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RESEARCH AND DEVELOPMENT DEPARTMENT

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

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I. SUMMARY

This Progress Report is the thirty-fifth 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 studies: Process Research, Chemical Engineering Studies, and Mechanical Development.

An attempt was made to study the affect of carbon dioxide and steam mixtures and their pressures on the solubility of silica in a sodium carbonate melt. The partial pressures of both gas phase components appear to affect silica solubility, but additional data will be obtained to determine the relationships more fully.

One atmosphere of carbon dioxide was found to completely prevent solubilization of either bituminous or anthracite ash in sodium carbonate at 1840°F. When nitrogen was used in place of carbon dioxide, the freezing point of the melt dropped substantially (indicating that ash was dissolving.) However, when the carbon dioxide was switched back, the freezing point rose back to its initial value, thereby precipitating the ash back out of solution.

Since preliminary experiments indicated that sodium sulfate may build up to rather high concentrations in the ash removal step, an experiment was run to determine whether this material could be selectively crystallized out from the bicarbonate solution. The results proved negative indicating that such techniques will not allow sodium sulfate to be removed from the system.

In an attempt to determine the predominant form of sulfur in the gasifier, an experiment was carried out in which sodium sulfate was charged to a sodium carbonate melt and sampled. Following this, a charge of anthracite was added and samples taken. The results indicate that essentially all of the sulfate was converted to sulfide by carbon reduction within one hour. When air was added to the melt, the sulfide was almost immediately converted back to sulfate. When steam was added, to the sulfide-containing melt, a slow conversion back to sulfate occurs as the carbon level decreases. No sulfur-containing gases were detected during any of the above operations.

Another experiment was conducted to determine the disposition of sodium sulfide during carbonation. The results indicated that practically all the sulfur is liberated in the form of hydrogen sulfide.

An attempt was made to further confirm the earlier finding that steam and carbon dioxide oxidize sulfide to sulfate in a carbonate melt. Great precautions were taken to insure that no oxygen was present in the feed gases. The results indicated that there is indeed a slow, but steady, oxidation of the sulfide to the sulfate.

The Status Report and Proposal were completed and forwarded to the OCR.

Some process revisions were made to the Ash Removal section of the pilot plant to allow for a concentration of the quench solution prior to the ash filtration step. Tests had indicated that a more concentrated ash slurry was desirable for filtration. These changes have been made with little, if any, effect on the process.

Work on the preparation of the Process Release was begun, and the process design of the synthesis-gas-from-coal plant has been resumed.

A plastic model of the pilot plant gasifier-combustor has been constructed. The purpose of this model is to enable process simulations to be made to allow visual observation of the internal circulation within the vessels. Such information will help to insure that proper deaerating space is provided in the regions of melt withdrawal and that there is sufficient agitation in the melt.

Corrosion test #12 of Monofrax A, a simulated gasification test, was terminated at 515 hours. The average corrosion rate for this period was 0.276 in./yr., with a maximum of 0.423 in./yr. measured across a pitted surface which prevented precise measurement. Surface pits were found in the sides of the specimens which had been on the outside surface of the original block. These pits were found to be extensions of bubbles which were originally present in the block as a result of casting. Similarly, several cracks were also present in theoriginal samples which were enlarged somewhat by the action of the melt. A sample of diamond cut Monofrax has been obtained, free from such flaws, and will be used in further tests. It is anticipated that this sample should show much lower rates of corrosion.

II. PROCESS RESEARCH

A. Accomplishments

1. Additional Study of Na_2Co_3- SiO_2 Melt under Pressure

The attempt was made to study the effect of pressure of carbon dioxide and steam on solubility of silica in a melt of 8% silica in sodium carbonate at 1840°F and two atmospheres total pressure. The following results were obtained and are compared to others reported last month.

Melt	P_{CO_2} (atm.)	P_{H_2O} (atm.)	°F Freezing Point Lowering over Pure Na_2CO_3
Na_2CO_3	0.5	0.5	46
8%SiO_2 in Na_2CO_3	0.5	0.5	84
8%SiO_2 in Na_2CO_3	1.0	1.0	44
Na_2CO_3	1.5	0.5	26
8%SiO_2 in Na_2CO_3	1.5	0.5	65, 42

In the first series with a 1 to 1 ratio of carbon dioxide to steam, an increase in total pressure to two atmospheres eliminated the solubilization of silica. However, two atmospheres of total pressure did not eliminate silica solubilization when the carbon dioxide content of the gas was increased. At this time the effect of the pressures of carbon dioxide and steam on solubility of silica in sodium carbonate melts cannot be defined and will have to be redetermined.

2. Effect of Ash on Na_2CO_3 Melts

Bituminous coal ash at the 8% level was mixed in Na_2CO_3 and held at 1840°F for 1 hour in 1 atmosphere of carbon dioxide. The freezing point was the same as pure sodium carbonate indicating no solubilization of any ash components had occurred. When nitrogen replaced the carbon dioxide and afte 3.5 hours, the freezing point was lowered 37°F showing some ash had dissolved. After replacing the nitrogen and blowing carbon dioxide through the melt for one hour, the freezing point returned to that of pure sodium carbonate.

With an 8% anthracite ash in sodium carbonate melt the results were quite similar. One atmosphere of carbon dioxide was sufficient to prevent solubilization, but in N_2 after 2, 4, and 6 hours the freezing point lowerings were 21, 55, and 62°F, respectively, showing the slow but steady solubilization of ash. One atmosphere of carbon dioxide was enough to precipitate the dissolved ash out of solution.

3. Disposition of Sulfur in Process

Although the complete determination of the disposition of the sulfur (in coal) in the process has not as yet been fully determined, very good indications are now available. In addition, considerable work has been done on the removal of sulfur from the system. As soon as an exhaust system over the laboratory reactor is installed, coal will be able to be fed to a melt to determine the extent of sulfur uptake by the melt.

Coal contains essentially three types of sulfur compounds - pyrites (FeS_2), organically bound sulfur and some sulfur as sulfate. One would expect the sulfate sulfur to enter the melt directly as sulfate; pyrites to react with sodium carbonate to form sodium sulfide; the organic compound-containing sulfur to be thermally decomposed and further attacked by the steam. It is felt that this sulfur will ultimately become sodium sulfide and perhaps a small amount will escape from the melt as carbonyl sulfide and/or hydrogen sulfide. With about four percent carbon present in the melt, the sulfate sulfur should reduce to sulfide. As soon as this melt enters the combustor, the sodium sulfide should be immediately oxidized to sodium sulfate. The present flow sheet calls for ash removal from the melt exiting from the combustor. Thus the initial work was done on sodium sulfate in the melt.

a. Crystallization of Sodium Sulfate in Ash Removal Section

Some preliminary experiments established that sodium sulfate would build up to a fairly high concentration in the sodium carbonate-bicarbonate solutions. A solution was prepared at 190°F which simulated the filtrate after removal of the ash; this solution contained 6.7% $NaHCO_3$, 10.6% Na_2CO_3, and 14.9% Na_2SO_4. The solution was cooled to 85°F, a solid filtered off in hopes that it would be sodium sulfate but it turned out to be sodium bicarbonate. It was concluded that crystallization techniques would not allow excess sodium sulfate to be removed easily.

b. Behavior of Sodium Sulfide in Ash Removal Section

First it was necessary to prove that sodium sulfide would be the major sulfur compound in the melt from the gasifier. A sample of a frozen melt containing 8% ash and 4% carbon made at 1900°F was found to contain mainly sulfide sulfur and a trace of sulfate sulfur. The sulfur introduced in the ash was mainly sulfate, thus the carbon must have reduced the sulfate to sulfide in the melt.

A direct determination was made by preparing a melt of 4% sodium sulfate in sodium carbonate at 1740°F. This melt was sampled, then 4% carbon as anthracite was added and the melt sampled at 5, 10, and 55 minutes. Nitrogen was bubbled through the melt at all times. Gas samples were analyzed for sulfur compounds by gas chromatography. The gas analyses did not detect any sulfur compounds present. Qualitative analysis on the melt samples showed sulfate to be strongly present in the first sample, as expected, before the carbon addition and only a trace present in the 5, 10, and 55 minute samples; sulfide was not present in the original sample but present to a large extent in the other samples. This quite conclusively established that sulfate is easily and quickly reduced to sulfide by carbon in the melt.

Experiments were continued on the melt from above to establish the disposition of sulfur during gasification. Steam and carbon were reacted, samples of melt and gas analyzed as shown in the following tabulation.

Time-min	Note	Qualitative Melt $S^{=}$	Test $SO_4^{=}$ *	Gas Analysis - % CO_2	CO	H_2	N_2
-	CO_2 in	+++	+	71	29	-	-
-	Air in for 5 minutes	-	++++	1.2	-	-	80
0	Steam in 5 minutes, then anthracite added (time zero)						
5	Gasification	+++	+	23.0	15.0	53.5	8.5
15	Gasification	+++	+	25.0	10.0	51.5	13.5
45	Gasficiation	+++	+	23.0	4.0	50.0	23.0
75	Gasification	+++	++	15.5	1.0	41.5	42.0
95	Gasification	++	+++	13.5	1.0	37.5	48.0
110	End, freezing point 1306°F						

These results show that air oxidizes sulfide to sulfate extremely fast, that carbon does reduce sulfate to sulfide during gasification even in the presence of a large excess of steam but that as the carbon becomes depleted, the steam and/or carbon dioxide tends to reoxidize the sulfide to sulfate (qualitative test only). Although all gas samples were analyzed for sulfurous gases, none were detected at any time. The level of detectability was 0.01 to 0.1%

Consideration was now given to what would happen to the sodium sulfide in the ash removal-sodium recovery section. Initially, the melt is quenched and the sodium compounds dissolved in a 7-9% sodium bicarbonate solution from which the ash is removed by filtration. The next operation is carbonation to convert the dissolved sodium carbonate to bicarbonate. Preliminary qualitative experiments quickly established that solutions of sodium sulfide with and without the presence of sodium bicarbonate or carbonate liberated hydrogen sulfide when treated with carbon dioxide. A literature study verified this. A solution of 7.8% sodium bicarbonate, 13.7% sodium carbonate, and 2.6% sodium sulfide was prepared at 150°F and carbon dioxide bubbled in through a sparger in a graduate. Hydrogren sulfide was liberated over a period of 2.5 hours even after all the sodium carbonate had been converted to bicarbonate and all the excess bicarbonate precipitated out of solution. The final solution showed practically all the sulfide had been liberated. This indicated a quantitative experiment should be performed.

*In a qualitative manner, the number of plus signs indicates the amount of the component present.

Using the flowsheet for the pilot plant (4/18/67) and the sulfur content of our bituminous coal it was calculated that about 1% sulfur was present in the melt going to the ash removal-sodium recovery section. The filtrate from the ash removal filter was then calculated to contain 78.2% H_2O, 7.7% N_aHCO_3, 13.7% Na_2CO_3, and 0.4% Na_2S. A solution weighing a total of 469 grams simulated the above filtrate composition. With an inlet meter to measure CO_2 gas in and an outlet meter (kerosene filled) to measure CO_2 and H_2S out a rate of sulfur removal under carbonation conditions with the above solution was obtained - gas analysis for H_2S were made every five minutes on the outlet gas from the carbonation tower. The uptake of carbon dioxide and the evolution of hydrogen sulfide placed on an outlet basis are shown in Figure 1.

The significant break in the hydrogen sulfide curve represents the point at which most of the carbonate had been converted to bicarbonate and the carbon dioxide was now displacing the bulk of the sulfide. This is further substantiated by the break in the carbon dioxide curve.

These data suggest that the carbonation tower should be run almost to the break in the H_2S curve in order to recycle the carbon dioxide with a low concentration of hydrogen sulfide. This solution should then be further carbonated in a separate zone to complete the precipitation of sodium bicarbonate and drive off the majority of the hydrogen sulfide to give a high enough concentration of hydrogen sulfide in the exit gas which will aid its separation from the carbon dioxide. Although the final solution contains a low concentration of sulfide it will be recycled to the quench zone thus causing no difficulties. Methods of removal of hydrogen sulfide from carbon dioxide will be literature searched before experimentation.

c. Oxidation of Sodium Sulfide by Steam-Carbon Dioxide

As reported last month, it was indicated that steam-carbon dioxide oxidized sulfide to sulfate in a carbonate melt. Further verification of this was obtained by a similar experiment. In case oxygen from the gases, although of high purity, or from the freezing of the melt sample in air may have caused the oxidation, greater precautions were taken. The hydrogen, nitrogen, and carbon dioxide gases were passed through a copper deoxygenator, the water deaerated completely before use and the melt samples taken into a carbon dioxide atmosphere. Over a three hour period with 50/50 steam/carbon dioxide passing into a 5% sodium sulfide in sodium carbonate melt, melt samples progressively showed higher sulfate and lower sulfide content. The reaction does not appear to be fast. It is possible that the Inconel reactor may play a role in this behavior. Thus the experiment will be repeated using a McDanel alumina refractory tube in place of Inconel.

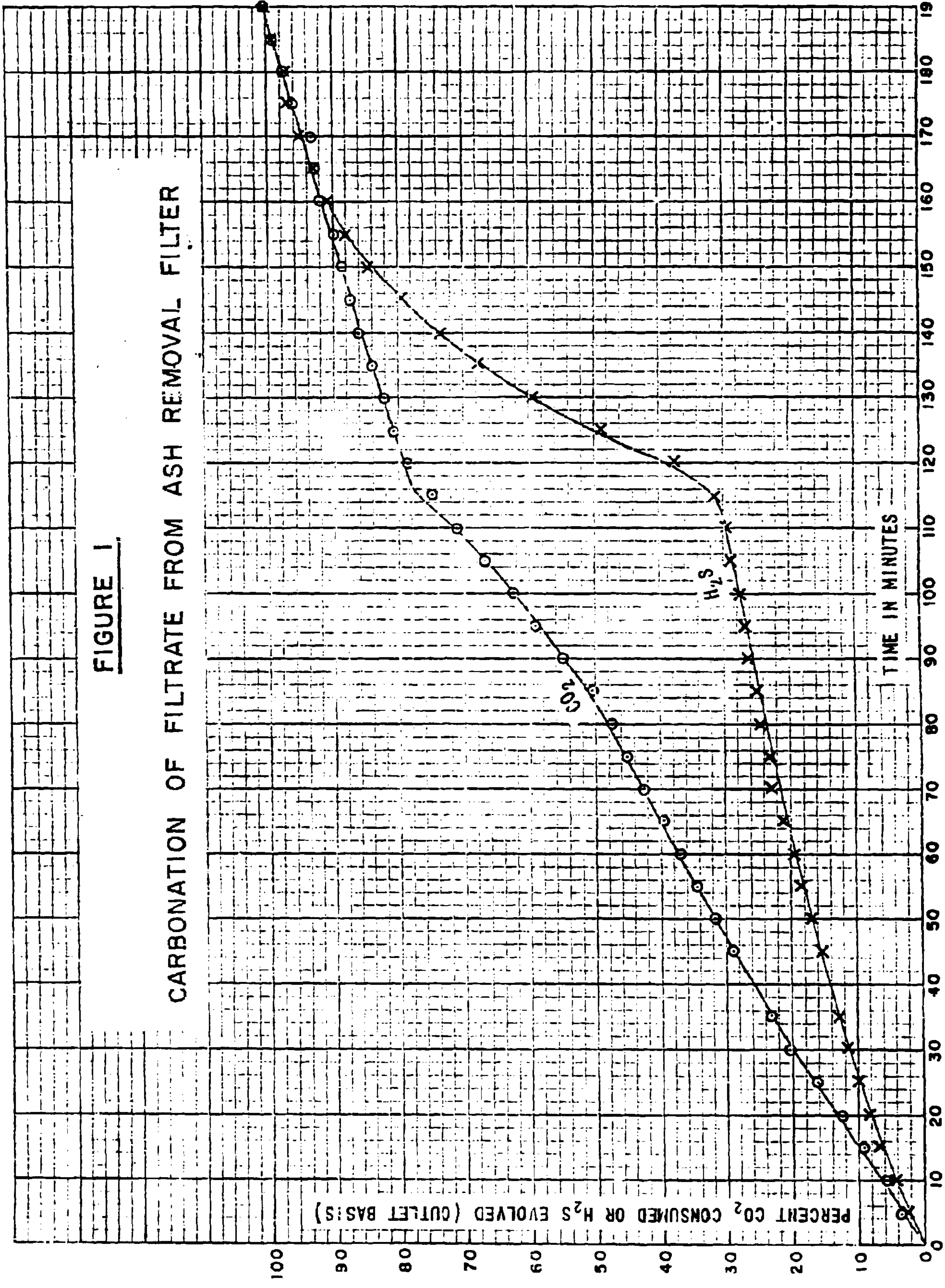

FIGURE I

CARBONATION OF FILTRATE FROM ASH REMOVAL FILTER

B. Projections:

The following remain to be investigated:

1. Does all the coal sulfur stay in the melt when coal is bottom fed during gasification?

2. Is sodium sulfide in the melt oxidized by steam-carbon dioxide?

3. When pyrites, FeS_2, is reacted with a melt, what is the chemistry?

4. Prepare 8% ash, 4% carbon, 1% sulfur in a melt at 1900°F in an alumina tube to eliminate contamination from Inconel. Study ash removal, sulfur removal and sodium recovery. This could also be done by starting from coal and gasifying until the ash is built up in the melt.

5. Investigate sulfur recovery methods for 2-10% hydrogen sulfide in carbon dioxide.

6. Effect of steam-carbon dioxide pressure on the solubilization of silica and alumina in molten salt.

III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

1. Pilot Plant

The Status Report and Proposal were completed and forwarded to the OCR during June.

Process revisions were made to the Ash Removal section of the pilot plant to allow for a concentration of the quench solution prior to the ash filtration step. Tests run by a filter manufacturer (Eimco) indicated that filtration rates could be greatly enhanced by increasing the ash content of the solution to the filter from the previous two percent level to about 30 percent. This has been accomplished using a pre-filtration thickener and will not result in an appreciable cost change in this section.

Work has begun to prepare process load sheets for inclusion in the final pilot plant Process Release.

2. Flowsheet Studies

Work on the process design of the synthesis gas plant, temporarily suspended due to the press of preparing the Proposal and Status Report, has been resumed.

B. Projections

1. Pilot Plant

Work on the Process Release, with particular emphasis on the preparation of load sheets, will continue.

2. Flowsheet Studies

Process design of the synthesis gas plant will proceed. In addition, work will commence to complete the hydrogen flowsheet so that the "process package" for hydrogen can be completed.

IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Mechanical Characteristics Testing

A transparent plastic model of the proposed pilot plant gasifier-combustor has been constructed. This model, when operated with materials simulating the properties of the molten salt, will allow visual observation of the internal circulation within the vessels. Information of this sort is needed to insure that proper deaerating space is provided in the regions of melt withdrawal, and that there is sufficient agitation in the molten bed itself. Some observations will also be made as to the overhead space required to minimize melt carry-over from the vessels into the gas outlet piping.

2. Corrosion Testing of High Temperature Materials

Corrosion Test #12 of Monofrax A was terminated at 515 hours during this report period, and the specimens examined. The average corrosion rate for the 515 hours was found to be 0.276 in./year, with a maximum of 0.423 in./year measured across a pitted surface which prevented precise measurement. Rather severe surface pits were found in the sides of the test specimens which had been the outside surface of the original Monofrax block. These pits, on further examination, were found to have started as small "bubbles" which had been formed when the ceramic was cast; the molten salt penetrated these and enlarged them, but caused no pitting unless these bubbles were present initially. Several small cracks that were present in the samples prior to testing were found to have been enlarged by the action of the molten salt, but not enough to endanger the integrity of the block.

This test verifies the premise that it is important to have Monofrax A that is as free from flaws, both voids and cracks, as possible. To this end, a sample Diamond Cut Lug (DCL) block of Monofrax A has been obtained, and will be used for further tests. This version of Monofrax A is free from internal defects that have been present in all specimens of this material tested to date. To insure the soundness of future test specimens, they will be ultrasonically inspected prior to testing.

B. Projections

1. Mechanical Characteristics Testing

Visual observation of flow patterns obtainable in the simulated reactor will be made to check circulation and general operation.

A test facility will be constructed to investigate the possibility of using a slip-joint in molten salt at process temperature. This construction is proposed for use in the pilot plant, and must be evaluated as to realiability.

2. Corrosion Testing of High Temperature Materials

Testing of Monofrax A will continue, using DCL specimens that have been ultrasonically inspected for soundness. In addition, a program will be started to investigate the suitability of INSULAG as a thermal insulation behind the Monofrax A. This program will involve primarily the investigation of INSULAG'S strength at temperature, and its susceptibility to crushing due to repeated thermal cycling.

V. MANPOWER AND COST ESTIMATES

Figure 2 shows the projected breakdown for Phase 1 for 1967 as well as the actual effort that was made. It can be seen that a 12.8 man-effort was made during June. Figures for May have been revised to include charges which were erroneously omitted from May's billing.

Figure 3 shows expenditures during June. For the month $21,664 was expended, not including fee and G & A. The total expenditures through June were $695,018. (Again, figures for May have been adjusted to include the previous omission.). Including fee and G & A, the total expenditures were $792,230. This is 72% of the encumbered funds.

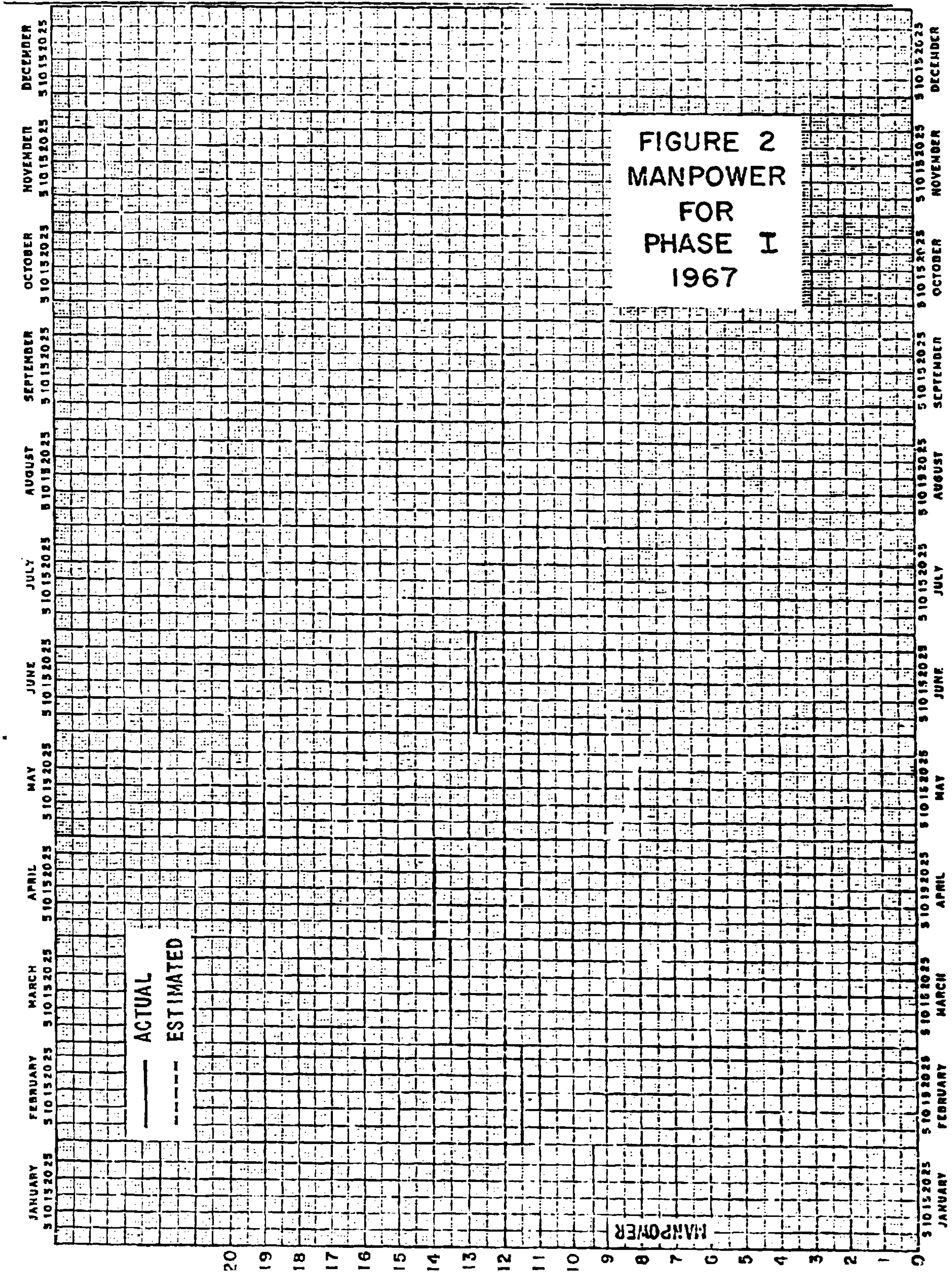

FIGURE 2
MANPOWER
FOR
PHASE I
1967

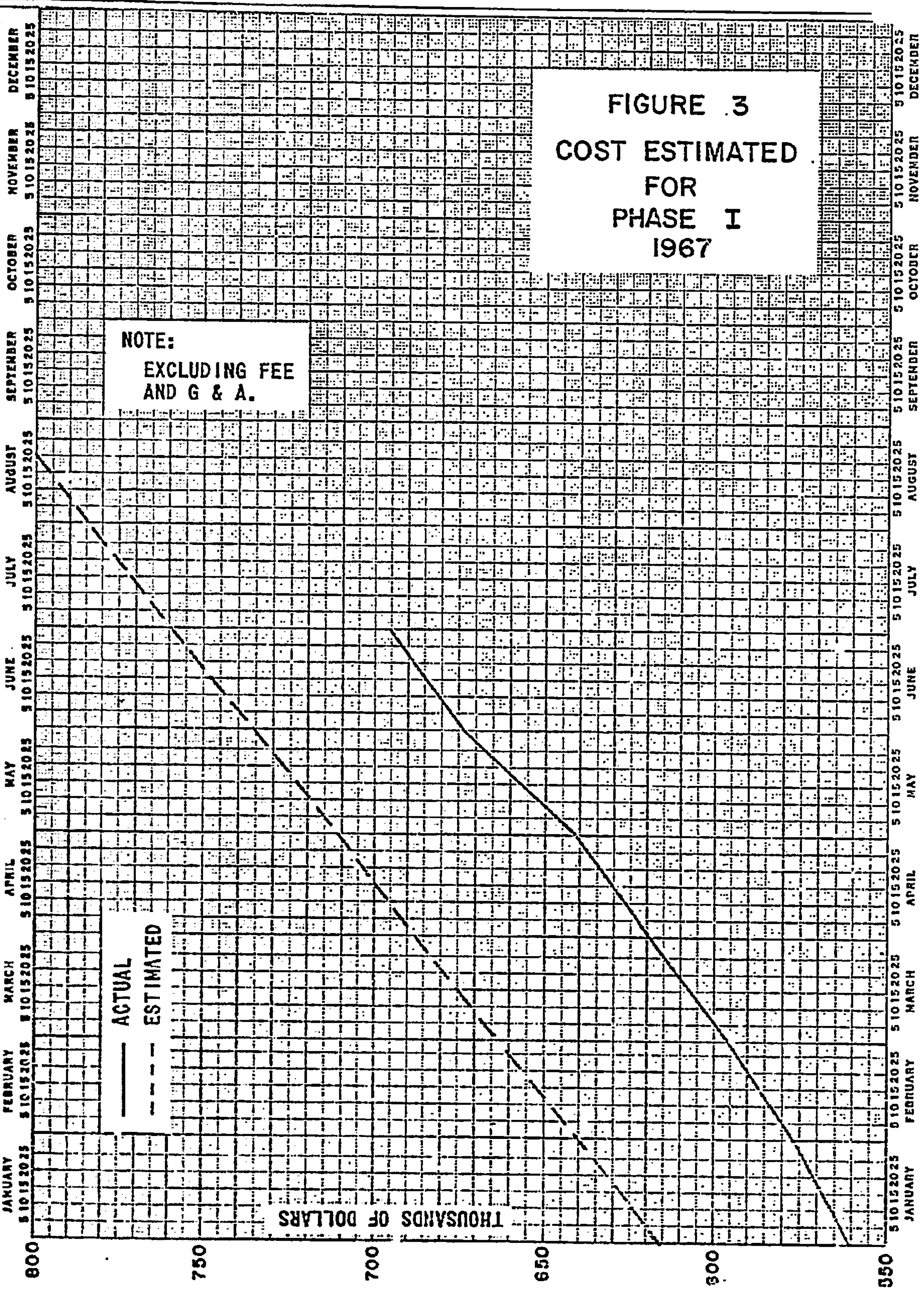

FIGURE 3
COST ESTIMATED
FOR
PHASE I
1967

NOTE:
EXCLUDING FEE
AND G & A.