5
1.7
TRANSFER VELOCITY (FT/SEC)

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 9.5 man-effort was made during December.

Figure 8 shows the expenditures during December. For the month, $16,335 was expended, not including fee and G & A. The total expenditures through December were $561,047. Including fee and G & A, the total expenditures were $641,346. This is 58% of the encumbered funds.

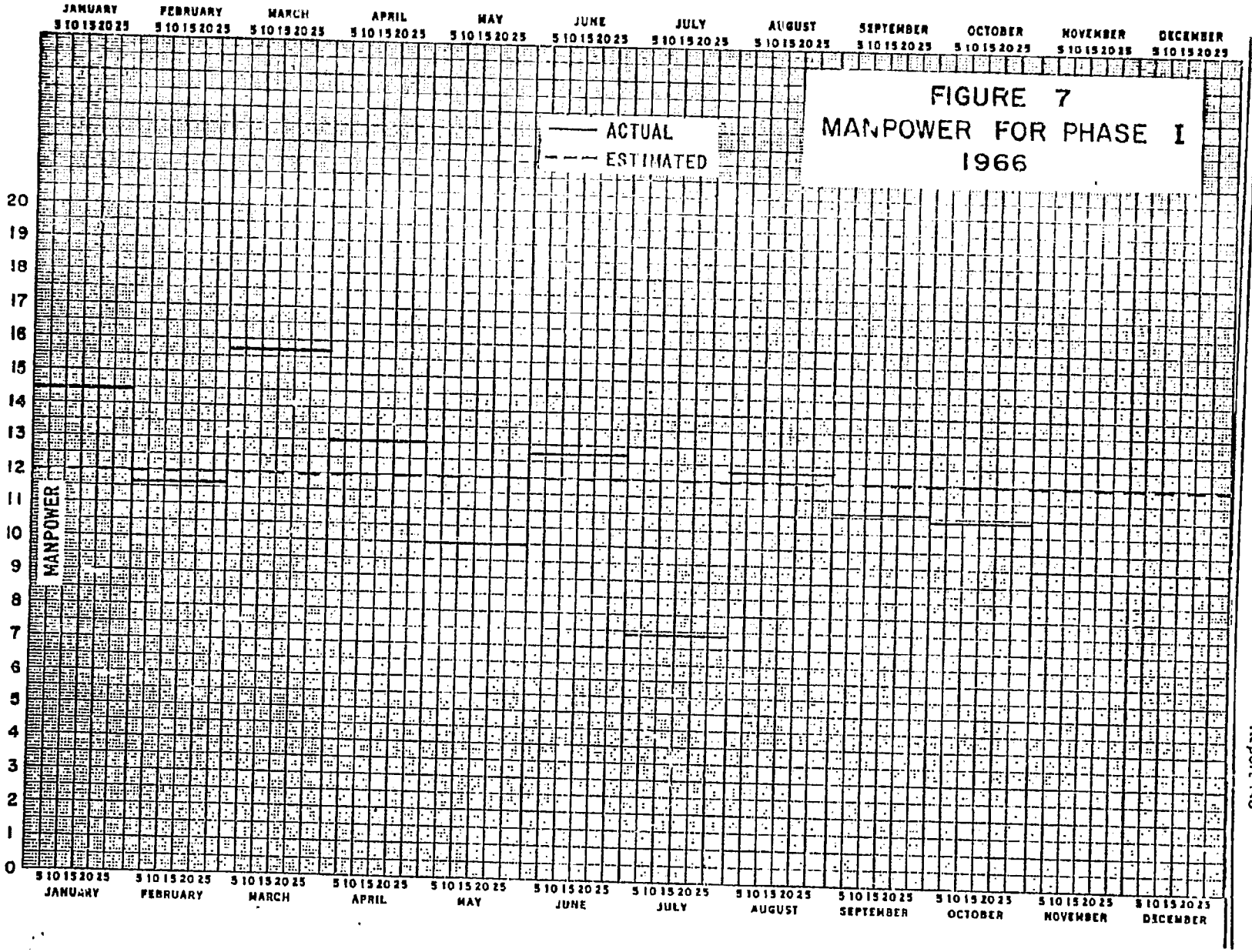


FIGURE 7
MANPOWER FOR PHASE I
1966

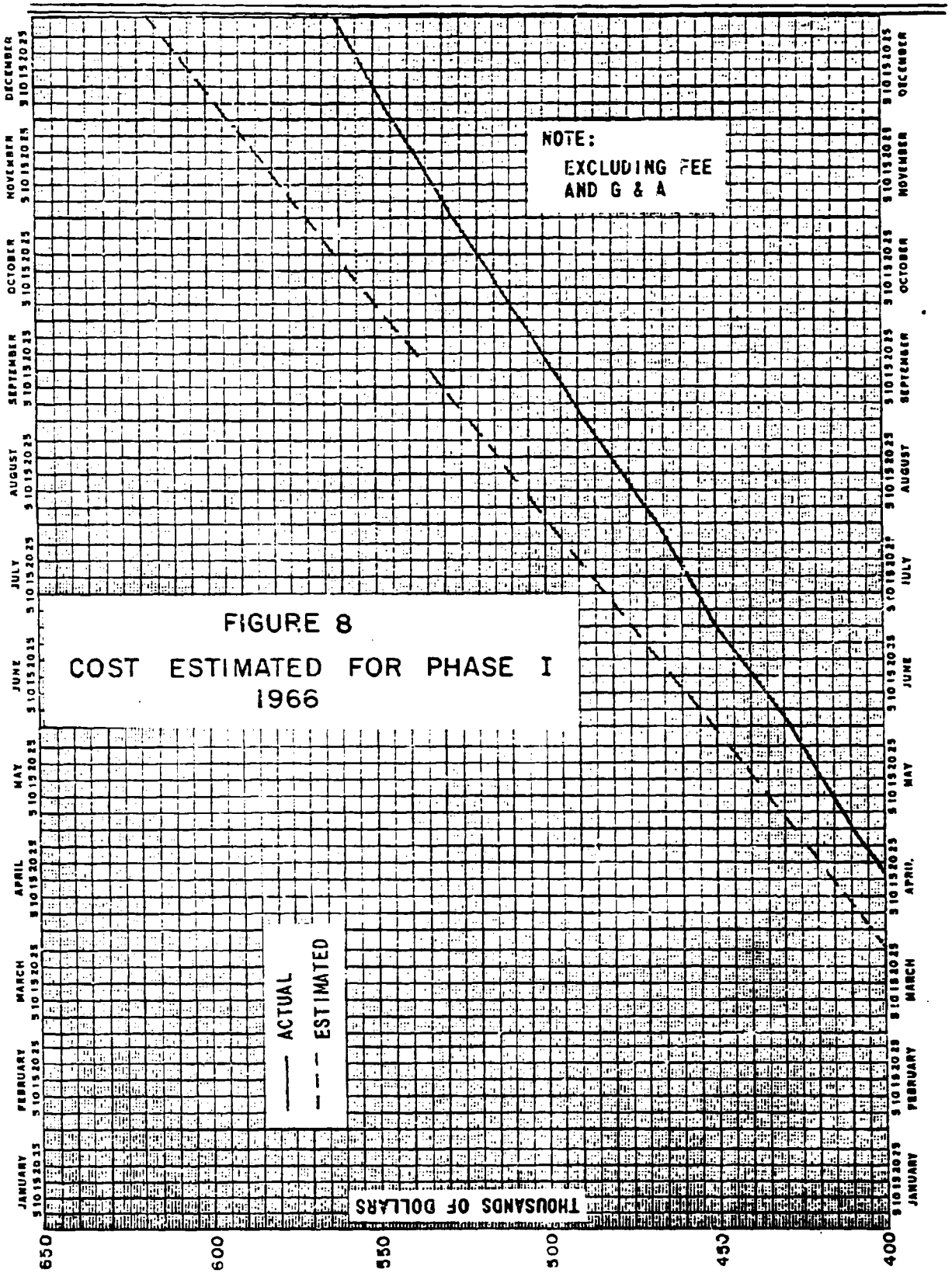


FIGURE 8

COST ESTIMATED FOR PHASE I
1966

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