MWK-MPR-31

RESEARCH AND DEVELOPMENT DEPARTMENT

# DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

February 28, 1967

Progress Report No. 31

APPROVED: _____
Project Manager

_____
MANAGER
RESEARCH & DEVELOPMENT DEPARTMENT

## I. SUMMARY

This progress report is the thirty-first 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.

Nine new combustion runs were made with anthracite to determine the effects on rate of varying air pressure, superficial gas velocity and ash content (and type.) As was the case for bituminous, air pressure in the range of three to eight atmospheres was found to have no effect on the combustion rate of anthracite. Increasing the superficial air velocity from 0.5 to 2 feet per second resulted in an increase in rate of almost 50 percent.

In making these studies it was found that ash formed in situ, i.e. material left in the melt from combustion, was more effective in increasing combustion rate than ash formed externally. This effect has been attributed to a difference in sulfur (or sulfate) content of the two types of ash. Sulfate, of course, has previously been shown to be an effective catalyst for the combustion process.

Five new runs have been made using a gas sampling probe to determine the efficiency of combustion to carbon dioxide. Considerable variation in this efficiency was observed as a function of carbon level, but in all cases the carbon monoxide content of the gases just above the melt surface was less than 15 percent of the total carbon oxides.

A preliminary pilot plant process design has been completed and was turned over to the Mechanical Development group for review. In the course of preparing this flowsheet, a list of process questions was developed in an effort to determine the areas where further bench-scale experimentation is warranted. Development of such programs is now underway.

Capital cost estimation of hydrogen flowsheet was continued and is now near completion. In addition, work was continued on the preparation of the design of the synthesis gas plant.

Additional experiments have been carried out to determine the time required to degasify a melt which has been aerated with carbon dioxide at velocities up to three feet per second. Most of the degasification takes place within 10 to 20 seconds

regardless of the aeration velocity. These results indicate that a relatively small stilling section will be adequate to keep cross-flow contamination of the gasifier to an acceptable level.

Further work has been done on melt circulation to extend the predictions to the zero lift condition contemplated in the pilot plant design. These results indicate that the previously used prediction methods are in reasonable agreement with the results obtained for water and a 100 cp. glycerine-water mixture. These prediction methods are presently being used to determine the circulation rates and to size the melt transfer lines for the proposed pilot plant.

## II. PROCESS RESEARCH

### A. Accomplishments

Anthracite has been used to study the effects on combustion of air pressure, superficial gas velocity, ash formed in situ, and the composition of the product gas by use of a probe. The results of these experiments are shown in Tables 1 and 2.

#### 1. Effect of Air Pressure on Combustion of Anthracite

It was previously shown that air pressure in the range of 1 to 8 atmospheres had no effect on the combustion rate of bituminous coke (Progress Report No. 27, 10/31/66). It is now shown that runs with air pressures of three (Run 165) and eight (Run 160) atmospheres gave the same combustion rate of about 9 lbs. C burned/hr./cu.ft. melt for anthracite. It was found absolutely essential that conditions be identical, especially with regard to the level of ash and/or sulfate buildup in the melt. Runs 161, 162, 163 which used the same melt, but which varied the pressure, showed increasing rates of combustion with increasing ash content as is seen in the following tabulation.

| Run | % Ash in Melt | Pressure-psia | Combustion Rate lbs. C/hr/cu.ft.melt |
|---|---|---|---|
| 160 | 2.0 | 121 | 9 |
| 161 | 2.6 | 15 | 14 |
| 162 | 3.2 | 45 | 22 |
| 163 | 3.8 | 15 | 22 |
| 165 | 2.0 | 46 | 9 |

Although going from 2.0 to 2.6% ash appeared to improve the rate from 9 to 14 lbs. C/hr-CF one other factor must be taken into account. Sulfur, as sulfate, has an exceptional catalytic effect on the combustion of carbon (Progress Report 28,11/30/66). Anthracite has 0.52% sulfur content (ultimate analysis, dry basis) which, if all present in the ash, would correspond to 4.4%. However, the actual sulfur content of the ash is only 0.24%, indicating that a considerable amount of sulfur is driven off during ashing. When anthracite is charged to molten sodium carbonate in nitrogen and then burned, the amount of the total sulfur that remains in the melt and forms sulfate is an unknown entity. Although the changes in combustion rate are presently related to the ash level in the melt, a better correlation must exist for sulfate content. In effect, it

appears that the ash added in situ, by the anthracite is considerably more effective in increasing the rate than the ash added from externally oxidized anthractie (as in Run 160). This suggests some sulfur above that present in the pre-ashed material is retained by the alkaline melt.

2. Effect of Superficial Air Velocity on Combustion of Anthracite

The remaining runs in Table 1, 165 to 168, attempted to determine the effect of superficial air velocity on the combustion rate of anthracite. This was done with fresh melts of sodium carbonate and 2.0% externally produced anthracite ash for each run. The results show a slight, but positive, effect of superficial air velocity on the combustion rate.

| Run | SGV-ft./sec. | Combustion Rate |
|---|---|---|
| 167 | 0.53 | 7.1 |
| 165 | 0.98 | 8.6 |
| 166 | 1.61 | 9.1 |
| 168 | 2.04 | 10.3 |

It is difficult to reconcile this small effect of velocity and the large effect of melt height with a distribution problem of the carbonaceous solid as was done with the gasification studies. Nevertheless, it is believed that distribution of the carbon particles is still a problem, but, that the size of the air bubbles (as a function of bed depth) is considerably different than the steam bubbles or that the film through which diffusion of oxygen and products occurs is grossly different than the film for steam-carbon reactions.

3. Probe Experiments on Anthracite Combustion

The experiment reported in October 1965, in which a probe sampler was used to determine the composition of the combustion gas directly above the melt before excess air could oxidize carbon monoxide led to the conclusion that carbon monoxide did exit from the melt but that the amount decreased to nil when the carbon concentration in the melt became about 3.5% or less. The same $CO_2$ - cooled probe has been used in a series of five experiments, Runs 169 to 173, to obtain additional data in this crucial and important area. This probe was placed 8.5 to 11 inches

## TABLE I

### SUMMARY OF COMBUSTION RUNS IN MOLTEN SODIUM CARBONATE(1)

| Run No. H- | 160 | 161 | 162 | 163 | 164 | 165 | 166 | 167 | 168 |
|---|---|---|---|---|---|---|---|---|---|
| Date 1967 | 1/26 | 1/27 | 1/30 | 1/31 | 2/2 | 2/6 | 2/9 | 2/13 | 2/15 |
| **Feed** | | | | | | | | | |
| % Fixed Carbon | ← Anthracite → | | | | | | | | |
| % Total Carbon | ← - → | | | | | | | | |
| % Volatile Matter | ← 90.8 → | | | | | | | | |
| % Ash | ← 5.9 → | | | | | | | | |
| Gms. Charge | ← 11.7 → | | | | | | | | |
| Mesh Size | ← 21.35 → | | | | | | | | |
| % Carbon in Melt - Initial | ← 12/20 → | | | | | | | | |
| | ← 4 → | | | | | | | | |
| **Melt** | | | | | | | | | |
| Gms $Na_2CO_3$ | 405.7 | (3) | (3) | (3) | 405.7 | 405.7 | 405.7 | 405.7 | 405.7 |
| Gms. Ash | 8.3 | - | - | - | 8.3 | 8.3 | 8.3 | 8.3 | 8.3 |
| % Ash in Melt | 2.0 | 2.59 | 3.17 | 3.76 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Height - Inches | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Conditions** | | | | | | | | | |
| Temp. °F - Initial | 1844 | 1844 | 1845 | 1844 | 1841 | 1843 | 1845 | 1845 | 1845 |
| - Average(2) | 1834 | 1847 | 1856 | 1855 | 1840 | 1840 | 1839 | 1840 | 1838 |
| - Maximum | 1846 | 1867 | 1880 | 1873 | 1857 | 1852 | 1862 | 1858 | 1865 |
| Pressure - psia | 120.5 | 15 | 44.7 | 15 | 15 | 45.5 | 45.0 | 44.8 | 45.0 |
| Sup. Gas Vel. - ft/sec | 1.02 | 1.29 | 1.03 | 0.95 | 1.07 | 0.98 | 1.61 | 0.53 | 2.04 |
| Run Time - min | 55 | 60 | 30 | 15(4) | 10(4) | 65 | 60 | 80 | 60 |
| Air Rate - liters/min | 69.4 | 10.8 | 26.0 | 7.9 | 8.9 | 24.8 | 40.7 | 19.7 | 51.8 |
| **Results - Product Gas** | | | | | | | | | |
| % $CO_2$ - 5 min | 1.05 | 8.6 | 5.1 | 17.0 | 6.9 | 2.6 | 1.7 | 3.4 | 1.35 |
| - 35 min | 0.8 | 2.7 | - | - | - | 2.1 | 1.05 | 3.0 | 0.75 |
| - end | 0.6 | 0.7 | 1.1 | 12.5 | 6.3 | 0.8 | 0.42 | 0.9 | 0.4 |
| % $O_2$ - 5 min | 19.5 | 11.5 | 15.5 | 4.0 | 13.5 | 18.0 | 18.5 | 17.5 | 19.0 |
| - 35 min | 20.5 | 17.5 | - | - | - | 19.0 | 19.5 | 18.0 | 19.3 |
| - end | 20.5 | 19.6 | 19.8 | 9.5 | 13.8 | 20.0 | 20.5 | 20.3 | 20.6 |
| Combustion Rate Constant | 0.75 | 1.18 | 1.89 | 1.85 | 1.12 | 0.73 | 0.77 | 0.60 | 0.87 |
| % Fixed Carbon Consumed | 100 | 101 | 99 | 74 | 33 | 98 | 97 | 101 | 99 |
| Rate - Lbs C/hr/cu ft at 4% carbon init. | 8.9 | 13.9 | 22.3 | 21.8 | 13.2 | 8.6 | 9.1 | 7.1 | 10.3 |
| % Total Carbon - Devolatilized | 10.0 | 16.3 | 17.4 | 22.3 | 15.0 | 15.0 | 13.1 | 12.2 | 14.5 |
| - Combusted | 90.2 | 84.4 | 81.9 | 51.4 | 18.3 | 83.3 | 83.9 | 88.8 | 84.2 |
| - Left + Loss | - | - | 1.0 | 26 | 67 | 1.7 | 3.0 | - | 1.3 |

(1) In 2-inch I.D. Inconel reactor; coal charged into $N_2$ at 0.1 ft/sec SGV and held 5 minutes before air in.

(2) Average temperature in 50% carbon consumed period.

(3) Reused melt from previous run.

(4) Run terminated due to plug in outlet of condenser.

from the bottom of the reactor while employing the normal 4 inch quiescent bed depth. Splashing of the melt into the probe nozzle did cause plugging difficulties in the first three runs. At a height of 11 inches, the least amount of plugging occurred. A summary of the runs is presented in Table II and discussed below.

Table II shows that the first run, with 4% carbon initially, gave only a trace of CO after 5 minutes of combustion. Direct reaction of the anthracite and the melt lowered the carbon level to about 3.3% before air was introduced. Difficulty with sampling was experienced so that the probe analyses at 5 and 10 minutes are not too reliable. The use of 6% carbon initially in the succeeding runs was adopted to be able to follow carbon concentration in the melt and carbon monoxide concentration in the product gas over a wider range. With each charge of anthracite, the sulfur and ash level in the reused melt became greater. This increased the reaction rate, thus enabling probe samples to be taken over a range of rates, from 6 to 17 lbs. C burned/hr./cu.ft. of melt and to as low as 1.5% oxygen in the combustion gas.

The table shows that an appreciable amount of carbon reacts in the devolatilization period (no air) and that the devolatilized gas is rich in carbon monoxide. This is a desirable situation, since this will occur in the gasifier where the coal is fed. Only the devolatilized coal will circulate to the combustor for air oxidation.

Figure 1 presents the relationship of percent carbon monoxide in the product gas carbon (i. e., $CO \times 100/CO + CO_2$) and the percent carbon left in the melt. Naturally, considerable variation in the results (saw toothed curves) is evident. Notably, in the 3 to 5% carbon level in the melt, the amount of carbon monoxide is of the order of 6 to 13% of the total carbon oxides produced. Below 3% carbon in the melt, carbon monoxide is less than 6-7% of the total oxides. Even the probe samples, taken 2.5-3 minutes after the air was turned on, showed only 7.4 to 12.2% CO in the carbon oxides (not shown in Figure 1). Such CO levels in the commercial unit would not result in a significant cost increase due to the efficiency loss.

It is concluded that the melt does a reasonably efficient job in conversion of carbon to carbon dioxide in the 2 inch test unit. It is felt that the sodium carbonate catalyzes the reaction of carbon monoxide to carbon dioxide. In addition, it is anticipated that the presence of steam in the air will further catalyze the CO to $CO_2$ reaction as is known in the literature(1) as well as catalyzing the overall conversion as previously demonstrated(2).

B. Projections

It is planned to determine the effect of 20% $CO_2$ in air on the combustion rate of anthracite. The determination of the effect of the concentration of sodium sulfate in the melt on the combustion of coke will be completed. Attempts will be made to enhance the rate of gasification of anthracite.

(1) Lowry, H. H., "Chemistry of Coal Utilization", Supplementary Volume, pg. 776, Wiley and Sons (1963).

(2) Progress Report 14, September 30, 1965.

TABLE IV

ANTHRACITE COMBUSTION RUN SUMMARY USING PROBE SAMPLER(1)

| Run No. H- | 169 | 170 | 171 | 172 | 173 |
|---|---|---|---|---|---|
| Date 1967 | 2/17 | 2/17 | 2/20 | 2/21 | 2/22 |
| Anthracite - gms | 21.35 | 32.03 | 32.03 | 32.03 | 32.03 |
| % C in Melt | 4 | 6 | 6 | 6 | 6 |
| $Na_2CO_3$ - gms | 405.7 | (3) | (3) | (3) | (3) |
| Ash - gms | 8.3 | - | - | - | - |
| % Ash in Melt | 2.0 | 2.5 | 3.5 | 4.35 | 5.15 |
| Temp. °F - initial | 1841 | 1834 | 1837 | 1844 | 1845 |
| - average(2) | 1840 | 1840 | 1840 | 1840 | 1840 |
| - maximum | 1853 | 1870 | 1871 | 1871 | 1890 |
| Pressure - psia | 15 | 15 | 15 | 15 | 15 |
| Sup. Gas Vel. - ft/sec | 0.94 | 0.88 | 0.95 | 0.98 | 0.90 |
| Run Time - min | 10(4) | 40(4) | 17(4) | 50 | 52 |
| Air Rate - l/min | 7.8 | 7.3 | 7.9 | 8.1 | 7.5 |
| Spec. Rate Constant | 0.50 | 0.65 | 1.03 | 1.45 | 1.40 |
| Rate - lbs C/hr/cu ft | 5.9 | 7.7 | 12.2 | 17.1 | 16.5 |
| % Total C - Devol. | 17 | 8 | 17 | 20 | 20 |
| Comb. | 15 | 58 | 40 | 79 | 79 |
| Left | 68 | 34 | 43 | 1 | 1 |
| Gas Analyses | | | | | |
| Devol. Gas - % CO | 27.5 | 18.4 | 41.2 | 37.4 | 43.7 |
| % $CO_2$ | 12.3 | 6.8 | 9.4 | 12.0 | 10.5 |
| Probe - Time - min | - | 2.5 | 3 | 2.5 | 2.5 |
| % CO | - | 0.85 | 1.7 | 2.4 | 2.0 |
| % $CO_2$ | - | 10.7 | 13.6 | 17.2 | 16.5 |
| % $O_2$ | - | 8.2 | 5.4 | 1.5 | 1.7 |
| Time - min | 5 | 5 | 5 | 5 | 5 |
| % CO | tr | 0.98 | 1.5 | 2.6 | 2.0 |
| % $CO_2$ | 5.7 | 13.25 | 14.0 | 17.5 | 17.5 |
| % $O_2$ | 15.5 | 6.5 | 5.4 | 1.6 | 1.6 |
| Time - min | 10 | 10 | 12 | 15 | 11 |
| % CO | tr | 1.1 | 0.7 | 0.9 | 1.1 |
| % $CO_2$ | 5.2 | 9.7 | 13.5 | 14.0 | 15.8 |
| % $O_2$ | 16.2 | 10.6 | 6.8 | 7.7 | 2.8 |
| Probe Height - in. from btm. | 8.5 | 10 | 11 | 11 | 11 |

(1) In 2-inch I.D. Inconel reactor; coal charged in $N_2$ at 0.1 ft/sec SGV and held 5 minutes before air in.

(2) Average temperature in rate determined period.

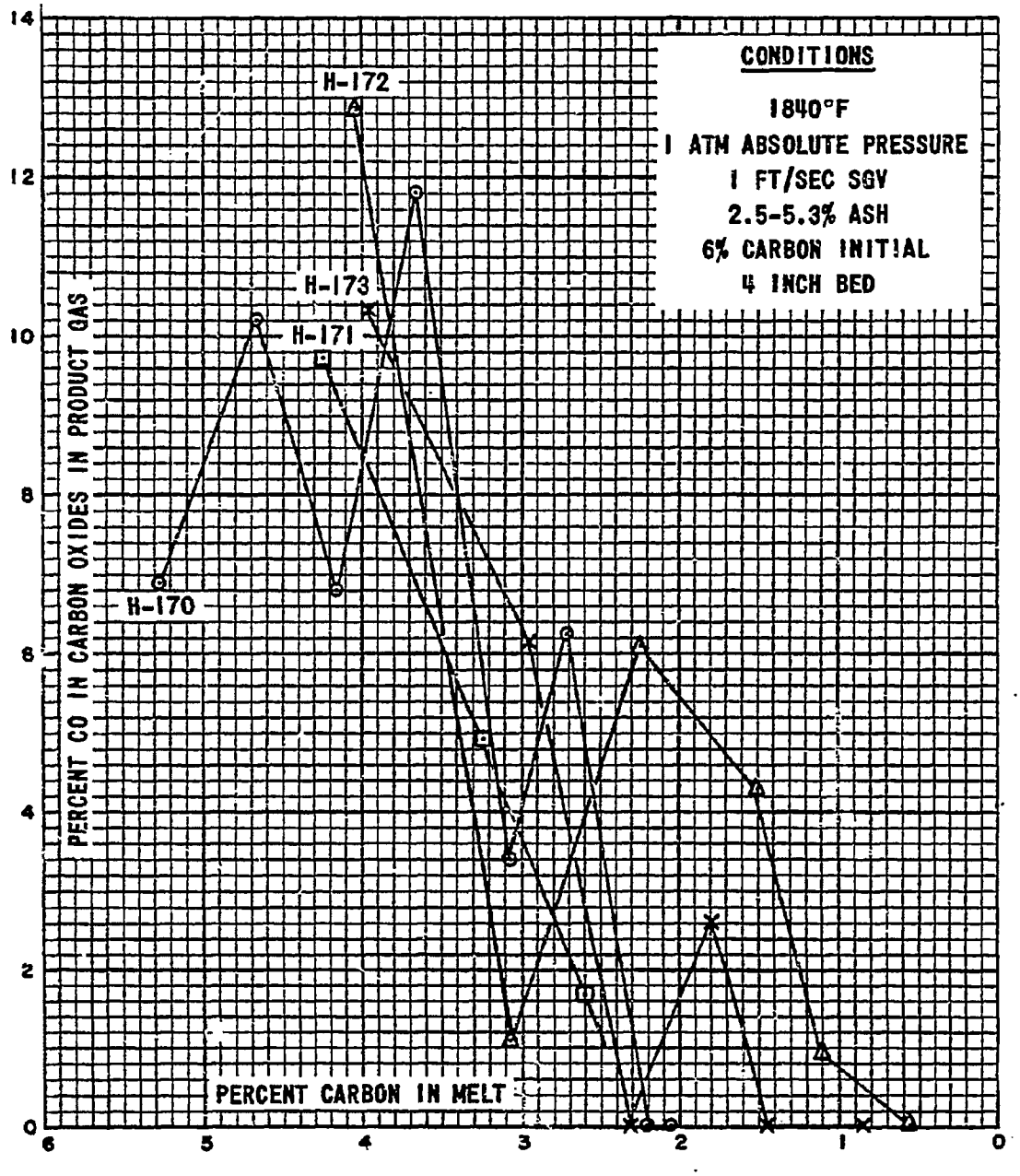
(3) Reused melt from previous run.

(4) Run ended due to plug in probe.

M 20 - Part

# FIGURE 1

## RELATIONSHIP OF CARBON MONOXIDE CONTENT IN PROBE PRODUCT GAS TO CARBON LEVEL IN MELT FROM ANTHRACITE COMBUSTION



# III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

## A. Accomplishments

### 1. Pilot Plant Design

A preliminary process design of the one-ton-per-hour gasification pilot plant has been completed. The flowsheet has been turned over to the Mechanical Development Department for sizing of the melt transfer lines and for estimation of the required amounts of the lift gases (air and steam) needed to circulate the melt at design rates. Further study of this flowsheet is continuing in an effort to "fix" a final process design as soon as possible.

A list of process questions has been drawn up in an effort to delineate those areas where additional experimental work is required before commercialization of the process. It is also anticipated that such a list will serve as a basis for planning the future Process and Mechanical Research programs in order that the pilot plant may be built and operated with the highest degree of certainty.

### 2. Flowsheet Studies

Capital cost estimation of the hydrogen-from-coal plant continued through February and costs of essentially all of the major process equipment have been obtained. Estimation of the erection cost is now underway. The major delay in determining this cost has been due to conflicts in scheduling in the Estimating Section - a section available to all phases of the Research Department. However, these problems have now been cleared up, and there should be no difficulty in proceeding through to completion of the estimate.

Work on the design of a plant capable of producing synthesis gas from bituminous coal has also continued.

## B. Projections

### 1. Pilot Plant Design

Modifications to the pilot plant process design will be made in accordance with the present review and the suggestions made by the Mechanical Development Department. Complete equipment specifications of the items on the final flowsheet will then be made so that the process can undergo a complete mechanical design.

2. Flowsheet Studies

Work will continue and hopefully conclude, on the cost estimation of the hydrogen plant. Gas costs using this figure will then be calculated.

Process design of the synthesis gas plant will also continue during March.

# IV. MECHANICAL DEVELOPMENT

## A. Accomplishments

### 1. Mechanical Characteristics Testing

Additional tests have been conducted to determine degasification time for a molten sodium carbonate bed with eight percent ash. Carbon dioxide was used to aerate the bed at superficial velocities up to three feet per second in the test apparatus previously used to determine melt bed expansion.

The electrical dip stick was placed at various heights above the bed and the time was measured from the time the gas supply was shut off until contact was broken between the melt and the dip stick. The results of these tests are shown on Figures 2 and 3. As can be seen in Figure 3, the degasification time sharply increases below a 1/2-inch gap.

The data indicates the majority of degasification takes place within 10 to 20 seconds regardless of the aeration superficial velocity. Complete degasification would appear to take in the order of two to five minutes based on extention of the data to zero gap. A 1/2-inch gap represents a contamination level of 0.007 cubic feet of gas per cubic feet of melt and is within the acceptable limit presently set. Thus, a stilling section providing 10 to 20 seconds hold-up would appear adequate to reduce the cross-flow contamination to an acceptable level.

### 2. Melt Circulation

Both experimental and analytical work has been done to extend melt circulation predictions to the essentially zero lift condition contemplated in the pilot plant design. Figures 4 and 5 show the results of this work. On Figure 4 it is interesting to note that maximum flow rates are obtained with air lift superficial velocities between two and five feet per second and that significant reductions in flow rate are obtained only below two feet per second for water and one foot per second for the 100 cp. mixture.

The analytically predicted flow rate for water at five fps air lift superficial velocity was exactly that obtained experimentally. For the 100 cp. mixture the predicted value was approximately 35 percent below the actual value which was to be expected based on previous calculations.

As a result of this work, we are prepared to predict melt circulation rates and size transfer lines for the proposed pilot plant. A computer program is being prepared to assist in the necessary prediction calculations.

## B. Projections

### 1. Mechanical Characteristics Testing

An experimental test setup to determine entrainment in the aeration gas exiting a sodium carbonate melt bed is being constructed. Figure 6 shows the proposed test setup. Temperature measurements will be taken along the length of the outlet line so that if carry-over deposits are found at particular locations a deposit temperature can be obtained. Total carry-over will be determined by weighing the exit line and filter before and after each run.

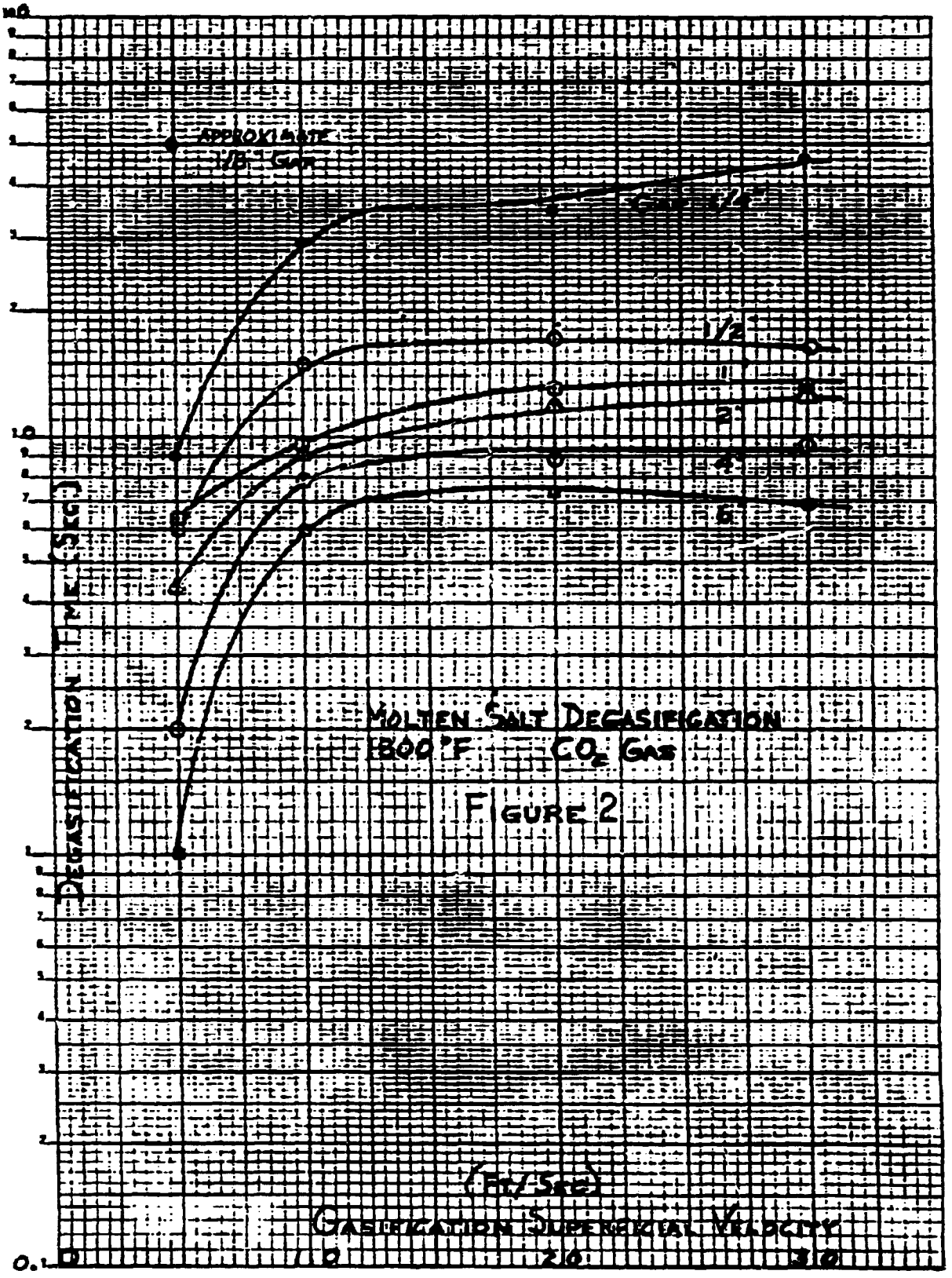

APPROXIMATE
1/8 Size
1/2
2
4
6
DEGASIFICATION TIME (Hrs)
MOLTEN SALT DEGASIFICATION
1800°F $CO_2$ Gas
(Ft/Sec)
GASIFICATION SUPERFICIAL VELOCITY
0.1
10
20
30

FIGURE 2

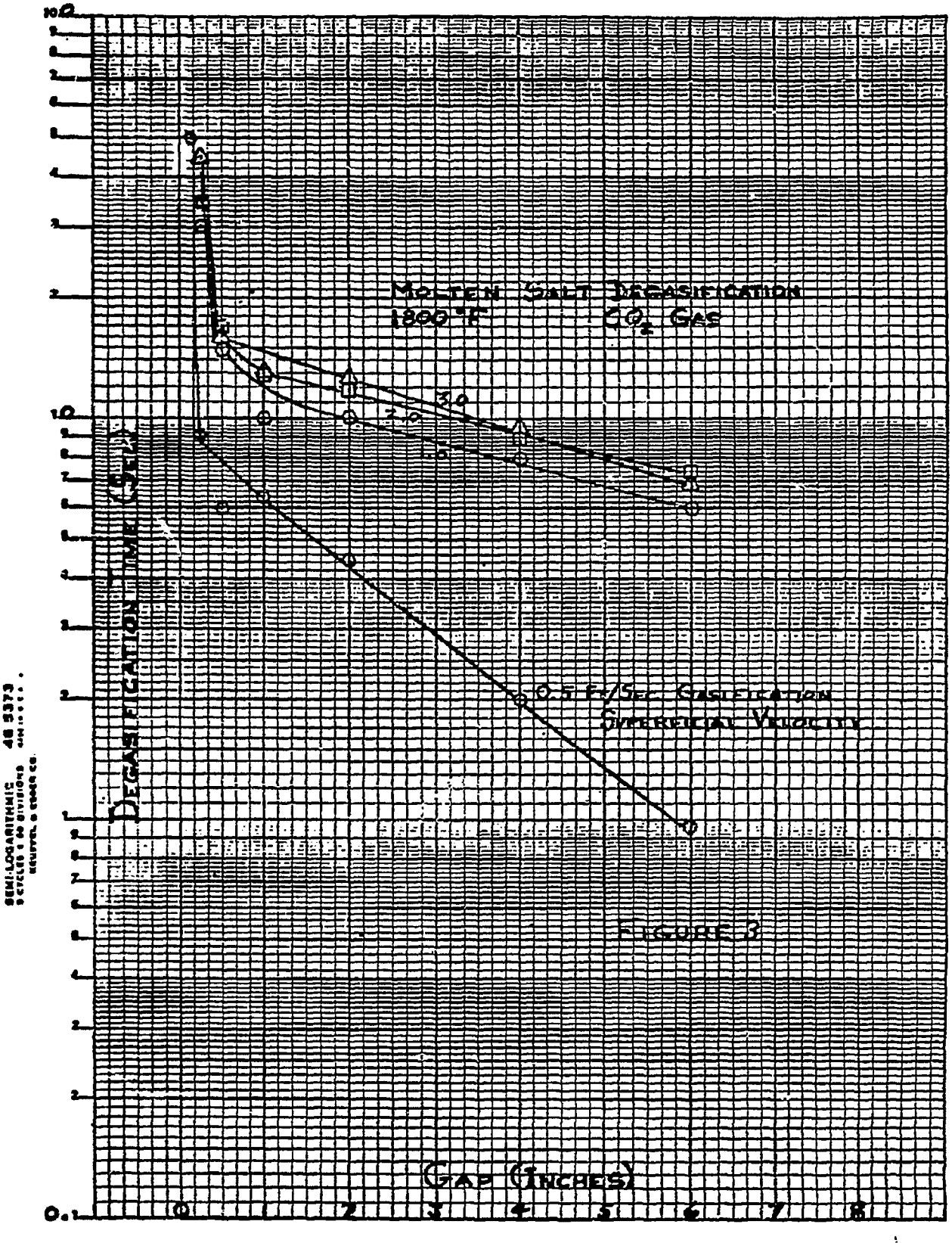
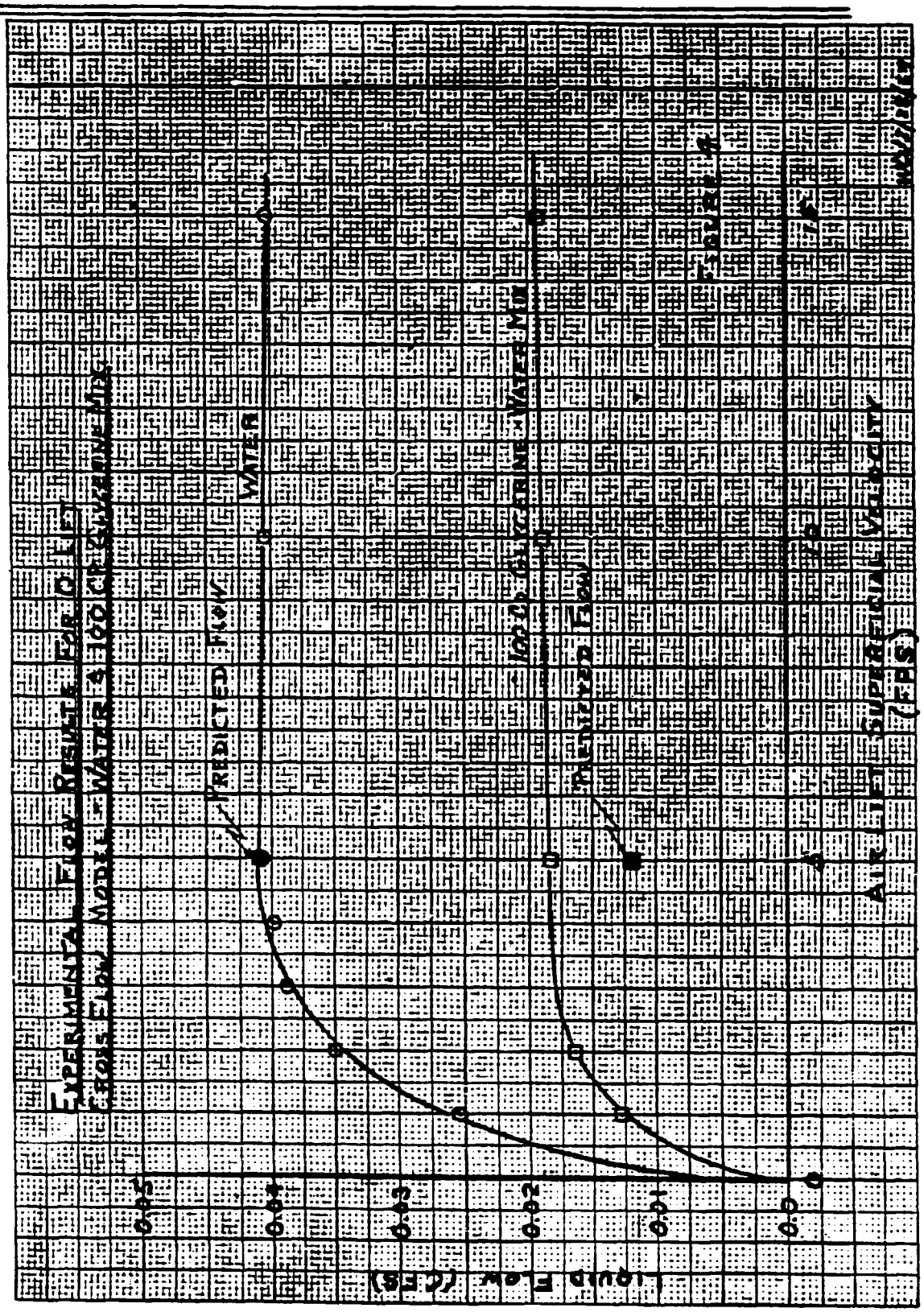
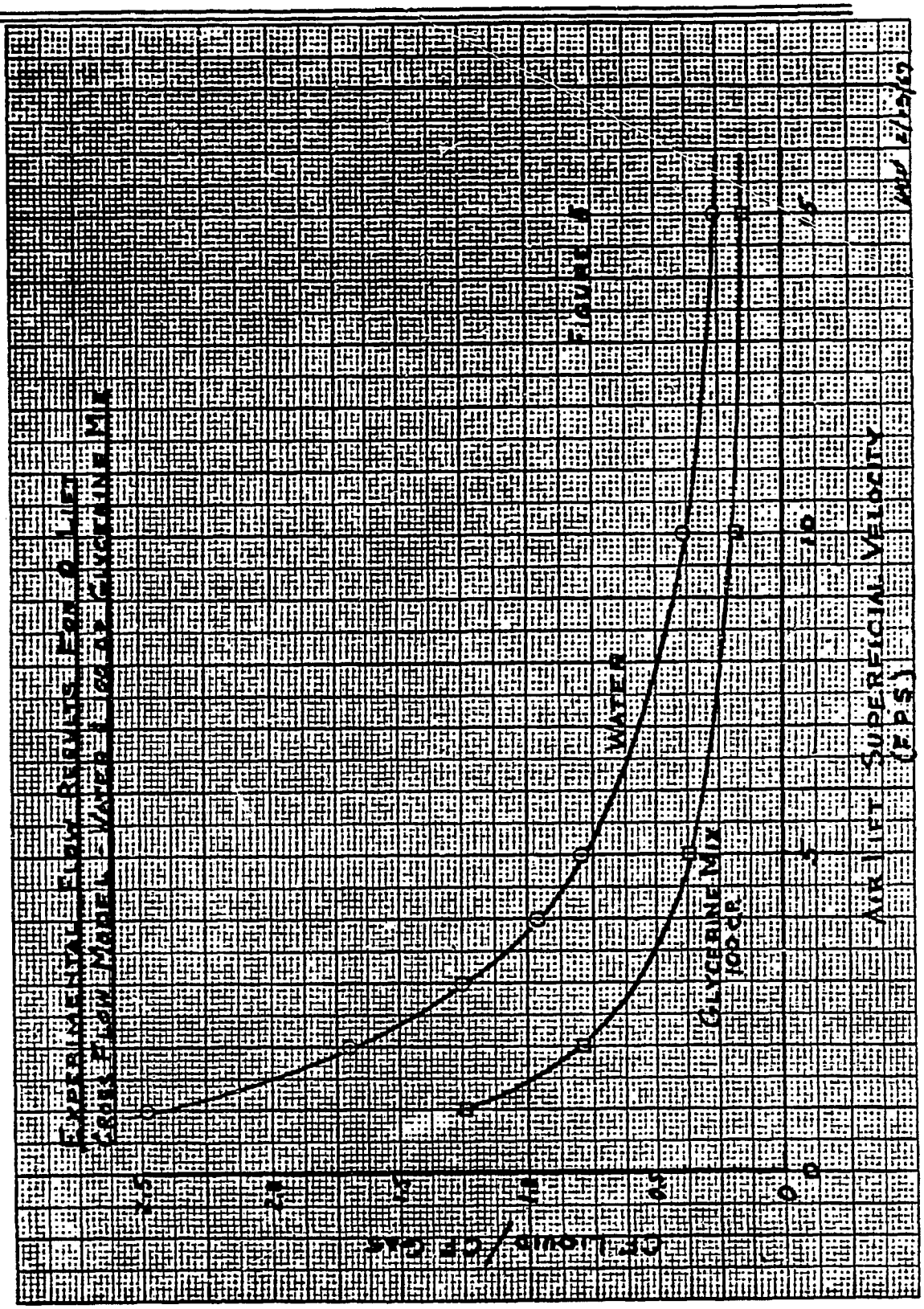

Molten Salt Degasification
1800°F
$CO_2$ Gas
0.5 Ft/Sec Superficial Velocity
Degasification Time (Sec)
Gap (Inches)
100
10
1
0.1
0
2
3
4
5
6
7
8

FIGURE 3


EXPERIMENTAL FLOW RESULTS FOR OUTLET CROSS FLOW MODEL - WATER & 100 CENTISTOKE MIX
PREDICTED FLOW, WATER
MEASURED FLOW, 100 CENTISTOKE MIX
FIGURE 15
AIR JET SUPERFICIAL VELOCITY (FPS)
0.05
0.04
0.03
0.02
0.01
0.0
LIQUID FLOW (CFS)


EXPERIMENTAL FLOW RATES FOR LIQUID FROM MODEL WATER-GLYCERINE MIX
WATER
100 CP.
GLYCERINE MIX
VELOCITY (F.P.S.)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
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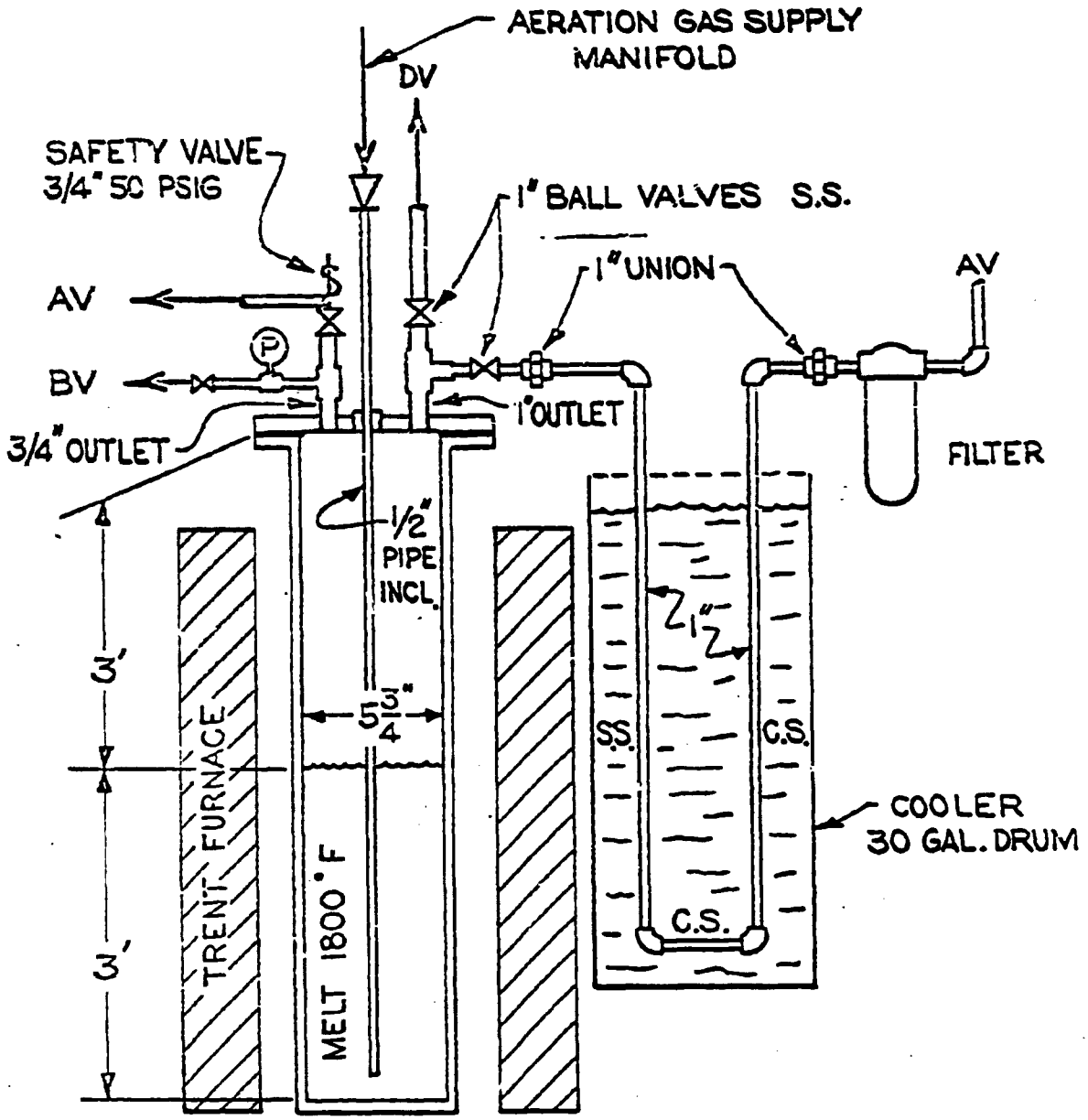
985
990
995
1000




A.V. ATMOSPHERIC VENT
D.V. DUCT VENT
B.V. BLEED VENT

FIGURE 6

# O.C.R. COAL GASIFICATION CARRYOVER TESTS