

MUR-MPR-36

RESEARCH AND ENGINEERING DEVELOPMENT



DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

CONTRACT NO. 14-01-0001-380

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PROGRESS REPORT NO. 36

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A DIVISION OF PULLMAN INCORPORATED



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I. SUMMARY

This progress report is the thirty-sixth 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.

Analytical results have been obtained which verify earlier qualitative observations concerning the form in which sulfur is present in the melt. The conclusions of this work are that sulfur in the gasifier will be present as sulfide and in the combustor as sulfate. In addition, all of the sulfur should stay in the melt and none should be lost in the effluent gases. This will make it possible to decrease sulfur removal costs substantially and thus yield lower gas costs.

Experiments were performed to determine what will happen to pyrites, FeS_2 , brought in with the coal. These results indicated that the pyrites most probably will react with sodium carbonate to yield sodium sulfide (in the gasifier) and magnetite, Fe_3O_4 , which will be removed in the ash removal section.

Additional work has been done to determine the degree to which a steam-carbon dioxide mixture will oxidize sodium sulfide in the melt. Careful precautions were taken to prevent oxidation due to air leakage or metal oxides present on the surface of an Inconel reactor by the use of a pure alumina reactor. Qualitative results thus far indicate that there is a slow, but continuous, oxidation of sulfide as the gaseous products of reaction are removed. It is felt, however, that the presence of carbon in the gasifier will maintain the sulfur in the sulfide form.

A literature search has indicated that the Claus Process for conversion of hydrogen sulfide to sulfur should be applicable to the carbon dioxide-hydrogen sulfide off gas from the carbonation tower in the ash removal section.

Flowsheet calculations and equipment sizing for the synthesis gas plant have been completed and a cost estimate is being prepared.

Work has continued on updating the pilot plant flowsheet in preparation for a process release.

Simulation tests designed to check on the efficiency of melt circulation indicated a good circulation pattern with no obvious problems. A relatively high degree of mixing and good pumping action in both vessels and in the lift lines were observed.

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Efforts were made to setup a new machine capable of cutting Monofrax "A" samples for use in corrosion tests. It is anticipated that these cut samples will be free from the casting defects which have previously led to above normal corrosion rates.



II. PROCESS RESEARCH

A. Accomplishments

1. Sulfur Form in Gasifier and Combustor:

Analytical results have been obtained which verify the qualitative observations and conclusions presented in the last summary. A melt of 4% sodium sulfate in sodium carbonate (corresponding to 0.9% sulfur in melt) at 1740° F, which had been treated with anthracite and stirred with 0.5 ft./sec. nitrogen, was subjected to gasification conditions and samples of the melt were analyzed for sulfide sulfur and sulfate sulfur at each condition.

| -- Melt Analyses -- | | | |
|---------------------|--|-------------------|-------------------|
| Time Min. | Condition | Sulfide Sulfur | Sulfate Sulfur |
| -- | CO ₂ replaced N ₂ | 0.54 | 0.15 |
| -- | Air replaced CO ₂ - 5 min. | 0.00 | 0.87 |
| 0 | Steam replaced air, anthracite added (zero time) | | |
| 5 | Gasification | 0.65 | 0.17 |
| 15 | " | 0.59 | 0.19 |
| 30 | " | 0.67 | 0.19 |
| 45 | " | 0.73 | 0.15 |
| 75 | " | 0.34 | 0.58 |
| 95 | " | 0.00 | 0.90 |

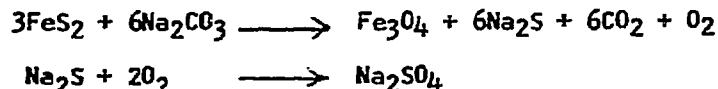
The analytical results show that air oxidizes sulfide to sulfate extremely fast, that carbon rapidly reduces sulfate to sulfide under gasification conditions with a large excess of steam, and upon depletion of the carbon and in the presence of steam reoxidation of sulfide to sulfate occurs. The presence of a constant amount of sulfate, about 20% of the total sulfur, during gasification may be real or may be due to air oxidation while removing the sample from the melt and reactor. All the sulfur appears to stay in the melt and none is lost to the gas phase.

Thus, it is concluded from the above and other results that sulfur in the gasifier and combustor of the process will be present as sulfide and sulfate, respectively.



2. Disposition of Pyrites in Melt:

Pyrites, FeS_2 , will enter the melt since it is present in the raw coal. A melt of 5% pyrites in sodium carbonate was heated to $1840^{\circ}F$ in an alumina tube with pure carbon dioxide at 0.5 ft./sec. superficial gas velocity. The melt was sampled and analyzed. A part of the sample was qualitatively found to be high in sulfide sulfur and low in sulfate sulfur. It is believed the following reactions took place:



The black color of the melt suggested the presence of magnetite, Fe_3O_4 . Formation of sulfate occurred internally from the sulfide and oxygen.

It is concluded that pyrites will yield sulfide in the gasifier and that the iron as magnetite will ultimately show up in the ash removal section.

3. Oxidation of Sulfide in Melt by Steam - Carbon Dioxide:

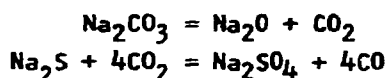
The oxidation of sodium sulfide in a sodium carbonate melt by a one to one ratio of steam to carbon dioxide has been mentioned in prior summaries. Precautions to prevent oxidation of the sample by impure gases or air have been made and now the elimination of any effect of the Inconel reactor by use of a McDanel pure alumina reactor and gas inlet tube has been done. A melt of 5% sodium sulfide in sodium carbonate at $1840^{\circ}F$ with pure nitrogen at 0.5 ft./sec. for agitation was sampled, then the nitrogen was replaced with a 1/1 mixture of purified steam and carbon dioxide and samples of the melt taken after 0.5, 1 and 2 hours. Although quantitative results are not available as yet, qualitative tests for sulfide and sulfate are given in the following table.

| <u>Time - hours</u> | <u>Qualitative for (1)</u> | |
|---------------------|----------------------------|----------------|
| | <u>Sulfide</u> | <u>Sulfate</u> |
| 0 | ++++ | + |
| 0.5 | +++ | ++ |
| 1 | ++ | +++ |
| 2 | + | ++++ |

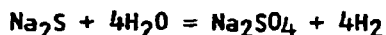
(1) Higher concentration with increasing number of +.



The results indicate that some sodium sulfide is oxidized by the carbon dioxide which results from decomposition of sodium carbonate, according to the following equations:



The oxidation is slow but continues with the constant removal of the product gases with nitrogen. Introduction of steam which carbon dioxide appears to increase the oxidation rate somewhat, probably by the following reaction:



Constant removal of the hydrogen by the excess steam-carbon dioxide accounts for the continual increase in oxidation of the sulfide to sulfate which is still a relatively slow reaction. In the gasifier, the presence of carbon in the melt will maintain the sulfur in the sulfide form.

4. Recovery of Sulfur:

Details were given last month of the method for recovery of sulfur. A preliminary search of the literature revealed that commercial units are in operation which recover sulfur by the Claus Process on a gas of 10 to 20% hydrogen sulfide in carbon dioxide (Chemical Engineering, April 1, 1963, pg. 38). This composition should be easily obtained in the final part of carbonation of the sodium carbonate-bicarbonate-sulfide filtrate from ash removal.

B. Projections

1. Ash Removal Studies:

In cooperation with Mechanical Development, a reactor set-up will be assembled to enable continuous gasification studies to be carried out at about 1800° F. The melt in the reactor will be allowed to build up to about 8% ash and 4% carbon at which time it will be frozen. The solid melt will be ground and an appropriate amount will be used to study ash removal, sodium recovery and sulfur recovery with an actual, rather than simulated, melt.



III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

1. Flowsheet Studies:

The flowsheet calculations and equipment sizing for the synthesis gas plant have been completed and a capital cost estimate is being prepared. Also the flowsheet for the hydrogen-from-coal plant has been completed and will be drafted in final form.

2. Pilot Plant Design:

Work has continued on updating the pilot plant flowsheet in preparation for a process release.

B. Projections

1. Flowsheet Studies:

The estimation of equipment cost for the synthesis gas plant should be completed and on the gas cost will be calculated. All of this information will be presented together in the form of a complete process package. Also the final flowsheet for the hydrogen-from-coal plant should be completed and will be presented with the material balances and utilities requirements. The costs for this process have been previously given in Progress Report No. 33.

2. Pilot Plant Design:

Work will continue on updating the pilot plant flowsheet and preparing equipment load sheets so that a process release can be made.



IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Mechanical Characteristics Testing:

Some preliminary tests conducted in the plastic model described last month indicated a good circulation pattern with no obvious problems occurring. The visual observations indicated a relatively high degree of mixing and good pumping action in both vessels and the lift lines.

Due to the short work period this month caused by vacation shut down, no further observations have been made.

2. Corrosion Testing of High Temperature Materials:

A machine to cut the Monofrax "A" samples to be used in these tests was obtained and partially installed during this period. No further testing has been started, as it is necessary to prepare new specimens before testing can resume. With this new machine, specimen preparation will be easier and faster than in the past.

B. Projections

1. Mechanical Characteristics Testing:

Some further observations as to the circulation in the test model will be made.

2. Corrosion Testing of High Temperature Materials:

Testing of Monofrax "A" will resume as soon as new specimens can be prepared. The testing of INSULAG as a thermal insulation behind the Monofrax "A" will begin as soon as its test facility can be completed.



V. MANPOWER AND COST ESTIMATES

Figure 1 shows the projected breakdown for Phase 1 for 1967 as well as the actual effort that was made. It can be seen that a 6.8 man-effort was made during July. The reduced level of effort is due to the Laboratory shut-down for the last two weeks of the month.

Figure 2 shows the expenditures during July. For the month \$12,827 was expended, not including fee and G & A. The total expenditures through July were \$707,845. Including fee and G & A, the total expenditures were \$807,363. This is 74% of the encumbered funds.

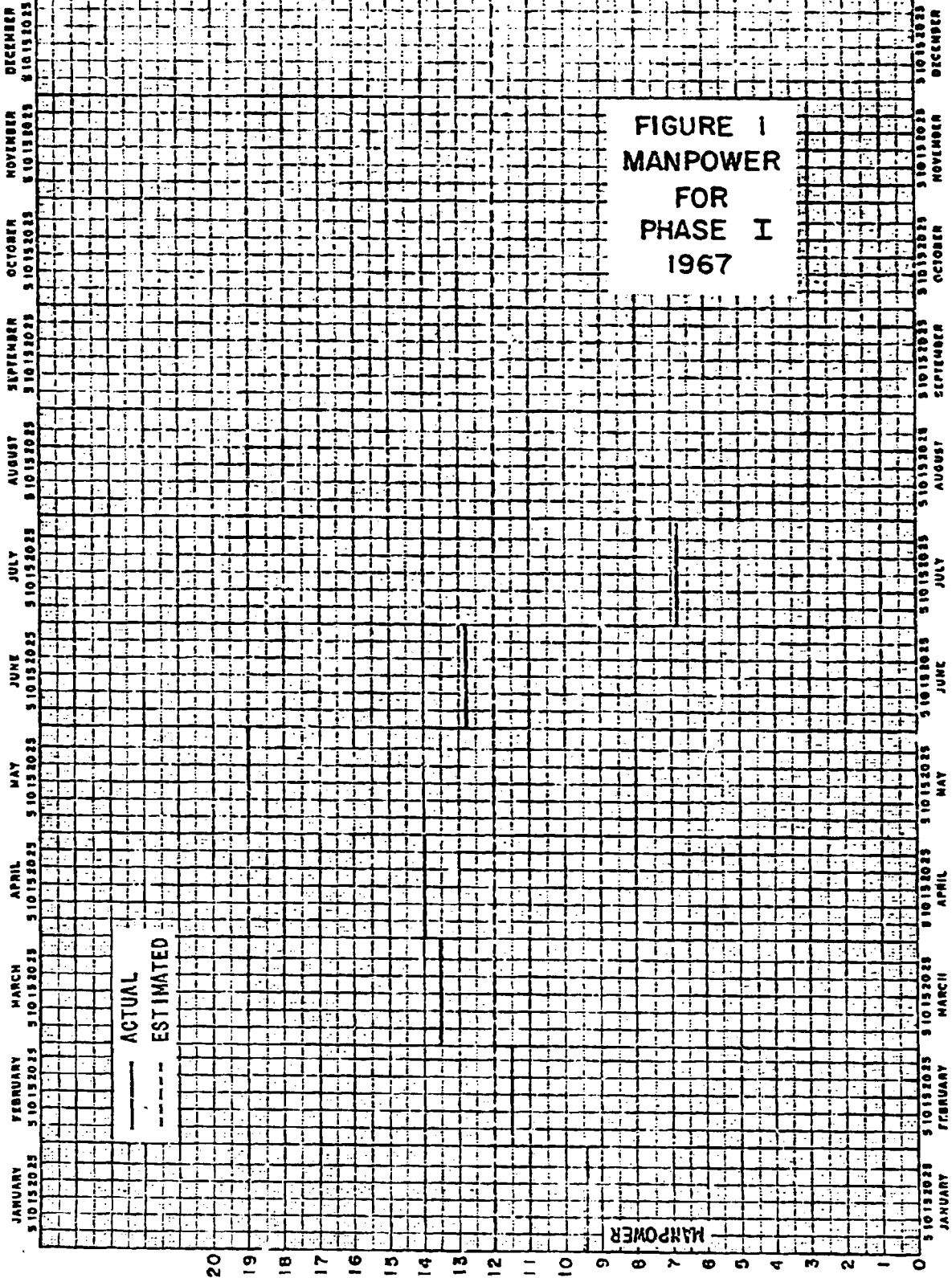


FIGURE I
 MANPOWER
 FOR
 PHASE I
 1967

MANPOWER

