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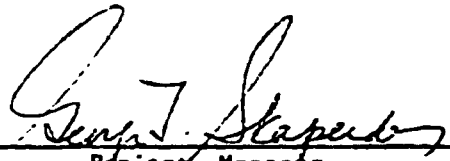
DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

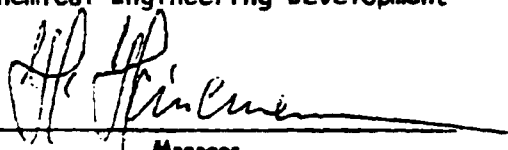
November 30, 1965

Progress Report No. 16

APPROVED:

  
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REPORT NO. 16

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## I. INTRODUCTION

The objective of this contract with the Office of Coal Research is to develop the Kellogg Gasification Process to the point where it will be able, on a commercial scale, to convert coal into pipeline gas at a cost of 50¢/MSCF or hydrogen at 25¢/MSCF. Five raw materials are to be studied -- an anthracite, a high-volatile bituminous coal, a sub-bituminous coal, a lignite, and a char. Although Kellogg's experimental work will not extend beyond the production of raw synthesis gas, the overall project must make engineering evaluations for four ultimate end products -- pipeline gas, hydrogen, synthesis gas, and transport gas.

Basis for the Kellogg Gasification Process is the reaction between steam and fine coal in a molten salt bath to form synthesis gas, a mixture of hydrogen and carbon monoxide, according to the reaction:



The necessary heat of reaction is supplied by circulating a heated molten salt stream. In addition, the molten salt mixture is chosen to catalyze the gasification reaction so that it may be carried out at a relatively low temperature.

The program is divided into three phases of study extending over a five-year period. Phase I, which is now in progress, involves several concurrent efforts:

1. Bench-scale process research -- to investigate melt properties, reaction kinetics, and the effect of process variables.
2. Chemical engineering studies and development -- to determine the optimum process flowsheet and operating conditions and to coordinate experimental work with overall project objectives.
3. Mechanical development -- to find acceptable materials of construction and develop techniques for handling the molten salt and powdered coal.



Phase I will be concluded by the design of a pilot plant to gasify 2 $\frac{1}{2}$  tons of coal per day, if it is found that a pilot plant program is justified by the bench-scale experimentation and economic studies.

Phase II will be devoted largely to the construction and operation of a pilot plant to convert a variety of raw materials into raw synthesis gas. The effect of operating variables found to be significant in Phase I will be investigated to obtain data for design of a commercial plant.

Phase III will involve the detailed process design of a commercial plant to produce 250 million standard cubic feet a day of product gas, including cost estimates and projected economics for those areas of the country that appear to offer commercial possibilities.



## II. SUMMARY

This progress report is the sixteenth since the awarding of the contract. It is concerned with the first phase of the contract and outlines the progress that has been made in the three main areas now being studied: process research, chemical engineering studies, and mechanical development.

It is proposed to supply heat to the commercial process by burning coal in direct contact with the melt (molten salt plus coal ash). It is important to the economics that this combustion produce  $\text{CO}_2$ , not  $\text{CO}$ , at the melt surface so that the heat of combustion be liberated in the melt and not in the gas space above it. To study further the probability of achieving this goal a combustion experiment was made with thermocouples spaced at 1-inch vertical intervals in the reactor. Temperature profiles were taken in a blank run (gas flowing, but no carbon being burned) and then under combustion conditions. The gas above the melt was found to be only  $10^\circ\text{F}$  hotter than the melt during the early part of the run, indicating some gas-phase combustion of  $\text{CO}$ , but this difference disappeared by the time half the initial carbon was burned. It was, therefore, concluded that most of the heat liberated by combustion was transferred to the melt as desired. These results continue to be encouraging and are in agreement with those previously reported based on analyses of gas samples taken just above the bed during combustion.

The previously reported smaller effect of steam partial pressure on gasification rate at higher temperatures ( $1840$  vs  $1740^\circ\text{F}$ ) was confirmed by several more experiments. This finding, that the rate improvement at high pressure may be smaller than previously anticipated, is not detrimental to present commercial designs and cost projections because the rate actually measured at atmospheric pressure has been used in these calculations.

Two gasification runs were successfully made at conditions of temperature, initial carbon concentration, bed height, particle size, and steam partial pressure that have come to represent standard experimental procedure, but at twice the superficial gas velocity, i.e.,  $1.0$  ft/sec instead of  $0.5$  ft/sec. The results of these two runs



were identical (excellent reproducibility), but unexpectedly yielded rate constants about 70% larger than the standard particularly at low bed depths. The reason for this is not yet completely clear. Possible explanations include improved distribution of coal particles throughout the melt when higher velocity is used, and more efficient contacting of steam and coal close to the gas inlet point. Further studies are planned at high superficial velocity to examine these reactions and their controlling parameters. In any case, it appears that most of the gasification rates measured to date, encouraging as they are, may turn out to be conservative.

Two gasification experiments were made with hydrogen and carbon dioxide in the feed gas to simulate conditions near the top of a commercially deep melt, where these reaction products will be present. The effect of hydrogen was insignificant. The presence of 70% CO<sub>2</sub> in the feed steam appeared to reduce the rate of reaction by about 35%, but the precision of the experiment may have been low. More runs of this nature are planned. If these effects are no larger than discovered to date, retardation of the gasification reaction in the deeper commercial bed will be insignificant.

Carryover of melt constituents, probably in the form of physical entrainment and volatilized sodium compounds, into the downstream gas-handling equipment has been noted in the bench-scale experiments. The quantities of carryover involved would be intolerable in commercial operation. However, at least three factors would tend to reduce the magnitude of this problem on a commercial scale:

1. Greater disengaging heights in larger equipment would reduce physical entrainment.
2. Gas flow rate per unit of carbon gasified would be much lower because of higher pressure and lower steam/carbon ratios.
3. Experiments to date indicate that carryover is reduced by an order of magnitude when the melt contains 10% ash.

Further definition of this problem is needed at higher pressure on a larger scale.

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The experimental setup for studying gasification and combustion rates will be modified in the near future to investigate the effect of operating pressures up to 60 psia.

Corrosion tests on the high-purity, high-density alumina products of several manufacturers under simulated gasification and combustion conditions, in the absence of any extraneous metals or refractories (except for the sample holder), are planned. Equipment has been set up and the tests will begin shortly, with the objective of achieving 400 hours continuously on stream before shutdown.

Observation of the effect of vessel diameter on the efficiency of contacting between air and a liquid having properties similar to a melt of  $\text{Na}_2\text{CO}_3$  and coal ash led to the conclusion that a 5-1/2"-I.D. reactor should be used in the pre-pilot unit now being designed.

A preliminary correlation of experimental melt viscosity data has shown that the total concentration of ash plus coal in the melt should not exceed about 10% at 1700° F, or 15% at 1900° F, to maintain viscosity in the range where reasonable contacting efficiency can be obtained. This criterion was used in choosing the current flowsheet design figures of 8% ash plus 4% coal at 1830-1900° F.

The process design of a plant to produce pipeline gas from sub-bituminous coal was revised to incorporate improvements made possible by recent experimental results. A similar design based on bituminous coal is continuing. Economics for these two cases will be completed next month.



### III. PROCESS RESEARCH

#### A. Accomplishments

##### 1. Combustion Study

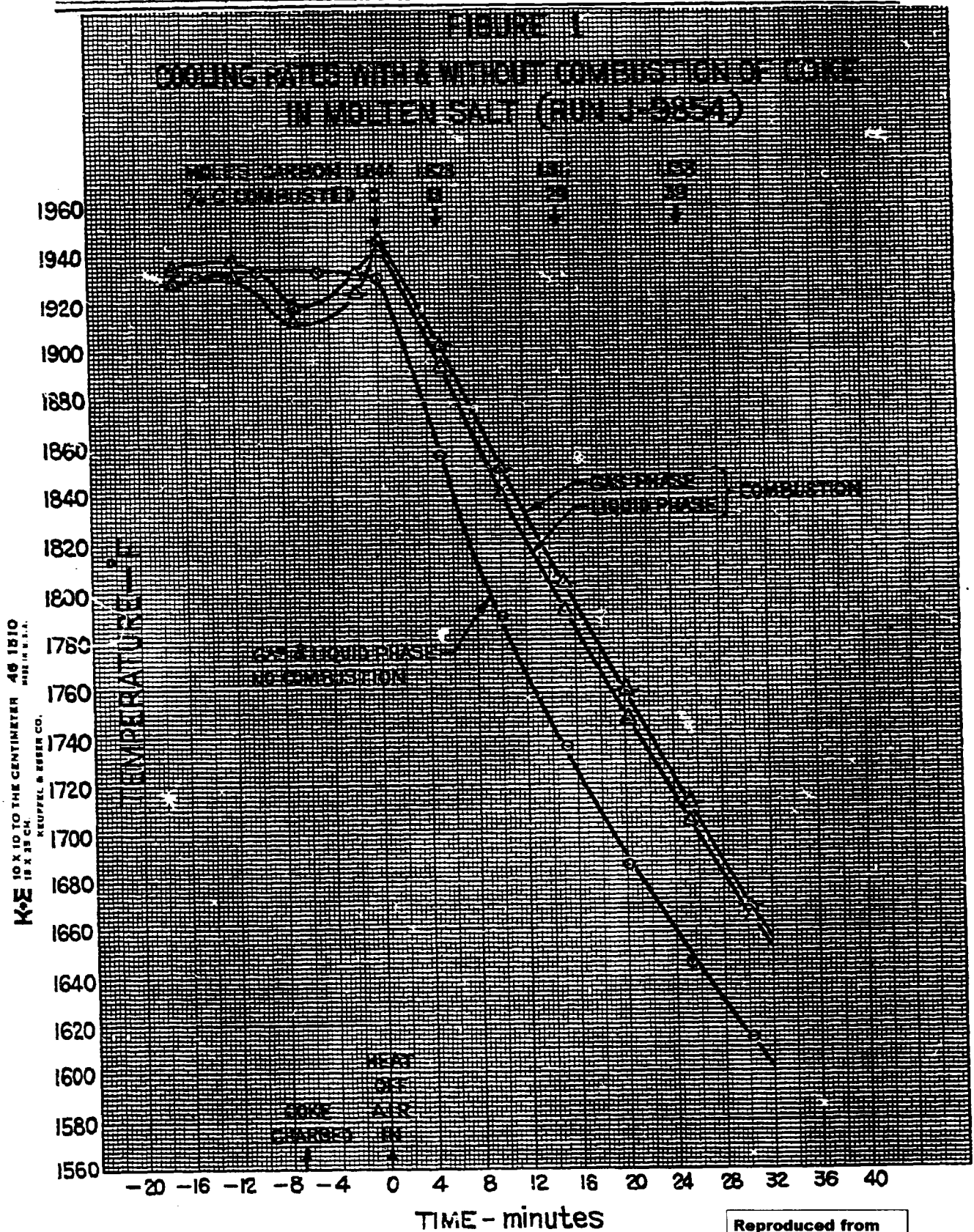
An additional combustion run, J-9854, was made to define further the nature of the combustion products and the transfer of heat to the molten salt. The standard sodium carbonate charge to the 2-inch reactor, namely a 4-inch quiescent bed height, was heated to 1930°F with 0.5 ft/sec superficial nitrogen velocity flowing, then the furnace was turned off. With twelve thermocouples an inch apart in the reactor, the cooling curves for the liquid and gas phases were determined under non-combustion conditions. After this, the temperature was brought back to 1930°F, a standard coke charge of 24 grams was made, and air was cut in at 0.5 ft/sec and the furnace turned off simultaneously. The cooling rate under combustion conditions was determined. The first five temperatures were averaged for the liquid phase and the top five temperatures were averaged for the gas phase. The five-minute averages are presented in Figure 1. The usual analytical data were also collected.

From the figure it can be seen that heat is readily transferred from the combustion of carbon to the molten salt and that under the conditions of the test system some additional heat is generated in the gas phase by combustion of carbon monoxide. The carbon monoxide decreased to nil in 25 to 30 minutes as determined by chemical and heat analysis. These results appear in agreement with previously reported results employing the probe sampler and other combustion data.

##### 2. Gasification Studies

The data on gasification runs are presented in Table I. Low-steam pressure, high superficial gas velocity, and the effect of hydrogen and carbon dioxide were investigated.





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Table 1  
Gasification of Bituminous Coal in Molten Na<sub>2</sub>CO<sub>3</sub> /1/

Run No. -J-	9853	9855	9911	9912	9913	9914	9915	9916
Date-1965	10/29	11/9	11/11	11/15	11/17	11/19	11/22	11/24
Feed	←-----Bituminous Coal-----→							
% Total Carbon				81.3				
% Volatiles				37.3				
% Ash				3.9				
gms. charged	20	40		20				
mesh size	←-----			12/20	-----→			
init. % C	←-----			3.8	-----→			
gms. Na <sub>2</sub> CO <sub>3</sub>	414	828		414				
bed ht.-inches	4	8		4				
Conditions	←-----							
Temp. °F				1840	-----→			
% Steam	30	81	92	30	30	90	90	92
Gas in Steam	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>
Ft/sec. Stm. & Gas	0.5	1.0	1.0	0.5	0.5	1.0	1.0	1.0
Preh't. Temp. °F.	750	750	720	680	720	750	750	720
Min. to 0% CO	65	55	35	55	-	-	-	30
Total Run-min.	65	55	55	85	75	-	-	45
Results	←-----							
% C to CO + CO <sub>2</sub>	96.3	96.9	93.2	86.3	79.4	-	-	84.8
% C to C <sub>1-3</sub>	2.1	4.7	0	7.2	6.7	-	-	3.4
% C to tar, etc.	5.5	5.5	5.5	5.5	5.5	-	-	5.5
Total % C	104	107	99	99	92	-	-	94
Spec. Gasif. Rate Const.	←-----							
Basis input	1.20	1.44	2.25	1.06	0.72	-	-	2.25
Rate-lbs.C.gasif./hr/CF	←-----							
at 10% C in bed	37	45	70	33	22	-	-	70
at 4% C in bed	14	17	27	12	9	-	-	27
Salt Carryover-gms.	11.2	14.4	21.0	14.0	16.1	-	-	21.6
Notes		/2/				/3/	/4/	

See next page for footnotes.

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- /1/ Atm. pressure, 2" ID inconel reactor, Island Creek #27 coal.
- /2/ Run previously attempted on 11/5 but inlet plugged up at start of run. Coal charged in 20 g. slugs for present run.
- /3/ Outlet of condenser plugged in 9 minutes prevented run.
- /4/ Same as /3/ but in 12 minutes, data indicated 56% of C gasified in 10 minutes.



The effect of 0.3 atmosphere of steam at 1840°F in an 8-inch deep bed of the standard 0.9 atmosphere was noted last month to be smaller than the effect at 1740°F. Another run with 0.3 atmosphere of steam was made with a 4-inch bed at 1840°F in order to verify this effect. Run 9853 gave a reaction rate constant of 1.2, which when compared to the standard rate constant of 1.3 for 0.9 atmosphere steam indicates very little effect of steam pressure at these two levels. The average value for the three 0.3 atmosphere runs (1.13, 0.95, 1.20) is 1.1, which indicates a small but real effect for the pressure difference.

The constancy of reaction rate constant, reported in last month's summary, with changing bed height from 4 to 8 to 12 inches at standard steam rate and coal charge, along with one run at 8-inch bed height, normal steam rate, but double the standard charge of coal (which gave a below par rate constant of only 78% of the above), was investigated further in run 9855. In this run at 8-inch bed height, the steam rate and coal charge were doubled over the normal run, thus giving a superficial gas velocity in the reactor of 1 ft/sec. instead of the usual 0.5 ft/sec. The reaction rate constant was improved from 1.00 to 1.44 by this increase in steam rate and superficial velocity.

The above data appear explainable on the basis of mixing and contact of steam and carbon. It implies that perhaps the carbon is located at or near the top of the molten salt bed. The increase in agitation by higher gas velocity should improve the steam-carbon contact, thus produce a higher rate constant, as was obtained. The lower rate constant result of 1.00 from the double coal charge at 0.5 ft/sec. steam-nitrogen indicates poorer contact of steam and carbon and suggests localization of the carbon at the surface of the melt.



This work led to the next run, 9911, where the steam-nitrogen rate was upped to 1 ft/sec. superficial gas velocity in a 4-inch bed. Quite unexpectedly this run showed an exceptional rate constant of 2.25 versus the standard value of 1.3 for 0.5 ft/sec. Verification of this result was ultimately made in run 9916 with several unit modifications due to two aborted runs, 9914 and 9915. Exact duplication was achieved and the points followed the first-order plot exceptionally well. These results appear to substantiate the premise of better contact of steam and carbon at the higher gas velocity and better agitation. The failure of the 8-inch bed run 9855 to show a larger increase in rate constant implies that contact of steam and carbon was not satisfactory and that the double charge of carbon may have concentrated at the surface where bubble action was poorest.

Two runs were made to determine the effect of hydrogen and carbon dioxide, products of the gasification reactions, upon gasification rate. This was done by employing 30% steam in these gases in runs 9912 and 9913. The reaction rate constants are compared in the following tabulation with the average 30% steam in nitrogen results determined earlier.

<u>30% Steam in</u>	<u>Reaction Rate Constant</u>
Nitrogen	1.1
Hydrogen	1.06
Carbon Dioxide	0.72

Hydrogen apparently had no effect on the kinetics. Carbon dioxide appeared to lower the reaction rate constant by about 35%. However, although it is felt that carbon dioxide did suppress the rate, the quantitative value must be used with caution. The reason for this is that 9.525 moles of  $\text{CO}_2$  were fed through the reactor and 10.601 moles of  $\text{CO}$  plus  $\text{CO}_2$  exited; the quantity of carbon gasified thus represents the difference between two large numbers and its precision must be judged in that light. Experimentally it appears



to be a valid run because the carbon balance was 92%, an excellent value for a run of this type. Additional runs along these lines will be made.

Composition of the exit gases naturally were changed by the presence of hydrogen and carbon dioxide in the steam, apparently by the water gas reaction. Hydrogen depressed the carbon dioxide yield and increased the carbon monoxide yield, as expected. Carbon dioxide increased the carbon monoxide yield and about 3% of the carbon dioxide fed was converted.

### 3. Corrosion Test

A circular coupon of high purity alumina from McDanel showed good corrosion resistance against highly corrosive molten sodium hydroxide in 17 hours at 1400°F. The sample was broken to remove it from the nickel crucible and although all the large pieces were easily recovered some small particles may have escaped collection. The corrosion rate was found to be 0.8 IPY. This material falls in the same class as the Coors alumina and could be employed for reactor service.

### 4. Salt Carryover

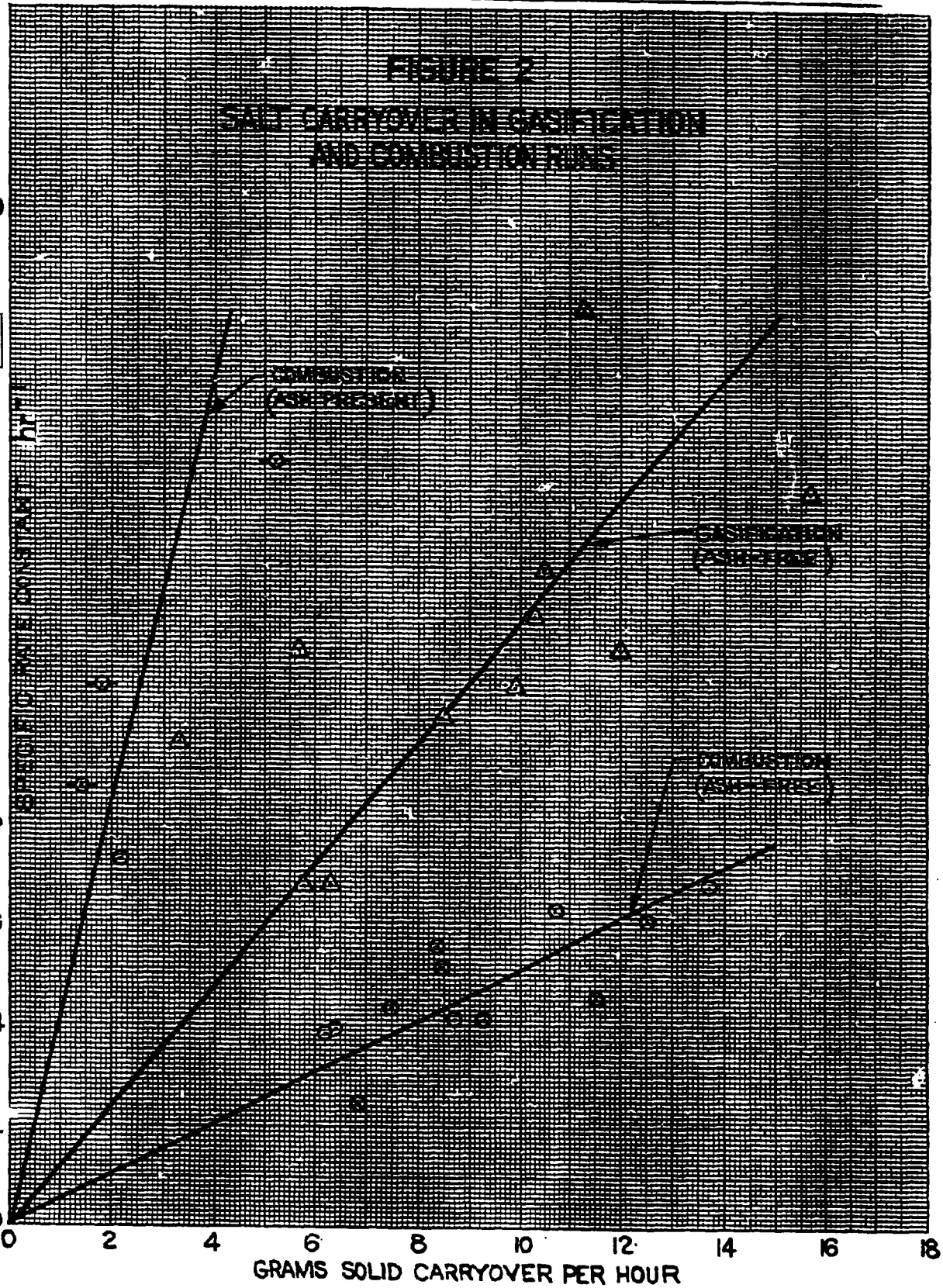
In most of the combustion runs and in most of the recent gasification runs, the amount of salt carried out of the reactor and into the condenser system has been collected at the end of the run. Initial attempts to correlate the data indicate that they line up reasonably well on the basis of grams solid carried over per hour plotted against the specific reaction rate constant for combustion or gasification. The preliminary correlation is presented in Figure 2.

Volatility of sodium oxide and hydroxide as well as some entrainment account for the carryover of sodium compounds. The results show greater salt carryover in combustion than in gasification when starting with an ash free melt. The higher volatility of sodium oxide over sodium hydroxide may account for this effect. Steam present in gasification would convert any sodium oxide immediately to hydroxide. The outstanding effect of ash in the melt on suppression of salt carryover is vividly shown in the figure. Ash constituents apparently immediately react with oxide and hydroxide and prevent volatilization.



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It can be calculated that at a rate of 30 lbs of carbon combusted per hour per cubic foot of melt, with ash present in the melt, about 45 lbs of salt are carried out of the reactor (under the present reactor set-up) per ton of carbon combusted at 10% carbon concentration or 95 lbs of salt carryover per ton carbon combusted at 5% carbon concentration. These, of course, are very preliminary figures. Further analyses will be made.

B. Projections

As soon as all the equipment is received to modify the test system, the effect of pressure up to 60 psia will be investigated. Follow up of the favorable results at higher superficial gas velocities and further study of the effects of gasification products on rate are on the agenda.





#### IV. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

##### A. Accomplishments

Experimental data showing the effects of temperature, ash concentration, and coke concentration on viscosity of melt were reviewed. A preliminary correlation of these data was made for use in process design work and is presented in Figure 3. Although a fair amount of interpretation and extrapolation were required, rendering the graph qualitative at best, it is still very useful. For example, to keep melt viscosity below 200 cp, which has been indicated in simulated bubbling experiments to be a desirable upper limit, total concentration of ash plus coke in the melt should be below about 10% at 1700° F, or below 15% at 1900° F.

Experimental data on rate of gasification were also reviewed and the effects of major variables were plotted for convenient use in the process design evaluation program. Figure 4 shows the effect of temperature on the specific rate constant for gasification,  $k$ , and Figure 5, the effect of ash concentration in the melt.

The process design of the plant for producing pipeline gas from sub-bituminous coal, which was discussed in the last Progress Report, was revised slightly to incorporate improvements made possible by recent experimental results, as discussed above. Specifically, a higher gasification rate constant and a higher superficial gas velocity in the gasifier have been used, both of which yield reductions in gasifier size and investment. Necessary changes are being made in the process flowsheet and in equipment specifications. The estimate of capital cost is in progress.

The process design for pipeline gas from bituminous coal is continuing.

A technical paper, entitled "Development of the Kellogg Coal Gasification Process", was prepared for presentation before the Symposium on Processing of Coal and Its By-Products, at the Philadelphia meeting of the American Institute of Chemical Engineers.

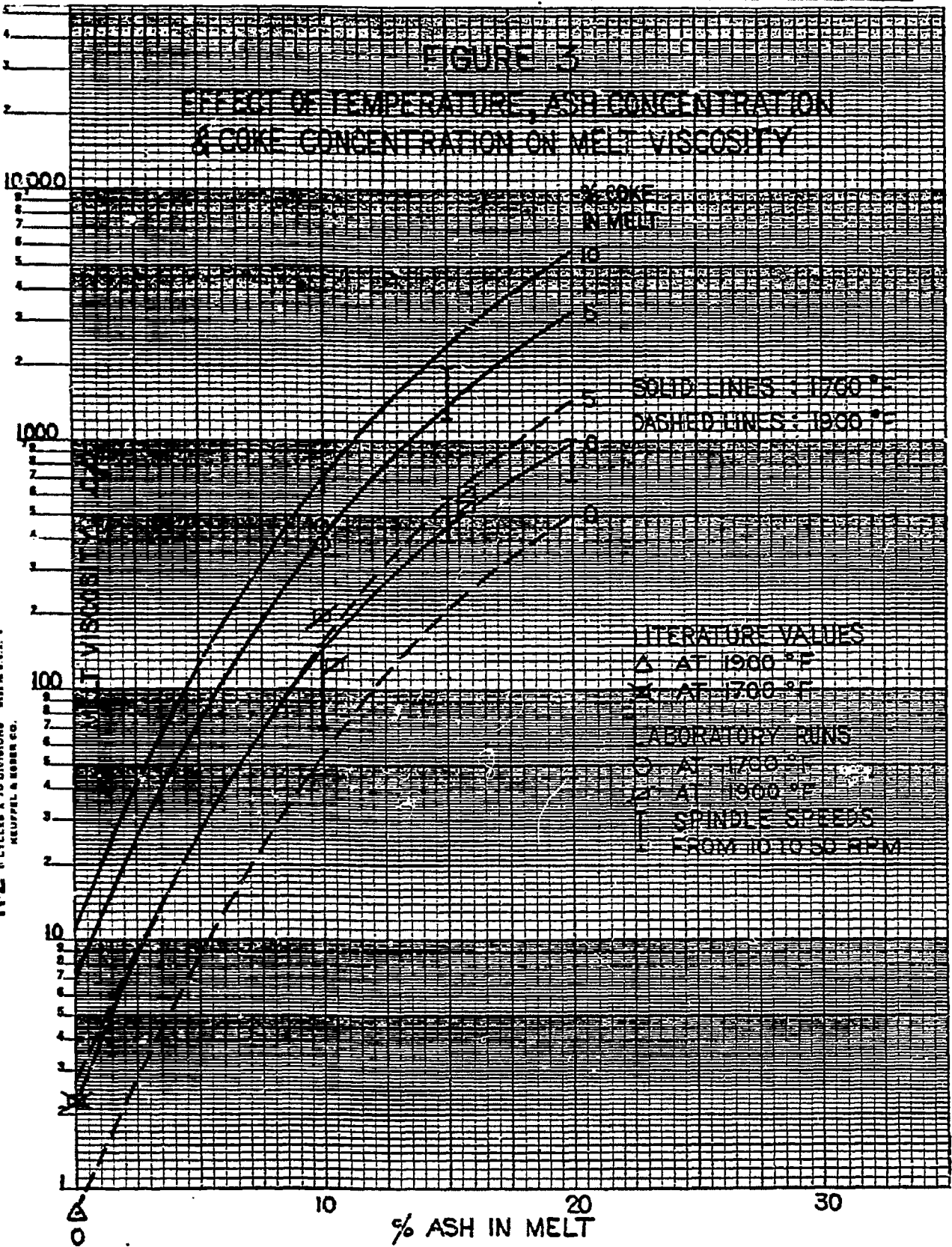
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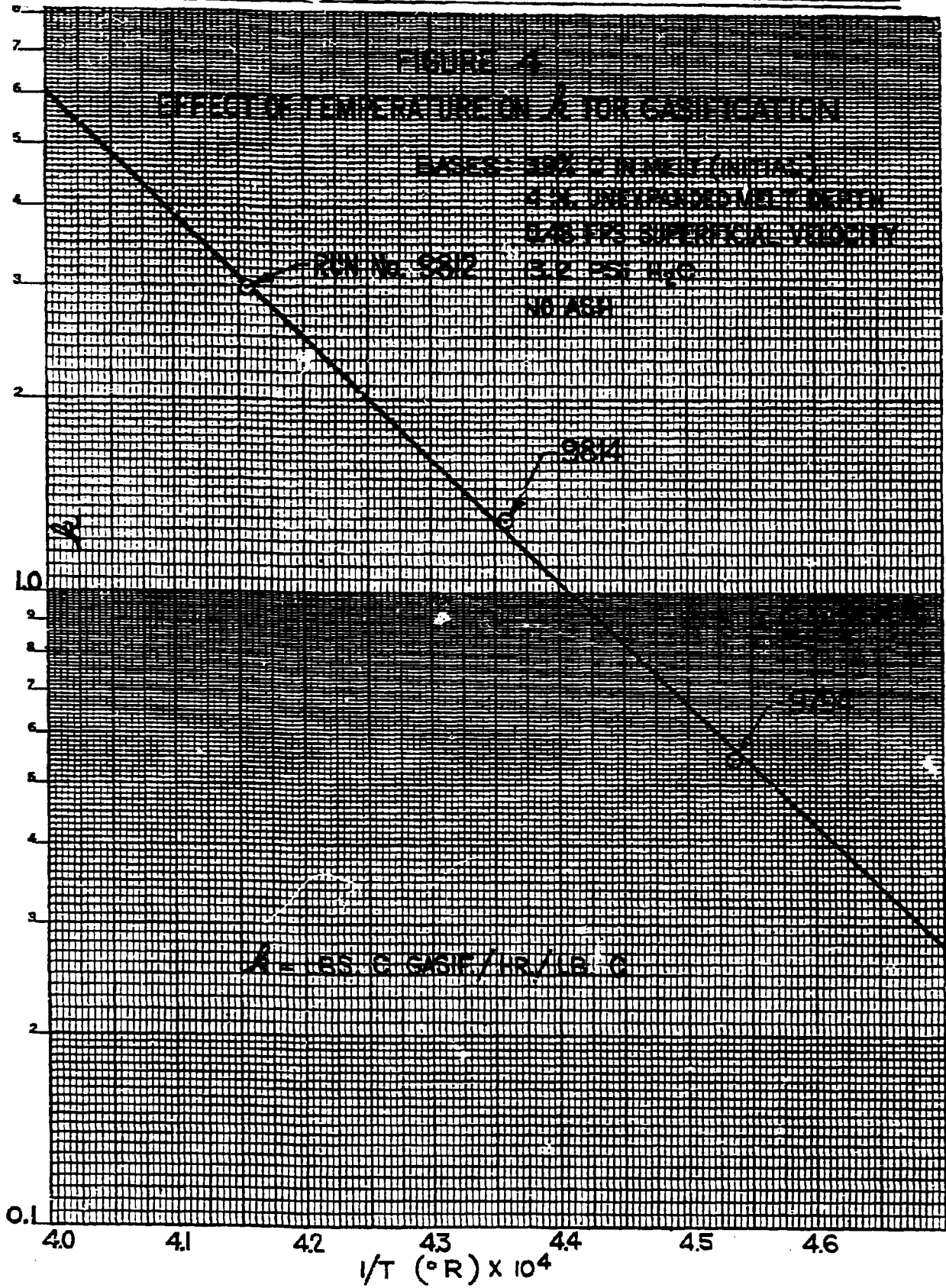


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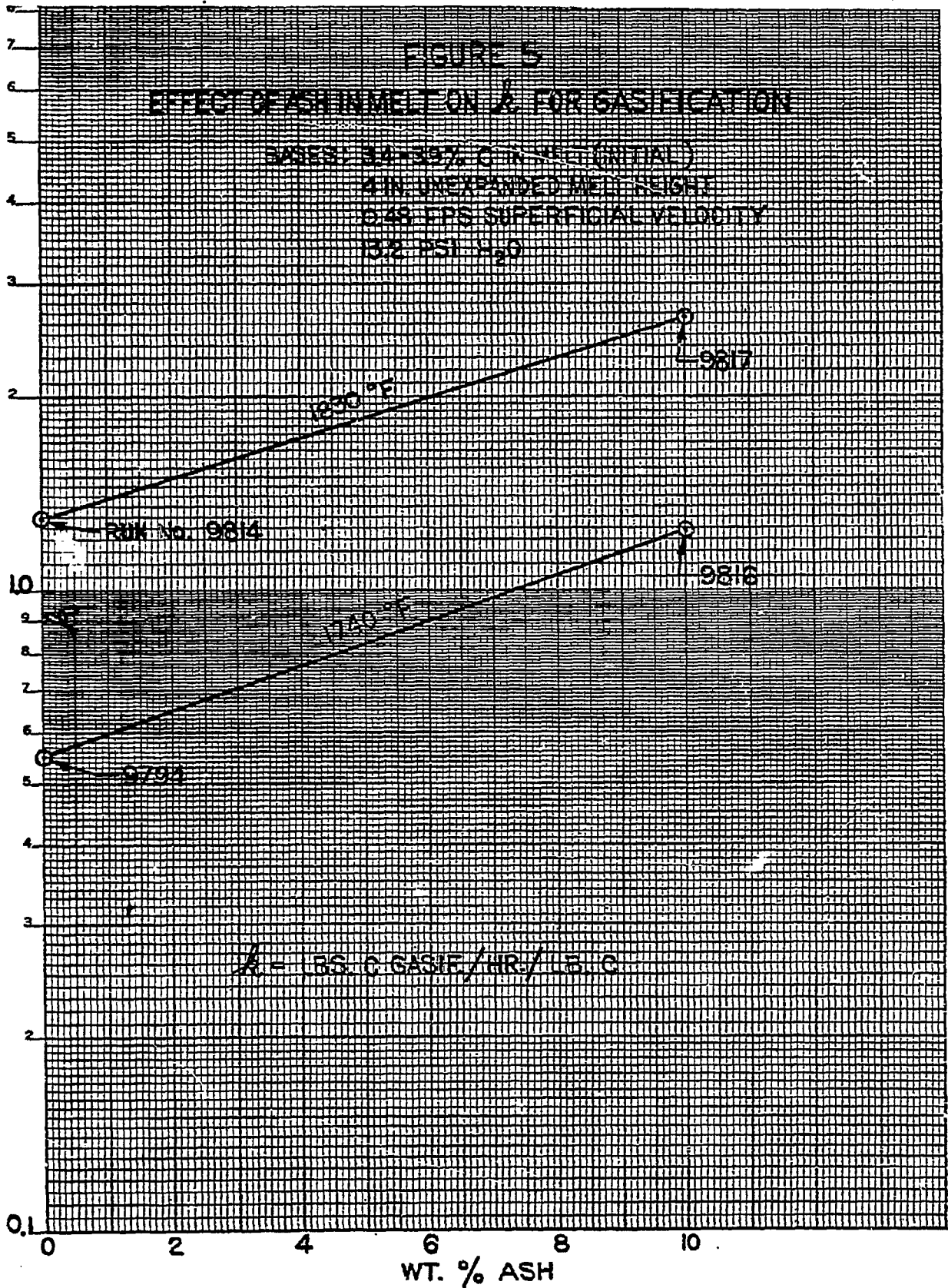
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B. Projections

The economic potential of the Kellogg Coal Gasification Process at this juncture of the development program will be realistically assessed. A process flowsheet, detailed cost estimate, and economic evaluation will be presented for pipeline gas from sub-bituminous coal. Estimated costs will also be prepared for the case of bituminous coal, although the complete process flowsheet and detailed cost estimate will probably not be ready for presentation next month. The sensitive areas in the design where further experimentation is necessary if the process is to realize its full potential will be clearly pointed out.



## V. MECHANICAL DEVELOPMENT

### A. Accomplishments

#### 1. Environmental Testing of High-Temperature Materials

The new reactor, a duplicate of Reactor #2, has been received. It is proposed to operate this reactor with a high-purity  $Al_2O_3$  liner for the next test. This liner has been procured and necessary modifications to the reactor have been made. The liner consists of a tube of McDanel AP-35 high-purity alumina 4" O. D. x 3-5/8" I.D. x 30" long, closed on the bottom end.

In addition to this test, a program has been undertaken to examine the reaction of high-purity alumina refractories in the presence of molten  $Na_2CO_3$  and an oxidizing atmosphere. The test set-up for this program consists of a tube of refractory (McDanel AP-35 2-1/4" O.D. x 2" I.D. x 24" long, closed on one end) which contains the melted  $Na_2CO_3$  in an electric furnace, and equipment for supplying air,  $CO_2$  and steam to the melt through a central tube. This test facility is nearing completion.

#### 2. Coal Feeding Studies

The full-range calibration tests of the bench-scale coal feeder have been completed and are presented as Figure 6. As soon as a suitable drive mechanism can be fabricated, it is contemplated that this feeder will be used in conjunction with the corrosion test reactor. Work was begun during this report period on a layout of a larger coal feeder for use with the pre-pilot-plant unit.

#### 3. Effect of Physical Properties on Bubble Size

Observations of bubble patterns in the 3" I.D. tower led to a conclusion that the small inside diameter caused interference with the bubble pattern and gave rise to large, fast-rising bubbles and poor



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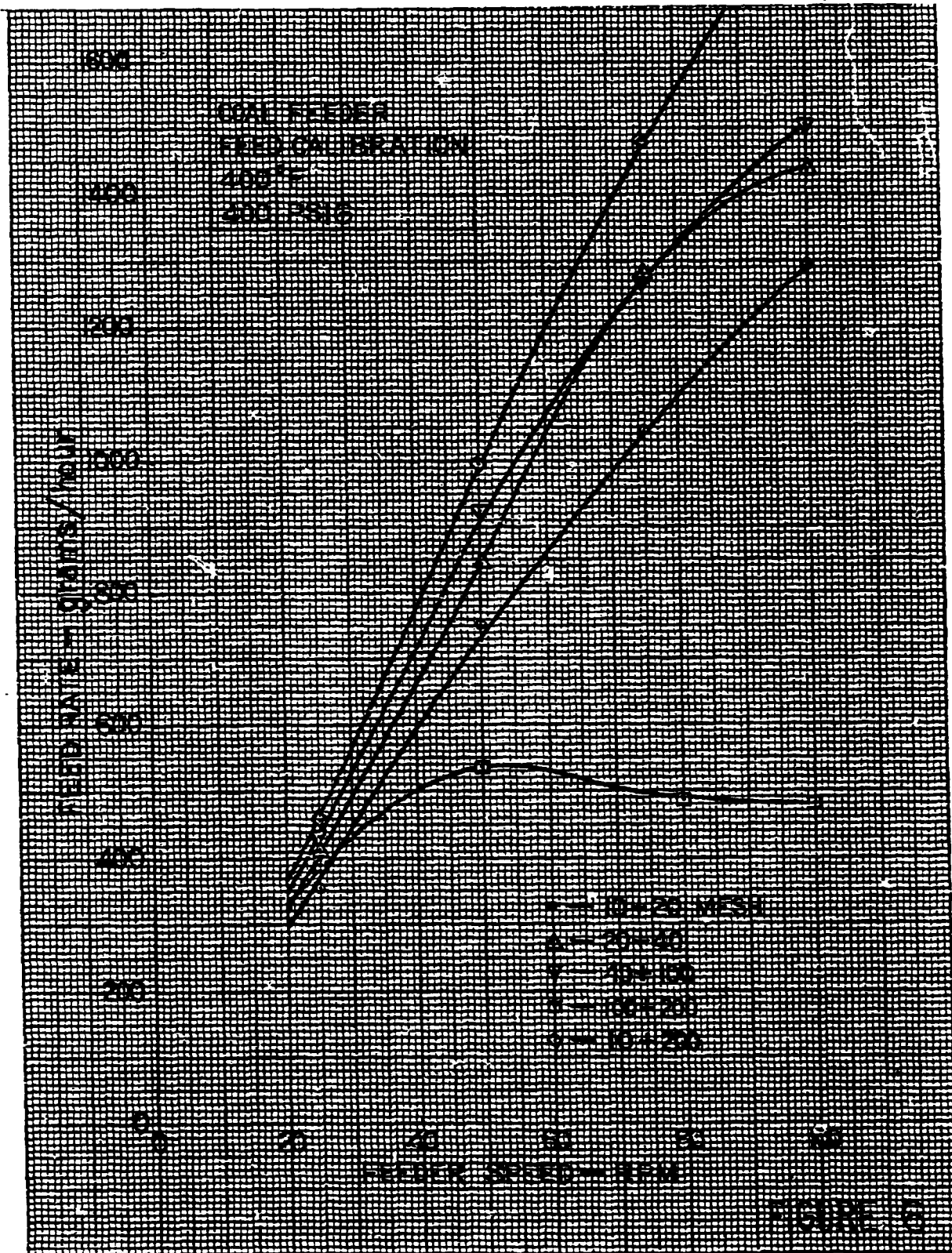


FIGURE 5



gas-liquid contacting. Therefore, a new tower was constructed of transparent plastic tube having a 5-1/2" I.D. Observation of bubbles formed in this tower, in a liquid simulating a  $\text{Na}_2\text{CO}_3$  melt, indicated that the tower walls offered less hindrance to the bubble motion and gave rise to better bubble patterns as well as better liquid circulation and gas-liquid contacting.

## B. Projections

### 1. Environmental Testing of High-Temperature Materials

As soon as Reactor #3 with its alumina liner can be installed in the test facility, the next test will begin. The following samples all high-density, high-purity alumina, are scheduled for this test:

McDane! AP-35 -- Both the reactor liner and test coupons.

Coors AD-99

Norton 4995

Monofrax A

This test is tentatively scheduled for approximately 400 hours to allow reporting the results in the next report. The study of the high-purity liner in the oxidizing atmosphere is planned to begin in the immediate future, and is also programmed for a duration of approximately 400 hours.

### 2. Coal Feeding Studies

When the required parts of the drive mechanism arrive, the coal feeder will be incorporated into the corrosion test reactor facility. Work will continue on designs for the pre-pilot-plant coal feeder.

### 3. Effect of Physical Properties on Bubble Size

No further work is planned on this phase of the project at this time.



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#### VI. MANPOWER AND COST ESTIMATES

Figure 7 shows the projected manpower breakdown for Phase I for 1965 as well as the actual effort that was made. It can be seen that a 12.7 man-effort was made during November.

Figure 8 shows the expenditures during November. For the month \$24,811 was expended, not including fee and G & A. The total expenditures through November were \$292,293. Including fee and G & A the total expenditures were \$337,114. This is 56% of the encumbered funds.

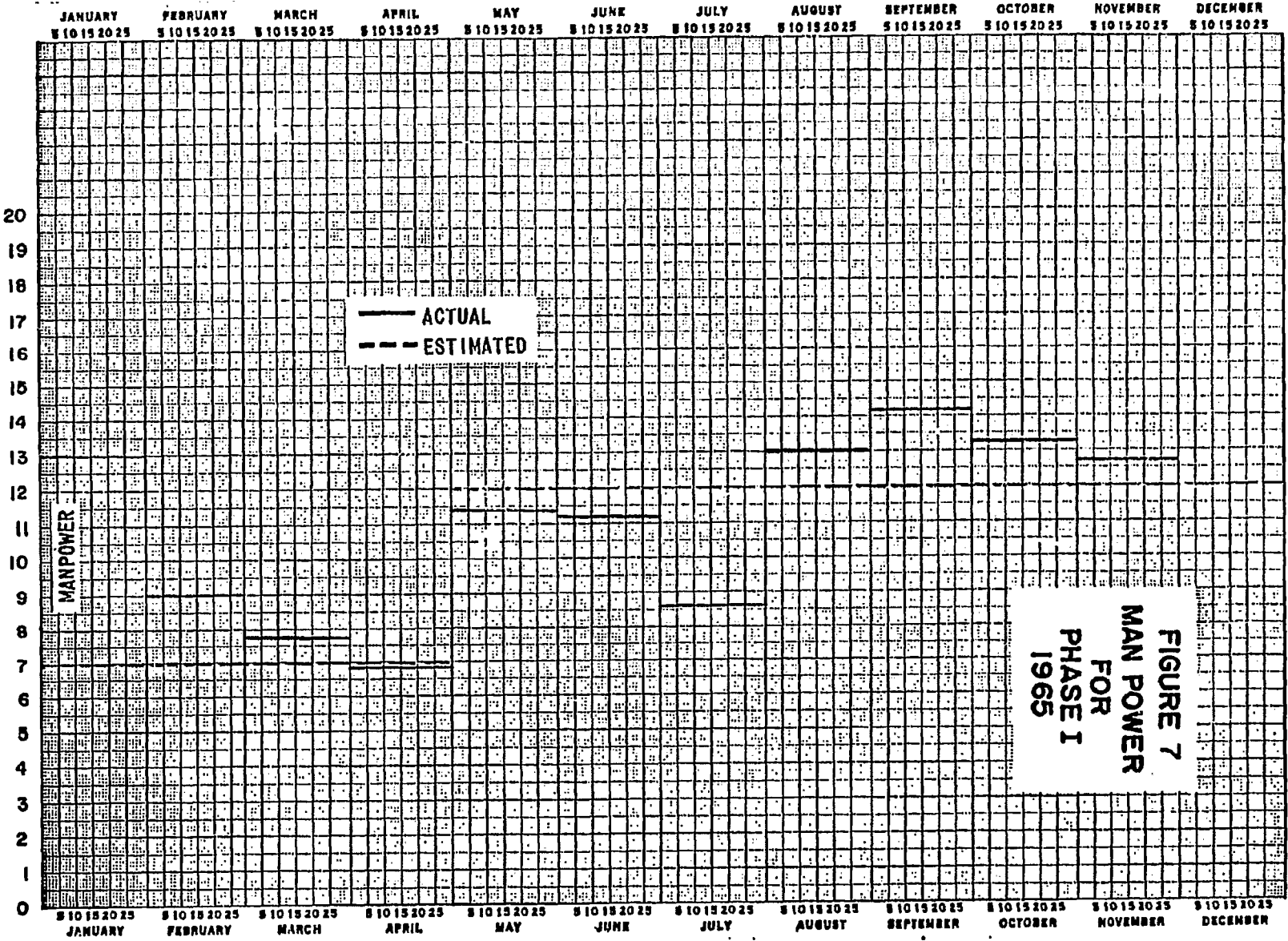


FIGURE 7  
 MAN POWER  
 FOR  
 PHASE I  
 1965

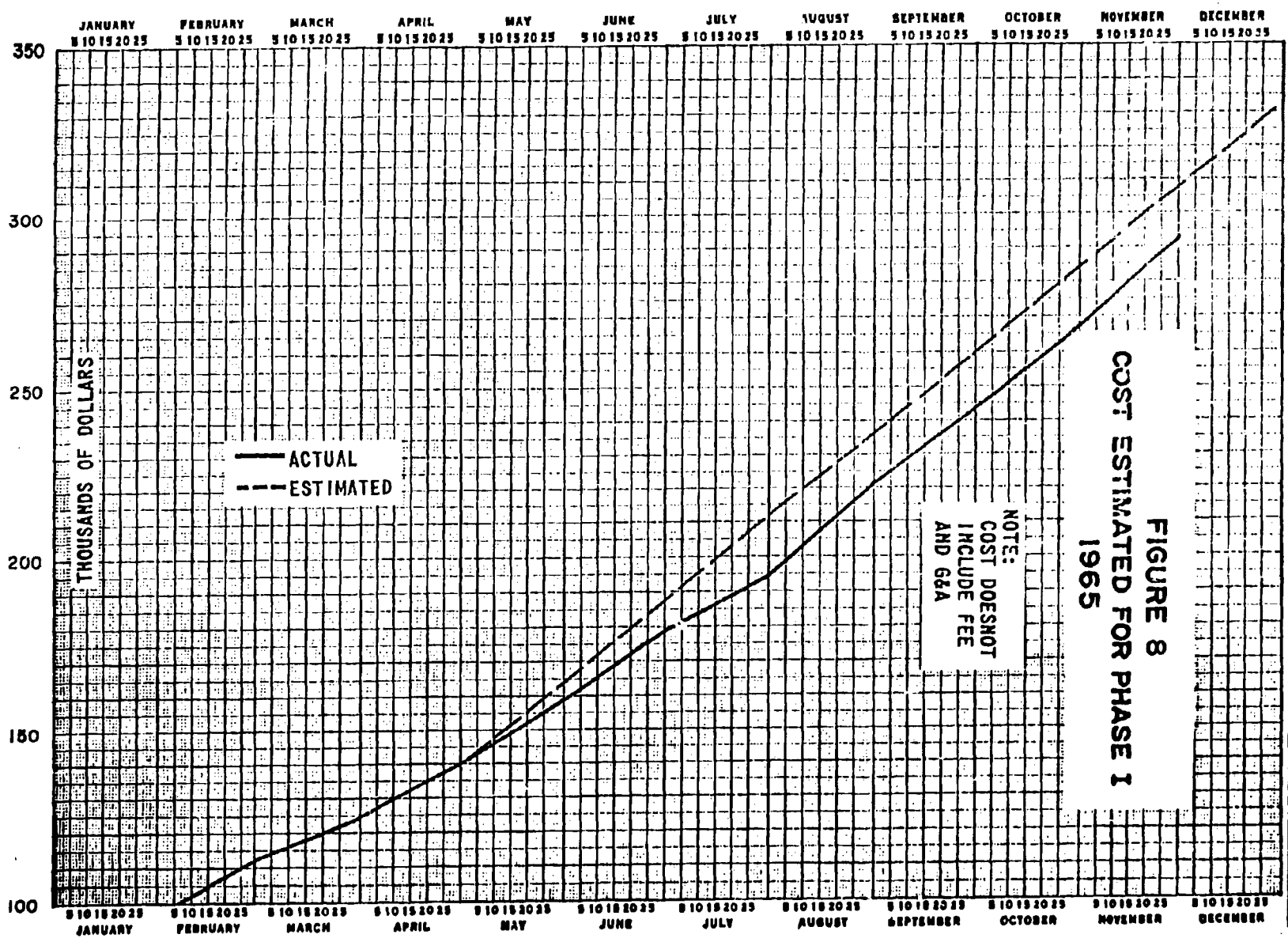


FIGURE 8  
COST ESTIMATED FOR PHASE I  
1965