139886

AMERICAN CYANAMID COMPANY
CALCO CHEMICAL DIVISION

PINEY RIVER PLANT

ACID RECOVERY PILOT PLANT

Stephen A. Lamanna

March 14, 1949

200002

AMERICAN CYANAMID COMPANY
CALCO CHEMICAL DIVISION
PINEY RIVER PLANT

ACID RECOVERY PILOT PLANT

Stephen A. Lamanna

March 14, 1949

200003

AMERICAN CYANAMID COMPANY
CALCO CHEMICAL DIVISION
PINEY RIVER PLANT

Mr. C. J. Kirkland

Typed: March 14, 1949

Stephen A. Lamanna

WASTE ACID RECOVERY PILOT PLANT

This report summarizes all the data obtained during the operation of a waste acid recovery pilot plant by the Chemical Construction Corporation at Piney River, Virginia.

The writer was assigned to the project as an observer and consultant. The writer's duties were to keep in contact with the work being done and see to it that the Chemical Construction Corporation personnel received the necessary cooperation to expedite their development work.

Our records show no delay in acid recovery development work due to lack of service from the Piney River Plant service departments.

This report is divided into three sections as follows:

Section I
Pilot Plant Operation
October 7, 1947 through May 22, 1948.

Section II
Pilot Plant Operation
September 14, 1948 through November 15, 1948

Section III
Cost Estimate for the Production of 70% Sulfuric Acid from Dilute Waste Acid.

Stephen A. Lamanna

/ow

Copies to: Mr. A. B. Hettrick
Dr. W. J. Cauwenberg
Mr. L. L. Hedgepeth
Mr. E. Hladky
Mr. V. L. King
Mr. C. J. Kirkland
Technical Files
(File) 2

200004

WASTE ACID RECOVERY PILOT PLANT

SECTION I

AMERICAN CYANAMID COMPANY
CALCO CHEMICAL DIVISION

PINEY RIVER PLANT

June 1, 1948

Mr. C. J. Kirkland

Stephen A. Lazzarra Typed: March 14, 1949

WASTE ACID RECOVERY PILOT PLANT

This report summarizes the operation of a waste acid recovery pilot plant at Piney River, Virginia by the Chemical Construction Corporation during the period beginning October 7, 1947 through May 22, 1948.

The purpose of the project was to develop a process utilizing submerged combustion type concentrators and a Dwight-Lloyd sintering machine to recover the acid value from the weak sulfuric acid solutions and ferrous sulfate rejected from the titanium dioxide process. It is also proposed that the process when established could be used to recover the acid values from steel mill pickle liquor wastes.

The proposed process involves the following process steps:

1. Low Stage Concentrator
Concentration of the weak acid to 60 - 70% H_2SO_4. At this concentration, all but less than 1% of the $FeSO_4$ in the acid solution is precipitated as $FeSO_4.H_2O$.

2. Filtration
Filtration of the acid - $FeSO_4.H_2O$ slurry discharged from the low stage concentrator. The filtrate is fed to a high stage concentrator and the monohydrate is conveyed to storage.

3. High Stage Concentrator
The filtered acid (60 - 70% H_2SO_4) is concentrated to 93% H_2SO_4. The concentrated acid is cooled and stored.

4. Pelletizer
Bins containing $FeSO_4.H_2O$, coal, pelletizer fines and sinter fines discharge on disc feeders into a screw conveyor which mixes and conveys to a rotary horizontal shaft pelletizer. The pellets are screened and the accepted pellets are conveyed to pellet storage. Pellet fines are returned to pelletizer feed.

5. Sintering
The accepted pellets are sintered on a Dwight-Lloyd sintering machine. A hearth layer will be used to extend pallet life. The sintering machine will produce gas containing 7.0 - 7.5% SO_2 which will be fed to a contact unit and converted to sulfuric acid.

The process includes a scrubbing tower and coke box to remove entrainment from the exhaust gases from the concentrators. Gases from the sintering machine are passed through a water scrubbing tower and coke box. The gas is cooled and mist removed. A flowsheet of the pilot plant installation as of May 22, 1948 is included in this report.

The concentration section of the proposed process was developed into a very satisfactory operation. Heat efficiency on concentration was high and most of the filtration difficulties were worked out. Considerable difficulty was encountered with the pelletizer and it was decided to shut down the pilot plant and do more basic work on some other form of pelletizing. Preliminary work on a small scale indicated that the sinter mix could be extruded, forming very good pellets. A short run on the sintering machine indicated that if good pellets could be made, no difficulty would be encountered in producing an acceptable gas. (7.0 to 8.0% SO_2).

During the operation of the pilot plant, approximately 7000 gallons of 93% sulfuric acid was produced. This acid was analyzed and a complete analysis with a comparative analysis of our contact plant acid is included in this memorandum. The Research Department made digestions using 30% recovered acid and 70% new acid. They reported a pigment of 89 Y 1 color produced when utilizing the recovered acid while a check digestion using new acid produced a pigment with 92 B 1 color. The concentrated acid contained colloidal matter which on standing appeared to partially settle forming a hard cement-like mass. Liquor from pilot plant digestions, utilizing recovered acid, when concentrated appear to have the same type of colloidal matter suspended in it. This colloidal matter is not removed when the liquor is clarified by the usual process used in the titanium dioxide process.

An operation diagram representing average results obtained on several runs is included. Results indicate that the process has high heat efficiency and high recovery when concentrating the weak acid up to 70% H_2SO_4. Heat efficiency and recovery drop when concentration is carried higher than 70% H_2SO_4. Minor changes in design can be made to increase heat efficiency and recovery higher than is shown on the operation diagram if it is found necessary to concentrate up to 93% H_2SO_4.

Mr. C. J. Kirkland

March 14, 1949

ANALYSIS OF RECOVERY PLANT SAMPLES

	H_2SO_4	$FeSO_4$	Fe_2O_3	TiO_2	Cr_2O_3	V_2O_5	MnO
Weak Acid From Low Stage	65% Approx.	0.70	-	.0018	0.012	0.054	0.052
Wash Water From Filter	-	14.1	-	0.34	0.024	0.044	0.10
Filter Cake	-	50.2	-	2.48	0.071	0.22	0.56
93% Recovered Acid Centrifuged	93.0	-	<.03	0.012	.0073	0.012	0.077
Recovery Acid Used For: Pilot Plant Digestion #463	90.4	-	-	-	0.012	0.013	0.069
Digestion #464	86.4	-	-	-	0.012	0.011	0.052
Contact Plant Acid	93.0	-	-	-	<0.001	0.003	<0.001

200008

General information on operation, operating results, equipment maintenance and equipment changes on each step in the process is as follows:

Low Stage Concentrator

The low stage concentrator was started on October 7, 1947. From October 7, 1947 to April 1, 1948, all development work was devoted to the operation of the low stage concentrator and the Oliver filter.

The electrical spark ignitor used to ignite the oil in the concentrator worked efficiently from the start. The original design called for fixed electrodes. A retractable installation was made to remove the electrodes from the flame after ignition, thus extending the life of the electrodes. This type of installation was made on both the low stage and the high stage and no difficulties were encountered throughout the entire run.

Acid concentrations were varied from 45% H_2SO_4 to 70% H_2SO_4. It was found that optimum results were obtained when operating between 65 - 70% H_2SO_4. The precipitated $FeSO_4.H_2O$ crystals were easy to filter and wash. A run was made concentrating the acid to 80%, but difficulty was encountered with the filter cloth. In most of the pilot plant work, end liquor as discharged from the titanium plant was used as feed to the pilot plant. Several runs were made using an H_2SO_4 - $FeSO_4$ slurry which would represent the type of acid recovery plant feed if all the copperas from crystallization were added to the end liquor. The higher $FeSO_4$ content improved the filtration results and did not seem to affect the operation of the concentrator.

The original combustion chamber in the concentrators was made up into two sections each approximately 36 inches high. The upper section was made of stainless steel and the lower section which was immersed in the acid being concentrated was made of Hastelloy "D". The whole chamber was lined with 2 inches of zirconium silicate rings. A 1 inch lip on the lower end of the Hastelloy "D" supported the refractory.

The concentrator was equipped with a Schute-Koerting burner. Two tips were used for this burner, one supplying 100 pounds oil per hour and the other 205 pounds oil per hour. In all cases, combustion was not complete. Air was varied to give optimum combustion. While this burner was in use, the concentrated liquors contained a carbon scum which affected the operation of the filter. A check was made on the required combustion volumes for oil and it was shown that the concentrator combustion chamber volume was lower than all specifications available. (Specifications from U. S. Navy, Hauck Combustion Engineers, Trinks Industrial Furnaces). The Chemical Construction people felt that they had adequate combustion volume and no change was necessary at the time. Flame-back of the flame was

noticed and the size of the entrance venturi to the chamber was reduced to increase the air velocity. This change eliminated the flare-back.

On October 22, 1947, the dip pipe section of the combustion chamber failed. Failure of the lip section which supported the refractory caused the refractory to fall out exposing the metal to the high flame temperature. A dip pipe was fabricated with 316 SMO stainless steel. The lower 4 inches of the dip pipe was lined with 4 inch acid brick. The brick extended 4 inches below the metal section of the dip pipe and were supported by a 1 inch ring which had been welded to the dip pipe. The rest of the dip pipe was lined with 2 inches of A. P. Green Superplastic. The dip pipe was removed after 16 hours operation. The acid brick broke where they protruded below the dip pipe. The refractory (A. P. Green) spalled badly in the section which was exposed to the acid. The 316 stainless corroded enough to indicate that it would not be suitable as installed.

A dip pipe was made up with Hastelloy "D" and lined with 2 inch Karbofrax (silicon carbide). Karbofrax has approximately the same heat transfer coefficient as stainless steel. The concentrator was operated for 40 hours burning approximately 100 pounds oil per hour. The Hastelloy "D" was badly corroded, especially at the welds. The welds were not annealed. The upper 16 inches which were not exposed to the acid were burned, metal was melted and oxidized. The Karbofrax lining was not affected.

On November 17, 1947, the dip pipe was removed from the high stage and installed in the low stage concentrator. The dip pipe was lined as shown in sketch included in this report. The lower lip was not large enough to support the refractory, so a 316 stainless ring was used to supplement the Hastelloy "D" lip. When operation was discontinued, the Hastelloy "D" had not been affected in anyway. The 316 ring supporting the refractory was corroded. The concentrator was operated for several hundred hours. No exact operating time is available.

In order to obtain better combustion, the combustion chamber was enlarged. At the same time, the Schutte-Koerting burner was replaced with a Hauck burner. Actual construction and dimensions of the final combustion chamber are given on the sketch of the combustion chamber included in this report. No further difficulties were encountered with combustion.

The formation of a hard cement-like material (mostly $FeSO_4$) on the discharge of the combustion chamber caused some difficulty. A circular knife was installed which breaks the material, keeping the discharge clear. On normal operations, cleaning was necessary about once an hour. A 1 inch steel rod lead-covered screen 30 inches in diameter was installed in the concentrator cone to keep large pieces of material broken from the end of the dip pipe from plugging the concentrator discharge pump.

The concentrator discharge pump was originally located approximately 20 ft. below the concentrator. In this location, it was impossible to maintain packing in the pump. The pump was moved up to within 4 ft. of the discharge and packing difficulties were minimized. It was found that a mechanical sealed pump was best for this operation. Worthite pumps have been used on the concentrator discharge. Pump life has varied from 1 to 30 days. It is believed that a Hastelloy "D" pump would be more suitable for this operation, but it would be necessary to prove this in an actual installation.

It was very difficult to coordinate the operation of the low stage concentrator and the Oliver Filter. A 2000 gallon wood-lined tank was installed to act as filter feed storage and to store low stage concentrator acid when the filter was down for repairs. At this same time, a distribution box was installed on the filter level. The distribution box made it possible to make a controlled split between liquor going to the filter feed storage tank and the liquor recycled to the concentrator. It was found that a high liquor recycling load to the concentrator was necessary to inhibit plugging of the concentrator system.

A flow meter was used to control flow to the concentrator. No difficulty was encountered in maintaining any desired level in the concentrator. A glass level gage was used to determine liquor level.

Several suggestions have been made on concentrator design and layout. Sketches incorporating these suggestions are included in this report.

Oliver United Lead Filter

The 3' 0" diameter by 4' 0" face lead filter was started as soon as low stage concentrated acid was available. The filter was covered with glass cloth and wound with 304 stainless steel wire. Considerable difficulty was encountered at start of work due to carbonaceous matter contained in the liquor being filtered. A great improvement was noticed in filter operation after combustion was improved and the carbon eliminated from the liquor.

It was known from the start that the filter was too large for the operation. Several means of reducing its capacity were tried, namely blanking off 1/2 of the drum with several thickness of filter cloth, and when that didn't work, the drum was blanked off with lead. In both cases, operation was poor. The filter was slowed down as much as possible and a filter feed storage tank was installed to take care of the difference in production rate between the filter and the low stage concentrator.

A large number of cloths were tried to determine the best cloth for optimum filter operation. It was found that the best operation was obtained when using Vinyon N-719. Cloths tried on filter were: glass of different weaves, Nylon, Vinyon N-111 and 702, Vinyon 8, 10 and 15. The liquors were cooled to 85°F when using Vinyon 8, 10 and 15. The glass cloth seem to lose strength in the hot strong acid solutions. The Nylon dissolved in 45% H_2SO_4 at 100°F.

The actual life of Vinyon N-719 has not been determined as all the cloths have been removed due to mechanical failure.

Stainless steel 304 and 316 wire were used to wrap the filter. The 304 wire broke after a very short run while the 316 wire was about half gone after 24 hours use. A rubber covered wire similar to the type used on the precoat sludge filter in the titanium plant has been used successfully.

The filter cake has always cracked allowing a large amount of air to be pulled through the filter. The combination of high load and corrosion from acid mist carry-over caused considerable trouble with the Oliver vacuum pump. A steam jet was installed to replace the vacuum pump and this proved very satisfactory. No actual check was made on steam cost for this operation.

When the mentioned changes had been made and a Vinyon N-719 cloth was being used, no difficulty was encountered in obtaining a cake containing 65% $FeSO_4$ and very little acid. The cake was washed with very fine sprays and discharged as a good dry cake which was easy to convey and store.

Coal equal to the C:$FeSO_4$ ratio necessary for sintering was added to try to improve filtration conditions. The coal did not improve filtration enough to make this procedure worthwhile. Coal and iron oxide were also tried, but the iron oxide settled out in the filter bowl and plugged the filter.

High Stage Concentrator

Operation of the high stage concentrator was started on April 1, 1948. Several runs were made. In each case, the run was terminated due to failure of the lead vapor stack.

The "know-how" obtained in the operation of the low stage concentrator was used in making changes to the high stage to result in good operation. No difficulty was encountered in combustion and concentration of acid to 93% H_2SO_4. Heat efficiency was low, but it is felt that minor changes can be made to improve efficiency. Recovery was also low, but here again losses could be collected and returned to the concentration system.

Concentrated acid was settled and transferred to storage. The acid produced was dark and even after settling contained a high percentage of suspended solids.

Concentrator Exhaust System

Concentrator gases and carryover were passed through a water scrubbing tower and from there through a coke box. This system was fairly efficient. However, when both the low stage and high stage were operating, an acid mist in the atmosphere was quite noticeable.

Pelletizer

The material to be pelletized was fed through disc feeders into a screw mixer conveyor and fed to an oil fired rotary pelletizer.

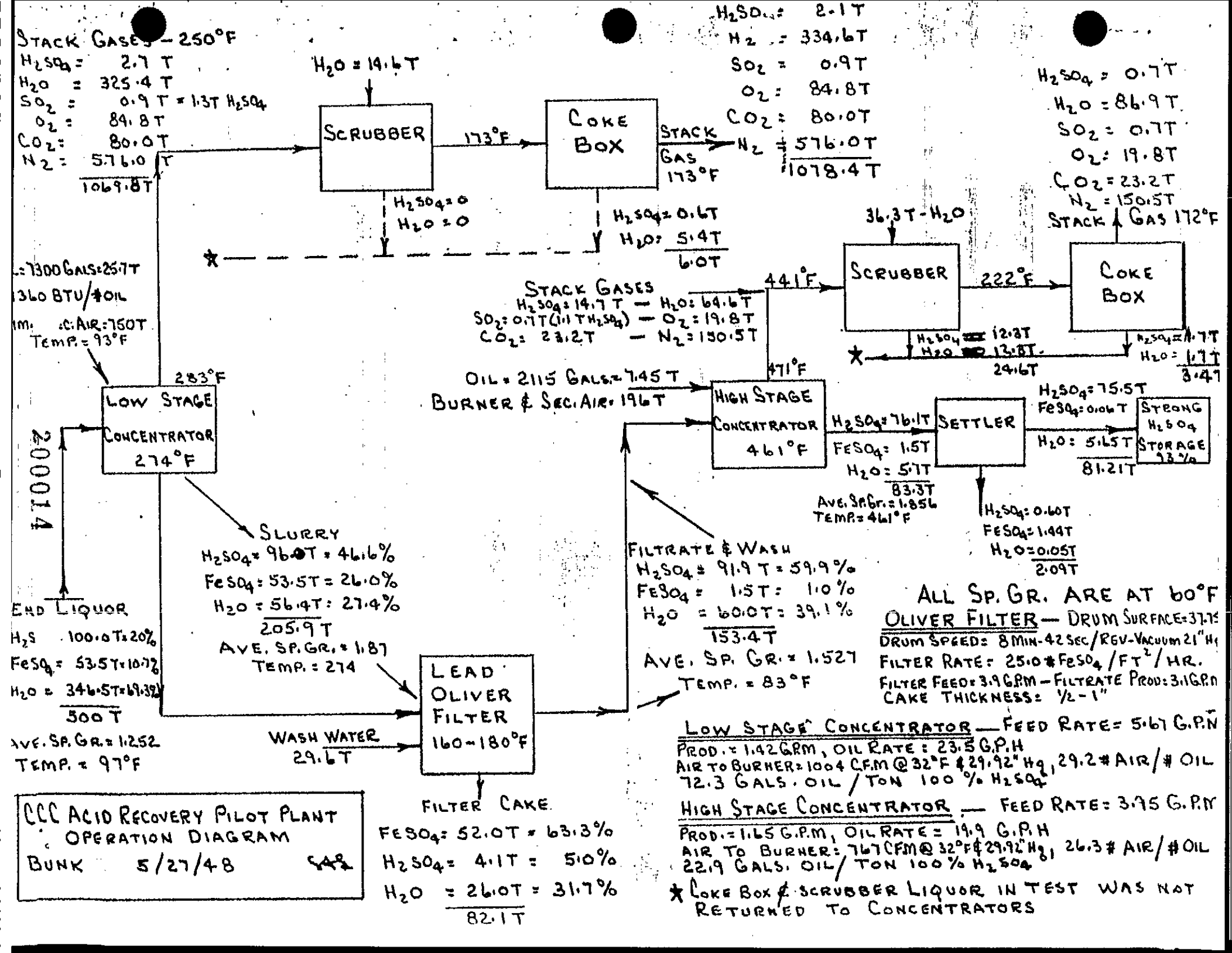
The material was not free flowing, causing trouble in adjusting the proper discharge of material. Disc feeders do not seem to be the proper type of equipment for this installation. The screw mixer conveyor also gave trouble by plugging. Several changes were made, but it was impossible to eliminate plugging entirely.

Pellets formed during the operation of the pelletizer were not suitable for efficient sintering. The pellets that met screen specifications represented a very small percentage of the total feed. Several changes in design were made with no marked improvement in results. It was finally decided that this type of pelletizer was not practical and pilot work would be discontinued to carry on small scale work on other types of equipment. Preliminary work indicated that an extruder could be used to form good pellets.

Dwight-Lloyd Sintering Machine

Two very short tests were made on the sintering machine using pellets made in the rotary pelletizer. The best gas obtained was equal to 5.6% SO_2. Everyone agreed that the weak gas was due to poor sintering caused by the improper composition of the pellets. Work was discontinued until proper pellets could be made.

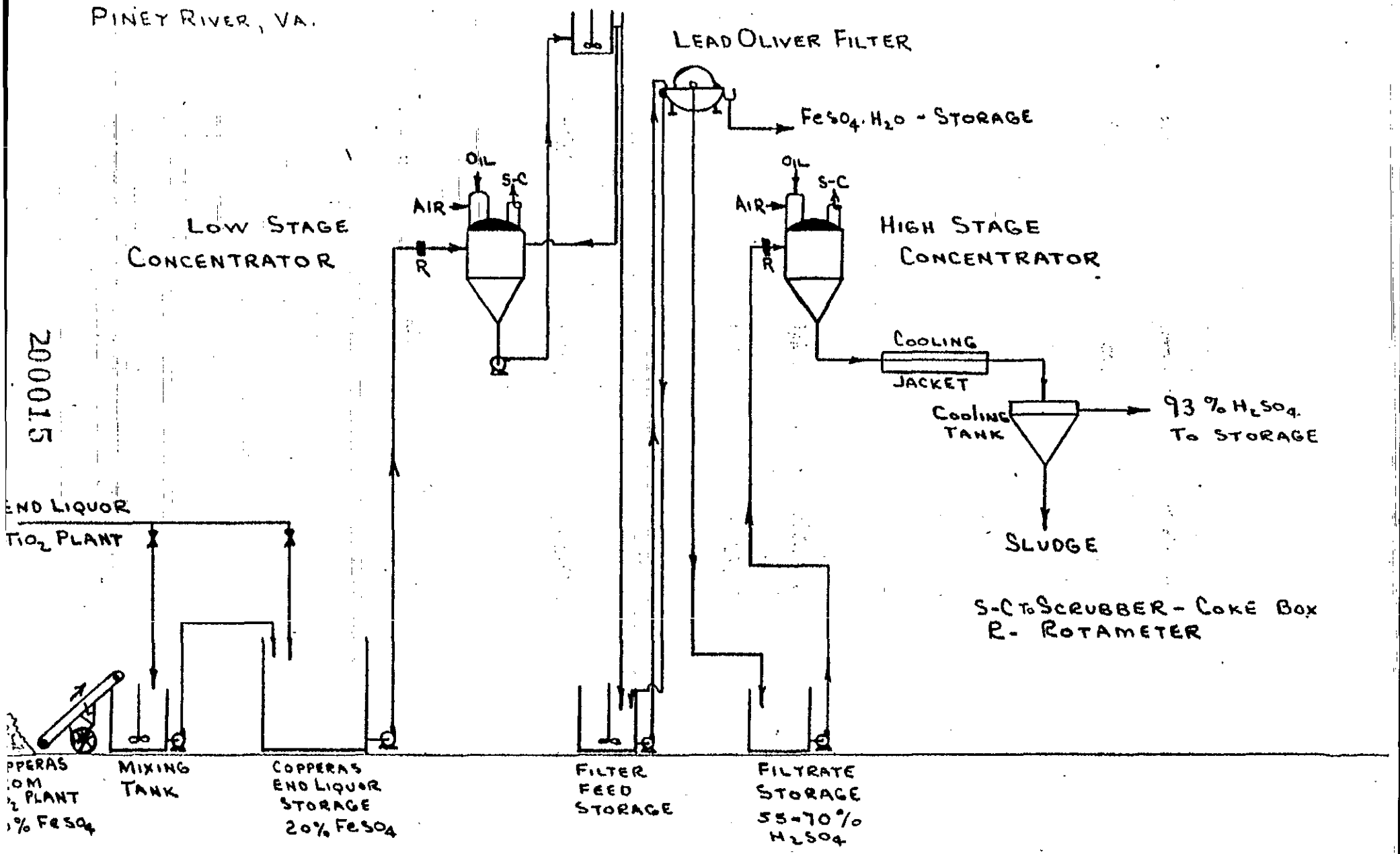
Stephen A. Lamanna


STACK GASES – 250°F
H2SO4 = 2.7 T
H2O = 325.4 T
SO2 = 0.9 T = 1.3T H2SO4
O2 = 84.8 T
CO2 = 80.0 T
N2 = 576.0 T
1069.8T
H2O = 14.6T
SCRUBBER
173°F
COKE BOX
STACK GAS 173°F
H2SO4 = 2.1T
H2 = 334.6T
SO2 = 0.9T
O2 = 84.8T
CO2 = 80.0T
N2 = 576.0T
1078.4T
H2SO4 = 0
H2O = 0
H2SO4 = 0.6T
H2O = 5.4T
6.0T
H2SO4 = 0.7T
H2O = 86.9T
SO2 = 0.7T
O2 = 19.8T
CO2 = 23.2T
N2 = 150.5T
STACK GAS 172°F
36.3T - H2O
SCRUBBER
222°F
COKE BOX
441°F
STACK GASES
H2SO4 = 14.7T — H2O = 64.6T
SO2 = 0.7T (1.1T H2SO4) — O2 = 19.8T
CO2 = 23.2T — N2 = 150.5T
H2SO4 = 12.3T
H2O = 12.3T
24.6T
H2SO4 = 1.7T
H2O = 1.7T
3.4T
= 7300 GALS = 25.7T
360 BTU/# OIL
AIR = 750T
TEMP. = 93°F
283°F
LOW STAGE CONCENTRATOR 274°F
OIL = 2115 GALS = 7.45T
BURNER & SEC. AIR = 196T
471°F
HIGH STAGE CONCENTRATOR 461°F
H2SO4 = 76.1T
FESO4 = 1.5T
H2O = 5.7T
83.3T
AVE. SP. GR. = 1.856
TEMP. = 461°F
SETTLER
H2SO4 = 75.5T
FESO4 = 0.06T
H2O = 5.65T
81.21T
STRONG H2SO4 STORAGE 93%
H2SO4 = 0.60T
FESO4 = 1.44T
H2O = 0.05T
2.09T
SLURRY
H2SO4 = 96.0T = 46.6%
FESO4 = 53.5T = 26.0%
H2O = 56.4T = 27.4%
205.9T
AVE. SP. GR. = 1.87
TEMP. = 274
END LIQUOR
H2S 100.0T = 20%
FESO4 = 53.5T = 10.7%
H2O = 346.5T = 69.3%
500T
AVE. SP. GR. = 1.252
TEMP. = 97°F
WASH WATER 29.6T
LEAD OLIVER FILTER 160-180°F
FILTRATE & WASH
H2SO4 = 91.9T = 59.9%
FESO4 = 1.5T = 1.0%
H2O = 60.0T = 39.1%
153.4T
AVE. SP. GR. = 1.527
TEMP. = 83°F
FILTER CAKE
FESO4 = 52.0T = 63.3%
H2SO4 = 4.1T = 5.0%
H2O = 26.0T = 31.7%
82.1T
CCC ACID RECOVERY PILOT PLANT
OPERATION DIAGRAM
BUNK 5/27/48
ALL SP. GR. ARE AT 60°F
OLIVER FILTER — DRUM SURFACE = 37.75
DRUM SPEED: 8 MIN-42 SEC/REV-VACUUM 21" Hg
FILTER RATE: 25.0 # FeSO4/FT²/HR.
FILTER FEED = 3.9 GPM — FILTRATE PROD: 3.1 GPM
CAKE THICKNESS: 1/2 - 1"
LOW STAGE CONCENTRATOR — FEED RATE = 5.67 G.P.M
PROD. = 1.42 GPM, OIL RATE = 23.5 G.P.H
AIR TO BURNER = 1004 C.F.M @ 32°F & 29.92" Hg, 29.2 # AIR/# OIL
72.3 GALS. OIL / TON 100% H2SO4
HIGH STAGE CONCENTRATOR — FEED RATE = 3.75 G.P.M
PROD. = 1.65 G.P.M, OIL RATE = 19.9 G.P.H
AIR TO BURNER = 767 CFM @ 32°F & 29.92" Hg, 26.3 # AIR/# OIL
22.9 GALS. OIL / TON 100% H2SO4
* COKE BOX & SCRUBBER LIQUOR IN TEST WAS NOT RETURNED TO CONCENTRATORS

200014

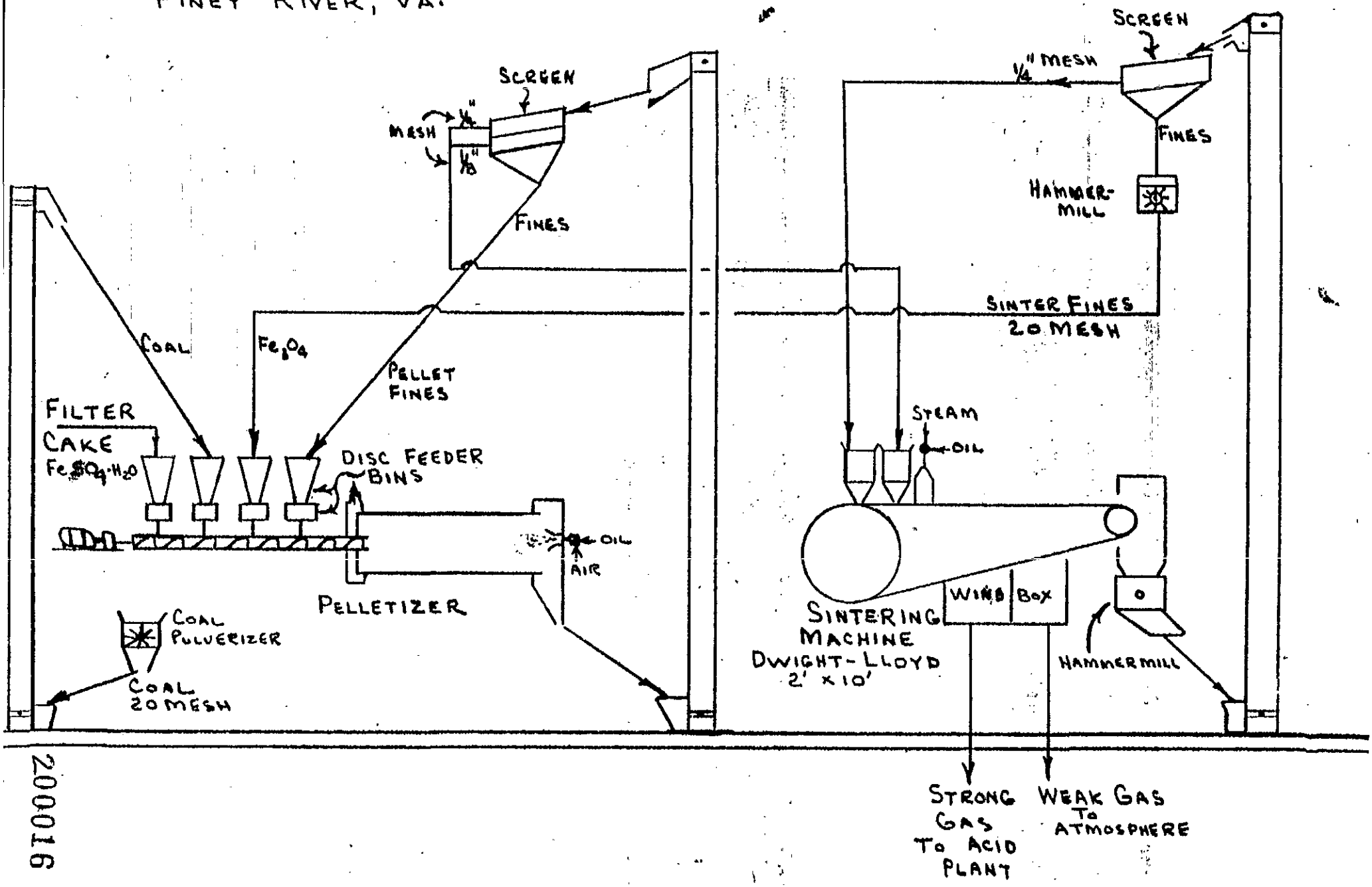
CON[illegible]NTRATION

CCC ACID RECOVERY PILOT PLANT
PINEY RIVER, VA.



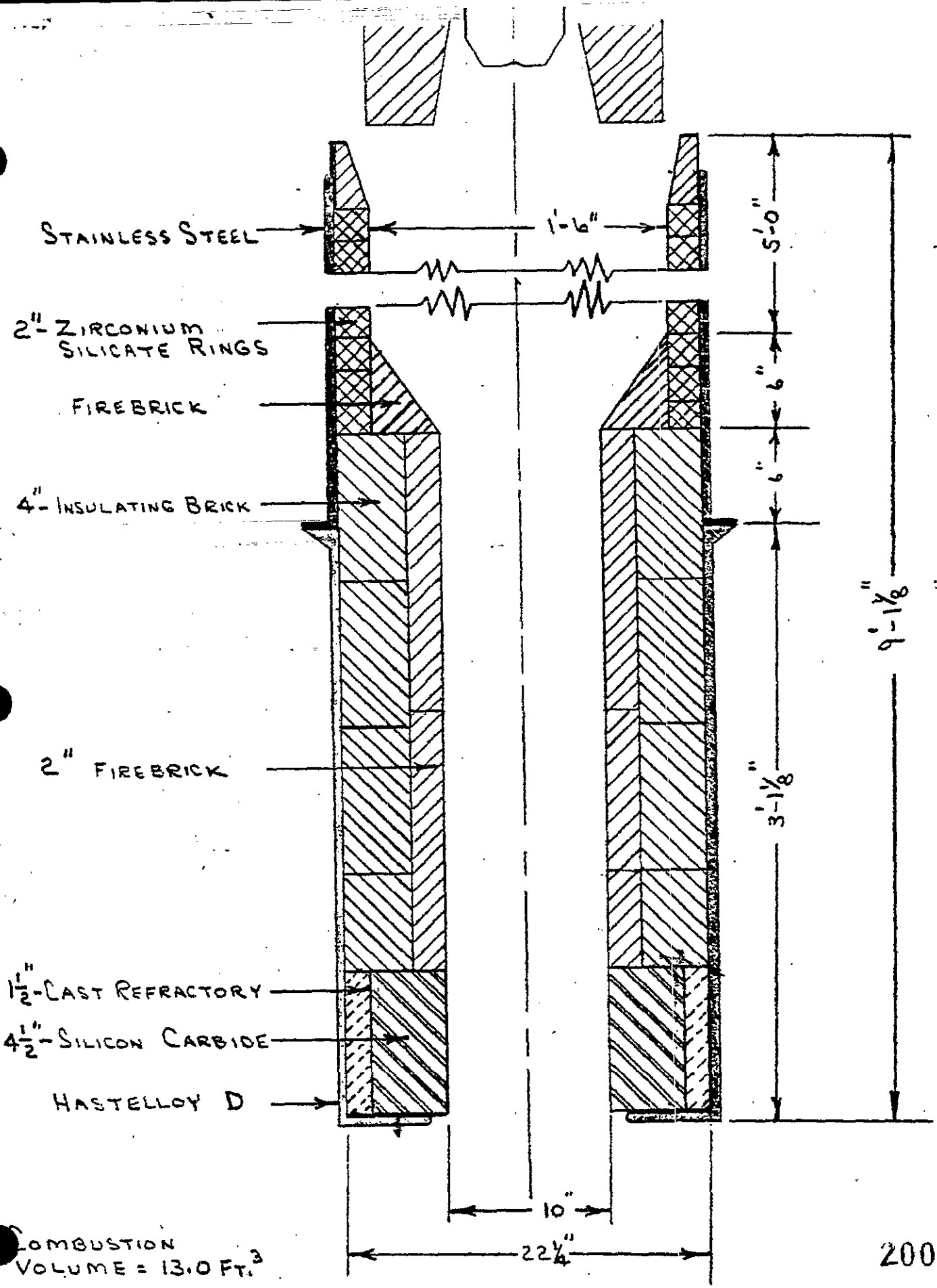
200015

PELLETIZING + SINTERING
CCC ACID RECOVERY PILOT PLANT
PINEY RIVER, VA.



200016

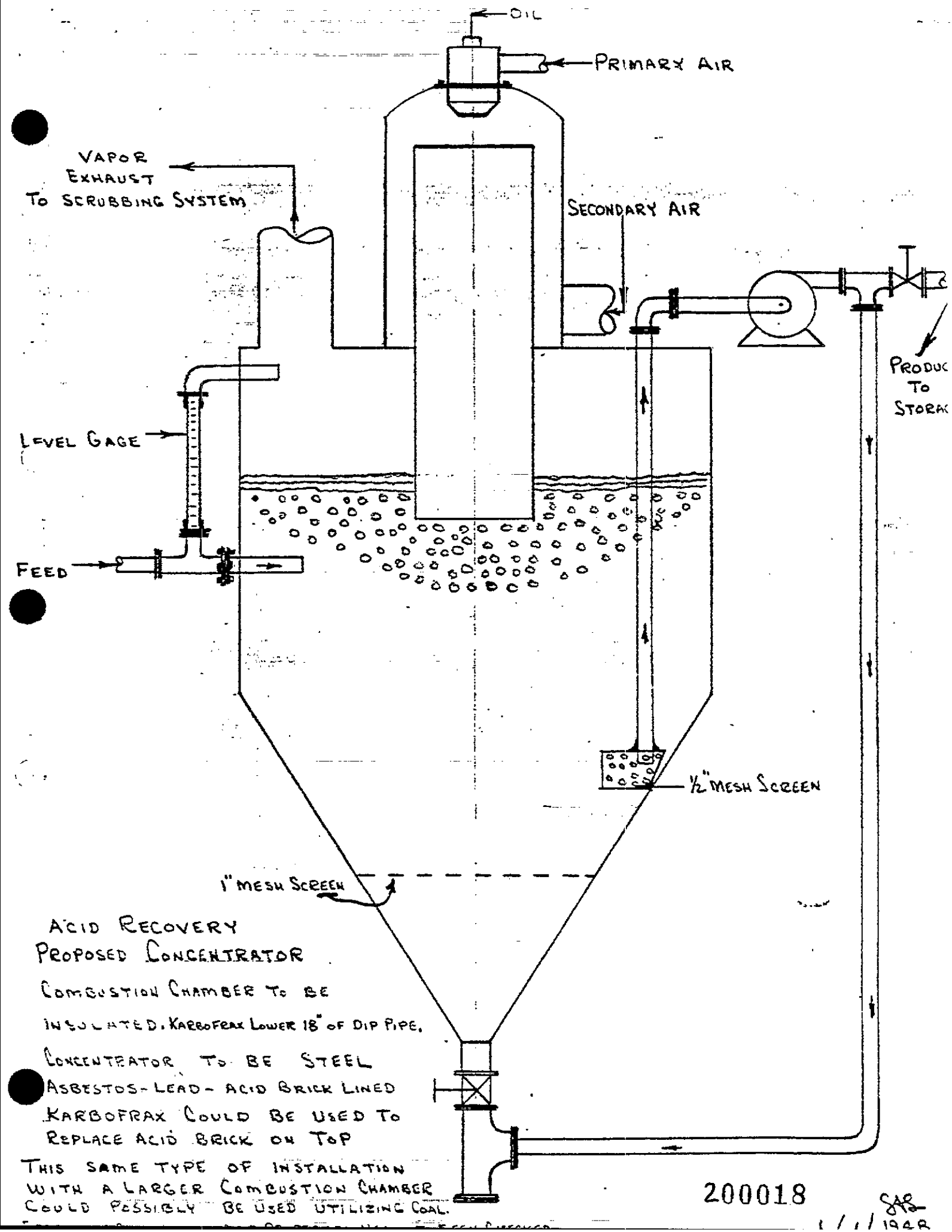
SAS

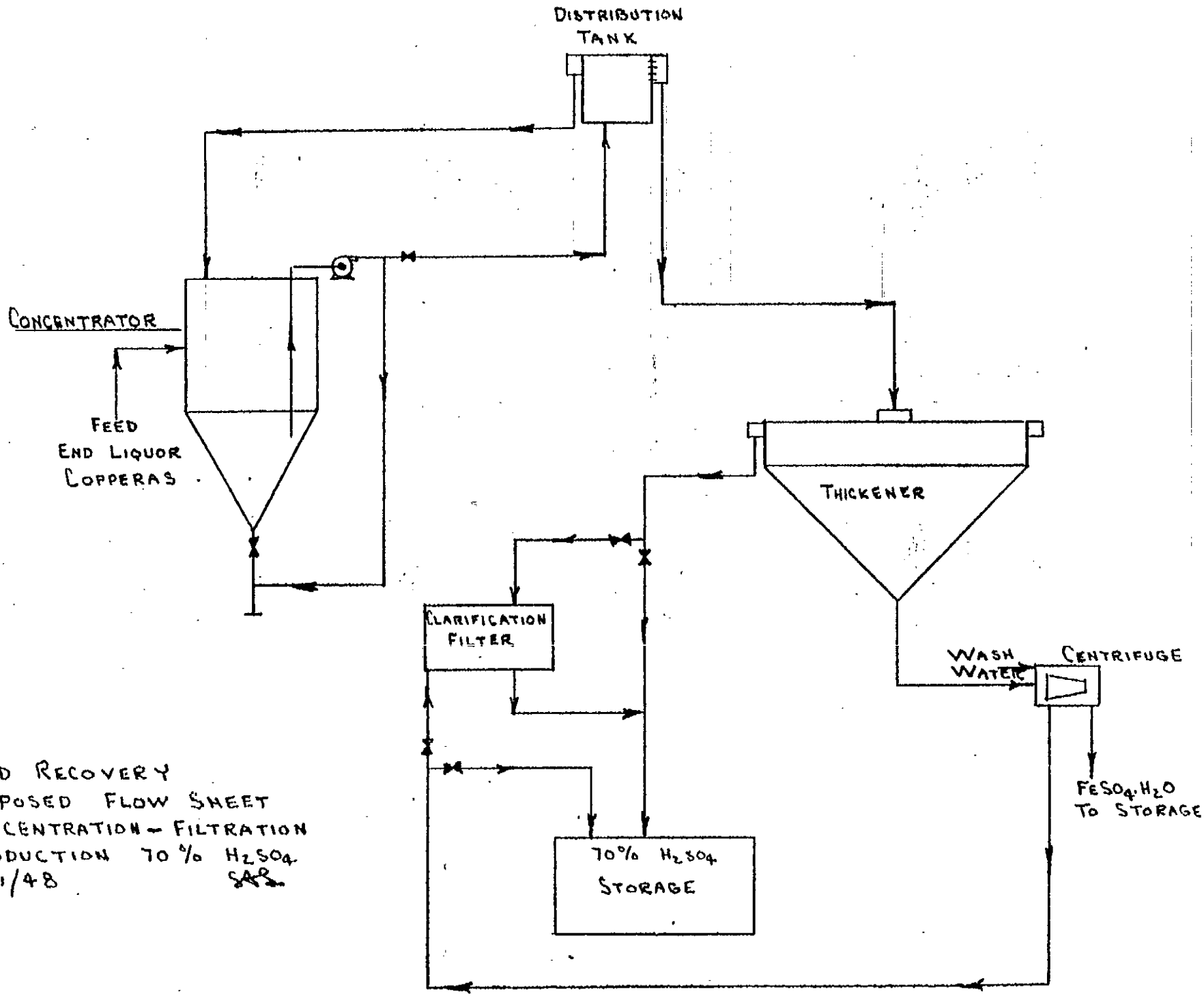


COMBUSTION VOLUME = 13.0 FT.^{3}

200017

ACID RECOVERY PILOT PLANT
CONCENTRATOR COMBUSTION CHAMBER


OIL
PRIMARY AIR
VAPOR
EXHAUST
TO SCRUBBING SYSTEM
SECONDARY AIR
PRODUC
TO
STORA
LEVEL GAGE
FEED
½" MESH SCREEN
1" MESH SCREEN
ACID RECOVERY
PROPOSED CONCENTRATOR
COMBUSTION CHAMBER TO BE
INSULATED. KARBOFRAX LOWER 18" OF DIP PIPE.
CONCENTRATOR TO BE STEEL
ASBESTOS-LEAD-ACID BRICK LINED
KARBOFRAX COULD BE USED TO
REPLACE ACID BRICK ON TOP
THIS SAME TYPE OF INSTALLATION
WITH A LARGER COMBUSTION CHAMBER
COULD POSSIBLY BE USED UTILIZING COAL.
200018
SAB
1/1/1968



ACID RECOVERY
PROPOSED FLOW SHEET
CONCENTRATION – FILTRATION
PRODUCTION 70% H_2SO_4
1/1/48
SAS

200019

WASTE ACID RECOVERY PILOT PLANT

SECTION II

AMERICAN CYANAMID COMPANY
CALCO CHEMICAL DIVISION

PINEY RIVER PLANT

December 1, 1948

Typed: March 14, 1949

Mr. C. J. Kirkland

Stephen A. Lamanna

WASTE ACID RECOVERY PILOT PLANT

This report summarizes the operation of the waste acid recovery pilot plant during the period beginning September 14, 1948 through November 15, 1948.

The purpose of this run was to test the production of pellets by extrusion. The pellets produced were to be sintered on a Dwight-Lloyd sintering machine to produce SO_2 and Fe_3O_4 sinter.

The pilot plant was shutdown on May 22, 1948 after several unsuccessful attempts had been made to produce pellets in a rotary pelletizer. Preliminary work indicated that pellets could be formed by extrusion.

Samples of the sinter mix were sent to the Bonnot Company, Canton, Ohio for extrusion tests. The results of these tests looked favorable and mixing and extrusion equipment were purchased.

Pilot plant changes were made and the plant started on September 14, 1948. Flowsheet showing pilot plant layout is included. An operation diagram showing operating results is also included. No additional work was done on acid concentration. Data recorded on concentration is that which was obtained in the previous pilot plant run.

The results of this test proved that good pellets could be formed by extrusion. These pellets could be easily dried and conveyed to storage with very little breakage. The pellets were successfully sintered producing a gas containing 7.0 - 7.5% SO_2. Gas losses were small and the sulfur content of the sinter was less than 1%.

General information and discussion on operation, operating results, equipment maintenance and equipment changes on each step in the processes is as follows:

Low Stage Concentrator

The operating procedure which was standardized on the previous run was essentially followed throughout this test run. Since it was felt that all necessary data on low stage concentration had been obtained, no further data were taken. Acid concentration was kept between 65 - 70% H_2SO_4. The concentrator was operated whenever sulphate cake was required for pelletizing.

A short test run was made increasing acid strength to 80% H_2SO_4, but this test was discontinued when difficulty was encountered with the cloth on the filter.

Oliver Filter

No further work was done on this step of the process. Operation of the filter further proved that Vinyon N-719 cloth gave better results than any other type of cloth used.

Pelletizing

Pellets were made using a Bonnot extruder. The ferrous sulfate cake, coal, sinter fines (Fe_3O_4) and pellet fines were mixed by hand, fed into a pug mill from which the mix discharged into the extruder. The extruded pellets dropped onto a small Dwight-Lloyd sintering machine where most of the moisture was driven off. The dried pellets were screened and the accepted pellets conveyed to storage. Pellet fines were fed back to the pellet mix.

Operation of the extruder was very satisfactory. Strong pellets which could be easily dried and conveyed were formed. Some difficulty was encountered with plugging of the pug mill and the feed section of the extruder. The extruder used in this test work was a small unit which handled only a small tonnage. It is difficult to determine what results would be obtained in a larger unit of this type. Maintenance cost data were not obtained on this operation. It was evident that operating life on a straight steel pug mill and extruder would be very short.

The pellets were easily dried on the small 1' x 4' Dwight-Lloyd sintering machine. Oil consumption for this operation was not obtained due to lack of metering equipment. It was stated that in a plant installation, the dryer would be eliminated and the wet pellet fed directly to the sintering machine. The sintering machine would have a dryer section ahead of the sintering section.

Sintering

The pellets prepared were successfully sintered on the Dwight-Lloyd sintering machine producing gases containing 7.0 to 8.0% SO_2 by volume and a sinter containing less than 1% S. The weak gases discharged from the sintering machine contained in most cases less than .3% SO_2. The strong gas was fed to the contact acid plant through the drying tower. This gas, although it was passed through a water scrubbing tower and a coke box, contained a considerable amount of acid mist. It is felt that this acid mist could be reduced by using coke instead of coal. However, it was the general opinion of all concerned that in a large installation, the gas would have to be passed

through a wet Cottrell or some other type of mist removing equipment before it was fed to a contact unit.

Grinding

The sinter from the sintering machine was discharged into a hammer mill. This material was ground and conveyed to a screen where a separation was made between + 1/4" and -1/4" material. The + 1/4" material was discharged into a storage bin and used for hearth layer on the sintering machine. Sinter product was all material in excess of that required for hearth layer. The -1/4 mesh material was ground in a hammer mill to -20 mesh. This fine iron oxide was used in making up the pellet mix.

Maintenance on the hammer mills was unreasonably high. It was soon obvious that a hammer mill was not the proper type of equipment for this operation. It was stated that in a large installation, a ball mill would be used. In a steel mill installation, all grinding could be eliminated as the steel people would want a coarse sinter. Fine iron oxides, such as flue dist, could be used to make up the sinter mix.

A demonstration run was made for concerns who were interested in the process. Representatives from the Great Lakes Steel Corporation of Detroit, Michigan and from DuPont observed the operation during this run.

The pilot plant was then shutdown and placed in a standby condition.

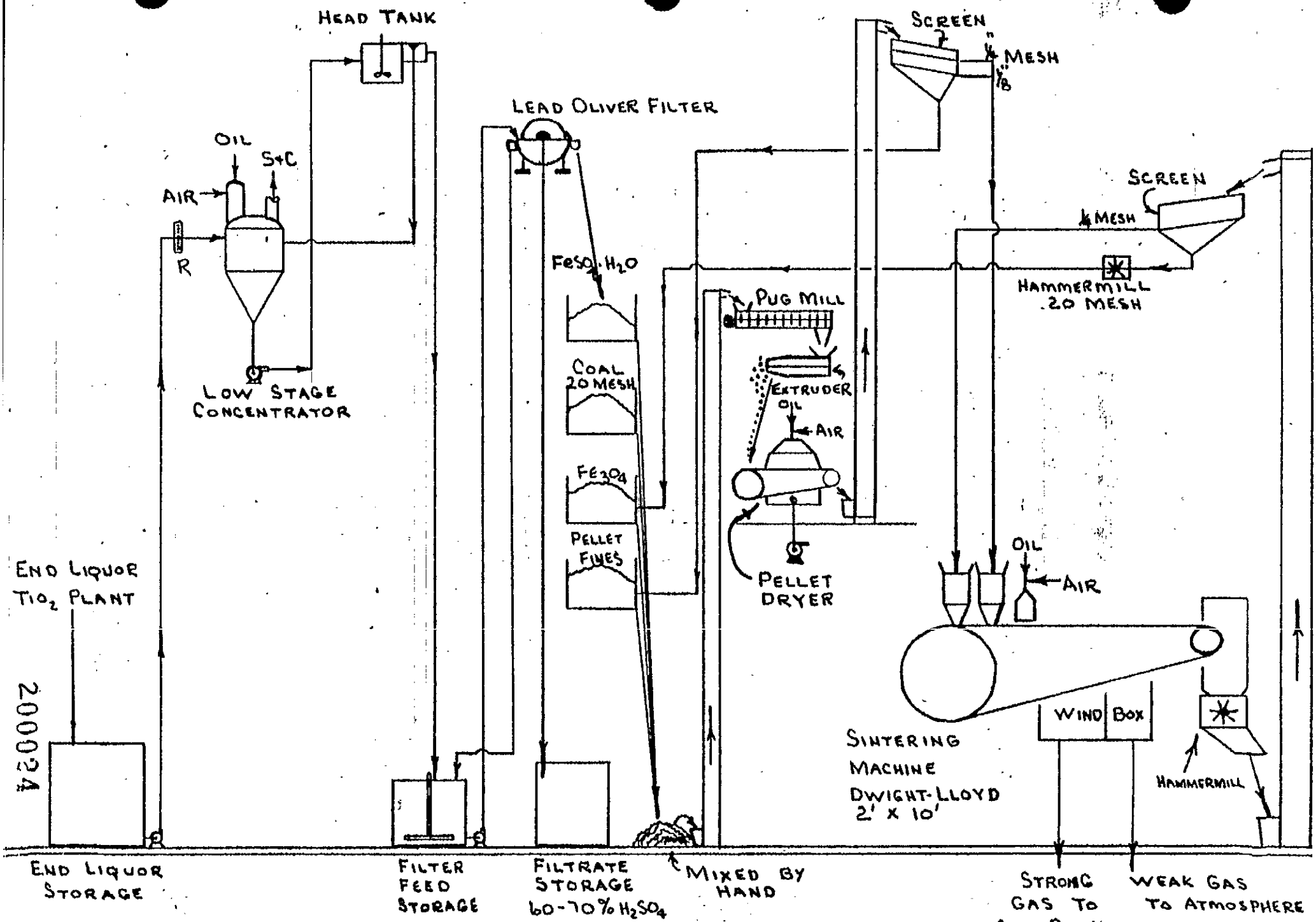
Another short demonstration run was made in January, 1949. During this run, the operation was observed by representatives of the following companies:

Blaw-Knox Company	Pittsburgh, Penna.
Great Lakes Steel Company	Detroit, Michigan
Sharon Steel Corporation	Sharon, Penna.

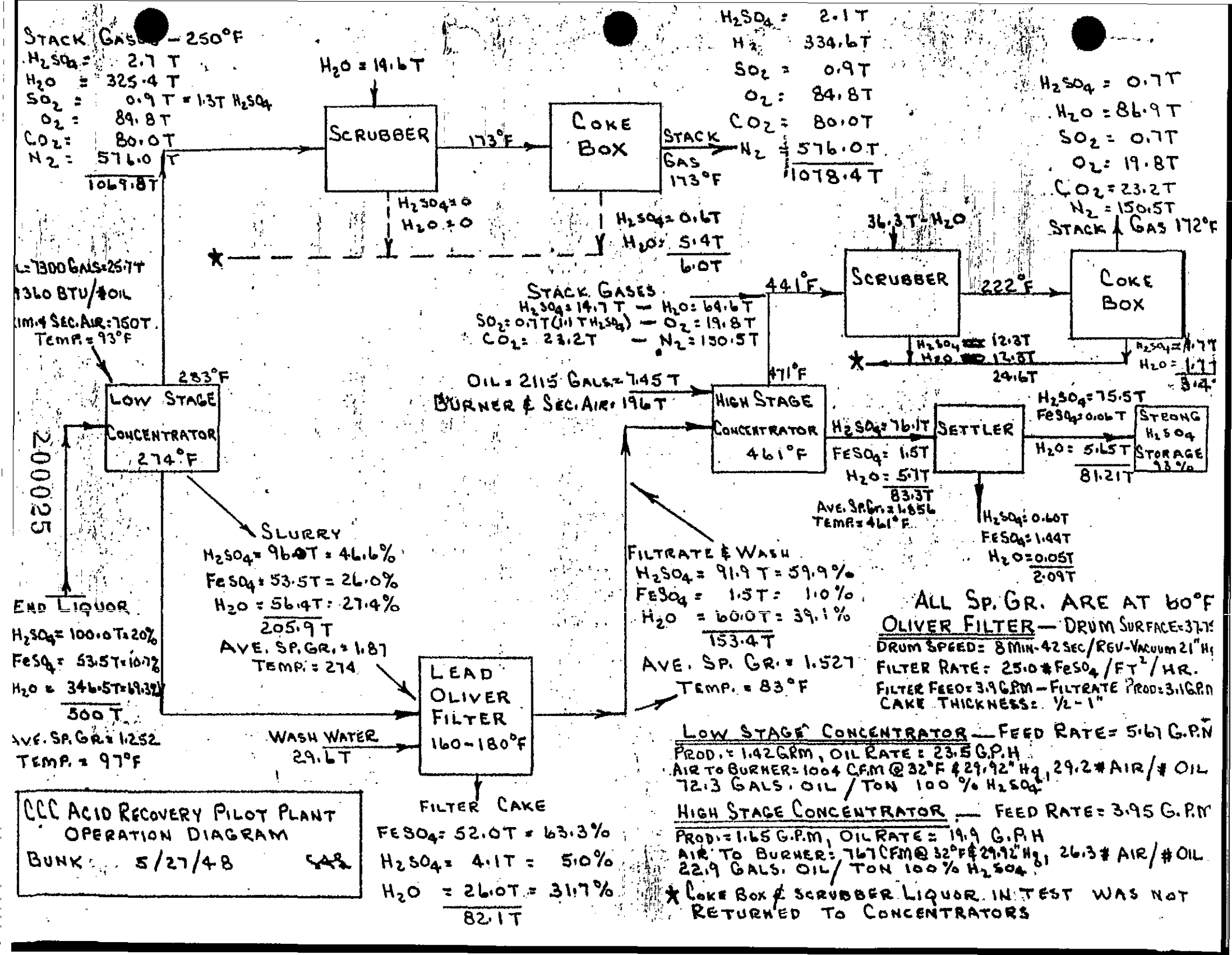
During this demonstration run, no data were obtained.

The pilot plant is now down and in a standby condition.

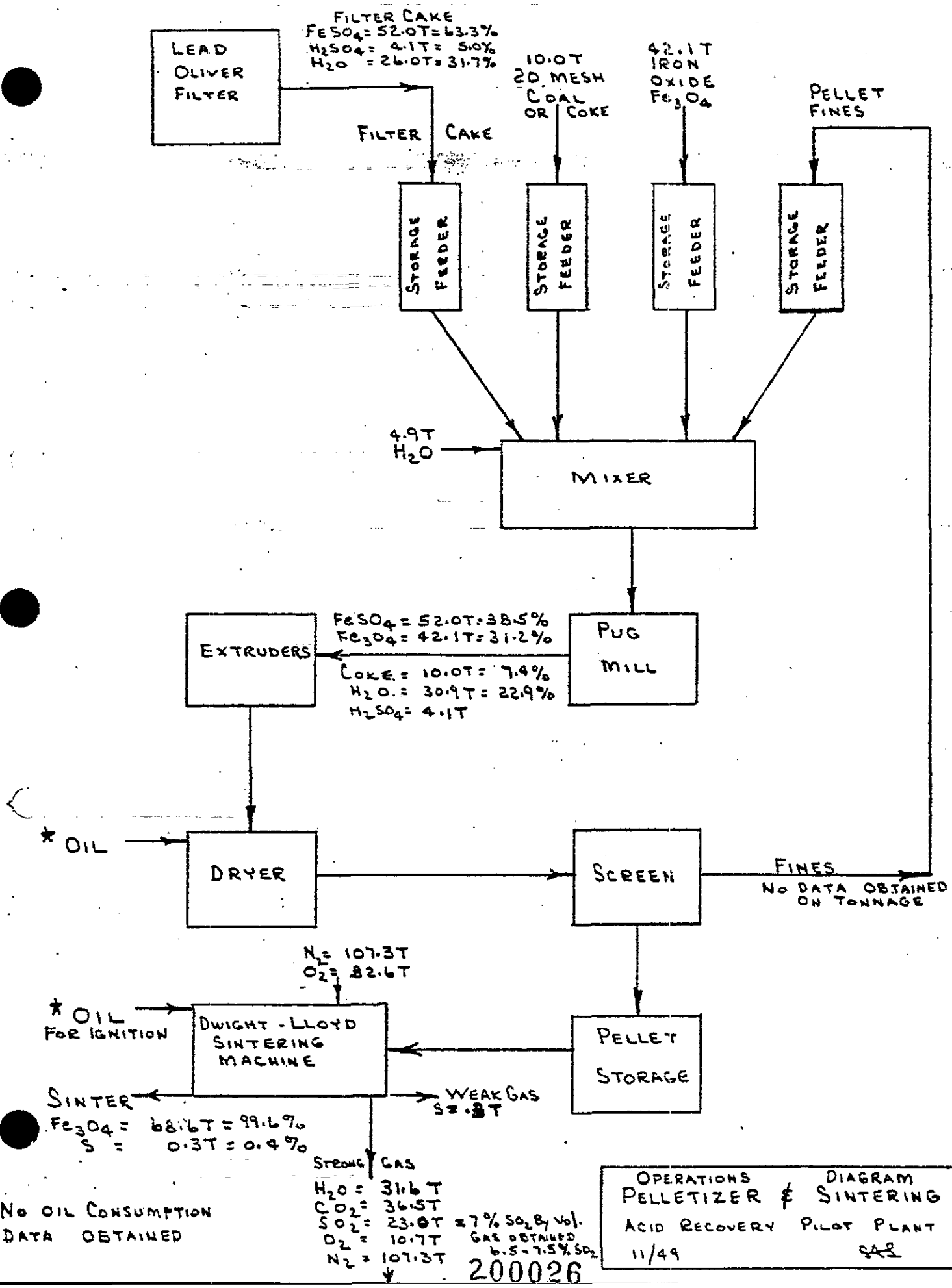
Stephen A. Iannuzzi

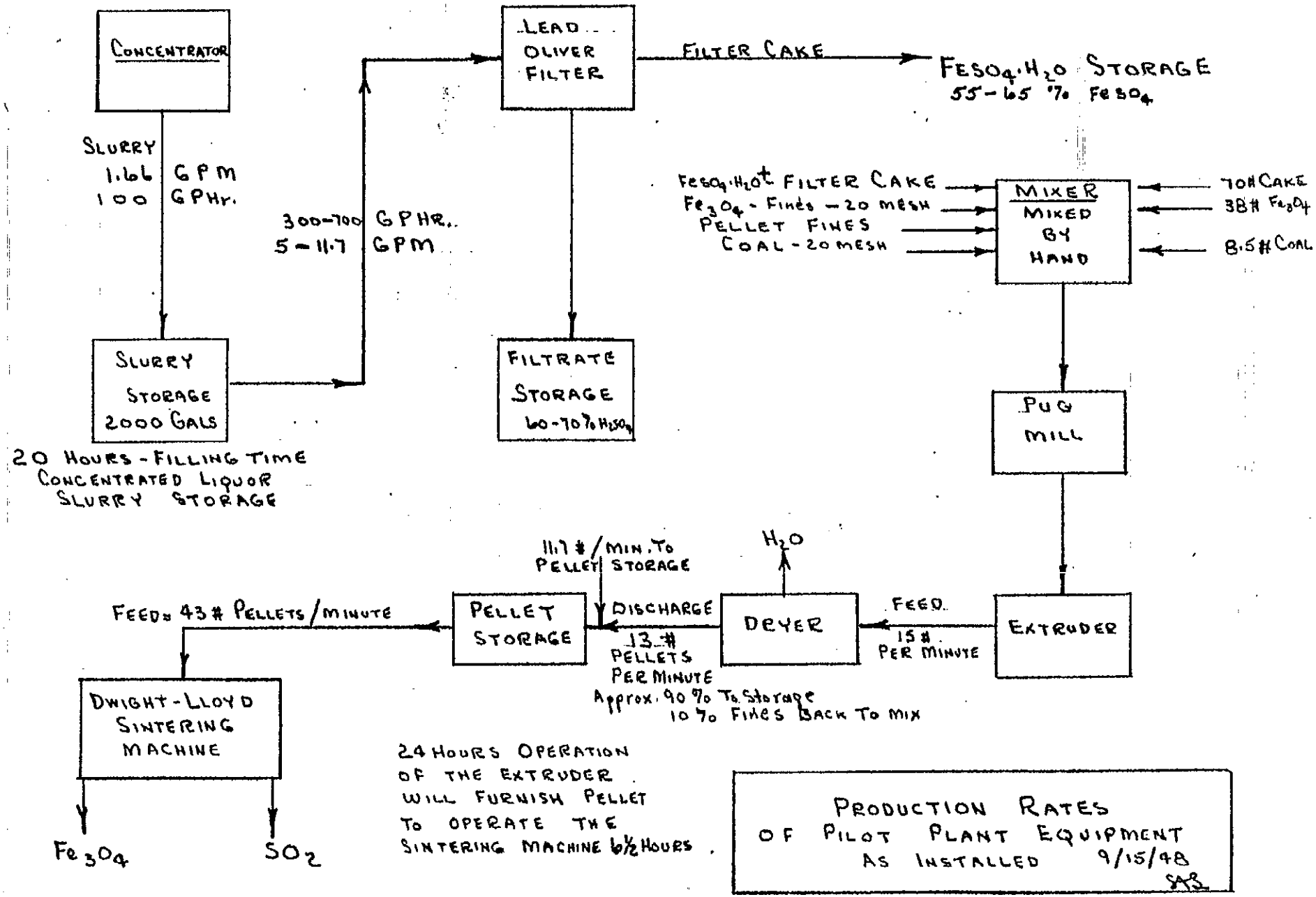

HEAD TANK
OIL
S+C
AIR
R
LOW STAGE CONCENTRATOR
END LIQUOR TiO2 PLANT
LEAD OLIVER FILTER
FeSO4·H2O
COAL 20 MESH
Fe3O4
PELLET FINES
PUG MILL
EXTRUDER
OIL
AIR
PELLET DRYER
SCREEN
1/4" MESH
1/8"
SCREEN
1/4 MESH
HAMMERMILL 20 MESH
OIL
AIR
SINTERING MACHINE DWIGHT-LLOYD 2' X 10'
WIND BOX
HAMMERMILL
END LIQUOR STORAGE
FILTER FEED STORAGE
FILTRATE STORAGE 60-70% H2SO4
MIXED BY HAND
STRONG GAS TO ACID PLANT
WEAK GAS TO ATMOSPHERE
S+C TO SCRUBBER AND COKE BOX
R- ROTAMETER
CCC WASTE ACID RECOVERY
PILOT PLANT - PINEY RIVER VA. 12/1/40 DAP

200024


STACK GASES – 250°F
H_2SO_4 = 2.7 T
H_2O = 325.4 T
SO_2 = 0.9 T = 1.3T H_2SO_4
O_2 = 89.8 T
CO_2 = 80.0 T
N_2 = 576.0 T
1069.8T
H_2O = 14.6T
SCRUBBER
173°F
COKE BOX
STACK GAS 173°F
H_2SO_4 = 2.1 T
H_2 334.6T
SO_2 = 0.9T
O_2 = 84.8T
CO_2 = 80.0T
N_2 = 576.0T
1078.4 T
H_2SO_4 = 0
H_2O = 0
H_2SO_4 = 0.6T
H_2O = 5.4T
6.0T
H_2SO_4 = 0.7T
H_2O = 86.9 T
SO_2 = 0.7T
O_2 = 19.8T
CO_2 = 23.2T
N_2 = 150.5T
STACK GAS 172°F
36.3T – H_2O
SCRUBBER
222°F
COKE BOX
H_2SO_4 = 12.3T
H_2O = 12.3T
24.6T
H_2SO_4 = 1.7T
H_2O = 1.7T
3.4T
STACK GASES
H_2SO_4 = 14.7 T — H_2O = 64.6T
SO_2 = 0.7T (1.1 T H_2SO_4) — O_2 = 19.8T
CO_2 = 23.2T — N_2 = 150.5T
441°F
471°F
OIL = 2115 GALS = 7.45 T
BURNER & SEC. AIR = 196T
HIGH STAGE CONCENTRATOR 461°F
H_2SO_4 = 76.1T
$FeSO_4$ = 1.5T
H_2O = 5.7T
83.3T
AVE. SP. GR. = 1.856
TEMP. = 461°F
SETTLER
H_2SO_4 = 75.5T
$FeSO_4$ = 0.06T
H_2O = 5.65T
81.21T
STRONG H_2SO_4 STORAGE 93%
H_2SO_4 = 0.60T
$FeSO_4$ = 1.44T
H_2O = 0.05T
2.09T
OIL = 7300 GALS = 25.7T
9360 BTU/# OIL
AIR & SEC. AIR = 750T
TEMP. = 93°F
283°F
LOW STAGE CONCENTRATOR 274°F
SLURRY
H_2SO_4 = 96.0T = 46.6%
$FeSO_4$ = 53.5T = 26.0%
H_2O = 56.4T = 27.4%
205.9 T
AVE. SP. GR. = 1.87
TEMP. = 274
END LIQUOR
H_2SO_4 = 100.0T = 20%
$FeSO_4$ = 53.5T = 10.7%
H_2O = 346.5T = 69.3%
500 T
AVE. SP. GR. = 1.252
TEMP. = 97°F
WASH WATER 29.6T
LEAD OLIVER FILTER 160–180°F
FILTER CAKE
$FeSO_4$ = 52.0T = 63.3%
H_2SO_4 = 4.1T = 5.0%
H_2O = 26.0T = 31.7%
82.1T
FILTRATE & WASH
H_2SO_4 = 91.9 T = 59.9%
$FeSO_4$ = 1.5T = 1.0%
H_2O = 60.0T = 39.1%
153.4T
AVE. SP. GR. = 1.527
TEMP. = 83°F
ALL SP. GR. ARE AT 60°F
OLIVER FILTER — DRUM SURFACE = 37.7
DRUM SPEED = 8 MIN-42 SEC/REV-VACUUM 21" Hg
FILTER RATE = 25.0 # $FeSO_4$ / FT^2 / HR.
FILTER FEED = 3.9 G.P.M — FILTRATE PROD = 3.1 G.P.M
CAKE THICKNESS = 1/2 – 1"
LOW STAGE CONCENTRATOR — FEED RATE = 5.67 G.P.M
PROD. = 1.42 GPM, OIL RATE = 23.5 G.P.H
AIR TO BURNER = 1004 CFM @ 32°F & 29.92" Hg, 29.2 # AIR / # OIL
72.3 GALS. OIL / TON 100% H_2SO_4
HIGH STAGE CONCENTRATOR — FEED RATE = 3.95 G.P.M
PROD. = 1.65 G.P.M, OIL RATE = 19.9 G.P.H
AIR TO BURNER = 767 CFM @ 32°F & 29.92" Hg, 26.3 # AIR / # OIL
22.9 GALS. OIL / TON 100% H_2SO_4
★ COKE BOX & SCRUBBER LIQUOR IN TEST WAS NOT RETURNED TO CONCENTRATORS
CCC ACID RECOVERY PILOT PLANT
OPERATION DIAGRAM
BUNK 5/27/48

200025


LEAD OLIVER FILTER
FILTER CAKE
$FeSO_4$ = 52.0T = 63.3%
H_2SO_4 = 4.1T = 5.0%
H_2O = 26.0T = 31.7%
FILTER CAKE
10.0T 20 MESH COAL OR COKE
42.1T IRON OXIDE Fe_3O_4
PELLET FINES
STORAGE FEEDER
STORAGE FEEDER
STORAGE FEEDER
STORAGE FEEDER
4.9T H_2O
MIXER
PUG MILL
$FeSO_4$ = 52.0T = 38.5%
Fe_3O_4 = 42.1T = 31.2%
COKE = 10.0T = 7.4%
H_2O = 30.9T = 22.9%
H_2SO_4 = 4.1T
EXTRUDERS
* OIL
DRYER
SCREEN
FINES
NO DATA OBTAINED ON TONNAGE
N_2 = 107.3T
O_2 = 82.6T
* OIL FOR IGNITION
DWIGHT-LLOYD SINTERING MACHINE
PELLET STORAGE
SINTER
Fe_3O_4 = 68.6T = 99.6%
S = 0.3T = 0.4%
WEAK GAS
S = .3T
STRONG GAS
H_2O = 31.6T
CO_2 = 36.5T
SO_2 = 23.0T ≈ 7% SO_2 by vol.
O_2 = 10.7T
N_2 = 107.3T
GAS OBTAINED 6.5 - 7.5% SO_2
NO OIL CONSUMPTION DATA OBTAINED
OPERATIONS DIAGRAM
PELLETIZER & SINTERING
ACID RECOVERY PILOT PLANT
11/49
200026


CONCENTRATOR
SLURRY
1.66 GPM
100 GPHr.
SLURRY STORAGE
2000 GALS
20 HOURS - FILLING TIME
CONCENTRATED LIQUOR
SLURRY STORAGE
300-700 GPHR.
5 - 11.7 GPM
LEAD OLIVER FILTER
FILTER CAKE
FESO4·H2O STORAGE
55-65 % FESO4
FILTRATE STORAGE
60-70% H2SO4
FESO4·H2O + FILTER CAKE
Fe3O4 - FINES - 20 MESH
PELLET FINES
COAL - 20 MESH
MIXER
MIXED BY HAND
70# CAKE
38# Fe3O4
8.5# COAL
PUG MILL
EXTRUDER
FEED
15# PER MINUTE
DRYER
H2O
DISCHARGE
13# PELLETS PER MINUTE
Approx. 90% To Storage
10% FINES BACK TO MIX
11.7 #/MIN. TO PELLET STORAGE
PELLET STORAGE
FEED = 43# PELLETS/MINUTE
DWIGHT-LLOYD SINTERING MACHINE
Fe3O4
SO2
24 HOURS OPERATION OF THE EXTRUDER WILL FURNISH PELLET TO OPERATE THE SINTERING MACHINE 6½ HOURS.
PRODUCTION RATES OF PILOT PLANT EQUIPMENT AS INSTALLED 9/15/48
SAB

200027

WASTE ACID RECOVERY PILOT PLANT

SECTION III

AMERICAN CYANAMID COMPANY
CALCO CHEMICAL DIVISION
PINEY RIVER PLANT

Typed: March 14, 1949

Mr. C. J. Kirkland

Stephen A. Lamanna

RECOVERED ACID COST ESTIMATE

As requested, I have prepared a cost estimate for the production of 70% sulfuric acid from dilute waste acid. A flowsheet and a plant cost estimate of the proposed plant are included.

The superphosphate industry uses 70% H_2SO_4 for acidulation of phosphate rock. It is proposed that waste acid be recovered as 70% H_2SO_4 and sold to the phosphate industry or used to produce superphosphate from the apatite produced at Piney River, Virginia.

Acid recovered as 70% H_2SO_4 will be equal to 1224 tons 100% H_2SO_4 per month. Acid cost will be $14.65 per net ton of 100% H_2SO_4.

Stephen A. Lamanna

/ms

200029

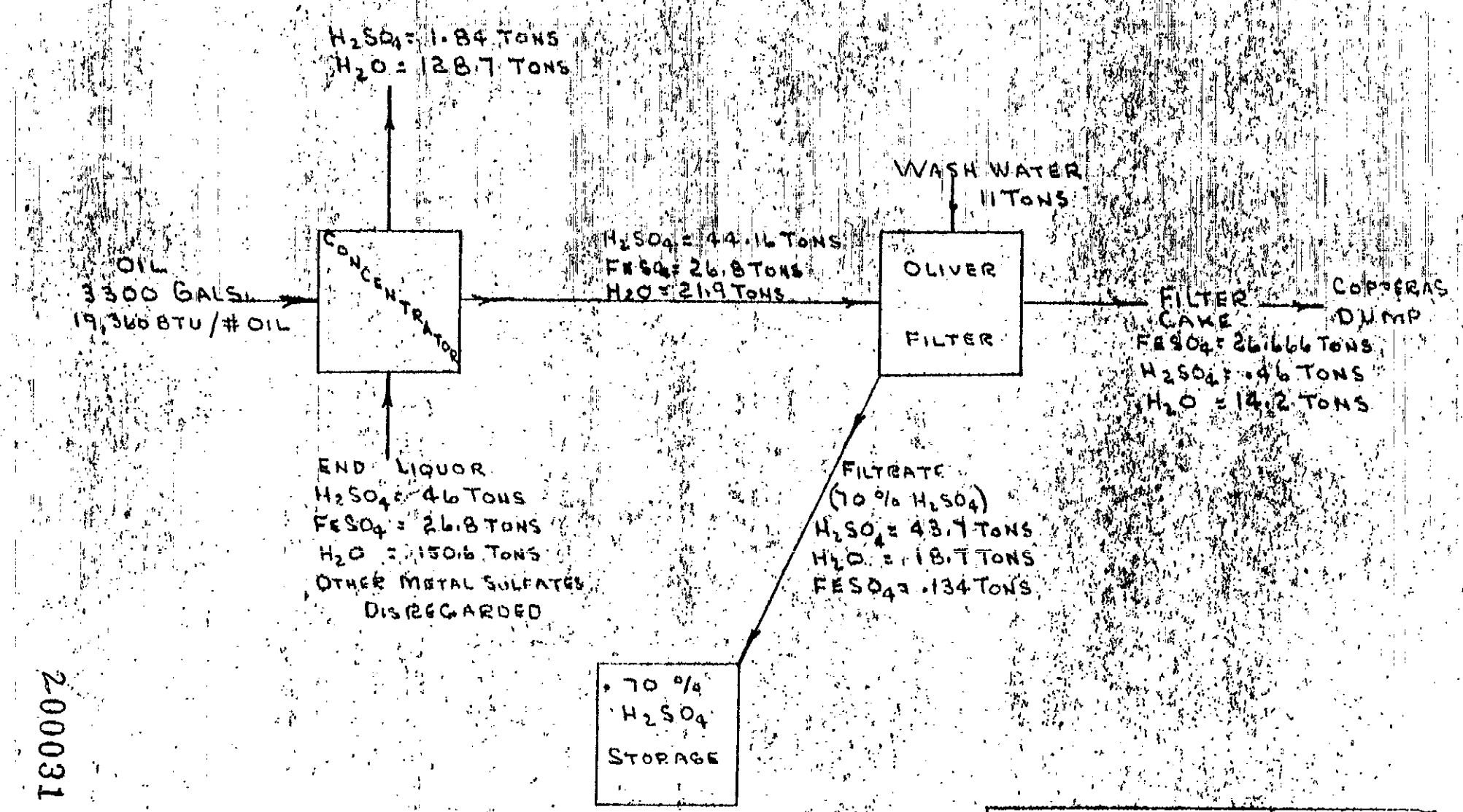
RECOVERED ACID COSTS
PROPOSED ACID RECOVERY PLANT
10,000 TONS TiO_2

PIDEX RIVER PLANT

Process Material	
Fuel Oil	$ 9,887.00
Productive Labor	2,420.00
Salaries & Wages - Supt.	200.00
Salaries & Wages - Foremen	-
Factory Supplies	50.00
Electricity	628.00
Insurance Compensation	19.00
Insurance, Other	6.00
Taxes - State & Local	60.00
Taxes - SUI, FUI, FOAP	39.00
Vacation Reserve	93.00
Miscellaneous Expense	50.00
Repair Labor	920.00
Repair Material	920.00
Depreciation	970.00
Service Department	
Yard Service	400.00
Chemical Engineering	100.00
Chemical Control Laboratory	100.00
Water	320.00
Boiler	225.00
Engineering	-
Receiving	50.00
Factory General	500.00
COST ABOVE	$ 5,650.00
GRAND TOTAL	$17,957.00
COST CHARGED TO ACID	$17,957.00

Tons 70% H_2SO_4 produced per month	=	1,747 Tons
Cost 70% H_2SO_4 $/Net Ton	=	$ 10.30
Acid as 100% H_2SO_4	=	1,224 Tons
Acid Costs 100% H_2SO_4 basis $/Net Ton	=	$ 14.65

200030



OPERATIONS DIAGRAM
BASIS: TONS PER DAY
28 DAYS PER MONTH
10,000 TONS TiO_2 PER YEAR

2000031

ASSUMPTION FOR COST ESTIMATE
PRODUCTION 70% H_2SO_4 FROM SPO LIQUOR
BASIS: 10,000 TONS TiO_2 PER YEAR
28 OPERATING DAYS PER MONTH

1. **Fuel Oil**

$0.107 per gallon (cost as of March, 1949). Oil consumption based on data obtained during the operation of the waste acid recovery pilot plant by Chemical Construction Corporation at Piney River, Virginia.
Oil consumed = 3300 gallons per day
3300 x 28 x $0.107 = $9,887.00

2. **Productive Labor**

1 operator per shift @ $1.21
1 helper per shift @ $1.01
1 truck driver per shift @ $1.01

Operator;
$\frac{365}{12}$ x 1 x 3 x 8 x $1.26 = $ 920.00

Helper & truck driver
$\frac{365}{12}$ x 2 x 3 x 8 x $1.06 = 1,500.00

$2,420.00 Per Month

3. **Salaries and Wages - Supt.**

Same as charged to Contact Plant = $ 200.00

4. **Salaries and Wages - Foremen**

No foremen required

5. **Factory Supplies** 50.00 Per Month

6. **Electricity**

Waste acid pilot plant = 2700 K.W.
Assume power consumption for plant to be same as pilot plant,
2700 x 28 x .0083 = $ 628.00

7. **Insurance Compensation**

.80424 of productive labor cost
2420 x .008042 = $ 19.36

200032

8. Insurance, Other

$0.04 Per $1000 investment
125 x $0.04 = $ 6.00

9. Taxes - State & Local

$0.40 per $1000 investment
125 x $0.40 = 60.00

10. Taxes - SUI, FUI, FOAB

1.6% Labor cost
2420 x .016 = 38.72

11. Vacation Reserve

1/26 of Productive Labor
1/26 x 2420 = 93.00

12. Miscellaneous Expenses = 50.00

13. Repair Labor

$0.75 Per ton 100% H_2SO_4 produced
43.7 x 28 x .75 = 920.00

14. Repair Material

Same as Repair Labor = 920.00

15. Depreciation

Equipment $110,000 @ 10% = 11,000
Building 15,000 @ 4% = 600
11,600 = 970.00

16. Yard Service

1 man per day
Five 8-hour days per week
4.33 x 5 x 8 x .97 = 168.00
Dumping charge for sludge
$0.20/Ton
41.4 x 28 x $0.20 = 232.00

17. Chemical Engineering

1 man 1/4 Time 100.00

200033

18. Chemical Control Laboratory

1 Analyst 1/3 Time	=	$ 100.00

19. Water

Same as Contact Plant	=	320.00

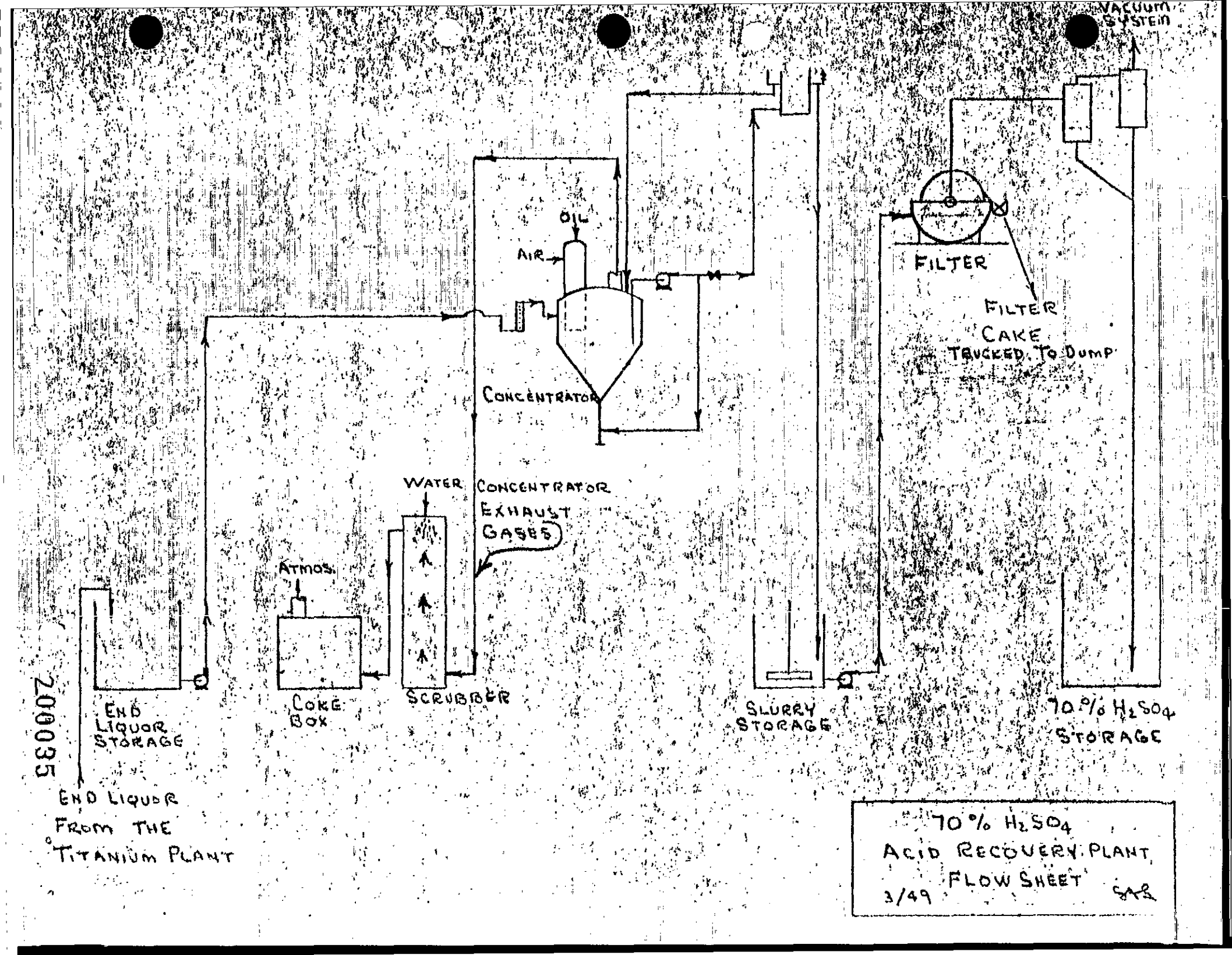
20. Boiler

Steam for heating	100,000		
Process steam	200,000		
	300,000		
At $0.75 Per 1000			
300 x $0.75		=	225.00

21. Engineering

No Charge

22. Shipping & Receiving	=	50.00
23. General Factory		
Assumed	=	500.00


VACUUM SYSTEM
OIL
AIR
CONCENTRATOR
FILTER
FILTER CAKE TRUCKED TO DUMP
WATER
CONCENTRATOR EXHAUST GASES
ATMOS.
END LIQUOR STORAGE
COKE BOX
SCRUBBER
SLURRY STORAGE
70% H_2SO_4 STORAGE
END LIQUOR FROM THE TITANIUM PLANT
70% H_2SO_4 ACID RECOVERY PLANT FLOW SHEET
3/49
200035

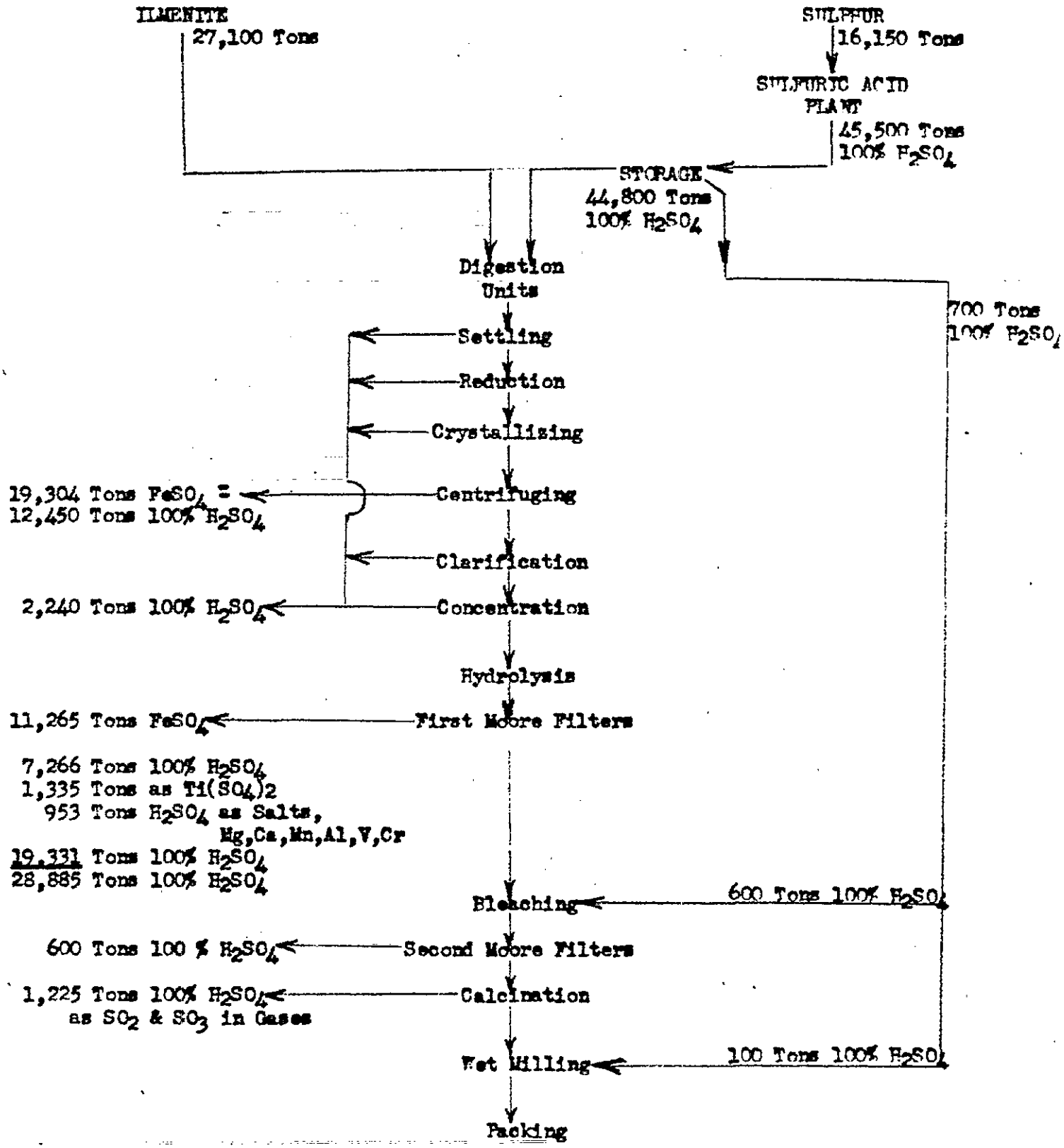
PLANT COST

	EQUIPMENT	INSTALLED
2	Concentrators @ $10,000	$ 20,000
1	Oil storage tank (8,000 - 10,000 Gals.)	1,000
1	12' x 12' wood lead-lined tank for end liquor storage	4,300
2	4' x 4' steel lead-lined distribution tanks @ $150.00	300
1	10' x 10' steel lead and brick lined tank with Nettco agitator for slurry storage	6,800
1	Oliver filter 4' ø x 5' face, acid resistant construction	10,000
1	25' x 18' steel tank acid brick lining filtrate receiver and 70% acid storage	15,000
6	1½" Worthite pumps @ $500.00	3,000
1	Scrubbing tower	3,000
1	Coke box	3,000
2	Spencer turbines @ $3,000	6,000
1	Oil pump	200
	Vacuum system (pump or ejectors)	3,000
	Piping	10,000
	Electrical Equipment	6,000
2	Dump trucks @ $3,000	6,000
	* Building to house concentrators and filter	15,000
	Miscellaneous	12,400
	TOTAL	$ 125,000

* Use concrete [illegible]
base used for
acid recovery pilot plant

TiO_2 MANUFACTURE
SULFURIC ACID DISTRIBUTION
VIRGINIA ILMENITE
PINEY RIVER PLANT

10,000 Tons Packed TiO_2 Per Year



200037

C
O
P
Y

April 16, 1948

Mr. E. Hladky

S. A. Lamanna

Mr. C. J. Kirkland
Mr. E. W. Samoden
(File)

Waste Acid to Recovery Plant

As you requested, I have prepared an estimate on the available waste acid to be delivered to the recovery plant from our present process; basis, 10,000 tons TiO_2 produced per year.

It is assumed that all of the copperas from the centrifuge step will be added to the end liquor recovered from the First Moore Filter. The end liquor recovered from the First Moore Filter will contain 80% of the free acid and metal sulfates contained in the hydrolysis liquor. The remaining 20% will be discharged as a dilute solution which cannot be economically recovered.

This estimate is based on acid consumption and waste acid distribution studies made in March, 1948.

Data shown is based on 336 operating days per year and expressed as tons per day delivered to the Acid Recovery Plant.

Copperas discharged from centrifuge	=	57.5	Tons $FeSO_4$/D.
Total weight discharged (as 50% $FeSO_4$)	=	115	Tons
End liquor discharged as 20% H_2SO_4 solution $\frac{46}{20}$ = total weight discharged	=	230	Tons
Total weight to recovery plant	=	345	Tons/D.

	From Copperas Centrifuge	From End Liquor	Total	% of Total Delivered to Recovery Plant
Free H_2SO_4	-	46.0	46.00	13.33
$FeSO_4$	57.5	26.80	84.30	24.44
$Ti(SO_4)_2$	-	3.90	3.90	1.13
$CaSO_4$	-	.29	.29	.08
$MgSO_4$	-	.56	.56	.16
$Al_2(SO_4)_3$	-	.84	.84	.24
$MnSO_4$	.12	.64	.76	.22
$Cr_2(SO_4)_3$	-	.12	.12	.03
$V_2(SO_4)_5$	-	.36	.36	.10
H_2O	57.33	150.59	207.92	60.26

S. A. Lamanna

200038