CR-160280

(NASA-CR-160280) SIMULTANEOUS STACK GAS SCRUBBING WASTEWATER PURIFICATION Final Report (Chemsoil Corp., Bakersfield, Calif.) 100 p HC A05/MF A01 CSCL 13B

N80-12620

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G3/45 38960

FINAL REPORT

SIMULTANEOUS STACK GAS SCRUBBING
WASTEWATER PURIFICATION

NASA CONTRACT - 9 - 14639

Prepared by

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SIMULTANEOUS STACK GAS SCRUBBING WASTEWATER PURIFICATION

Introduction and Background

About 1970 domestic supplies for possible fuel stopped increasing and demand went on escalating. Even more serious, the domestic oil supply didn't just level off, it began to decrease sharply in 1973, as shown in Figure 1.1. It can be seen in Figure 1.2 that the United States electrical energy demand increased similarly to the total energy demand. Without oil and gas availability, the demand must be met by coal and nuclear power. Figure 1.3 shows an estimate of the use of coal between 1970 and 1990. This value more than doubles in order to meet the electrical demand. To protect the environment from the adverse effects of using all this coal, a high level of SO_2 scrubbing must be attempted in the United States. Prior to the energy crisis, the Environment Protection Agency, which was formed by Congress as a result of public pressure for cleaner environment, had forced reduction in almost all forms of pollution. In stack gas emissions of sulfur dioxide from electric generating plants the reduction was primarily from the use of low sulfur coal and oil. However, with the onset of the energy crisis a demand in the need for substitute energy sources for gas and oil, the pressure to utilize "dirty fuel" such as high sulfur coal and high sulfur oil increased.

The Chemsoil Corporation has developed a process which we feel can economically reduce air pollution in plants using fossil fuels. The purpose of this test program was to develop

FIGURE 1

U.S. ENERGY DEMAND & SUPPLY

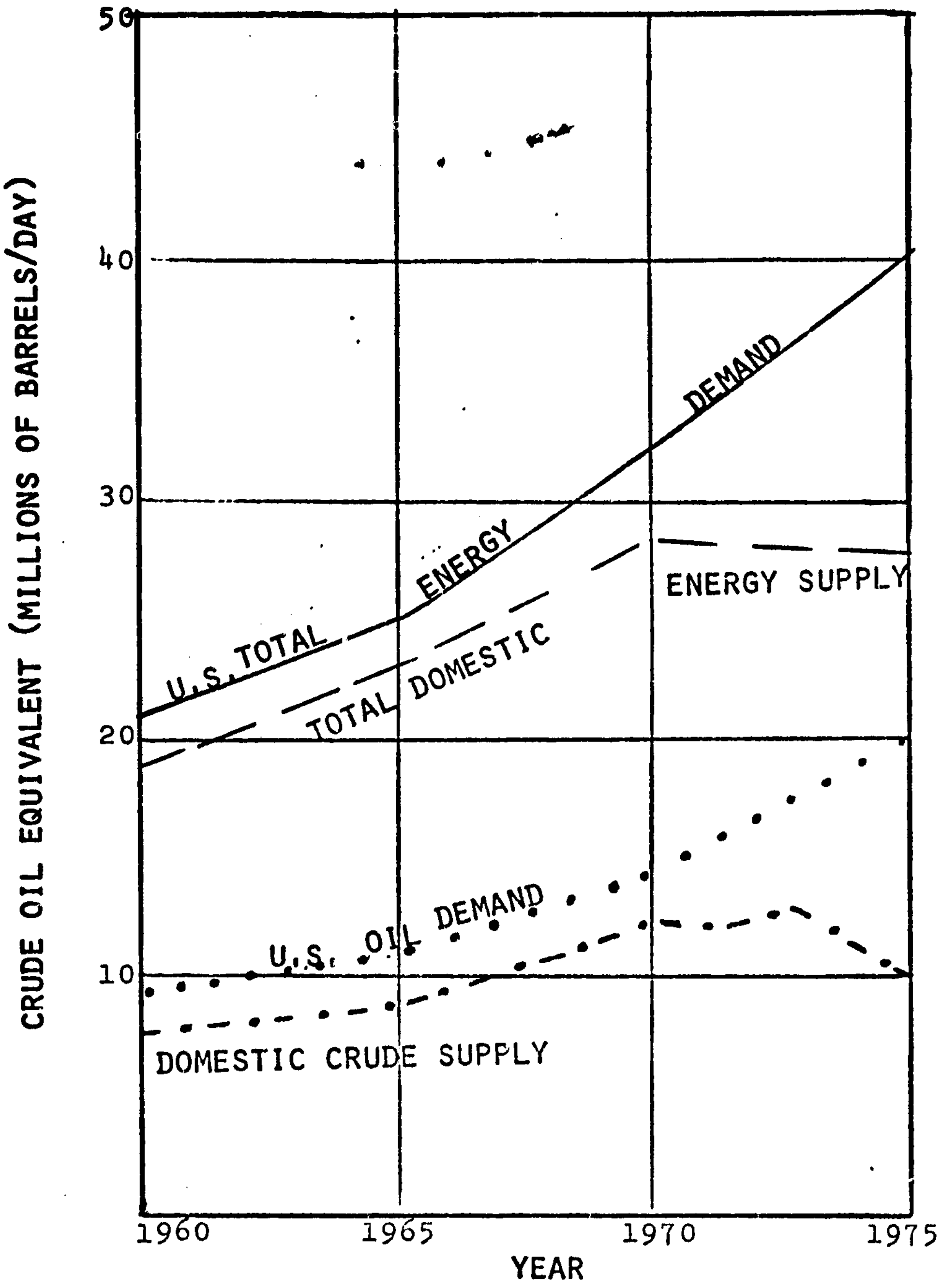


FIGURE 2

U.S. TOTAL ENERGY AND ELECTRICAL DEMAND

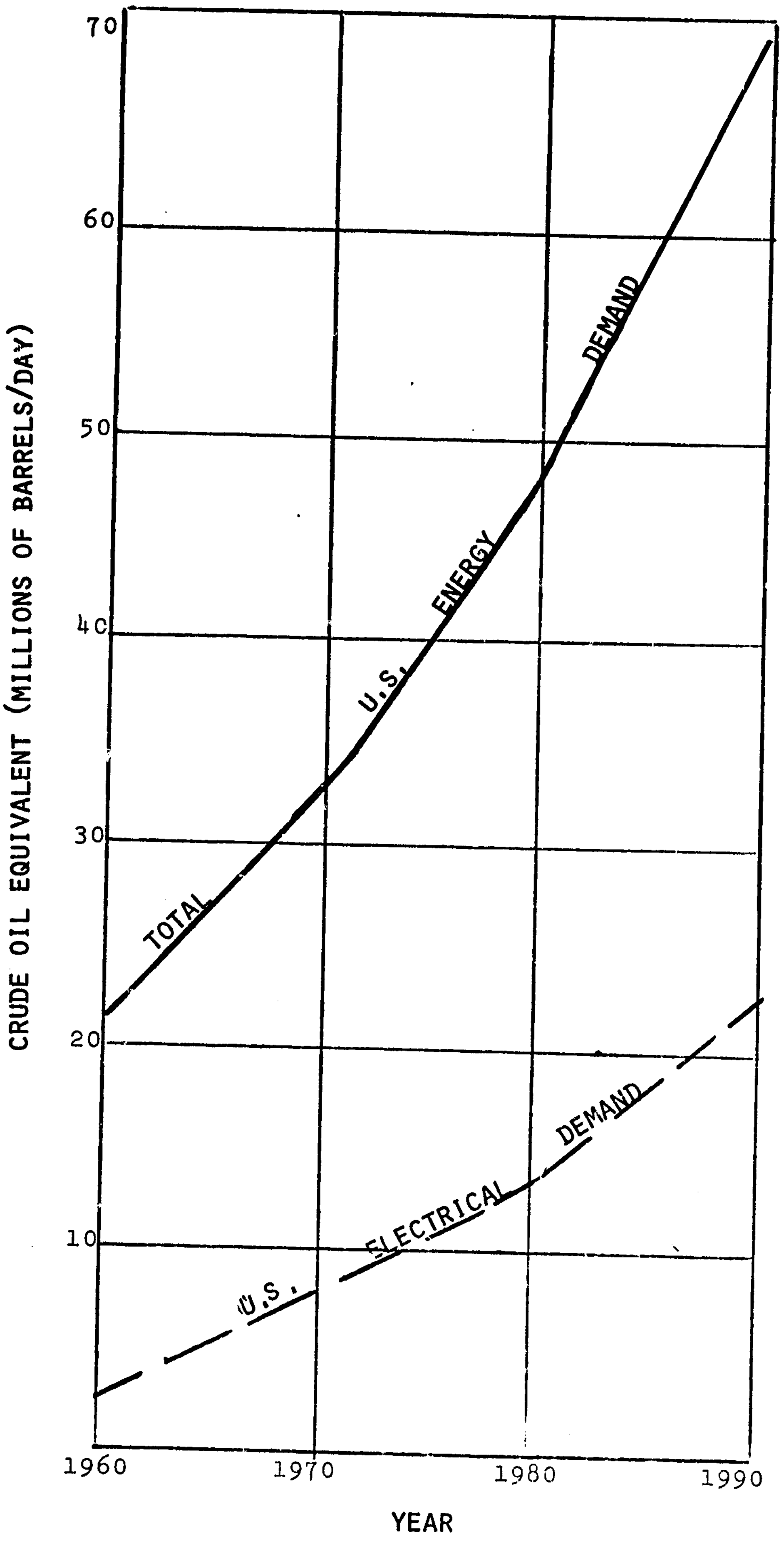
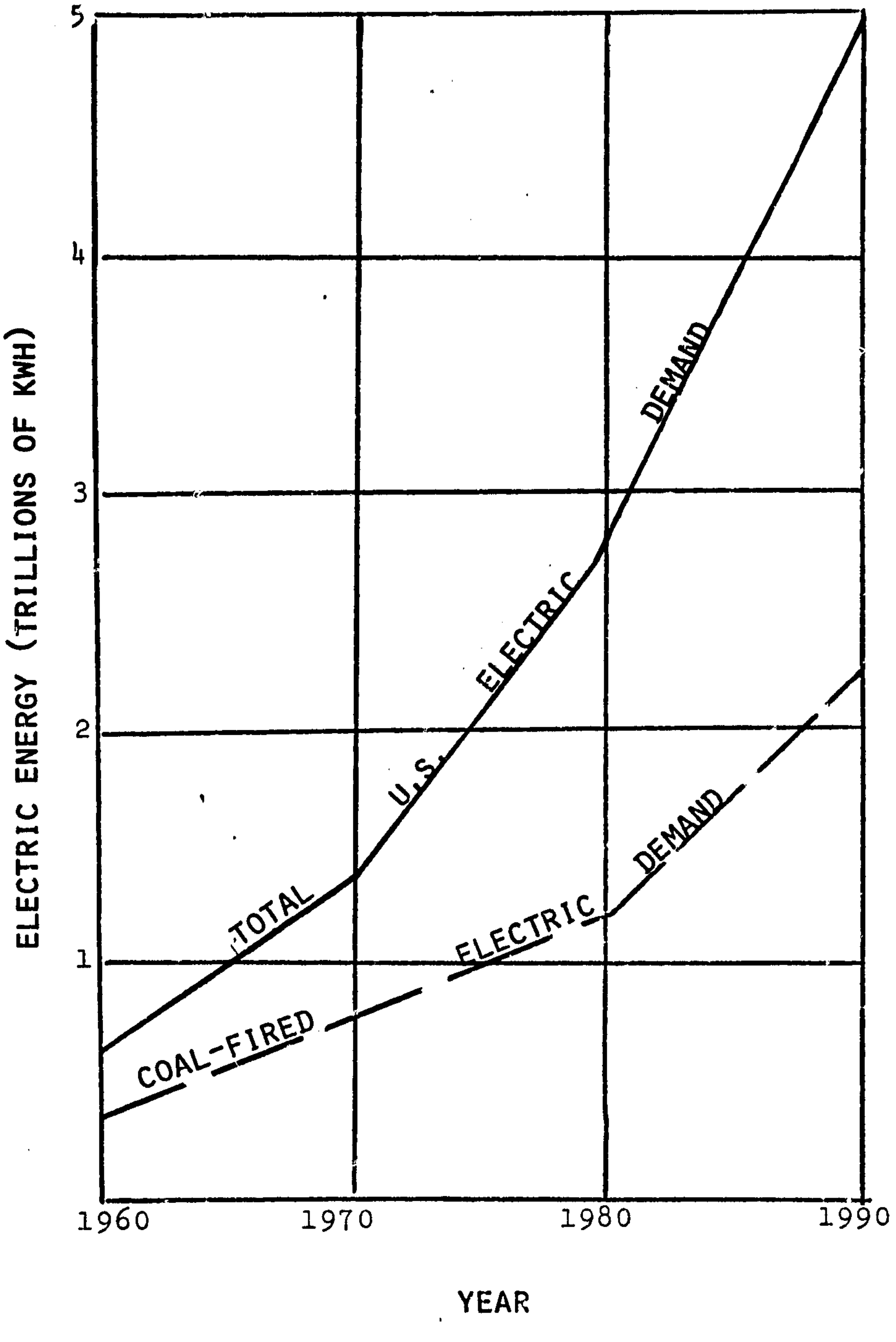


FIGURE 3

U.S. ELECTRIC DEMAND
(TOTAL AND COAL-FIRED)



through laboratory scale tests the information required to produce larger plants and to identify the technical problems involved with the scrubbing process. The Chemsoil process can be produced in several variations;a) Once-Thru system which lowers the pH of the scrubbing water from minor depressions to a pH of about 2.5 under certain conditions, b) a recycle system using iron for catalytic oxidation of sulfurous acid to sulfuric acid allowing very large amounts of sulfur dioxide to be absorbed in a small portion of water, c) partial recycle system using municipal wastewater and iron as a scrubbing media followed by neutralization of the wastewater with lime to produce an iron hydroxide percipitation which when removed produces tertiary quality treated wastewater. The development of processes for removing the SO_2 from stack gases and purifying municipal wastewater have developed along separate paths at the Chemsoil Corporation. One, the development of the sulfur dioxide permeater, and the other, the development of the Lin-Pro wastewater treatment system.

SO_2 Scrubber

Early in 1969 the Chemsoil Corporation undertook the method of converting elemental sulfur to sulfurous acid which could be used with irrigation waters to aid in water permeability to the soil. The problem involved oxidizing elemental sulfur to SO_2 and absorbing the SO_2 into the water to form consistent quality of sulfurous acid.

Early in 1972 a successful method was developed using cylintrical P.V.C. rings in an unflooded packed tower with counter current airflow to perform the scrubbing process. The company immediately began to produce what now is known as the Chemsoil SO_2 permeater which can be found in eleven western states and a number of other countries for neutralizing the alkaline soil. It was realized at this time that the same method of absorption could be utilized for controlling stack gas emission from power plants. A short test program was proposed to the city of Los Angeles, and this program was carried out under the direction of Los Angeles City engineers at the Scattergood power plant in Santa Monica, California.

Figure 4 shows a flow diagram and the measuring points for the SO_2 Scrubber at the Scattergood Power Plant. The flue gas was the slip stream from the large exhaust stack which was then taken through the permeater by a turbine. The water inlets and outlets are also shown. Both city tap water and sea water were used in the test.

Figure 5 shows the results of those tests in a liquid to gas ratio, commonly referred to L/G versus percent removal of SO_2. The test was run at 175 ppm SO_2 level which is quite low. It can be seen that L/G of 50 is where the 100% SO_2 removal occurs. This result may be skewed somewhat to the high L/G side, because with the gas flow rates of between 130-200 SCFM, the water flow rate required for complete removal is around 3 gpm which is approaching the point where total scrubbing is not

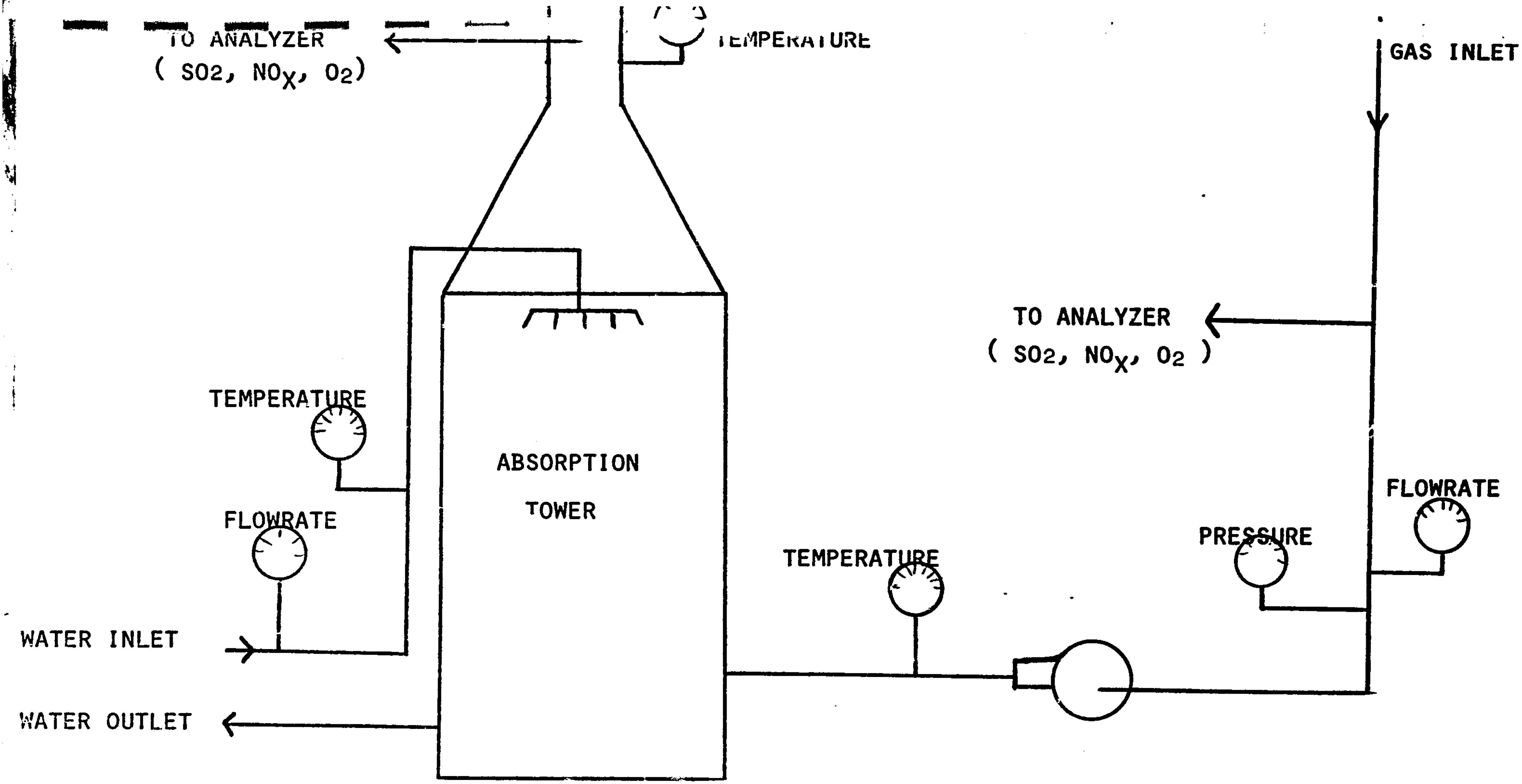


FIGURE 4

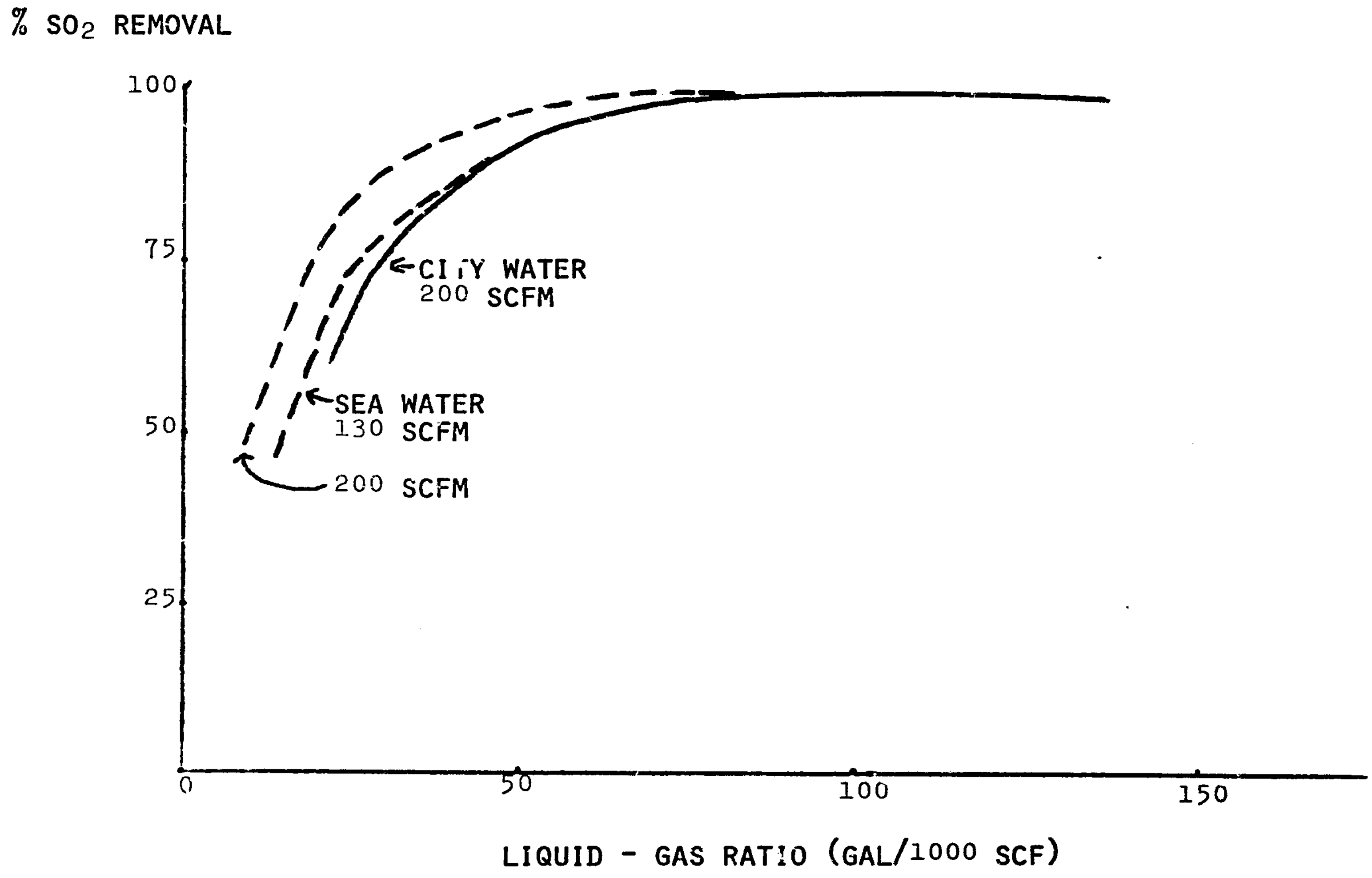
FLOW DIAGRAM AND MEASURING POINTS FOR SO_2 SCRUBBER

FIGURE 5

SO_2 REMOVAL VS. L/G RATIO

LA TESTS

175 PPM



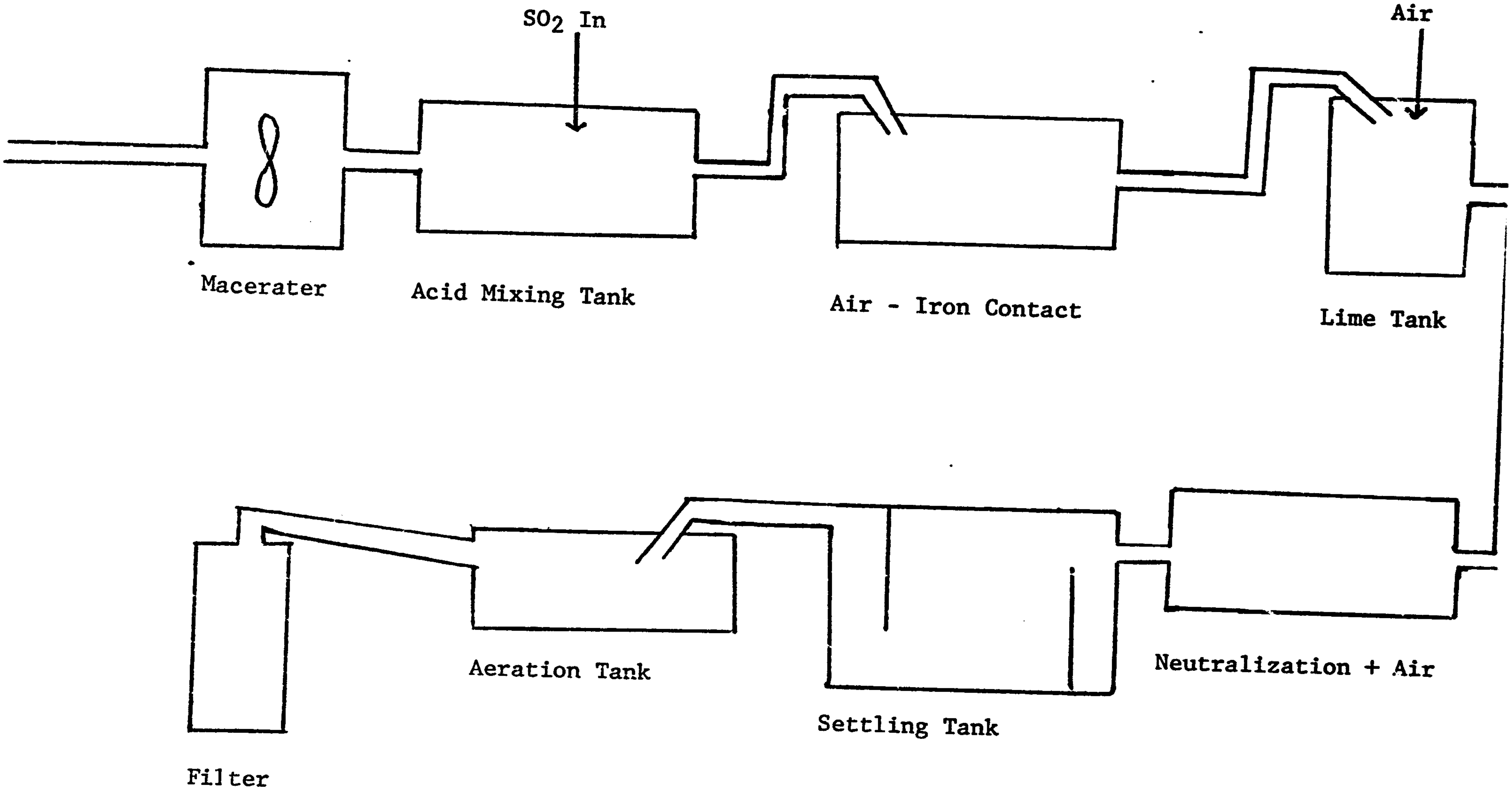
achieved because not enough water is available for complete packing coverage.

Three problem areas were identified by Los Angeles City engineers. They were; 1) a plume was visible in the exhaust, 2) gas reheat is required, and 3) there is a potential for plugging of packing material. Now, gas reheat is always a problem with a wet scrubber. No plugging was identified in any way during the Scattergood test nor in the test series completed. The visible plume was partly due to the spray system used to introduce the water in the tower. If gas reheat is used, no plume would be visible.

The conclusions of the report of the Scattergood test program were; 1) the recycle system was required in light of the national goal of zero discharge made by EPA, and 2) other systems are being developed so that further testing of the Chemsoil Unit was not required.

About the same time that the permeater was being developed the Chemsoil Corporation developed the Lin-Pro wastewater treatment system, which basically uses sulfurous acid or sulfur dioxide to act as a wastewater treatment chemical in a physical chemical treatment system. A schematic of a Lin-Pro system is seen in Figure 6. The wastewater enters the Lin-Pro system, goes through a massarator, or grinding step to reduce the size of the particles in the wastewater. At that point, the liquid from the massarator is pumped to an acid mixing tank where sulfur dioxide is added until the pH is reduced to about 2.5.

Figure 6
LIN-PRO WASTEWATER TREATMENT



The pH is maintained at 2.5 by an automatic sensing device which regulates the flow of sulfur dioxide into the water. The amount of sulfur dioxide required to maintain this pH level is somewhere between 1¼ and 2 pounds per thousand gallons of wastewater processed. From there the liquid passes to an iron tank for further treatment. The acidified liquid flows through iron, in the form of normal scrap iron, and air is injected at the same time. During a short mixing time there is sufficient opportunity for the acidic water to put ferrous and ferric ions into the solution. Once a sufficient amount of iron has been picked up, the liquid flows from the iron tank into a neutralization tank where lime slurry solution is added to the liquid flow. The amount of lime used varies from 1½ to 2 poinds per thousand gallons also. The whole mixture is agitated vigorously for approximately fifteen minutes. A thorough mixing in the neutralization tank is required in order to produce the desired chemical floculate. At this point, the wastewater flows to the settling tank and the floculate is permitted to settle out in the tank. The principle flock at this point in time is ferric hydroxide, and because of the initial acidification and then neutralization, the zata potential has been found to run around zero, so that rapid settling is attainable. After the settling has taken place the liquid flows into an aeration unit to make sure that the wastewater has the correct amount of dissolved oxygen before being discharged. After a short aeration time the final effulent is filtered to remove any traces of suspended solids. Average test performances have demonstrated that the coliform count can be reduced to less than 2.2 ppm per hundred mililiters. Chemical and biological oxygen demands can be reduced up to 98%. Phosphate can be reduced nearly 100%. However, varying amounts of reduction have been attained for the nitrogen, and this is still one of the questionable points in the process.

During 1974 Chemsoil Corporation and NASA engaged in technical discussions which culminated in June of 1975 with the contract award for the investigation of a simultaneous stack gas emission control and wastewater purification unit. Thus, SO_2 from a power plant stack gas emissions is used as the SO_2 ingredient, (sulfur dioxide) in the Lin-Pro type system using the permeater as a means of separating the SO_2 in the gas stream and injecting it into the wastewater solution.

Technical Requirements of the Contract

Basically contract NAS 9-14639[illegible] can be broken into three segments; technology evaluation, laboratory investigation, and process sequence design.

TECHNOLOGY EVALUATION

The Technology Evaluation was studied and it was decided that the NASA sponsored WESRAC program provided by the University of Southern California would provide the most prolific amount of information abailable on this subject.

A meeting was set up with Dr. Robert Mixer to determine which key words would be selected for the data bank interrogation. The major titles we selected for printout were a number of key words within the major titles. The major titles and number of hits received were as follows:

1. Sulfur Dioxide - 1252
2. Oxides of Nitrogen - 753
3. Ozone - 260

Copy of the print outs were sent to the NASA technical monitor in a review made by myself. We selected various hits which we felt were appropriate for our study and requested ESRAC to provide copies of the abstracts for analysis. The abstracts were studied and in cases of pertinent information, the entire article was acquired (translated if necessary) and studied.

At this point we asked WESRAC to additionally run retrospectives on:

a. Catalytic reactions of ozone
b. Calcium Sulfate, ferrous oxide and ferric oxide solubility

The same procedure relative to hits and acquistion of pertinent information was followed as above. WESRAC data bank search was drawn from the chemical abstract data base. In addition the National Technical Information Service Division of U.S. Department of Commerce (NTIS) was contracted and copies acquired on all information printed on the same subjects, relative to this report. These two professional data sources were added to the already existing library of the Chemsoil Corporation in order to provide what we believe to be a thorough bank of information relative to this subject matter.

LABORATORY INVESTIGATIONS

The Laboratory Investigation phase of the contract required testing of a great number of varying parameters to identify which ones were important and which ones were not. Photograph 1 shows the NASA-CHEMSOIL test facility with the tower packed to 16 feet.

In the Once-Thru testing, eight parameters were to be varied according to the contract. These included investigation of five different sulfur dioxide input levels, six water flow rates through the tower, four gas temperatures or reacting temperatures, five gas velocities, five detention times which were achieved by varying the height of the towers, three bed diameters, three packing sizes, and three different types of water. Looking at Figure 7, one can see a progression of the number of possible tests which could have been conducted under this contract. It was not the intent to test all those test points, but to test a representative number so that smooth line curves could be drawn to estimate the values of any of the intervening parameters. Through the test phase it was determined which parameters did not have to be fully investigated, or which parameters could not be fully investigated.

Table 1 shows that within the contact times and gas velocities required by the contract and a limitation of 16 feet placed in the contract on the maximum height of the tower, there were a number of tests which could not be performed. Those tests

Photograph 1

Figure 7

Once-Thru Potential Number of Tests

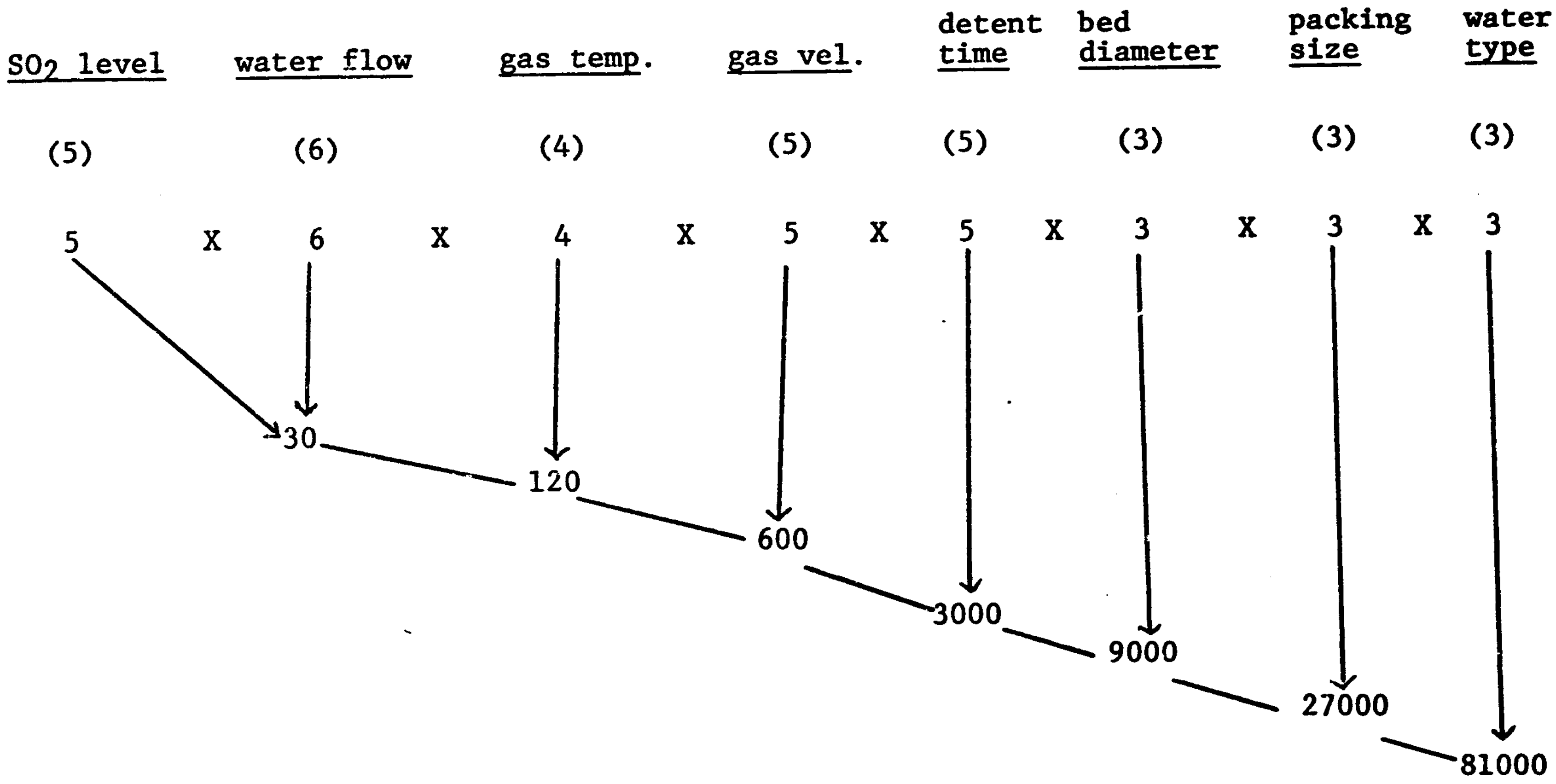
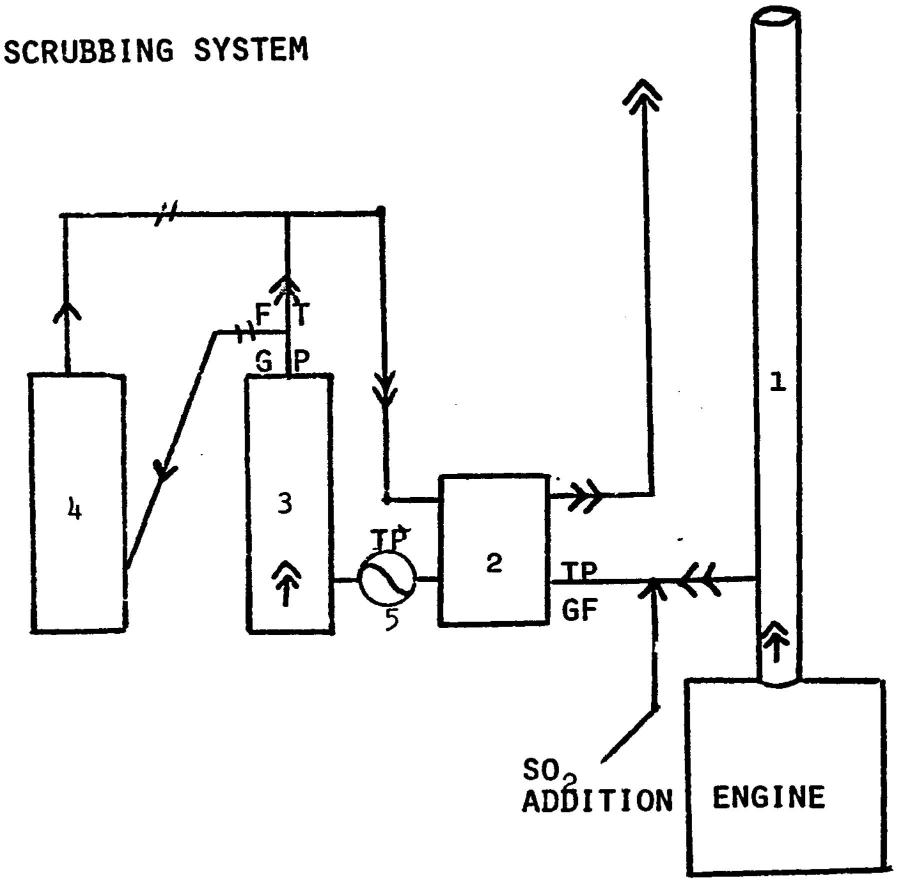


TABLE 1

AIR FLOW SCHEMATIC

SO_2 SCRUBBING SYSTEM



1. MAIN EXHAUST STACK
2. HEAT PIPE HEAT EXHANGER
3. SO_2 TOWER (NO. 1)
4. SO_2 TOWER (NO. 2)
5. TURBINE

for instance, at 8 seconds contact time, 3 and 3½ ft./sec., 20 seconds of contact time and gas velocity of 1, 3, 3, 3½ ft./sec., could not be tested. In addition, after testing began, it was found that tower configuration was unable to achieve velocities much in excess of 2½ ft./sec. because the gas velocity at that point tended to hold the water in the tower causing water flooding and tests were for an unflooded tower, thus testing at 3 to 3½ ft./sec. gas velocity could not be achieved under the physical constraints of the tower configuration. It was decided by the NASA technical monitor and the contractor to test at one, two, and three thousand ppm SO_2 levels, leaving out the five hundred and fifteen hundred levels described by the contract in order to save time and still cover a wide range of SO_2 concentrations. It had been known from NASA testing, for instance, that the difference between five hundred and a thousand, and fifteen hundred and two thousand were straight line curves; thus the information gained from one to three thousand was enough to extrapolate and interpolate between those points to find the actual values that could have been achieved through testing of the five to fifteen hundred ppm levels.

In actuality, although five detention times from one to twenty seconds were prescribed, there was a vastly larger number of contact times that fell out of the actual test itself, including a contact time as long as 32 seconds. The tower dimensions did not exceed 18 feet including the stack which meant a bed depth of 16 feet as prescribed by the contract. And tests were performed on three different packing dimensions as well as the three different types of water. A test was done early in the contract which determined that about one gallon per square footage of surface area of packing was the minimum flow which would produce reliable results. At that point the technical monitor and the contractor agreed to test at 1, 3, and 5 gpm per square foot surface area and interpolate to 4 gpm square foot levels. Tests were run at 110° and 140° as well as 85° to determine the effects of temperature, and information could be interpolated and extrapolated beyond those numbers. With all of the constraints mentioned and with the addition of a series of tests to identify the advantages and disadvantages of a distribution tray as a manner of water distribution over the pack versus a spray system, the total number of tests conducted in the Once-Thru series, approximately 695. These are summarized on Table 2 showing some 135 basic tests with 54 variations on those for 3 diameter tower, 59 on the one diameter tower, 120 tests at 140°F, 54 more at 115°F, 135 tests on various packing sizes, 18 tests on water types. For each one of these tests equilibrium had to be obtained and 12 measurements were taken, all summarized in Table 2. Each of these measurements had to be taken at least two times to varify that equilibrium had been reached. There were some 8200 final data points recorded. At least that many more had to be taken to varify equilibrium.

TABLE II

ONCE-THRU TEST SUMMARY

Basic		135
Tower Diameter	3 Ft.	54
	1 Ft.	59
Temp.	140	120
	115	54
Packing Size		135
Spray & Tray		120
Water Type		18
		695

Each test point measured the following parameters

1 gas flow
2 SO_2 level in
3 water flow
4 SO_2 level out
5 tower pH
6 SO_4 concentration ≈ 8200 data points
7 SO_3 concentration
8 gas temp in
9 gas temp out
10 water temp in
11 water temp out
12 tower Δ p

ANALYTICAL EQUIPMENT AND PROCEDURES

The following laboratory tests were conducted at the NASA test sight:

1) SO_3 and SO_4 content of the water (done by wet analysis)

2, Fe^{+2} and Fe^{+3} content of the water (done by wet analysis)

3) the pH of the water (Orion specific ion meter with a glass electrode)

4) the SO_2 content of the gas stream as it entered and exited the tower (Envirometrics 200 SO_2 - NO_x analyzer)

5) dissolved oxygen (Delta Scientific 1010 Dissolved Oxygen Meter)

6) Electro-Conductivity (Wheatstone Bridge)

The following is a more detailed description of the wet analyses run in the NASA field laboratory.

SULFITE
Titration Method
Hach Method
APHA Standard Methods 13th Ed. pg. 337

This method involves a water sample that must be acidified and treated with a starch indicator before being titrated. A 50 (ml) water sample was used in all cases and 1 (ml) of 1:1 H_2SO_4 was added for adicification before the 1 (ml) of starch solution was added. This solution was then titrated with a Potasium Iodide-Iodate standard solution (0.0025 or 0.075).

The acid releases free iodine which is reduced to colorless iodide by sulfite. Once the sulfite is expended, a blue color will appear due to excess iodine reacting with the starch. Below is the formula for calculating the ppm of sulfite present in a given sample.

Calculation

$$\frac{\text{(titration) (normality) (40,000)}}{\text{ml of sample}}$$

SULFATE
Turbidimetric Method
Hach Method
APHA Standard Methods 13th Ed. pg. 334

The procedure for determining sulfate is a modification of the Barium Sulfate Turbidimetric Method. A single dry powder reagent called Sulfa-Ver IV Sulfate Reagent will cause a milky percipate to form if sulfate is present. The sulfate reagent also contains a stabilizing agent to hold the percipitate in suspension for turbidimetric analysis. The amount of sulfate present is directly proportional to the amount of turbidity formed. Standard sulfate solutions were used for daily accuracy checks as well as for the formation of a curve which was used to determine the ppm of sulfate present by direct comparison with the percent transmittance of the sample.

Ferrous & Ferric Iron Analysis
1,10 - Phenanthroline Method
APHA Standard Methods 13th Ed. pg. 189

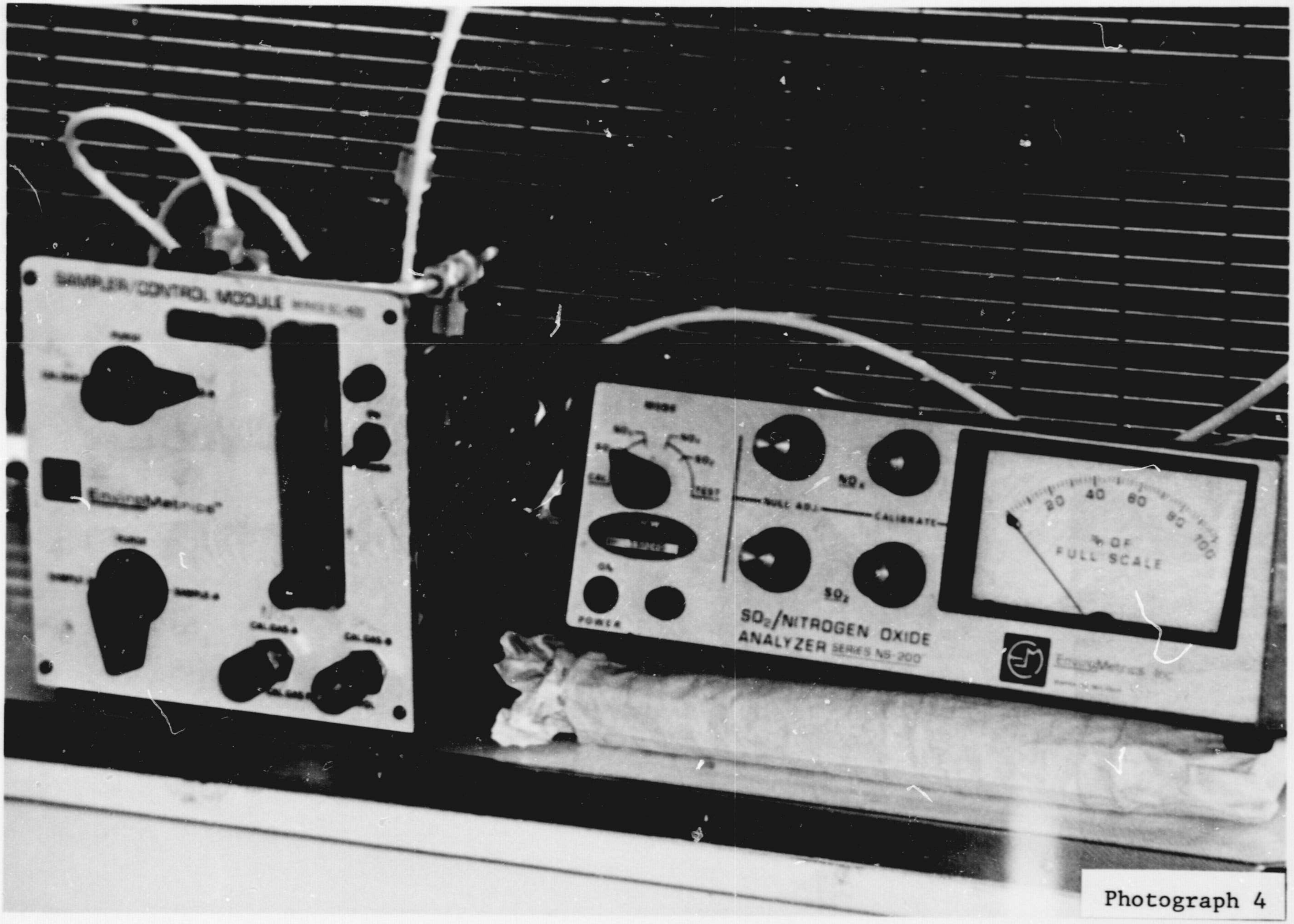
The 1,10 - Phenanthroline reagent gives an orange color with ferrous iron and is free from common interferences. The indicator is combined with a reducing agent for Total Iron analysis in a single powder formulation called Ferro-Ver Iron Reagent. The amount of ferric iron present can be determined as the difference between the amount of ferrous iron and the results of a total iron test. The Ferro-Ver Iron Reagent converts all the iron present to the ferrous state.

A standard iron solution was used daily to check the accuracy of this method. A curve was developed for converting from percent transmittance to ppm iron.

Sulfer Dioxide Analysis
SO_2-NO_x Analyzer

The SO_2 present in the system was monitored with an Envirometrics Series 200 SO_2-NO_x Analyzer. The sampling port for the SO_2 into the system was located at the point where the air containing the SO_2 and the diesel exhaust entered the tower. The sampling port for the SO_2 out of the system was located in the exhaust hose at the top of the tower. The sampling lines were run through cold traps prior to entering the analyzer. The analyzer was standardized with a standard SO_2 calibration gas daily to insure accuracy. The Envirometrics SO_2-NO_x analyzer and the valve and pressure gauge for it are shown in photographs 3 and 4.

Photograph 3



Photograph 4

REPRODUCIBILITY OF THE
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Due to a lack of laboratory space and technition time some analyses were sent to a local laboratory for testing. The tests run by B.C. Laboratory were mainly on wastewater samples and were as follows:

1) Coliform
2) Phosphate
3) Ammonium
4) BOD
5) COD (total and soluble)

Photograph 5 shows the inside of the NASA-CHEMSOIL field lab.

Photograph 5

Test Results

Once-Thru Scrubbing System. Figure 8 shows a schematic for the Once-Thru parametric flow test. On the right hand side one can see that when raised water temperatures were required, water was circulated through a water heater and into a holding tank until a large enough volume of water at the correct temperature was available for the test. Otherwise, tap water was pumped through a flow meter into the tower. At the same time gas was being collected from the exhaust of the diesel engine, SO_2 added, temperatures and flows measured through the turbine, and into the bottom of the tower. Sample points for the SO_2 from the inlet and the exhaust of the tower, which are taken sampling conditioner and into SO_2 monitor is also shown in the Figure.

At this point we'll go through the test results which identify the effects of the different parameters that were investigated. In addition to the parameters that were anticipated to be tested by the contract, one additional area was investigated in detail. This area is the effectiveness of tray distribution system versus the spray distribution system that was originally designed into the system. Early in the test program it was noted that unless the spray was very very accurately controlled, there were large variations in the test results. Because of this, a distribution tray was ordered for the 2 foot diameter tower. Subsequently, tests were run which identified the effectiveness of the tray versus the spray.

Figure 8

ONCE-THRU

PARAMETRIC

FLOW

TESTS

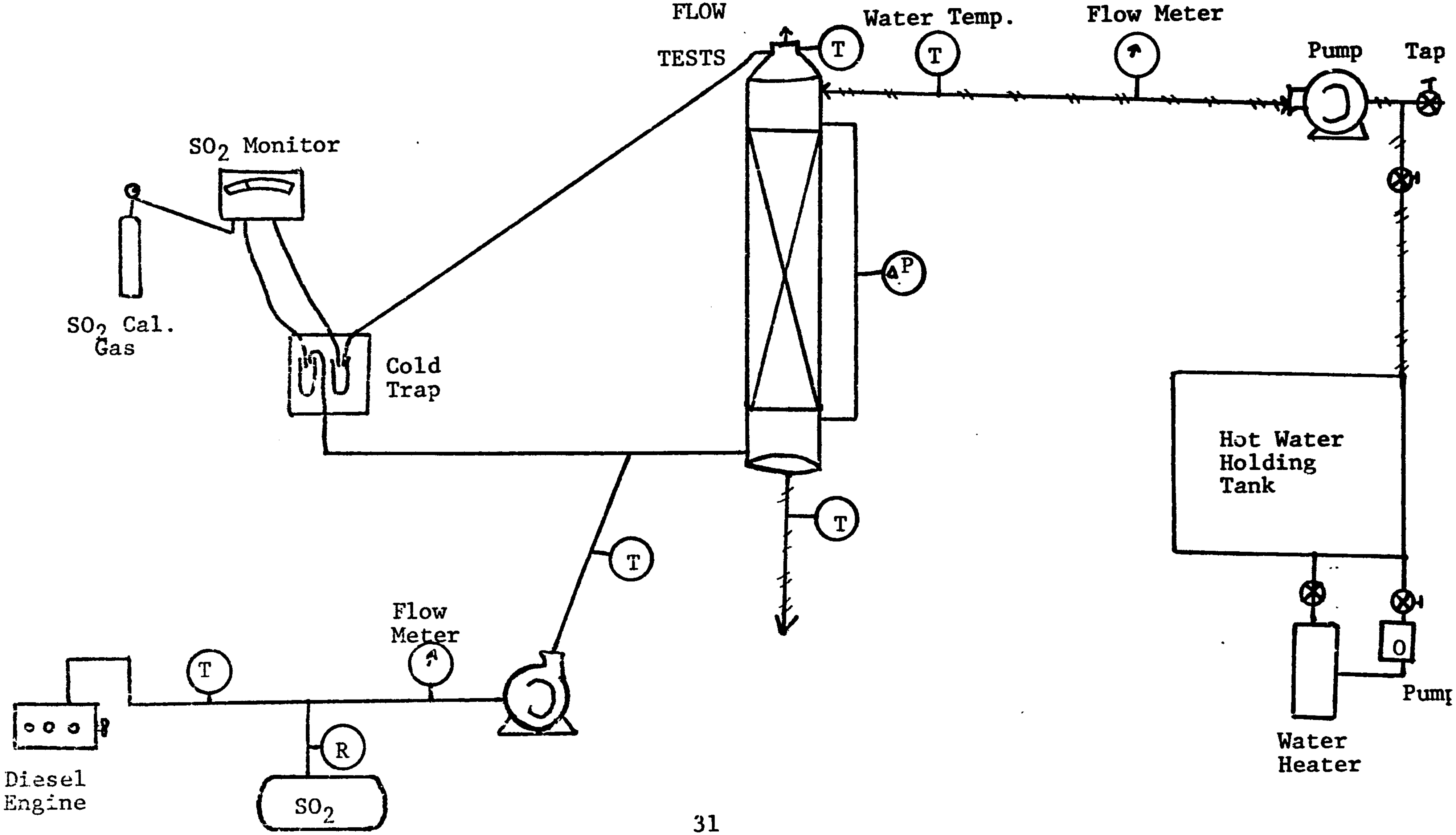


Figure 9 shows two different sets of test points for the one thousand, two thousand, and three thousand ppm input level of SO_2. These results are from a two foot diameter, four foot deep bed tower, at 4 gpm and they show that there is a distinctive difference in efficiency at the low cfm ratings. As the gas velocity increases the results from the tray and spray tests tend to merge. This trend was evident not only for the 4 gpm tests, but also for the 9 and 12 gpm tests. Basically, only at the low flow rates was there a significant difference in efficiency of the two systems.

Level of SO_2 Comparison. Because the SO_2 level at the inlet changes the partial pressure of SO_2 in the gas stream, there is more tendency to put higher levels of SO_2 into the water at higher levels of SO_2 concentration. This phenomena proved to be very reproducable; Figure 10 shows that at varying SO_2 levels, the amounts of SO_2 inserted into the gas through the scrubbing process was almost a straight line condition.

Levels obtained from the Chemsoil data were compared in Figure 11 to that which had been found in laboratory investigations through the years using distilled or deionized water. As can be seen the Chemsoil system puts more SO_2 into the water; however, because tap water was used, high carbonate content and thus more apparent absorption is to be expected.

Table 3 is a summary of the data collected from the Once-thru tests put into proper perspective by comparing the L/G ratio of the various tests. This table summarizes a great deal of information. The most important thing indicated is

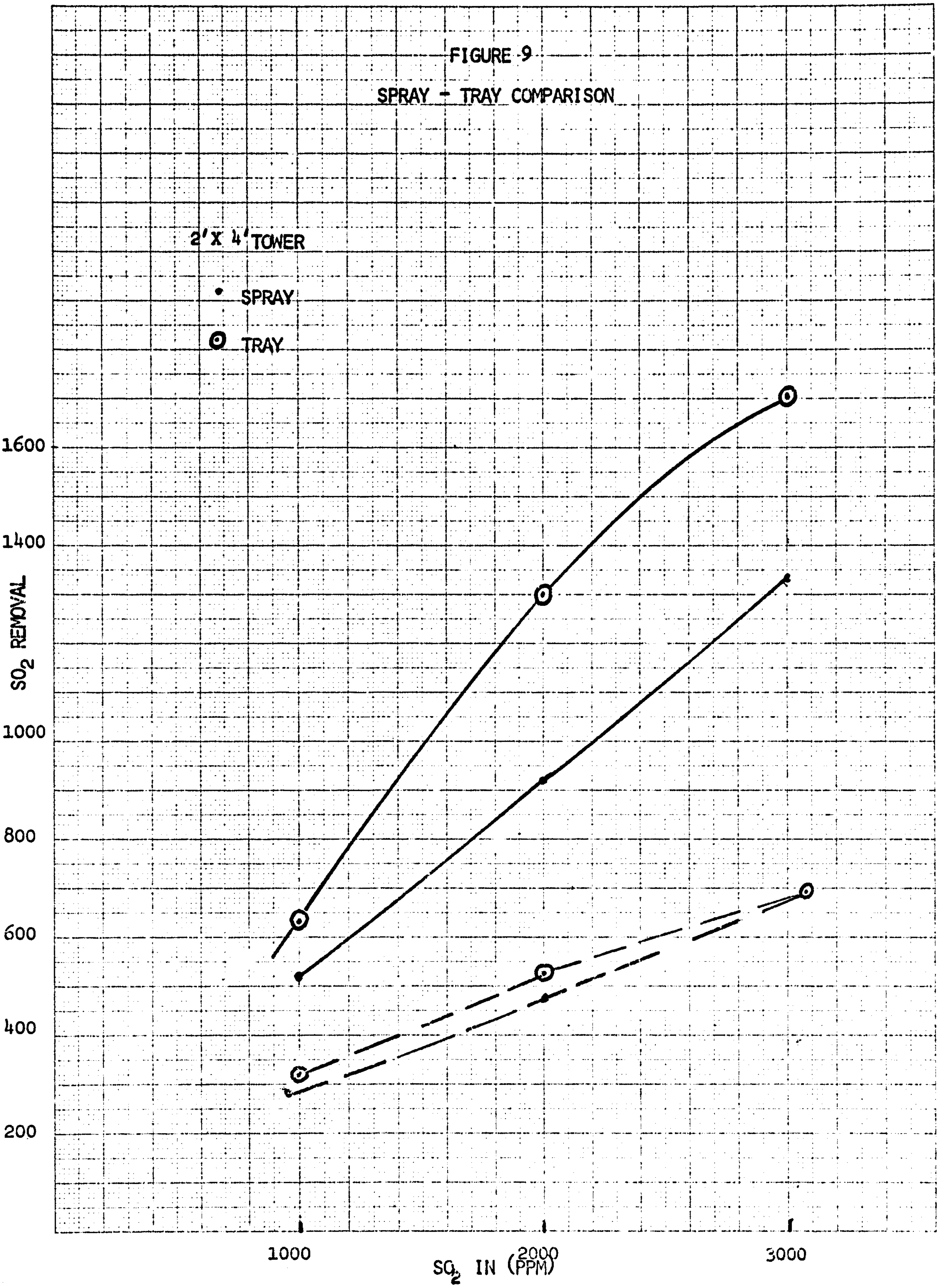


FIGURE 9

SPRAY - TRAY COMPARISON

FIGURE 10

WATER CAPACITY FROM TESTS

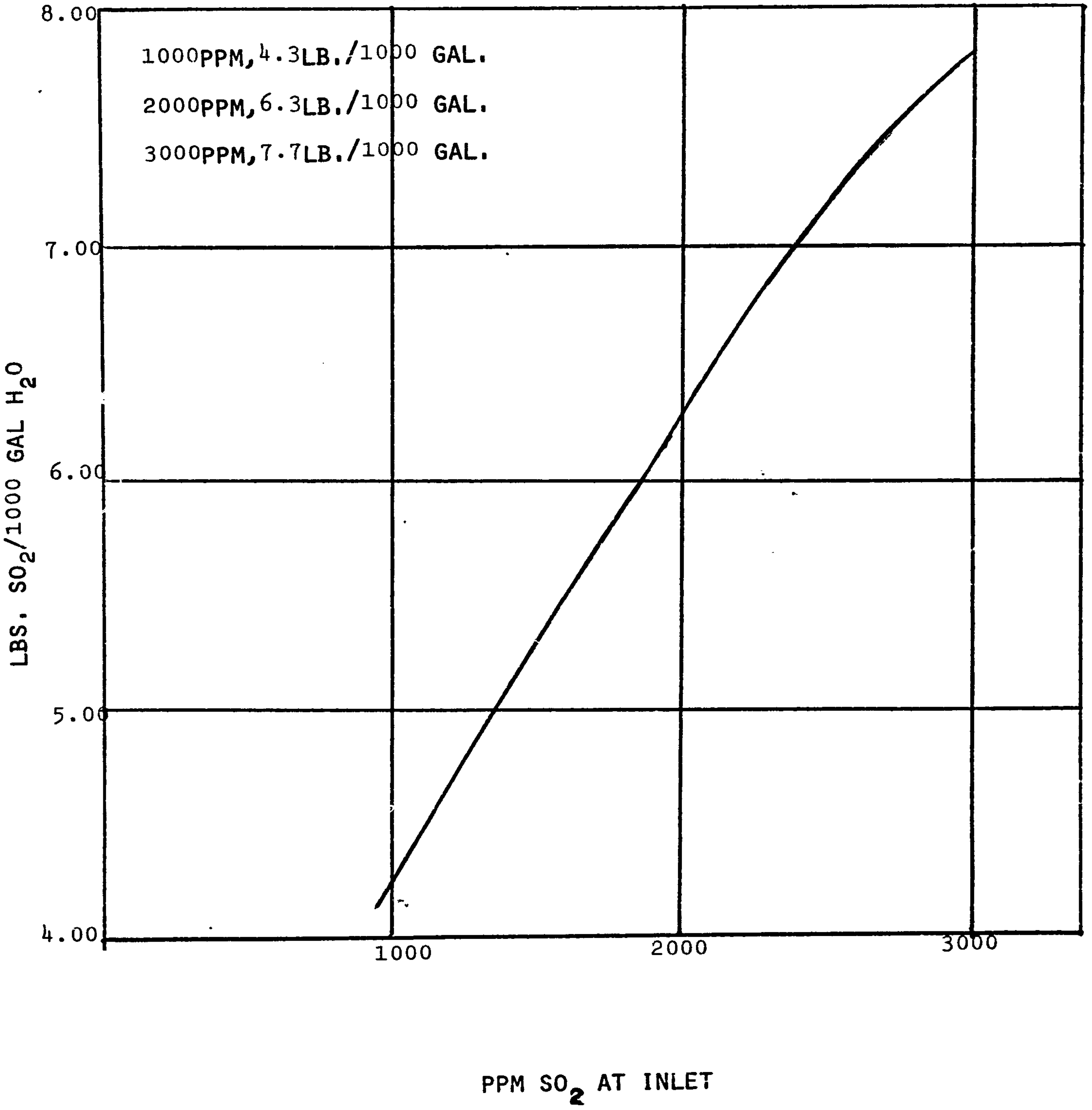
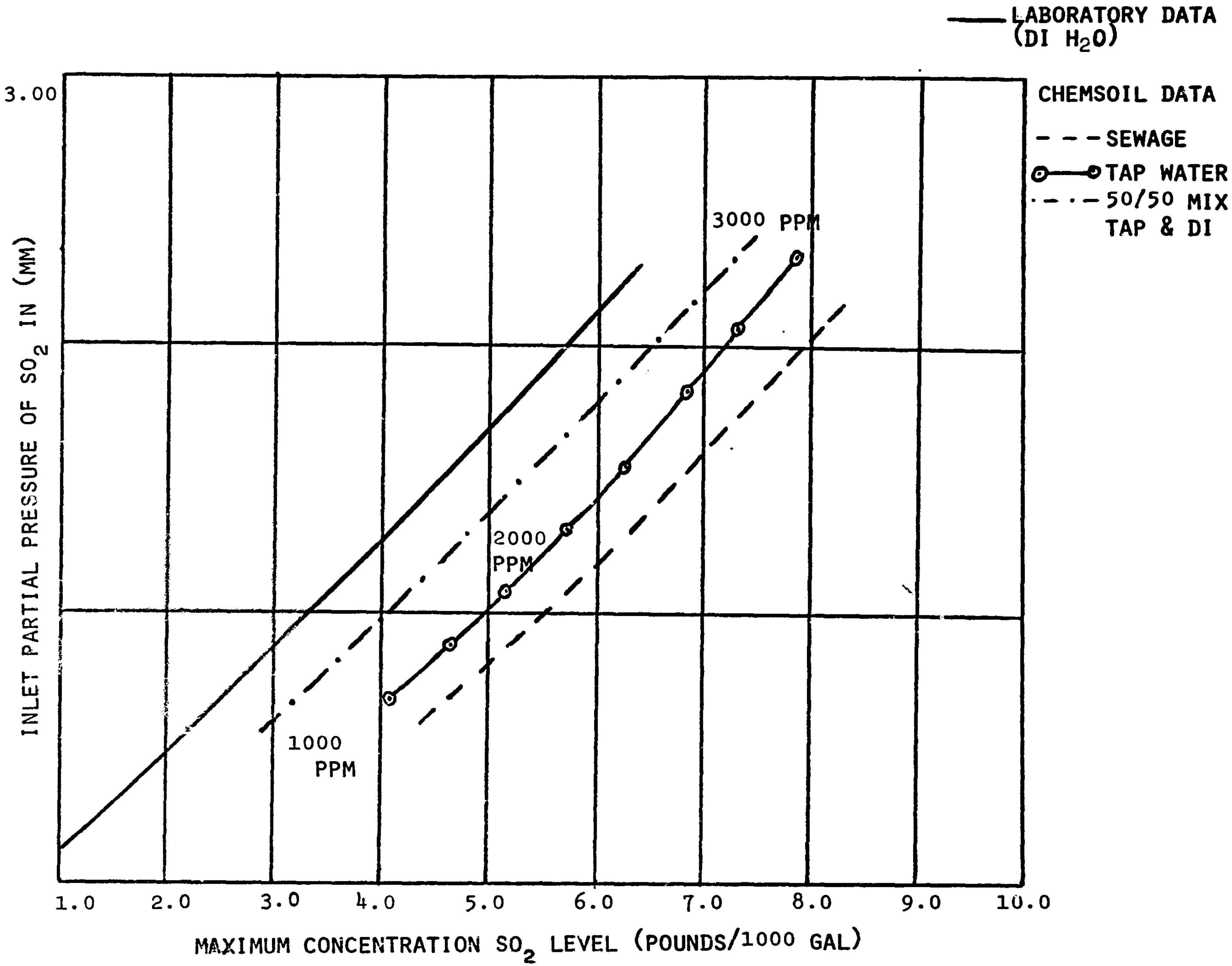


FIGURE 11



*NOTE: AVERAGE BICARBONATE CONCENTRATION EQUAL TO≈ 1.5 POUNDS OF SO_2 PER 1000 GAL

TABLE III

Once-Thru System Summary Data

Max. Gas Volume for 100% Removal

				Water Rate	
Temp.	SO_2 level	L/G	4 gpm	9 gpm	15 gpm
85° F	1000 ppm	46	87 SCFM	196 SCFM	326 SCFM
	2000 ppm	61	65	147	246
	3000 ppm	72	55	125	209
115° F	1000 ppm	66	61	136	227
	2000 ppm	85	47	106	176
	3000 ppm	120	33	75	125
140° F	1000 ppm	73	55	123	205
	2000 ppm	105	38	86	143
	3000 ppm	135	30	67	111

SCFM/gal. for 100% Absorption

85° F	1000 ppm	22	22	22
	2000 ppm	16	16	16
	3000 ppm	14	14	14
115° F	1000 ppm	15	15	15
	2000 ppm	12	12	11
	3000 ppm	8	8	7
140° F	1000 ppm	14	14	14
	2000 ppm	10	10	10
	3000 ppm	8	7	7

that with increasing temperature, the ability of the water to absorb SO_2 decreases. For instance, one thousand gpm at 85°F the L/G is 40; that is, it takes forty gallons of water per thousand standard cubic feet of gas to scrub all of the one thousand ppm SO_2 out of the gas stream. At 140°F the same conditions require sixty-four gallons of water, and so on. The lower portion of the table indicates that the water flow rates have essentially no effect whatsoever on the L/G, or on the ability to scrub the SO_2 from the gas. It was also found that the reason these tables can be written this way is that there was no basic effect of changing the gas velocity either. Within certain limitations detention time had no effect. This area will be covered later. Bed diameter had no effect, and except in the one foot diameter tower, packing size had no effect. At that point, however, it could be seen that the 1½ inch packing tower and short bed depths did reduce the scrubbing ability. A summary of the L/G versus water temperature can be seen in Figure 12. One additional piece of information seemed to fall out of all of the data, which is identified in Figure 13. That with a given pH level, a reasonable reproducable amount of SO_2 bypassing the system and exiting the stack, could be measured. Down to a pH of about 3 this is quite low; however, there is a rapid fall off in scrubbing between a pH 3 and a pH 2.5. Below a pH of 2.5 towards a pH of 2, there is essentially very little scrubbing ability left in the water, under the conditions tested.

FIGURE 12

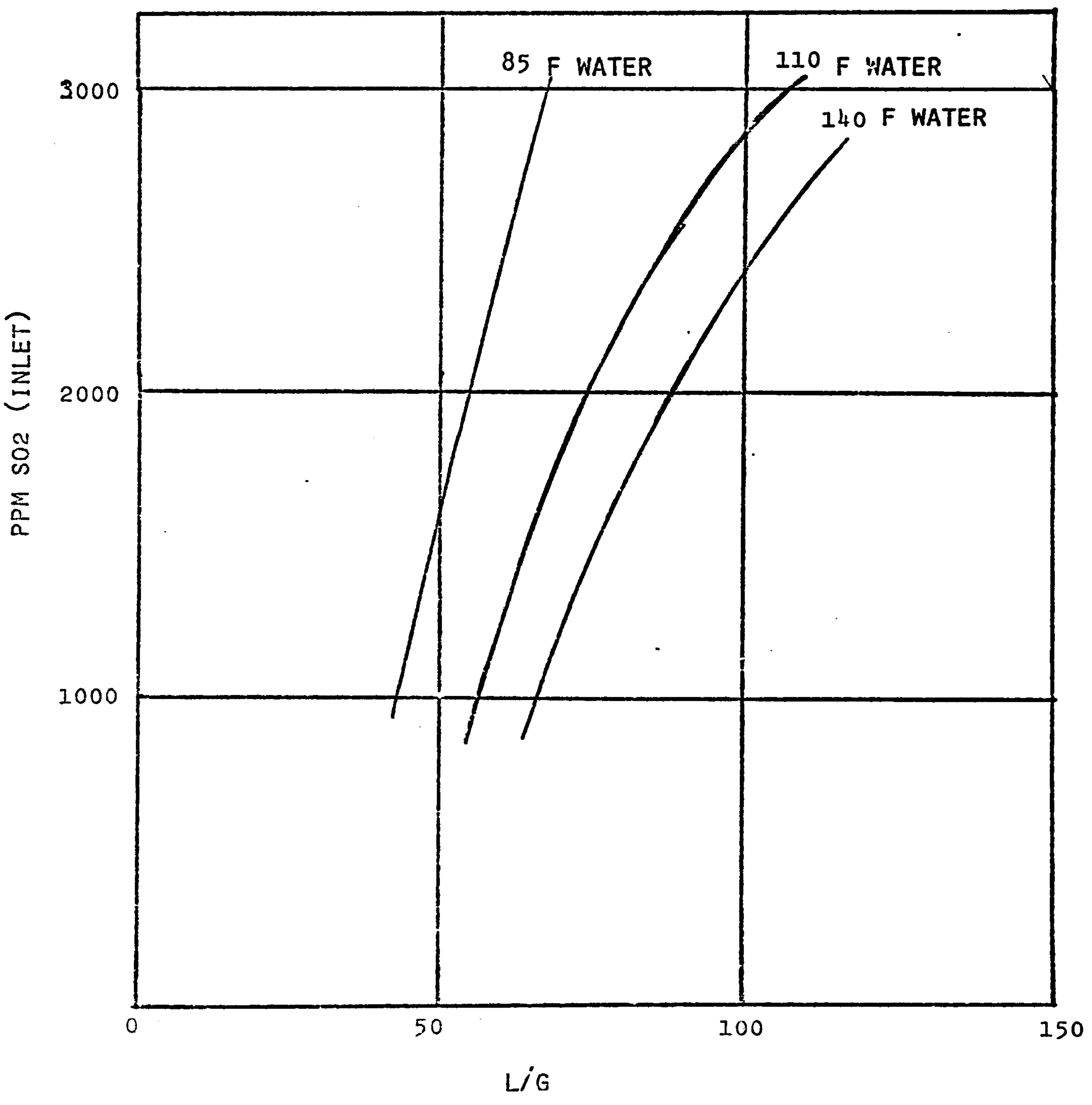
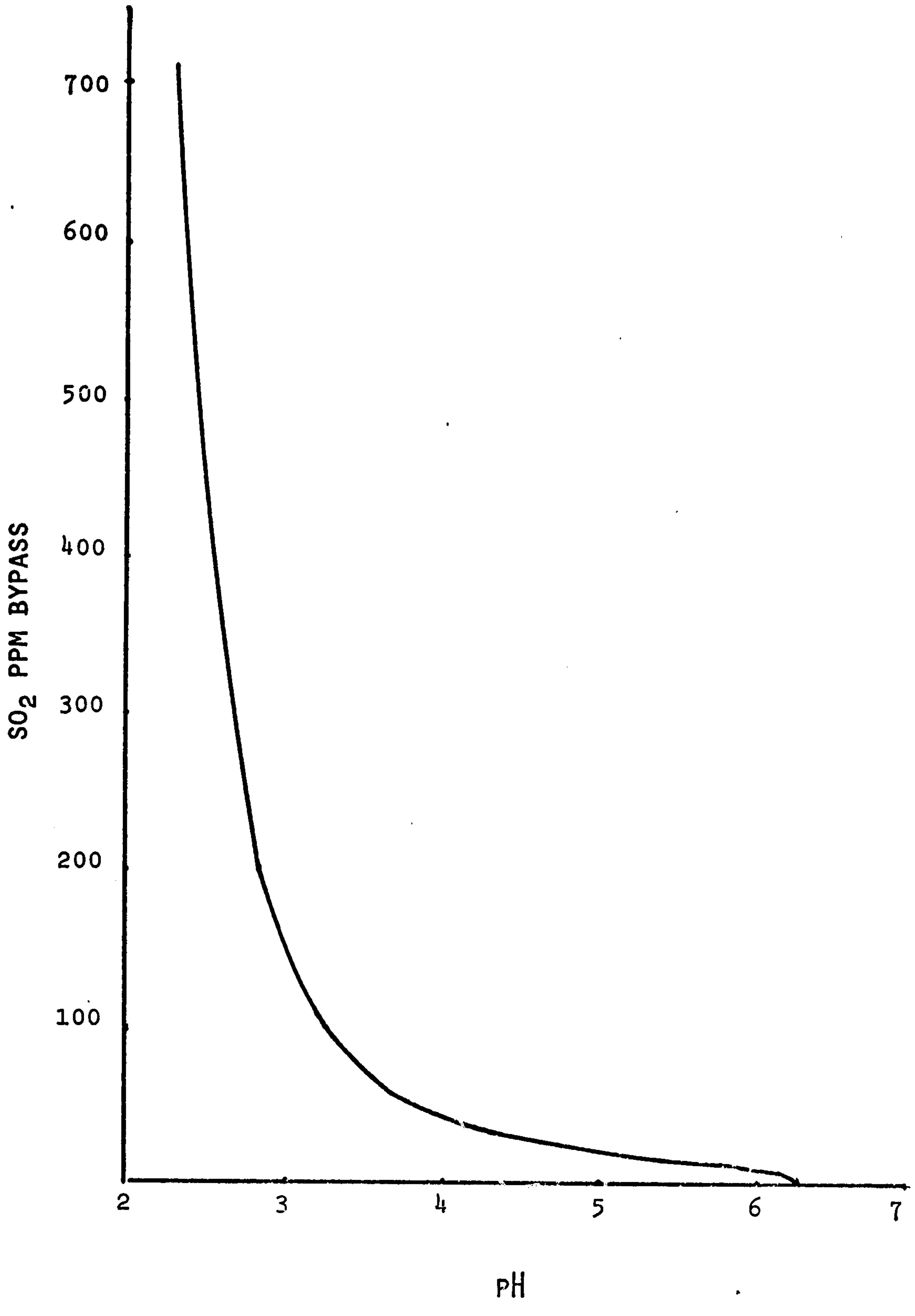

85 F WATER
110 F WATER
140 F WATER
3000
2000
1000
PPM SO2 (INLET)
0
50
100
150
L/G

FIGURE 13



A summary of all of the test points is shown in Figure 14 for the percentage of SO_2 removed from the gas stream at a given L/G for the one thousand, two thousand, and three thousand ppm SO_2 in the levels. The solid lines show that the scrubbing relationship for all bed depths from four to sixteen feet are quite reproducable at any gas velocity. Tests conducted on two foot deep packing showed an abrupt change from the other data, especially in SO_2 removal of 50% or more, showing that two feet is less than the minimum bed thickness required to contact the gas sufficiently to remove the SO_2. However, once a four foot bed depth was achieved, at least in the Once-Thru configuration, there was very little if any advantage in a deeper bed depth. Finally Figure 15 shows a series of L/G lines indicating what percent removal of a given L/G would have at various levels of SO_2 at the inlet.

Data Reduction

All the data reduction consisted of the same process of calculation. Certain corrections had to be made based on calibrations of the equipment. Basic assumptions, therefore, for the calculations are:

1. The correction of the gas turbine meter for inaccuracies using calibration data on those units can be found in Figures 16 and 17. Figure 16 takes the flow turbine reading and converts it to the actual flow through the turbine.

2. Gas temperatures in all the data were corrected to 110°. There was an oversight in the beginning and the temperature

FIGURE 14

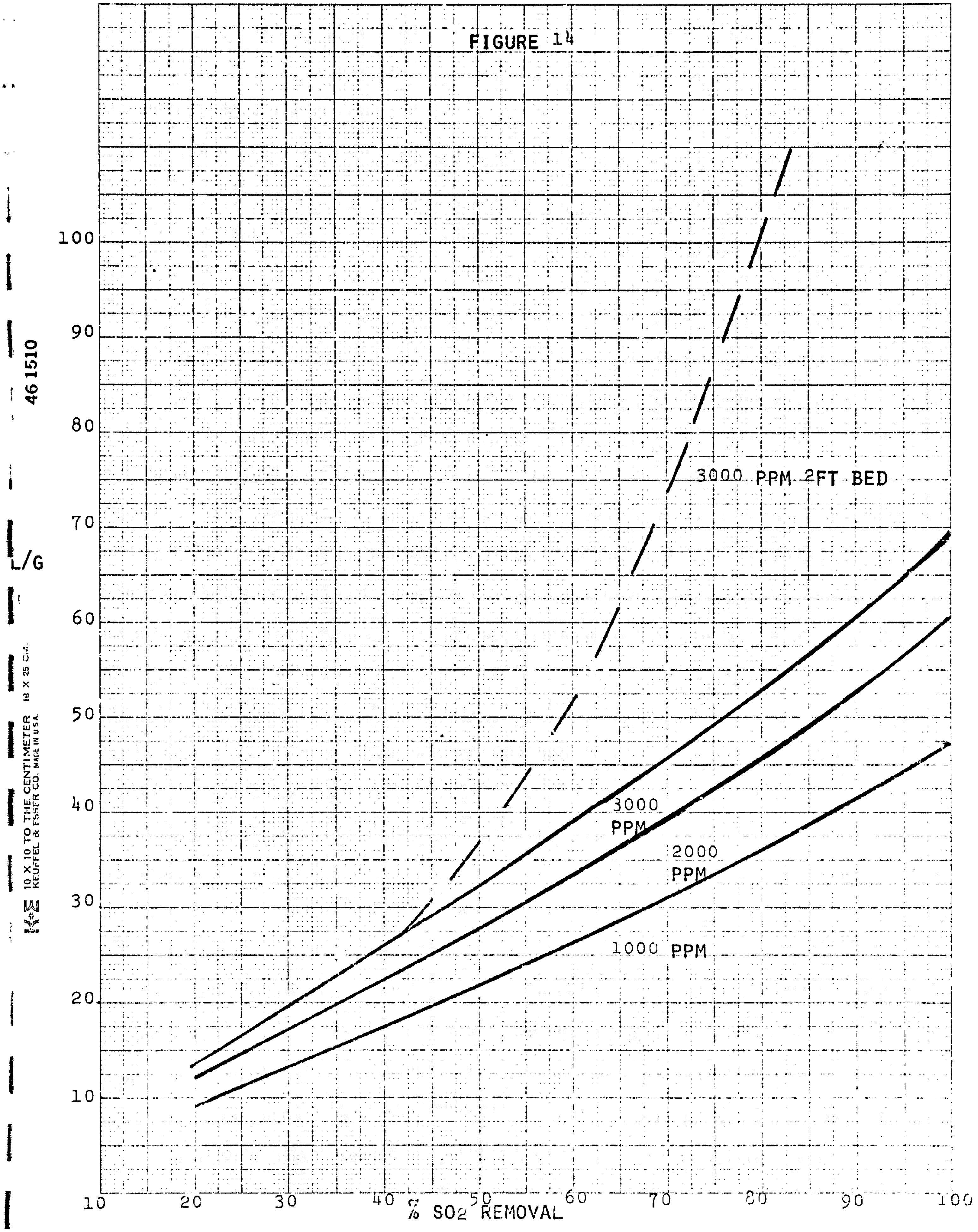

L/G
100
90
80
70
60
50
40
30
20
10
% SO2 REMOVAL
10
20
30
40
50
60
70
80
90
100
3000 PPM 2FT BED
3000 PPM
2000 PPM
1000 PPM

FIGURE 15

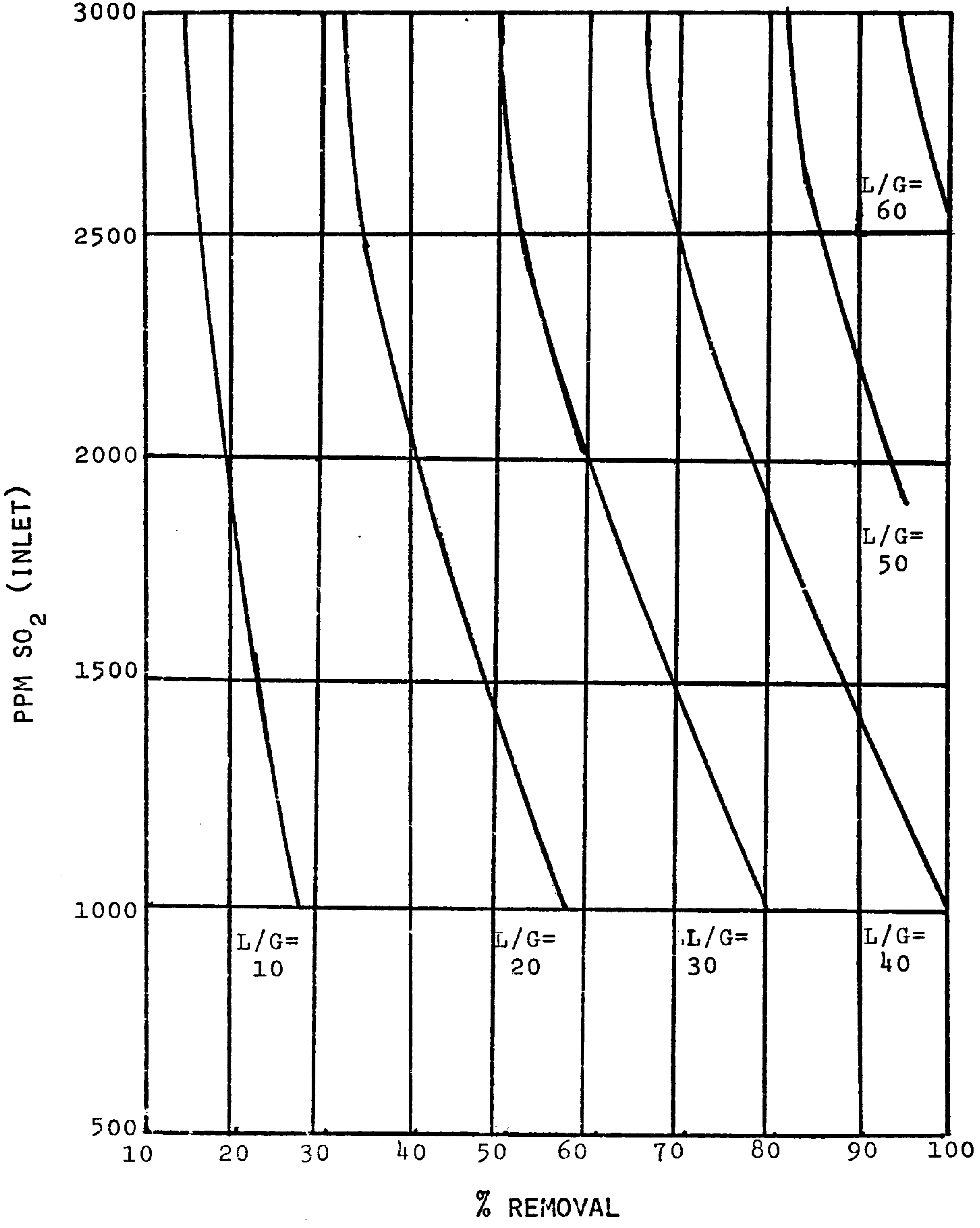

3000
2500
2000
1500
1000
500
PPM SO_2 (INLET)
10
20
30
40
50
60
70
80
90
100
% REMOVAL
L/G= 10
L/G= 20
L/G= 30
L/G= 40
L/G= 50
L/G= 60

TABLE IV

Basic Assumptions for Calculations

-- Correction of gas turbine flow meter using calibration
data and graphs
number 1 and 1a

-- Gas temperature in data corrected to 110°F as estimated
temperature
a 20°F error in that estimate would create about a 3.5%
error

-- Gas pressure correction based on turbine calibration data
as shown on Graph 2

-- Standard gas temperature and pressure used were 60°F 1 ATM.
Specific density used was .07650 pounds/cubic feet

-- Weight of SO_2 in gas calculated from the weight of gas times
.002133/1000 ppm of SO_2 in the gas

-- Universal meter flow data considered .80 accurate

-- Badger 25 meter flow data considered .80 accurate

-- Badger 40 meter flow data considered .92 accurate

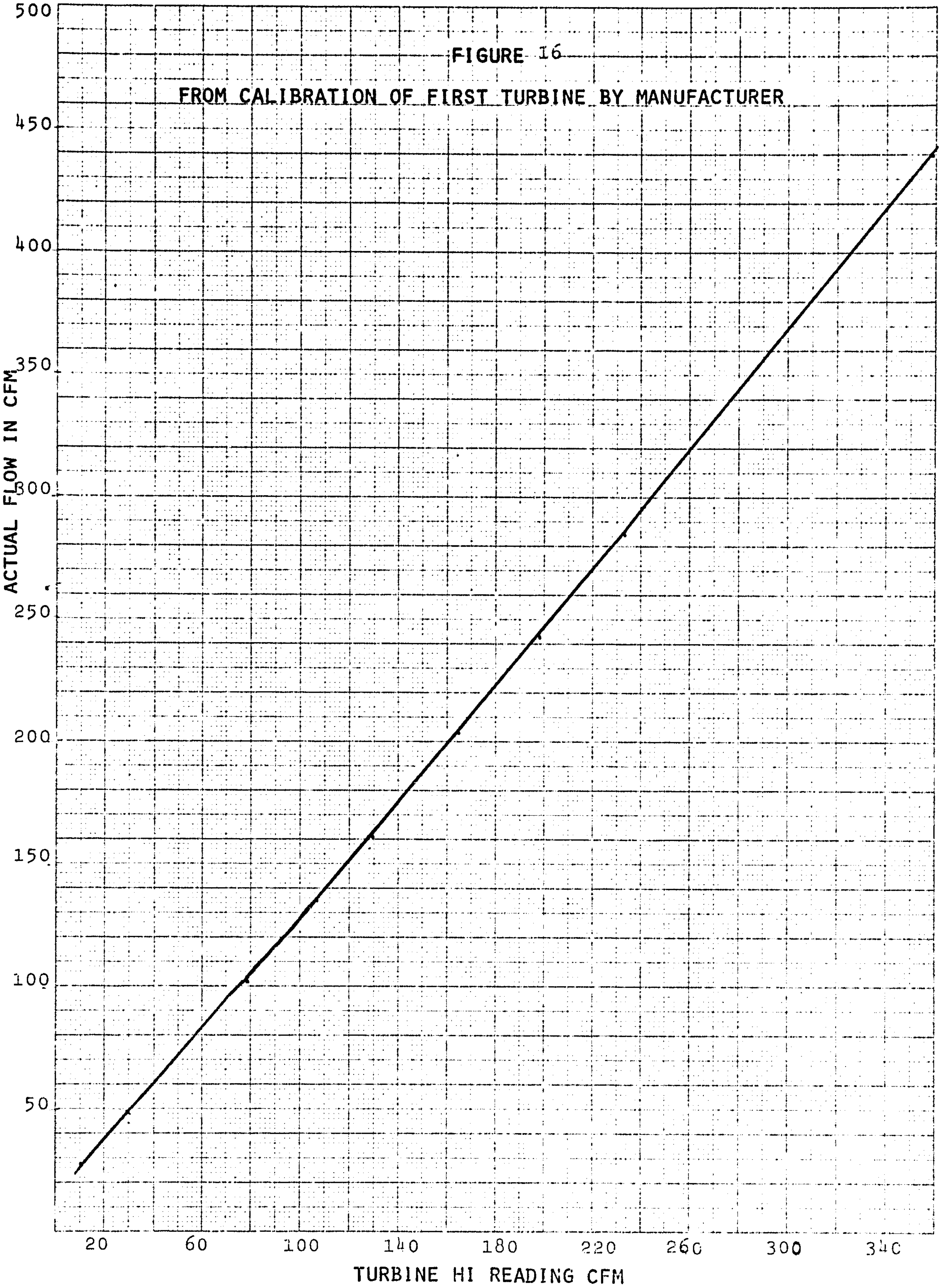
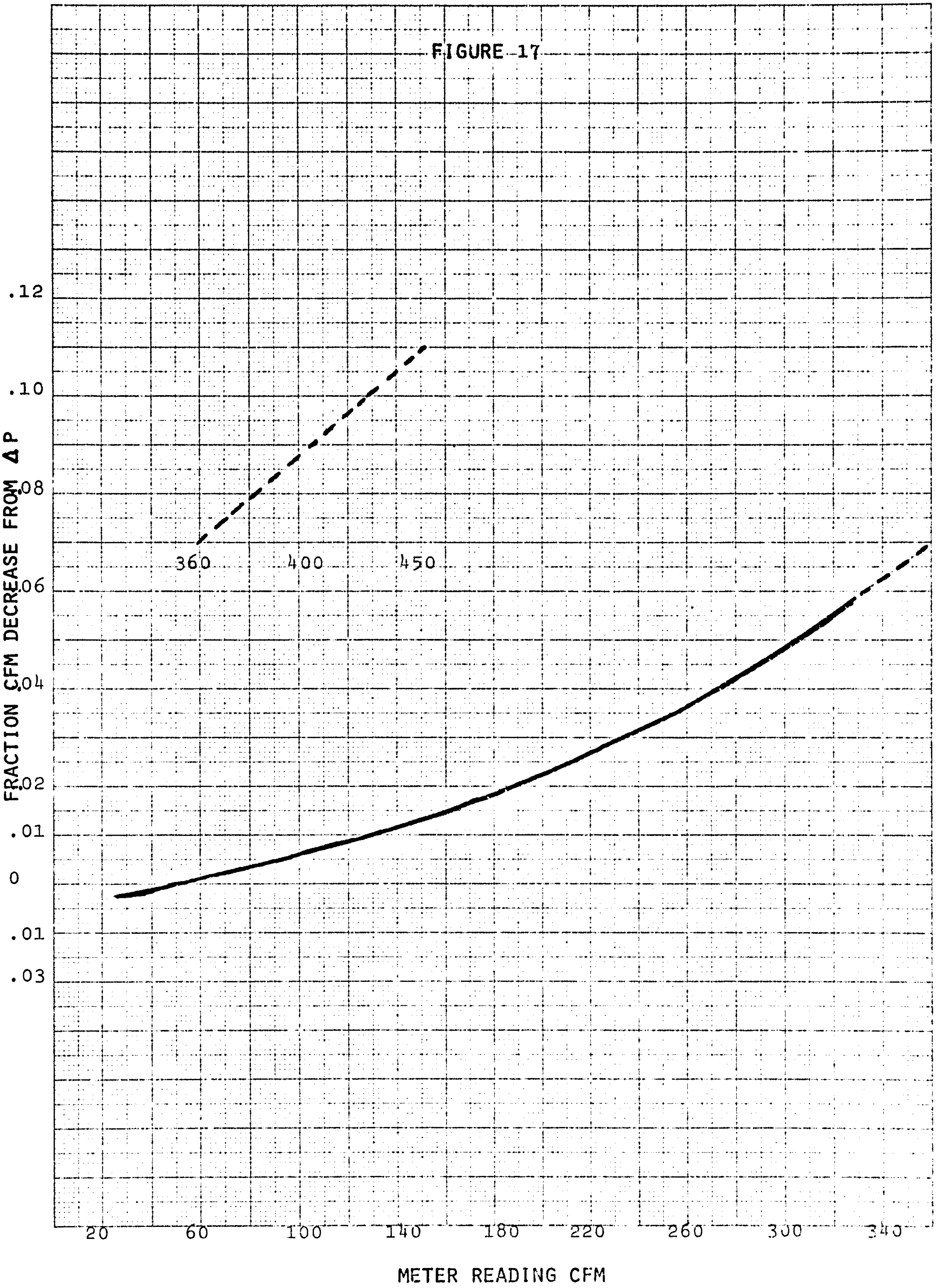


FIGURE 16

FROM CALIBRATION OF FIRST TURBINE BY MANUFACTURER

FIGURE 17


FRACTION CFM DECREASE FROM ΔP
.12
.10
.08
.06
.04
.02
.01
0
.01
.03
360
400
450
20
60
100
140
180
220
260
300
340
METER READING CFM

in the turbine was not monitored because it was not realized that there was a significant temperature build-up at the entrance of the flow turbine. However, later, when a temperature probe was inserted, it was found that under normal conditions about 110° was the stabilized temperature. To evaluate the magnitude of an error, it was found that a 20 degree error in the estimate would result in error in the air of temperature measurement about 3½% error in the amount of gas going through the meter.

3. Gas pressure correction based on the turbine calibration is seen in Figure 17.

4. The weight of the standard temperature and pressure gas at 60°F in one atmosphere was taken to be .07650 lbs./cubic feet.

5. Using the weight of SO^2 gas versus the weight just given for gas itself in lbs./cubic feet conversion ratio of .002133/thousand ppm of SO_2 was used.

6. The universal flow meter data was all corrected to 80% of actual flow rate. This was based on post-usage calibration showing that the 80% accuracy mark had been reached very rapidly.

7. The Badger 25 flow meter that was used was also calibrated to .80 accuracy, again based on the post-calibration measurements. The Badger 40 meter was much less susceptible to particulate clogging, and very rapidly reached an accuracy of .92, and held that level from that point on.

Using that calibration data and going through the conversions for gas flow, water flow, and for the SO_2 equivalents of the sulfite and sulfate in the water, Table 5 shows a sample calculation that was used on all points. This happens to be for test point 31, showing that the weight of SO_2 absorbed/hour calculated from the gas flow was .687 lbs./hr., and the SO_2 absorbed/hour calculated from the water flow was .661 giving a ratio of .962 when the SO_2 was calculated from water, and then checked against that which was calculated from the air.

All of the mass balances were summarized. There was a distinctive pattern which showed a peak of mass balance ratios as was just described, somewhere around 85% showing that there was a certain consistency. However, individually, the gas of the water calculations, were not accurate within 10%-15%. The bell-shaped curve in Figure 18 shows the essential variation of the mass balance water to air ratio.

Summary

In summation it has been shown that; 1) given the water temperature, the gas flow rate, and the SO_2 input level, a proper L/G can be determined for any gas stream, 2) any water flow rate above ½ ft./sec. and less than 2½ ft./sec. can be used in the tower to produce good scrubbing. With the packing material essentially .9 free space area in the tower, the above information can be used to size not only the tower, but the amount of water required for any given gas condition. Trade offs between gas flow rates which require varying turbine costs

TABLE V

Test Point 31 Worksheet

SO_2 in 1029

SO_2 out 647

SO_2 absorbed 382

Fraction SO_2 absorbed .371

Bed diameter 2'

Bed depth 8'

Water temp. 115°F

Water pH 2.4

Packing 3/4"

CFM meter 172

ACFM 205

Gas meter temp. 570°

Fraction ΔP increase vol. .017

SCFM 184

SCFH 11,027

Wt. of gas/hr. 844

Wt. of SO_2/hr. 1.852

Wt. of SO_2 absorbed/hr. .687

GPM meter 4

AGPM 5

LpH 1136

SO_4 measured 36

SO_4 equivalent to SO_2 24

SO_3 measured 300

SO_3 equivalent to SO_2 240

Total SO_2 equivalent 264

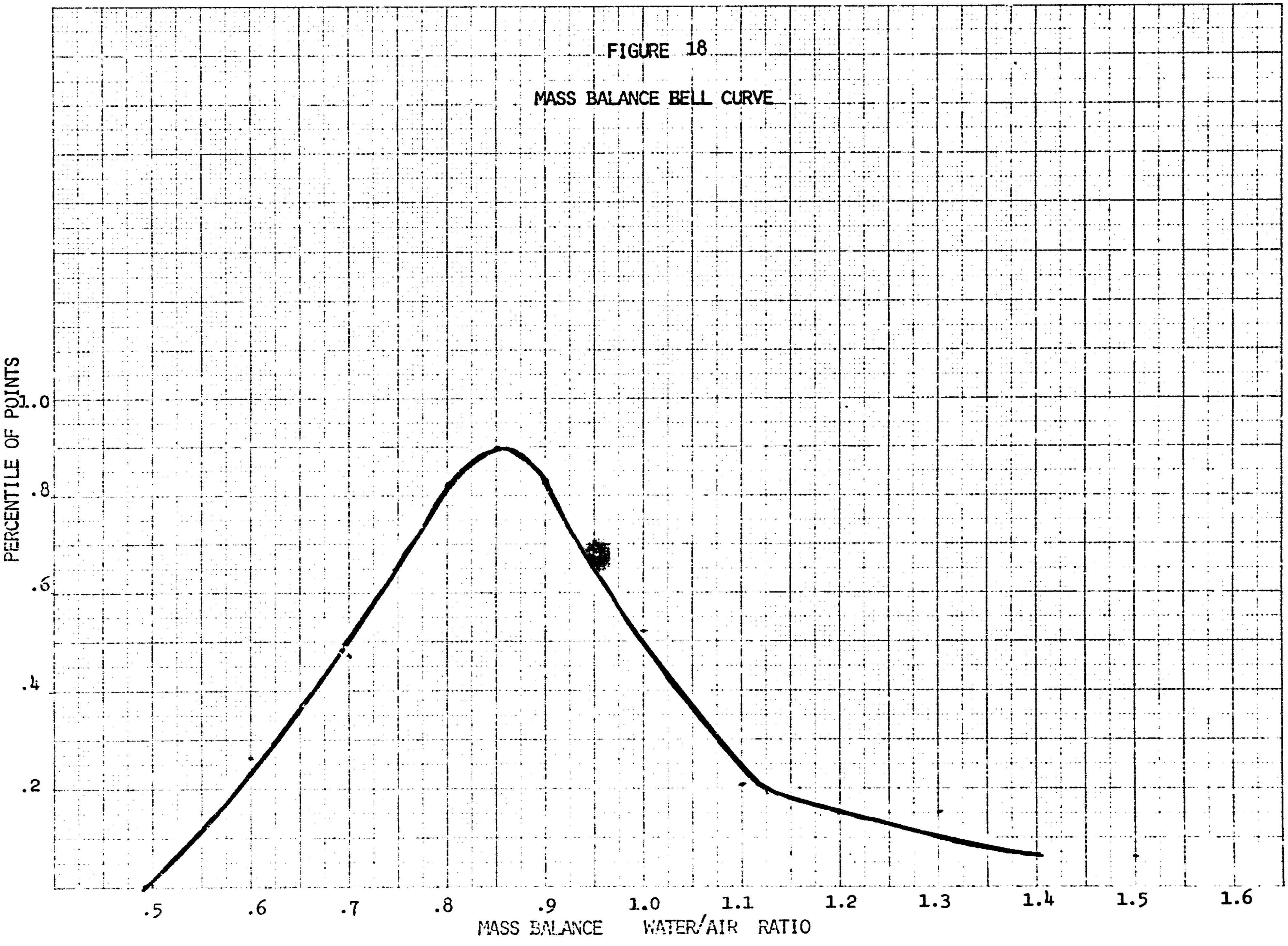
SO_2 absorbed/hr. .661

Ratio of SO_2 calc. water to air .962

L/G 27

FIGURE 18

MASS BALANCE BELL CURVE



and the costs of the various size towers can be made only with additional information about the specific sight; this can be done by any architectural or engineering firm.

Catalytically Enhanced Absorption of Sulfur Dioxide

Until this time it can be seen that the amount of SO_2 absorbed in a given quantity of water is directly related to the chemical make-up of the water itself, the temperature of the water, and the partial pressure of the sulfur dioxide entering the tower. Levels of absorption ranged from less than four pounds to around eight pounds per thousand gallons of water. Several investigations have found that oxidation takes place under certain conditions to convert sulfite to sulfate. Once the sulfate is created more sulfur dioxide can be absorbed in the water than would be possible with just the sulfite conversion. There are two possible ways that the oxidation could take place in the over-all mechanism. The oxidation could take place in the gaseous sulfur dioxide state to form sulfur trioxide or sulfuric anhydride, SO_3, or the reaction could take place after the SO_2 was absorbed in the water. If anhydride formation is predominate, it should be possible to obtain a fast absorption of very soluable sulfuric acid vapors in small quantities of water. If, however, oxidation takes place only after the SO_2 is dissolved, a limiting rate of the process is the rate of absorption of SO_2 and oxygen into water. The oxidation has been found to take place in the liquid state. Thus, the amount of water can be reduced by catalytically oxidizing the SO_2 in the liquid, but the contact surfact and the contact time are not particularly changed. The reaction rate is therefore based on the absorption rate of

TABLE VI A

Tower Facts
Gas

Note: S = CFM gas flow
V = Gas Velocity
D = Bed depth
( ) = Approx. lbs. of gas/hour

1 Ft. Tower Dia.	2 Ft. Tower Dia.	3 Ft. Tower Dia.
S = 20.5 (93.5) V = .49 D 4 = 8.2 8 = 16.3 12 = 24.4 16 = 32.6	S = 83 (378.5) V = .49 D 4 = 8.2 8 = 16.3 12 = 24.4 16 = 32.6	S = 185 (843.6) V = .49 D 4 = 8.2 8 = 16.3 12 = 24.4 16 = 32.6
S = 41 (187.0) V = .98 D 4 = 4.0 8 = 8.1 12 = 12.2 16 = 16.2	S = 165 (752.4) V = .98 D 4 = 4.0 8 = 8.1 12 = 12.2 16 = 16.2	S = 370 (1687.2) V = .98 D 4 = 4.0 8 = 8.1 12 = 12.2 16 = 16.2
S = 82 (373.9) V = 1.96 D 4 = 2.0 8 = 4.1 12 = 6.1 16 = 8.2	S = 330 (1504.8) V = 1.96 D 4 = 2.0 8 = 4.1 12 = 6.1 16 = 8.2	S = 740 (3374.4) V = 1.96 D 4 = 2.0 8 = 4.1 12 = 6.1 16 = 8.2
S = 105 (478.8) V = 2.50 D 4 = 1.6 8 = 3.2 12 = 4.8 16 = 6.4	S = 420 (1915.2) V = 2.50 D 4 = 1.6 8 = 3.2 12 = 4.8 16 = 6.4	S = 944 V = 2.50 D 4 = 1.6 8 = 3.2 12 = 4.8 16 = 6.4

TABLE VI B

Tower Facts
Water Loading Rate

1 Ft. Tower Dia.	2 Ft. Tower Dia.	3 Ft. Tower Dia.
1.25 gal/sq. ft. 1 gpm	1.25 gal/sq. ft. 4 gpm	1.25 gal/sq. ft. 9 gpm
2.85 gal/sq. ft. 22 gpm	2.85 gal/sq. ft. 9 gpm	2.85 gal/sq. ft. 20 gpm
4.75 gal/sq. ft. 3.8 gpm	4.75 gal/sq. ft. 15 gpm	4.75 gal/sq. ft. 34 gpm

SO_2 into water as well as the oxygen rate of absorption of the water. It has also been found that several metal salts catalytically do enhance the oxidation process. A large number of salts have been tested and reported in literature, and of these, Manganese and Iron, proved to be the best. Manganese salts oxidize very rapidly, however are easily poisoned by impurities in water or in stack gases. Iron has been found to be rather insensitive to impurities and therefore appears to be more practical. Although many subtle ion forms are actually created in the reaction, the over-all reaction expressing ion catalytic process can be shown in the equations below.

(18) $2Fe\ SO_4 + SO_2 + O_2$ ---- $Fe\ (SO_4)3$

(19) $H_2O + SO_2 + \frac{1}{2}O_2$ ---- H_2SO_4

(20) $Fe_2\ (SO_4) + SO_2 + H_2O$ ---- $Fe\ SO_4 + 2H_2SO_4$

In the actual treatment of wastewater, the predominate desire is for equations 18 and 19 to take place, rather than equation 20 which produces sulfurous acid. It has been found that the concentration of iron in the water, plus the temperature of the water changes the amounts of each reaction taking place in equations 18 and 20. With the warmer temperatures and lower iron concentration favoring the desirable reaction equation.

Results

A great deal of time was spent pursuing what was thought to be the most important parameter in this catalytic test program. That parameter was the effect of concentration or iron in the scrubbing solution. Many tests were run with various amounts of iron in the concentration trying to show the effect of the concentration versus contact time, gas velocity, and SO_2 level. Interposed in these tests were rapid changes in temperature that were taking place in the environment at the time. And although the tower was insulated, it was very difficult to hold constant water and gas temperatures in the tower at that time. Photograph 2 shows the insulated tower with the packing bed at 16 feet. It was found that the water temperature makes a great deal of difference in the efficiency of the conversion of SO_2 to sulfuric acid. However, because of the rapid temperature changes these effects could not be quantified. A number of trends, however, were identified and these can be seen in the following series of figures and tables.

Table 7 shows the catalytic test matrix defined for the program and the number of tests actually conducted by test number. The total could have been 180 different tests, including three sulfur dioxide input levels, five iron levels, four gas flows, and three tower heights. Each one of these tests, depending on the rapidity of SO_2 removal drop off, lasted from 1½ to 8 hours. The contract called for investigation of three iron levels, but was not specific in the number and types of tests that were to be run. Due to the long duration of the tests, a great portion of the time involved in testing was taken up by 25 different catalytic scrubbing tests that were performed.

Photograph 2

TABLE V11

Iron Tests

SO_2 Level	1K SO_2				2K SO_2				3K SO_2			
Iron Level	1K Fe	2K Fe	5K Fe	10K Fe	1K Fe	2K Fe	5K Fe	10K Fe	1K Fe	2K Fe	5K Fe	10K Fe
CFM												
42					20							
85	6				8		23				22	
	27				9							
165		2	17		7			11	1			
		3										
	5	4	18						15			
	12											
	13											
	14											
	16											
	19											
	21											
	24											
	25											
	26											
330					10							

During each test, two levels of test point information were recorded. These can be seen in Table 8. The level "a" test parameters were measured every five minutes, including water temperature, SO_2 level, the gas flow, the water flow, and SO_2 out. These were the main parameters that were measured. However, every fifteen minutes, every third level "a" test point, additional information was gathered; level "b" information. These included level "a" parameters plus the total iron and ferrous iron in the water, the water pH, the sulfate and the sulfite ion concentration at the bottom of the tower.

Table 9 shows the typical data sheet that was collected on each test. In this particular case, the test number was test No. 5 on October 21. Table 10 is a summary test key showing the test number, the temperatures involved, the SO_2 level, gas velocities, number of test points, the iron level, and the duration of the test. Figure 19 shows the test set up for the catalytic test program, showing that we had to make some variations in the original Once-Thru schematic in order to recirculate the iron, including facilities for adding sodium hydroxide in the tests which included NaOH neutralization.

Attacking the problem from the basis that the amount of iron and the amount of SO_2 were the major parameters investigated, several tests were run to try to quantify the effects of these variables. As can be seen from Figure 20 this did meet with some success. Test No.6, 83 cfm, a thousand ppm of sulfur dioxide in the 16 foot tower, had a better apparent removal rate

TABLE VIII

Analysis Level

Level "a"

1 time

2 water in temp.

3 SO_2 level in

4 gas flow

5 water flow

6 SO_2 out

7 gas temp. in

8 gas temp. out of tower

9 water temp out of tower

10 tower gas delta pressure

Level "b"

11 same as "a" plus

12 total iron level in water

13 ferrous iron level in water

14 water pH

15 water sulfate ion concentration

16 water sulfite ion concentration

TABLE IX a

T-6	Time	SO_2 in	SO_2 out	SO_2 absorbed	% removal	SO_4-2	Temp	gpm	pH	Fe+2	%Fe+2
168 cfm	10	918	22	896	98	960	100	4.1	1.6	200	20
	20	918	44	874	95	1390	100	6.3	1.5	97	10
	30	918	73	845	92	2775	100	8.2	1.5	135	13
88 cfm	40	918	95	823	90	1900	100	10.0	1.4	130	14
	55	918	36	882	96	2140	100	12.3	1.4	137	14
	70	955	22	933	98	2820	100	12.3	1.4	180	16
	85	955	29	963	97	2820	100	12.3	1.4	180	19
	100	1029	66	963	94	3454	100	12.3	1.3	180	16
	115	992	73	963	93	3350	100	12.3	1.2	197	18
	130	1029	80	949	92	4030	100	12.3	1.2	215	25
	145	1029	58	971	95	3915	100	12.3	1.2	202	18
	160	955	80	875	92	4065	100	12.3	1.2	180	18
	175	992	102	890	90	4590	110	12.3	1.1	202	20
	190	992	117	875	88	4820	110	12.3	1.1	185	17
	205	992	124	868	88	5080	110	12.3	1.1	197	18
	220	992	139	853	86	5020	110	12.3	1.1	215	20
	235	992	154	838	84	5710	110	12.3	1.0	175	19
	250	992	154	838	84	5830	110	12.3	1.1	207	20
	265	992	132	860	84	5020	110	12.3	1.2	175	18
	280	992	169	823	83	6115	110	12.3	1.3	172	18
	295	1029	198	831	81	6600	110	12.3	1.2	207	20

	Time	SO_2 in	SO_2 out	SO_2 absorbed	% removal	SO_4^{-2}	Temp	gpm	pH	Fe+2	%Fe+2
88 cfm	310	1029	205	824	80	6600	110	12.3	1.1	189	19
	325	992	213	779	78	7180	110	12.3	1.0	215	18
	340	992	220	776	78	7630	110	12.3	.9	190	17
	355	1029	235	794	77	6400	105	12.3	1.0	190	17
	370	992	242	750	76	6600	105	12.3	.95	190	17
	385	955	257	698	73	7180	105	12.3	.95	180	18
	400	955	257	698	73	6410	105	12.3	1.0	175	18
	415	955	249	706	74	6980	105	12.3	1.0	175	18
	430	955	257	698	73	8200	105	12.3	1.0	180	17
	445	955	271	684	72	8510	100	12.3	.9	180	18
	460	955	271	684	72	9250	100	12.3	1.1	180	18
	475	955	249	684	74	8510	100	12.3	1.0	180	18

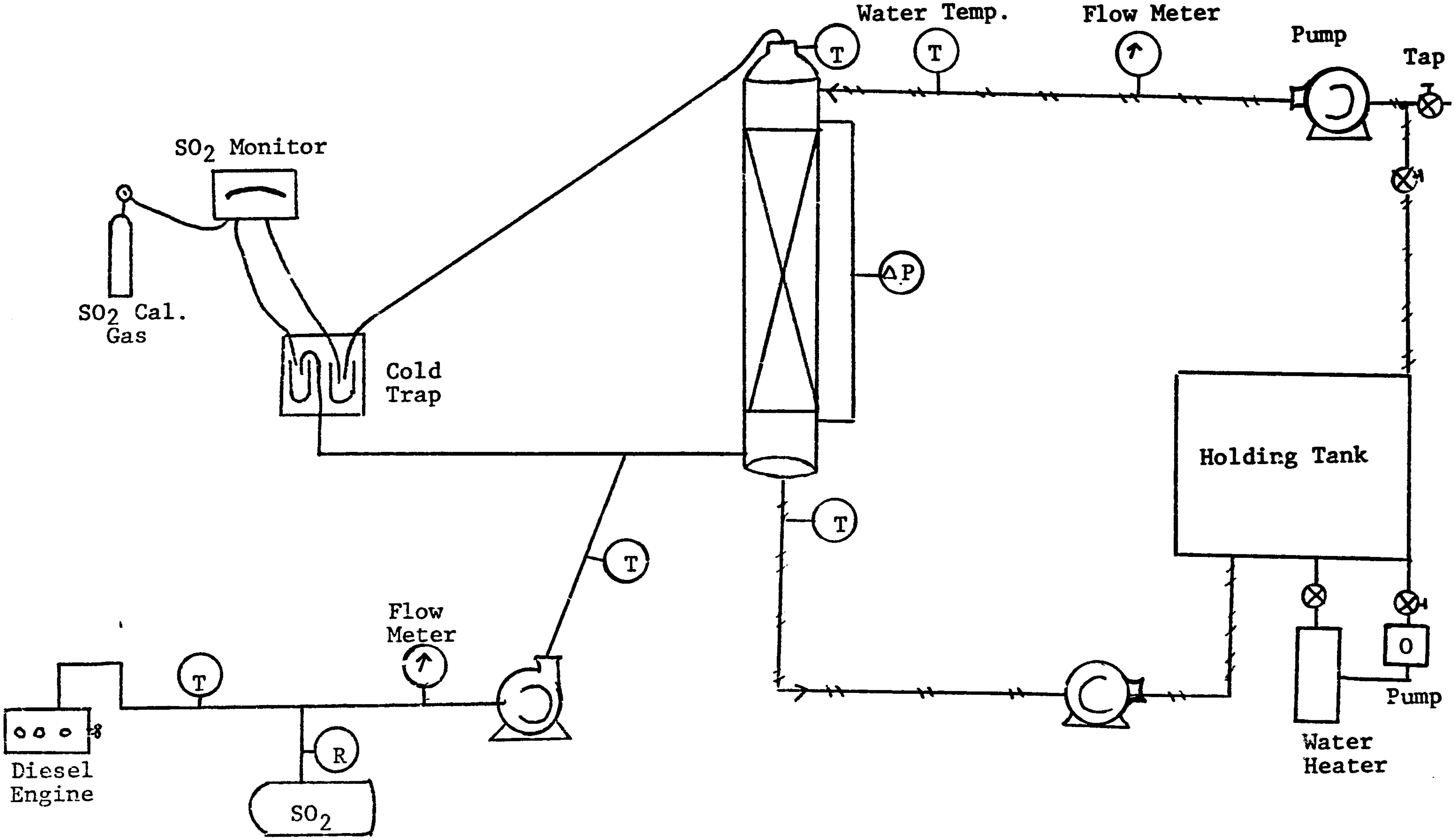
TABLE X

Test Key

Gal.	Test	Water Temp.	SO_2 Level	Gas Velocity	Level a TP	Level b TP	Fe Level	Duration	
100	1	100-120F	3000	200	40	20	1000	300	min.
	2	100-125	1000	171	18	9	1000	135	disc.
	3	110-125	1000	168	32	16	2000	246	
	4	110-120	1000	165	46	23	2000	347	
	5	105-120	1000	160	62	31	1000	470	
	6	95-110	1000	88	64	32	1000	480	
	7	95-120	2000	165	40	20	1000	310	
	8	110-120	2000	87	40	20	1000	310	
	9	110-115	2000	81	64	32	1000	485	
	10	100	2000	320	14	7	1000	105	
	11	90-100	2000	165	56	28	10,000	420	
	12	105-120	1000	170	12	6	1000) 4 ft. tower	90	
	13	100-120	1000	170	12	6	1000	90	
	14	85-90	1000	160	12	6	1000	90	
	15	85-90	3000	83	8	4	1000	60	
	16	75-90	1000	168	12	6	1000	90	
	17	85-90	1000	168	12	6	5000	90	
	18	85-100	1000	165	14	7	5000	115	
	19	80-90	1000	163	48	24	1000	360	
	20	80-95	2000	42	38	19	1000	290	
	21	80-95	1000	165	50	25	1000	375	NaOH
	22	90-100	3000	83	12	6	5000	95	
	23	85-95	2000	83	24	12	5000	180	
	24	80-95	1000	170	48	24	up to 1000	360	
200	25	95-120	1000	170	48	24	turnings 1000	360	
	26	100-120	1000	170	42	21	100 1100 2100	315	
150	27	85-110	1000	83	44	22	1000	330	
	28	100-120	3000	83-220	26	13	1000	200	
	29	100-120	2000	309		9	5000	135	

Figure 19

SCHEMATIC FOR CATALYTIC TESTS



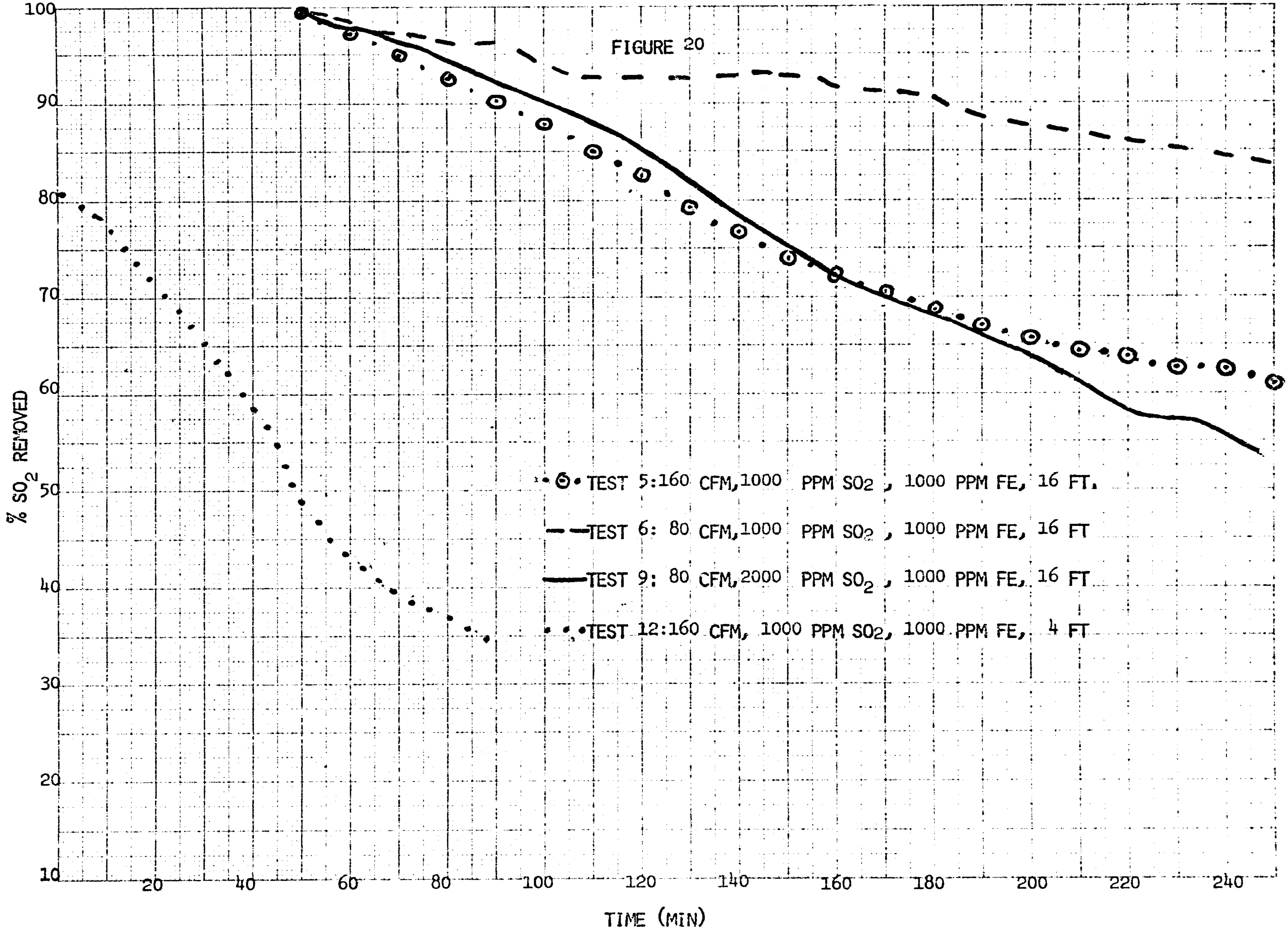


FIGURE 20

100
90
80
70
60
50
40
30
20
10
% SO_2 REMOVED
20
40
60
80
100
120
140
160
180
200
220
240
TIME (MIN)
TEST 5:160 CFM, 1000 PPM SO_2, 1000 PPM FE, 16 FT.
TEST 6: 80 CFM, 1000 PPM SO_2, 1000 PPM FE, 16 FT
TEST 9: 80 CFM, 2000 PPM SO_2, 1000 PPM FE, 16 FT
TEST 12:160 CFM, 1000 PPM SO_2, 1000 PPM FE, 4 FT

than did test No. 5 and No. 9, which in essence doubled the amount of SO_2 contacted in the tower during a given period of time. Whether the SO_2 is injected in higher concentrations or higher flow rates at lower concentrations showed similar removal results in tests No. 5 and No. 9, as can be seen on the figure. All these tests were done in the 16 foot tower with a contact time ranging anywhere from 16 to 32 seconds. However, in test No. 12 where conditions were similar to test No. 5, except that the contact time was reduced from 16 seconds to 4 seconds there is a tremendous reduction in the removal rate of SO_2. Basically, it can be concluded by this figure that within certain limits the amount of $SO2$ contacted at any given time is essentially equal without dependence upon velocity or SO_2 concentration level. However, there is a point at which there is not enough contact time in the tower to allow for oxidation to take place. As test No. 12 shows, scrubbing is reduced because the iron doesn't have enough time to convert the sulfite to sulfate in the tower and regenerate the iron. During this time variations in outside temperatures began to take place, and we started to notice erratic results. It was felt that temperature changes were the major contributor to the problem; and in the comparison of tests No. 5 and No. 9, a large variation in the effects brought about by temperature can be seen in Figure 21. These two test points are essentially the same except for the water temperature. Ferrous iron levels were affected by temperature. It can be seen that the ferrous ion level in warm water in test

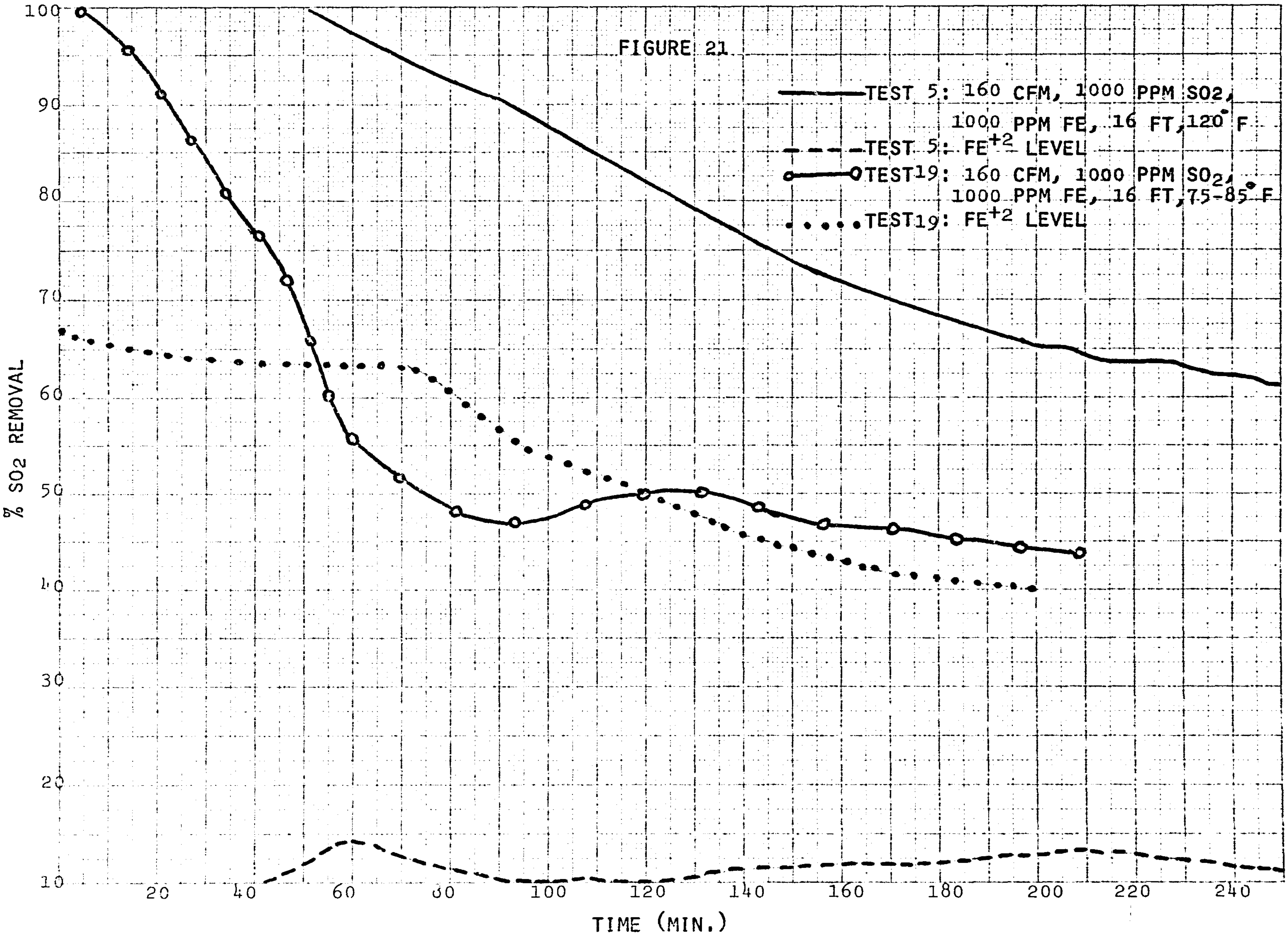


FIGURE 21

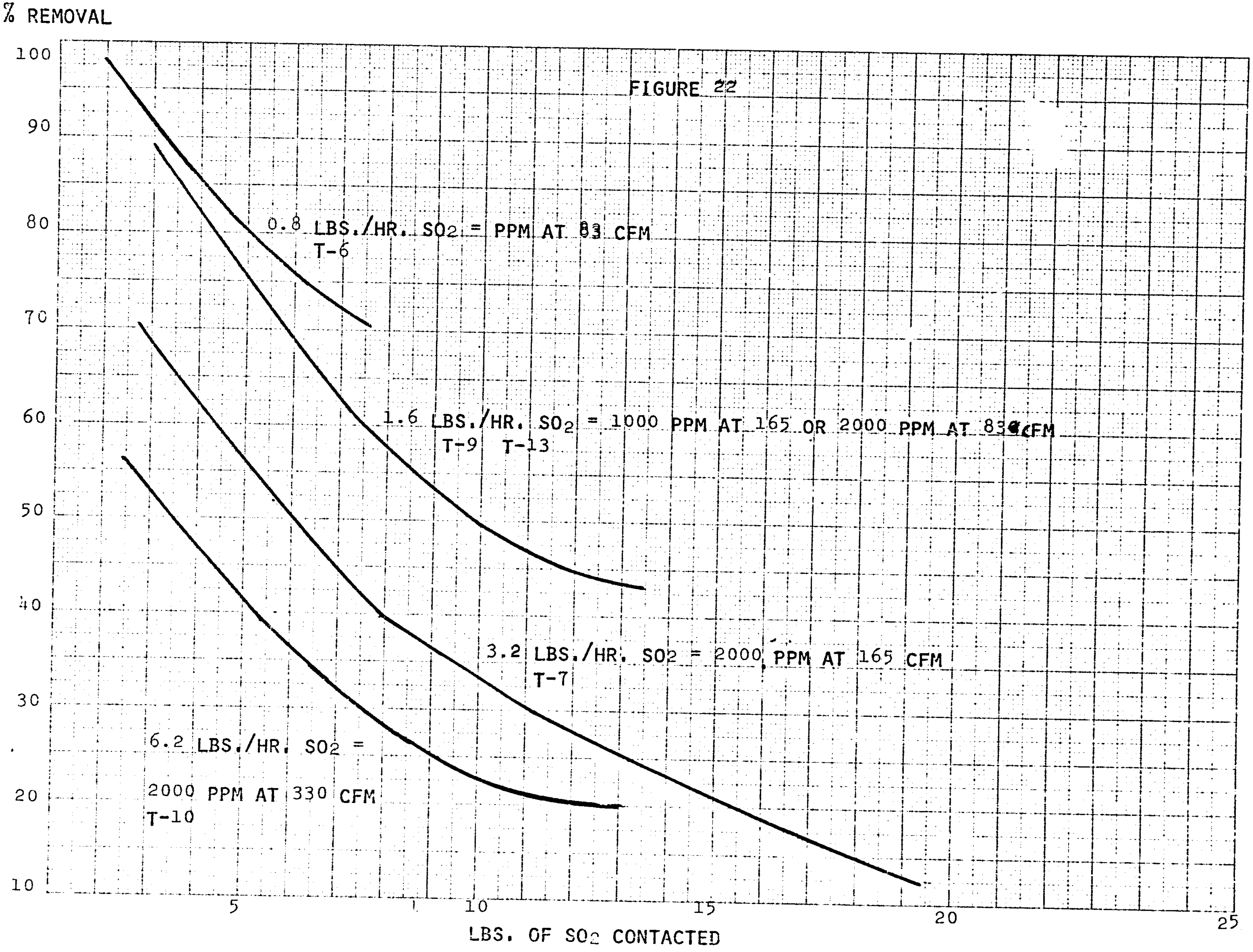
TEST 5: 160 CFM, 1000 PPM SO2, 1000 PPM FE, 16 FT, 120° F
TEST 5: FE+2 LEVEL
TEST19: 160 CFM, 1000 PPM SO2, 1000 PPM FE, 16 FT, 75-85° F
TEST19: FE+2 LEVEL
% SO2 REMOVAL
100
90
80
70
60
50
40
30
20
10
20
40
60
80
100
120
140
160
180
200
220
240
TIME (MIN.)

No. 5 was about 10% of the total iron level but with colder water in test No. 12 the ferrous ion percentage ranged from 30 to 40% of the total.

It can be seen that the higher water temperature of about 120° produced a great deal more scrubbing than the test which was conducted with water temperatures at 75° to 85°. Reviewing the more subtle data the major change that took place is the percentage of the iron which remains in the ferrous state, the Fe+2 state. This is apparently one of the keys to good scrubbing. The high levels of ferrous ion reduced the capability of the iron to oxidize the sulfite solution to sulfate. With this knowledge, a great deal of time was spent insulating lines, the tower, the surge tank, and everything that could be insulated, in an attempt to hold temperatures relatively stable, even though the environment around the test sight was changing rapidly from day to day, and even from hour to hour as cold fronts came through. The large amounts of time and energy we expended on this project produced very little in the way of positive results. There was always throughout the program a complete reflection of the environment on the test program, thus although we can make qualitative observations about the temperature, we can not quantify the magnitude of the variation in the tests due to temperature changes. It should be emphasized at this point that the problem of temperature control was mostly one of test configuration with only marginal ability to heat the scrubber water. Power plant scrubbers would not have the difficulties encountered in our test program.

It can be seen from Figure 22 that there is a relationship between the percentage of SO_2 removed versus the amount of SO_2 contacted with water. The problem here is that there is not only an interdependence upon the amount of SO_2 contacted, but also a direct relationship with the rate of contact. This parameter was not investigated thoroughly at more than one tower height so that it may be a situation that could be overcome with a longer contact time. It is obvious that the reason for the reduced removal at higher contact rates is the failure of the iron solution to be regenerated to the ferric state during the time the iron remained in contact with oxygen in the tower. For instance, the 6.2 lbs./hr. at the lower portion of the figure is contacted at 330 cfm. In comparison with the 1.6 or even the 3.2 lbs./hr. line the gas velocity has increased, thus reducing the contact time in the tower, because the tower remained at 16 feet. The difference between the top curve and the bottom curve is the factor of 4, thus the contact time went from 32 seconds at 83 cfm down to about 8 seconds at 330 cfm. The only points which would have enough data for direct comparison were in the region of 165 and 83 cfm. There appears to be little difference at these points; however the contact times are at least 16 seconds and it may be that with those low SO_2 contact rates of 1.6 lbs./hr. 16 seconds is more than enough contact time so there was very little variation in results. In other words, enough contact time in the tower was available to continue to regenerate the Fe^{+3} ions. At this point we still considered the concentration of iron in the solution to be a significant parameter.

FIGURE 22

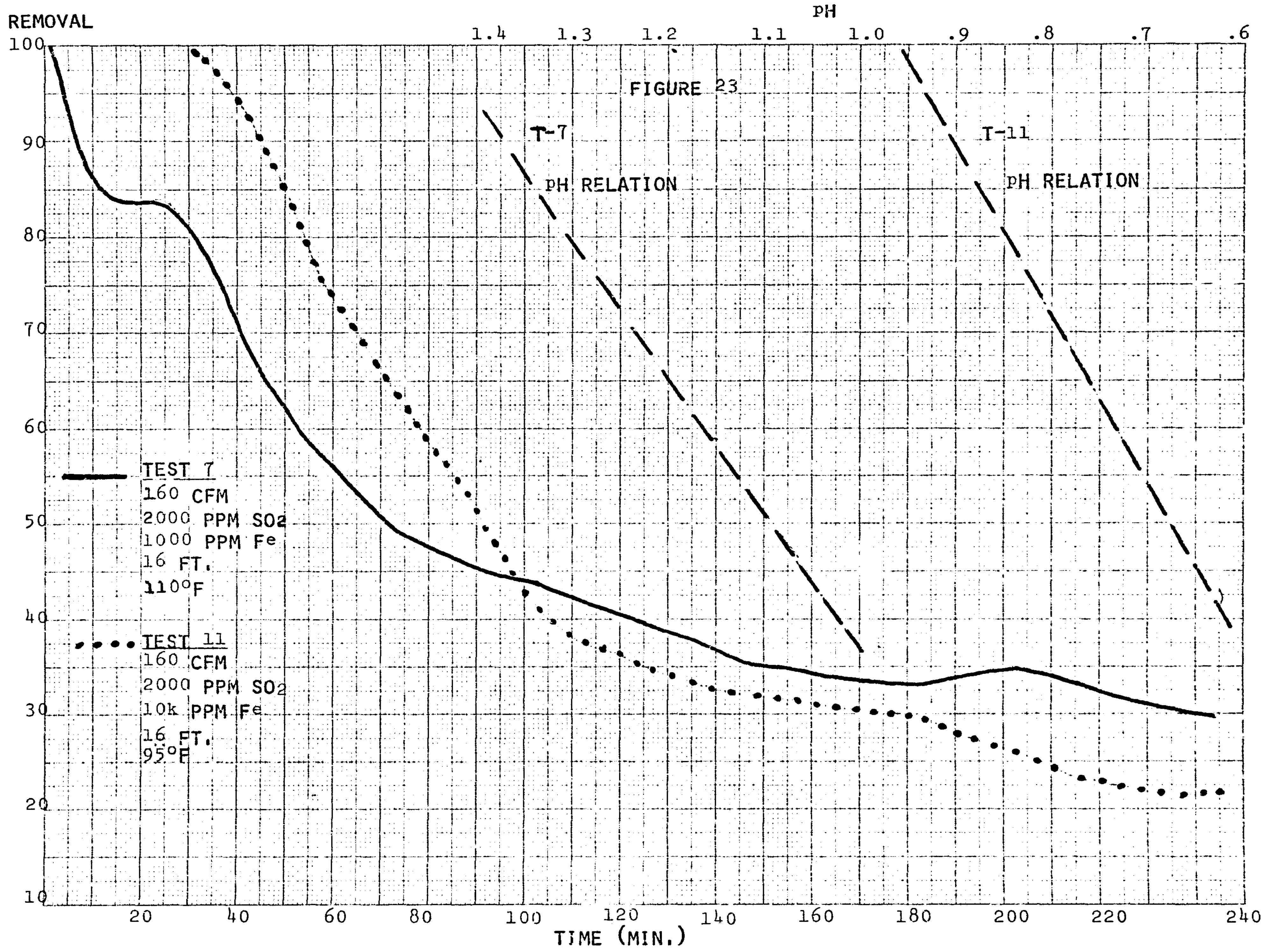

% REMOVAL
100
90
80
70
60
50
40
30
20
10
0.8 LBS./HR. SO_2 = PPM AT 83 CFM
T-6
1.6 LBS./HR. SO_2 = 1000 PPM AT 165 OR 2000 PPM AT 83 CFM
T-9 T-13
3.2 LBS./HR. SO_2 = 2000 PPM AT 165 CFM
T-7
6.2 LBS./HR. SO_2 =
2000 PPM AT 330 CFM
T-10
5
10
15
20
25
LBS. OF SO_2 CONTACTED

However, in tests No. 7 and No. 11 were essentially the same tests conducted at approximately the same temperature with the only major difference being the level of iron in the solution. Test No. 7 has a thousand ppm of iron and test No. 11 has ten thousand ppm of iron. Except for the point at which 100% scrubbing was no longer achieved one being early in the test, the other being about forty minutes, the two solutions at 100 minutes essentially have scrubbed at the same rate, and after that the solution with high concentration of iron actually produced a lower scrubbing capability.

Two things were noted in looking at the detailed data. There was a significant change in pH. This is recorded on the figure by the dashed lines. You can see that the pH for tests No. 7 and No. 11, for the same level of SO_2 removal, are considerably different with the pH being substantually lower in the high iron solution. However, it was further noted that in test No. 7 the percent of iron that was in the ferrous state was only 30%. whereas in solution 11 with the high iron concentration, 50% to 60% of the total iron remained in the ferrous state. It was concluded that iron concentration alone was not as important as previously thought.

Figure 24 is a good indication of the reproducability which can be achieved with the test set up just described when test conditions remain quite similar. This is a busy figure, however it attempts to put a lot of information on one graph for tests No. 3, No. 4, and No. 5. On the upper left, SO_2

FIGURE 23


REMOVAL
100
90
80
70
60
50
40
30
20
10
PH
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
T-7
PH RELATION
T-11
PH RELATION
TEST 7
160 CFM
2000 PPM SO2
1000 PPM Fe
16 FT.
110°F
TEST 11
160 CFM
2000 PPM SO2
10k PPM Fe
16 FT.
95°F
20
40
60
80
100
120
140
160
180
200
220
240
TIME (MIN.)

removal percentages lower going from about the 60% area on down. The pH which is high on the right hand side and continually drops. The horizontal across the bottom are percentages of the ferrous iron in the solution. The lower left to upper right diagonal lines are a measure of the SO_4 concentration in the solution for a given time.

Figure 24 is a busy chart that attempts to show that under relatively reproducable conditions the results are also reproducable. Careful attention has to be made to the scales on the left, percent removal of SO_2, and percent of ferrous iron, Fe+2. On the top, the time of the tests in minutes; along the right hand margin, the build-up of sulfate, (SO_4), scale and also the pH scale. One interesting note can be seen at the bottom of the page, where tests No. 3 and No. 4, which have an initial total iron concentration of two thousand ppm, end up with higher ferrous iron levels than does test No. 5 with an initial 1000 ppm total iron level. This condition which has been mentioned before, has been seen throughout the testing, and of course the level of SO_2 removed seems also to be closely related to percentage iron in the solution, which is in the form of ferrous iron.

With these test results and all the qualitative data available to us through previous testing, it appears that rather than the level of iron in the solution being the major driver in SO_2 removal, the pH and temperature share the role of most important factors. Once the level of iron in the solution is great enough to drive the catalytic reaction, pH and temperature

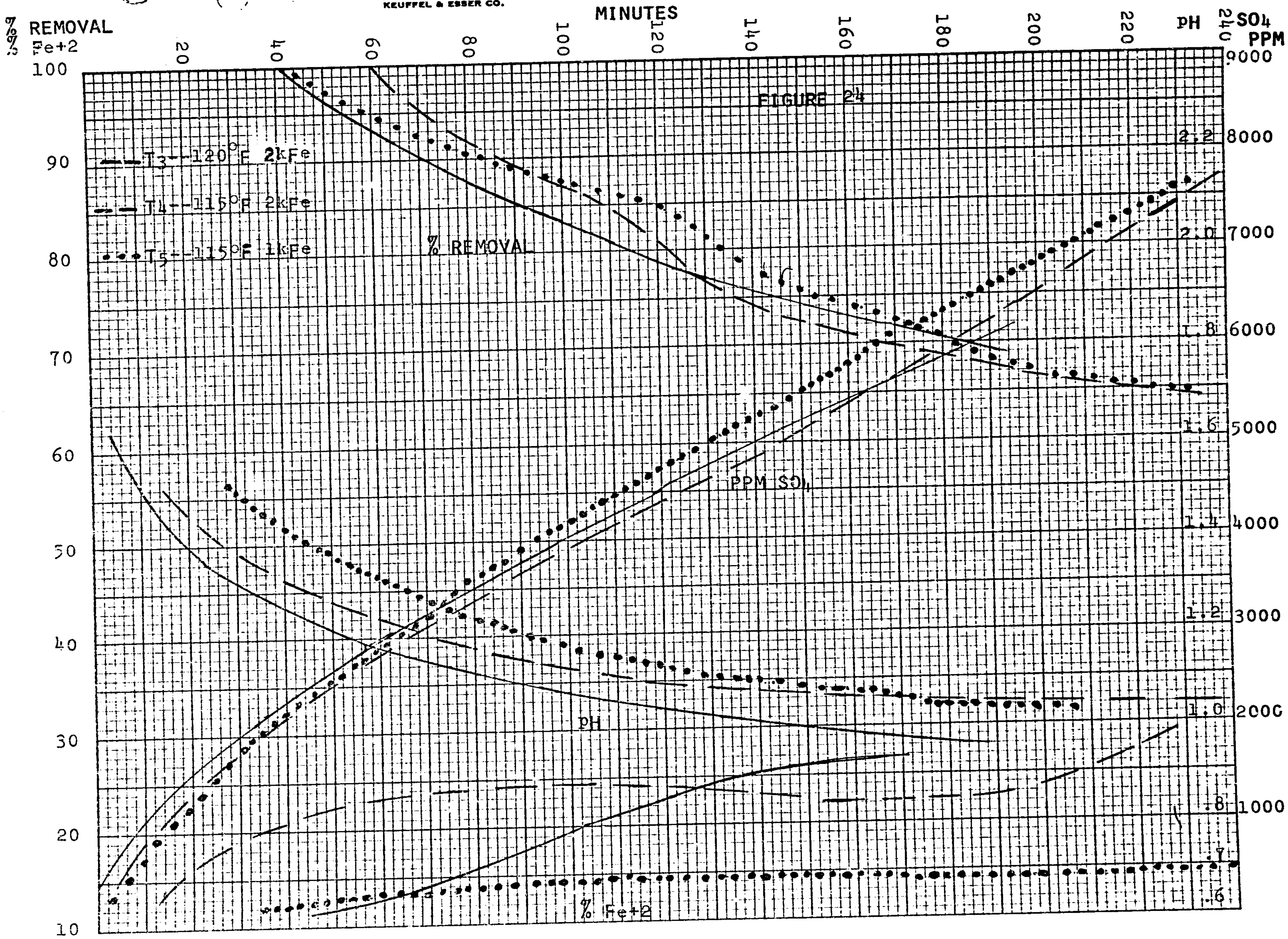


FIGURE 24

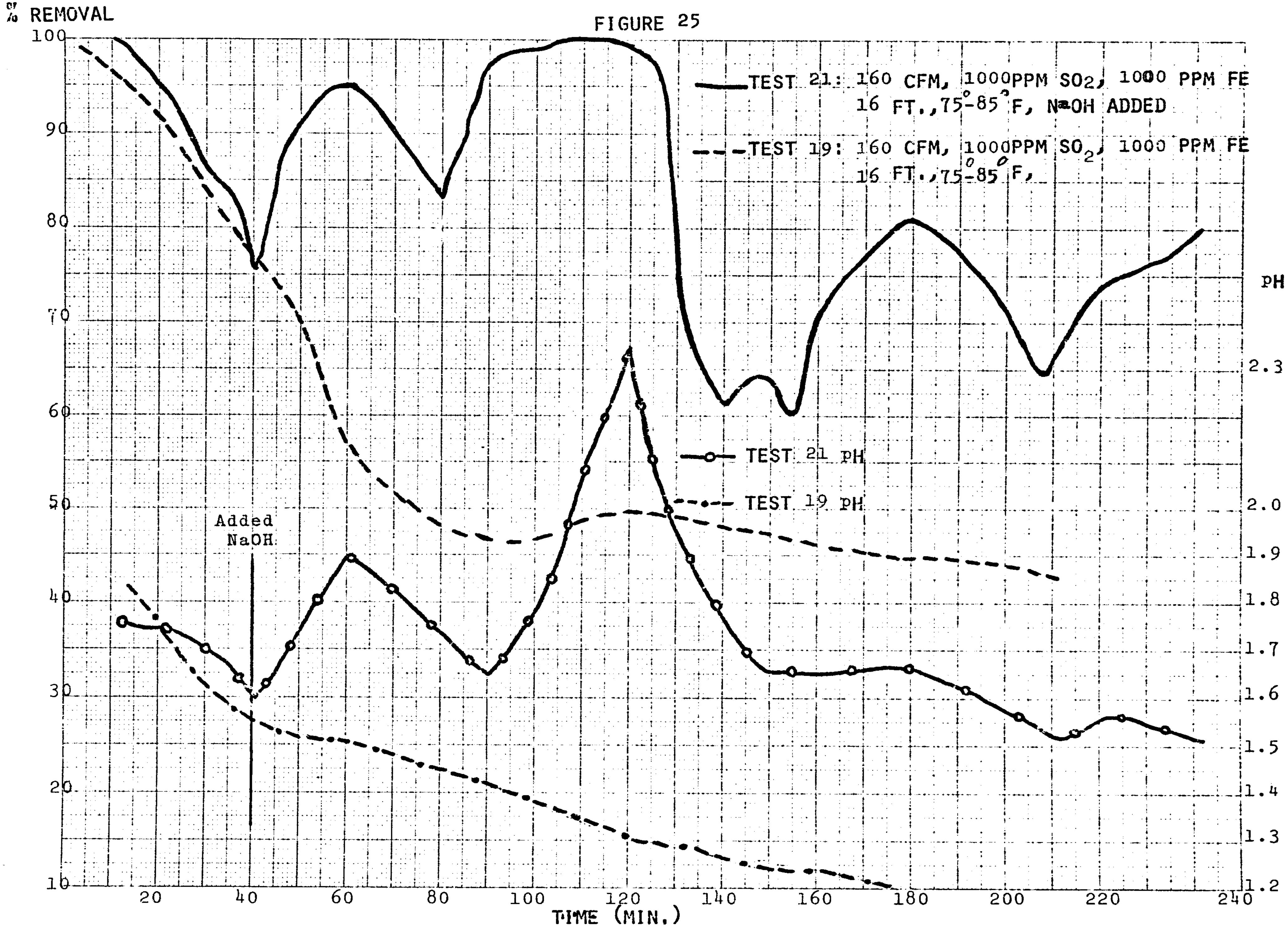
MINUTES
20
40
60
80
100
120
140
160
180
200
220
240
% REMOVAL
% Fe+2
100
90
80
70
60
50
40
30
20
10
pH
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.7
.6
SO4 PPM
9000
8000
7000
6000
5000
4000
3000
2000
1000
T3--120°F 2kFe
T4--115°F 2kFe
T5--115°F 1kFe
% REMOVAL
PPM SO4
pH
% Fe+2

control the rate. With time running out in the test program and the wastewater tests still to be performed, one additional test was devised to test the validity of the pH as the controlling factor in SO_2 removal.

Figure 25 is a comparison of test No. 21 and test No. 19. Both these tests were run under approximately the same conditions, with the exception being that in test No. 21, a controlled amount of sodium hydroxide was added to the solution in order to maintain a relatively steady pH. The amount of NaOH required was calculated based on the amount of sulfuric acid formed in test No. 19. The test system was not really set up to add the sodium hydroxide, so it was an add-on procedure that didn't work too smoothly. A pH controller should have been used but time and money constraints prohibited its use. However, the test results bear out the fact that the pH is a most significant factor. As can be seen in Figure 25, when the pH was raised by adding sodium hydroxide, there is an almost one to one following of the SO_2 removal with the pH. If there had been more time available, a second sodium hydroxide test would have been performed utilizing a smoother addition of sodium hydroxide. However, this was impossible. These test results, however, show a direct correlation between the pH and the sulfur dioxide removal.

Several quantitative conclusions can be made about the iron testing, a) above an unknown iron minimum level, additional iron seemed to be no particular aid in the SO_2 removal process, b) high water temperatures improved the reaction significantly;

FIGURE 25


% REMOVAL
100
90
80
70
60
50
40
30
20
10
PH
2.3
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
TEST 21: 160 CFM, 1000PPM SO2, 1000 PPM FE
16 FT., 75°-85°F, NaOH ADDED
TEST 19: 160 CFM, 1000PPM SO2, 1000 PPM FE
16 FT., 75°-85°F,
TEST 21 PH
TEST 19 PH
Added NaOH
20
40
60
80
100
120
140
160
180
200
220
240
TIME (MIN.)

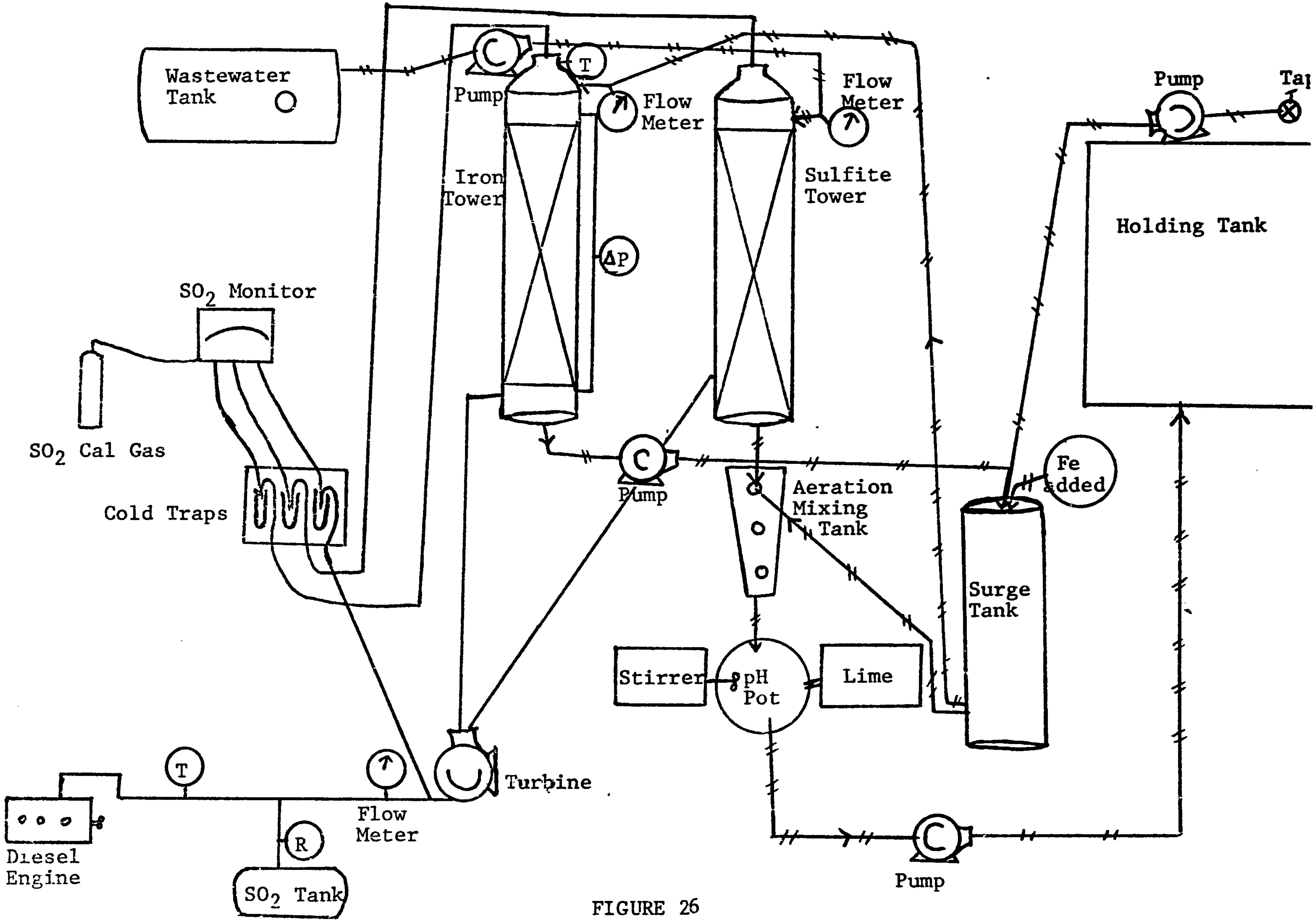


FIGURE 26
Parallel Towers

however, the absolute effect of the increase in temperature was not defined, c) with a thousand ppm of iron, L/G values approached or surpassed those on the Once-Thru water system with pH's above 2.0, d) the conditions which enhanced the formation of large amounts of Fe+2 or ferrous ions, such as low water temperature, high total iron content in the solution, and high sulfur dioxide input levels, reduced the solution's ability to remove the SO_2 from the gas stream, e) practically no sulfite ion was produced under any of the conditions tested, f) again quantitatively, the longer the contact time in the tower, the more efficient the process of scrubbing the SO_2 becomes.

Wastewater Testing

It had been anticipated in the contract that enough data would be known about the system, and the set-up of the system, to move right into wastewater testing, and finish up the program. However, it had been agreed upon in discussions between the NASA technical monitor and the contractor, that two ways could be devised to remove SO_2 with the wastewater scrubbing system. These two ways were, 1) a parallel set of towers, one using iron water recirculation, and the other tower, a pure sulfite removal tower as defined by the Once-Thru system tests, and 2) a series flow in which all the gas flow went through first the iron tower, and then the sulfite tower, or vice versa. The wastewater could then be blended from the two towers to produce the right concentration of iron for the wastewater treatment. Figure 26 and Figure 27 show respectively the parallel flow scheme, and the series flow scheme. The parallel tower looked like the most versatile way to go, and so using tap water as a scrubbing media, a parallel flow system was set up. The 16 foot tower was used for the iron solution, and the flow was set up at about 85 cfm. A 6 foot deep bed, 2 foot diameter tower was set up for sulfite Once-Thru type scrubbing, and the flow set at about 220 cfm. The sulfite tower can be seen on the left of photograph 6 with the iron tower on the right. Because the constraints in measuring equipment and in time, those numbers were only approximate. A 6 gpm wastewater flow through the sulfite tower was expected to scrub about

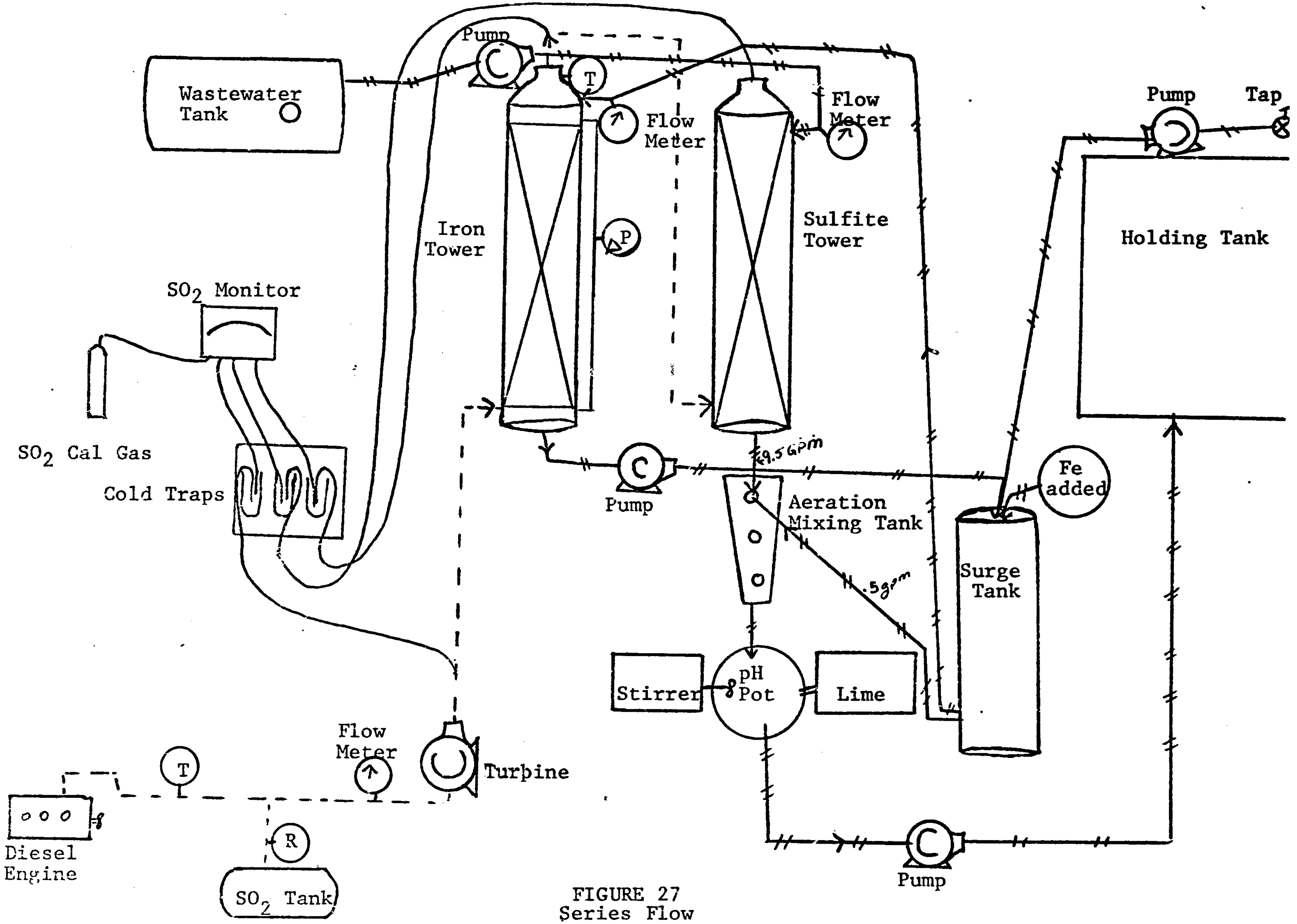
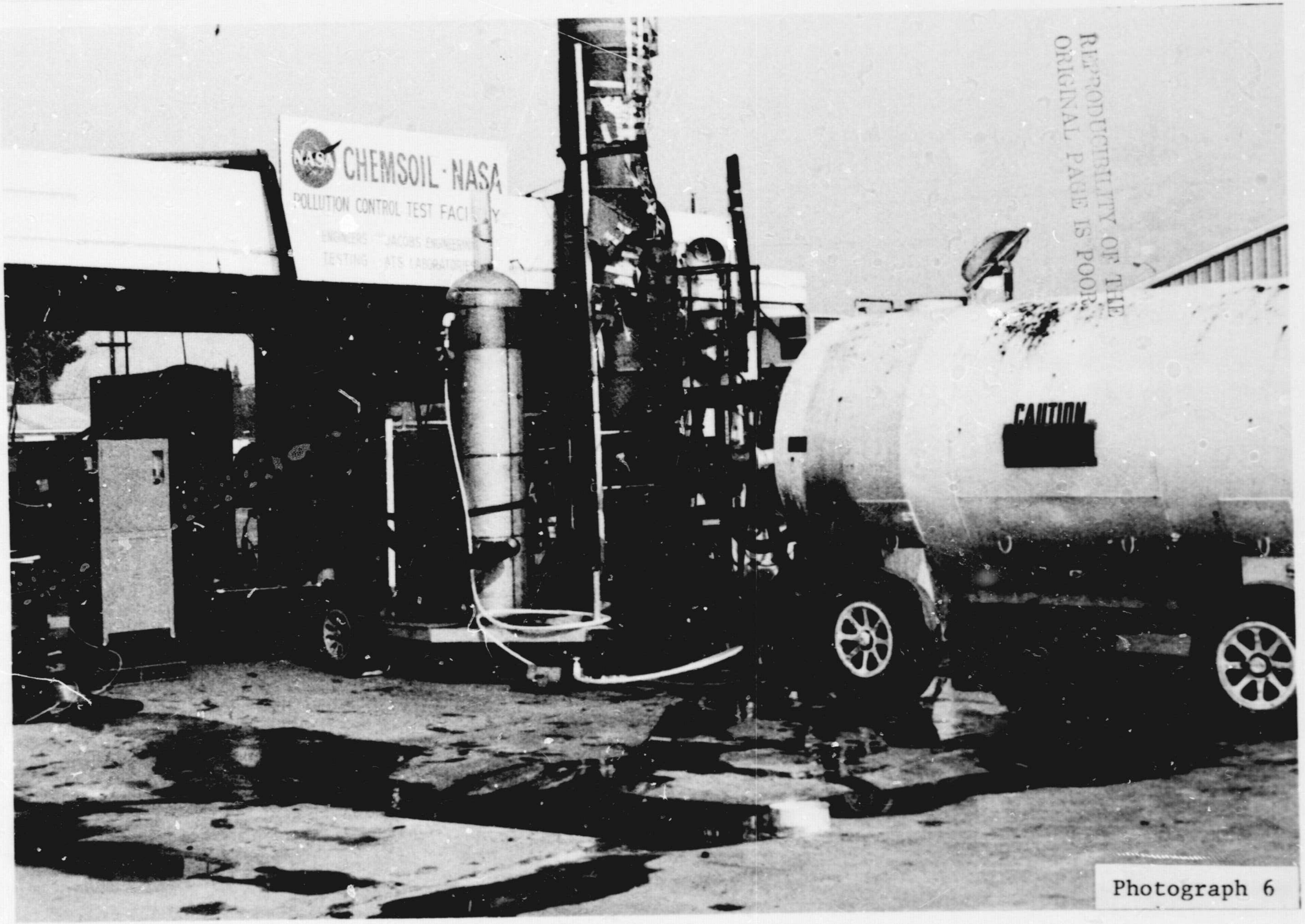


FIGURE 27
Series Flow



Photograph 6

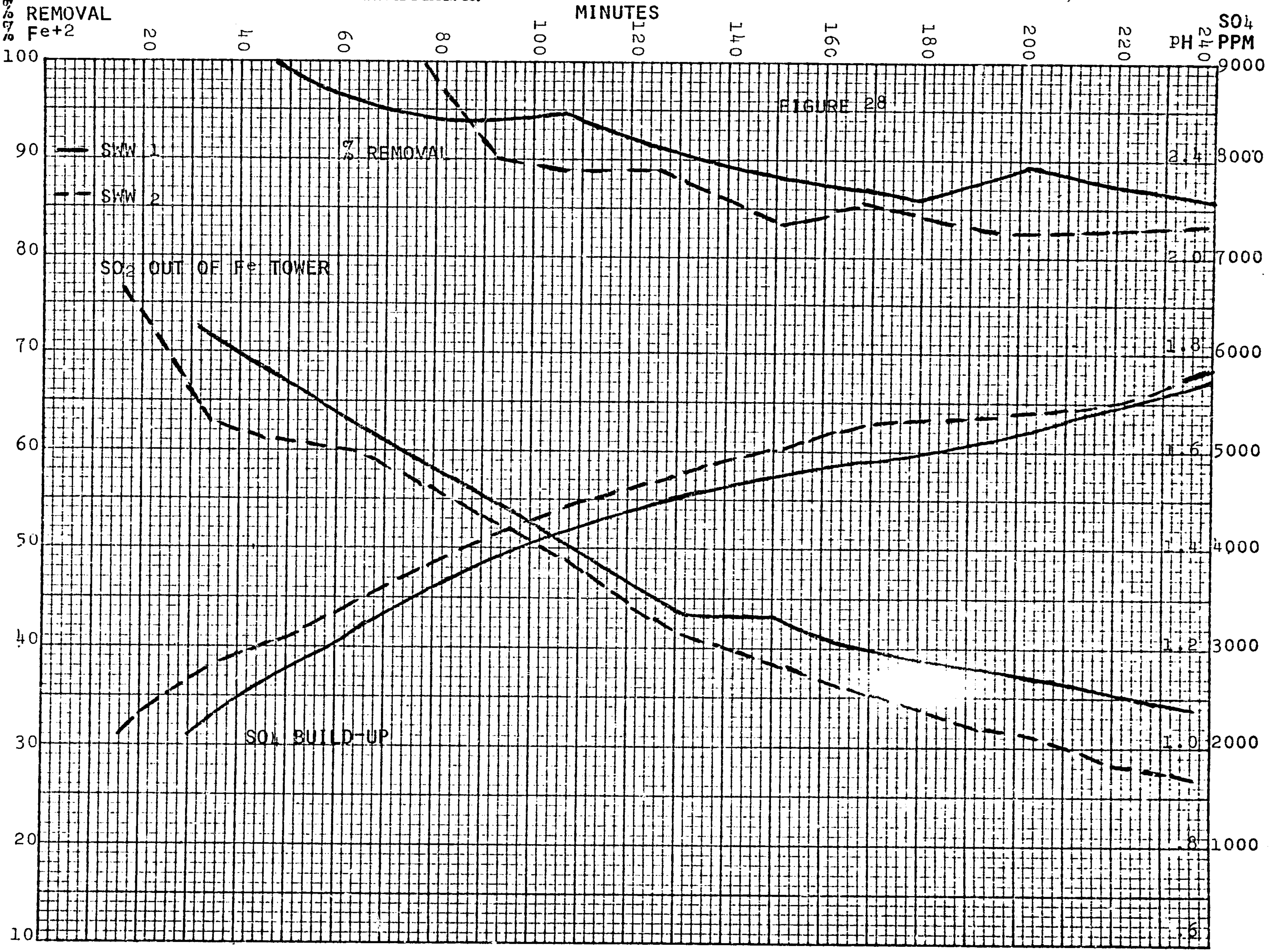
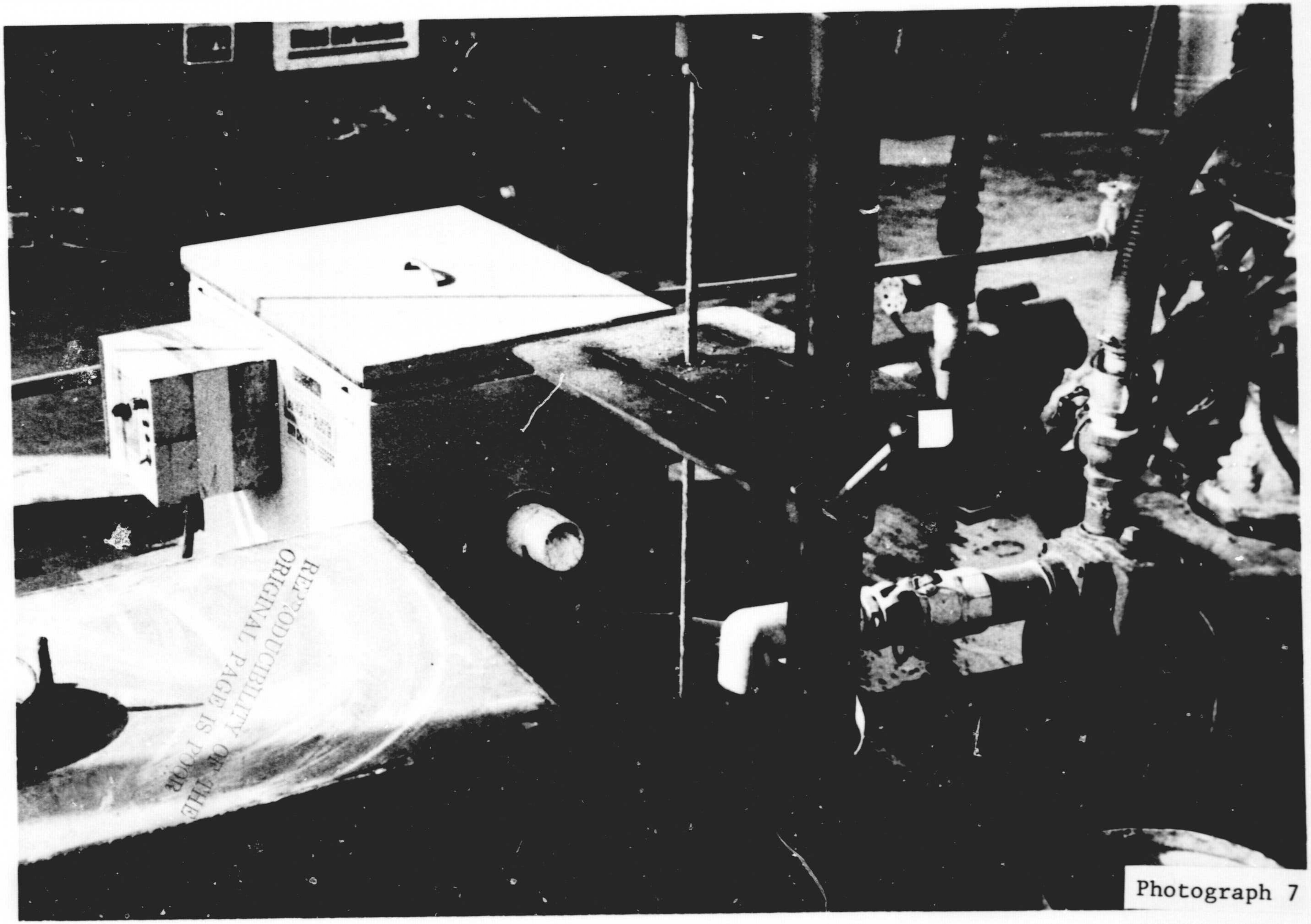

% REMOVAL Fe+2
MINUTES
20
40
60
80
100
120
140
160
180
200
220
240
100
90
80
70
60
50
40
30
20
10
pH
SO4 PPM
9000
2.4 8000
2.0 7000
1.8 6000
1.6 5000
1.4 4000
1.2 3000
1.0 2000
.8 1000
.6
SWW 1
SWW 2
% REMOVAL
SO2 OUT OF Fe TOWER
SO4 BUILD-UP

FIGURE 28

85%. Recirculation of the iron tower water at 12 gpm with a bleed-off of iron solution into the sulfite treated wastewater mixture was designed to produce about 85% scrubbing in the iron tower also.

The results of the first tests showed the iron tower worked very well, and the sulfite tower worked terribly. A mixture of a 90% sulfite tower water with 10% of the iron tower solution to form a 100 ppm iron level in the combined wastewater, a pH of less than 3 could not be achieved. Only 60% efficiency in the sulfite tower scrubbing was achieved, rather than the 85% that was anticipated. This system proved very difficult to control and operate correctly with no automatic control circuitry. Levels in the iron tower had to be maintained; levels in the surge tank also had to be maintained; the iron replenishment had to be operated at the correct rates; a blend of 9.5 gallons/minute of sulfited wastewater, and .5 gallon/minute of the iron tower wastewater had to be maintained; and the pH in the mixing pot, requiring varying amounts of lime had to be maintained. Photograph 7 shows the pH pot and the lime feeder.

After aeration, the levels of ferrous irons were low, .05 ppm, but sulfate was at 40° ppm, and ferric iron in particle form was at 15 ppm but could be removed with filtration. However the coliform counts were exceedingly high, showing that the pH of 3 or higher was not enough for sterilization.

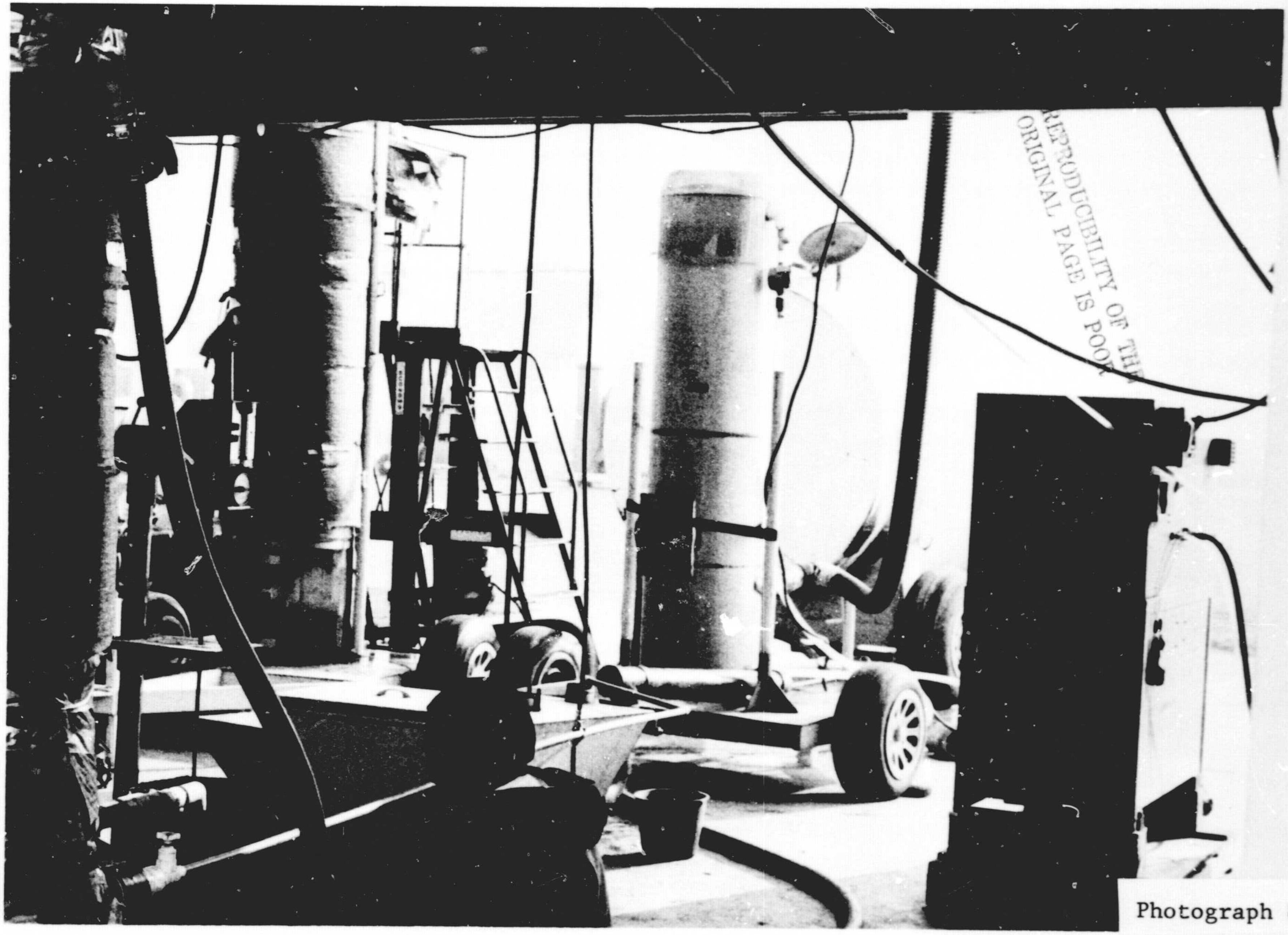


Photograph 7

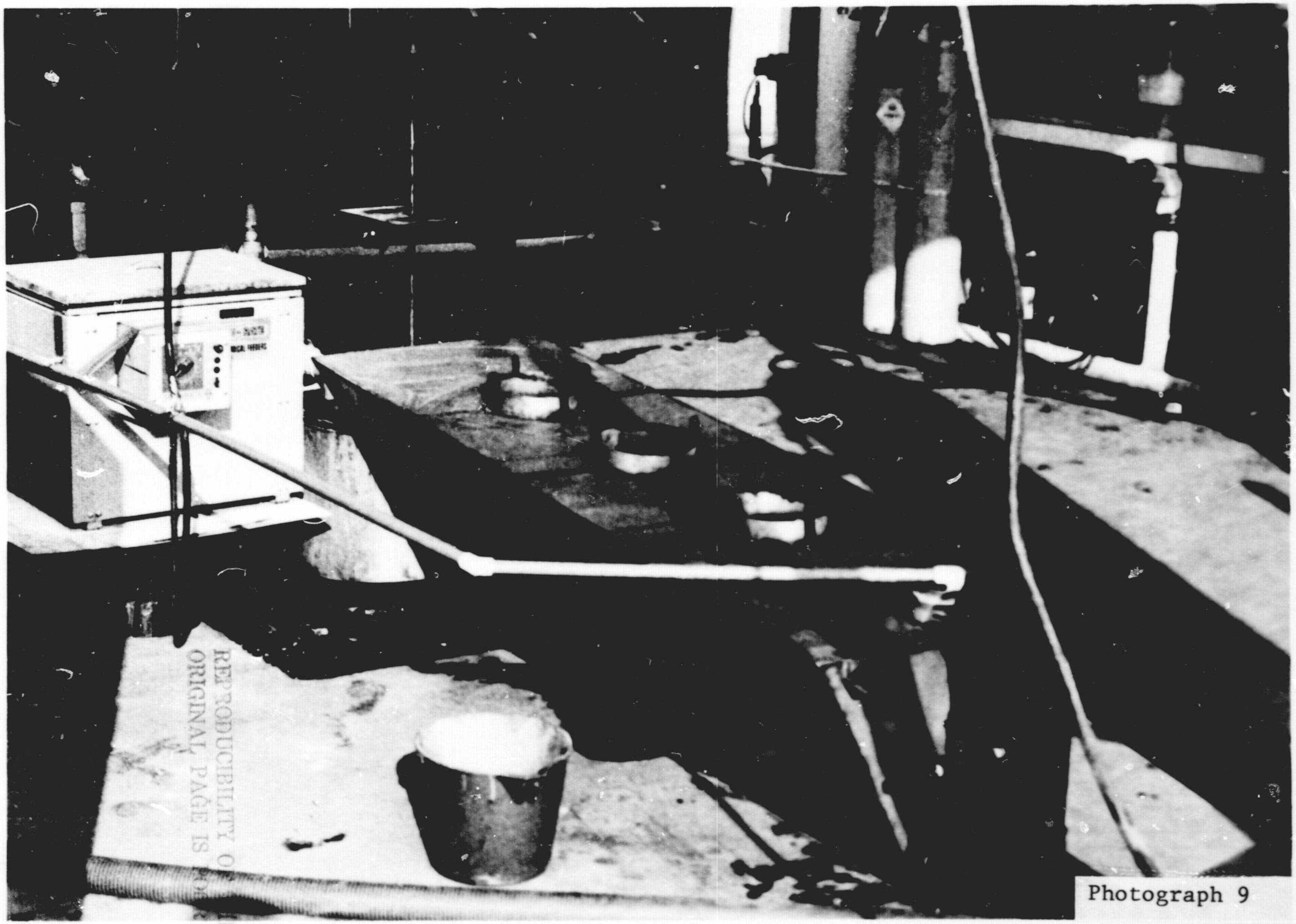
The next day was spent converting to the series flow. Here again, essentially the same conditions were set up, the total flow through each tower being about 300 cfm. Conditions improved to remove about 80% total of the SO_2 but again a pH of only 2.7 could be achieved in the sulfite tower. Again, without the low pH, a wastewater disinfection portion of the test was not good, and the test was considered a failure also from a standpoint of treating the wastewater. Photographs 8 and 9 show the series flow set-up and the pH pot set-up.

Figure 28 shows this test as SWW 1 and was followed by an attempt to duplicate the test after checking all of the equipment. This is shown as run SWW 2. In this test there was 7½% more SO_2 being injected and 5% more gas flow. These increases are reflected in apparent lower absorption rates, but a higher amount of SO_2 was removed and showed up as a higher sulfate build-up. On the second run, SWW 2, a pH of less than 2.5 had been achieved briefly.

With two days remaining in the regularly scheduled test program, a run was decided to be made utilizing primary settled wastewater under the same conditions as run SWW 2. SO_2 removal was excellent maintaining around 96% at the 200 minute mark. Correct flow from the iron tower and sulfite tower were maintained. The flow mixture of the two waters were maintained. The lime neutralization treatment was maintained, and all temperatures were pretty well controlled. One problem, however, was that the pH of the wastewater through the sulfite tower never fell below 2.8, and this resulted again



Photograph 8



Photograph 9

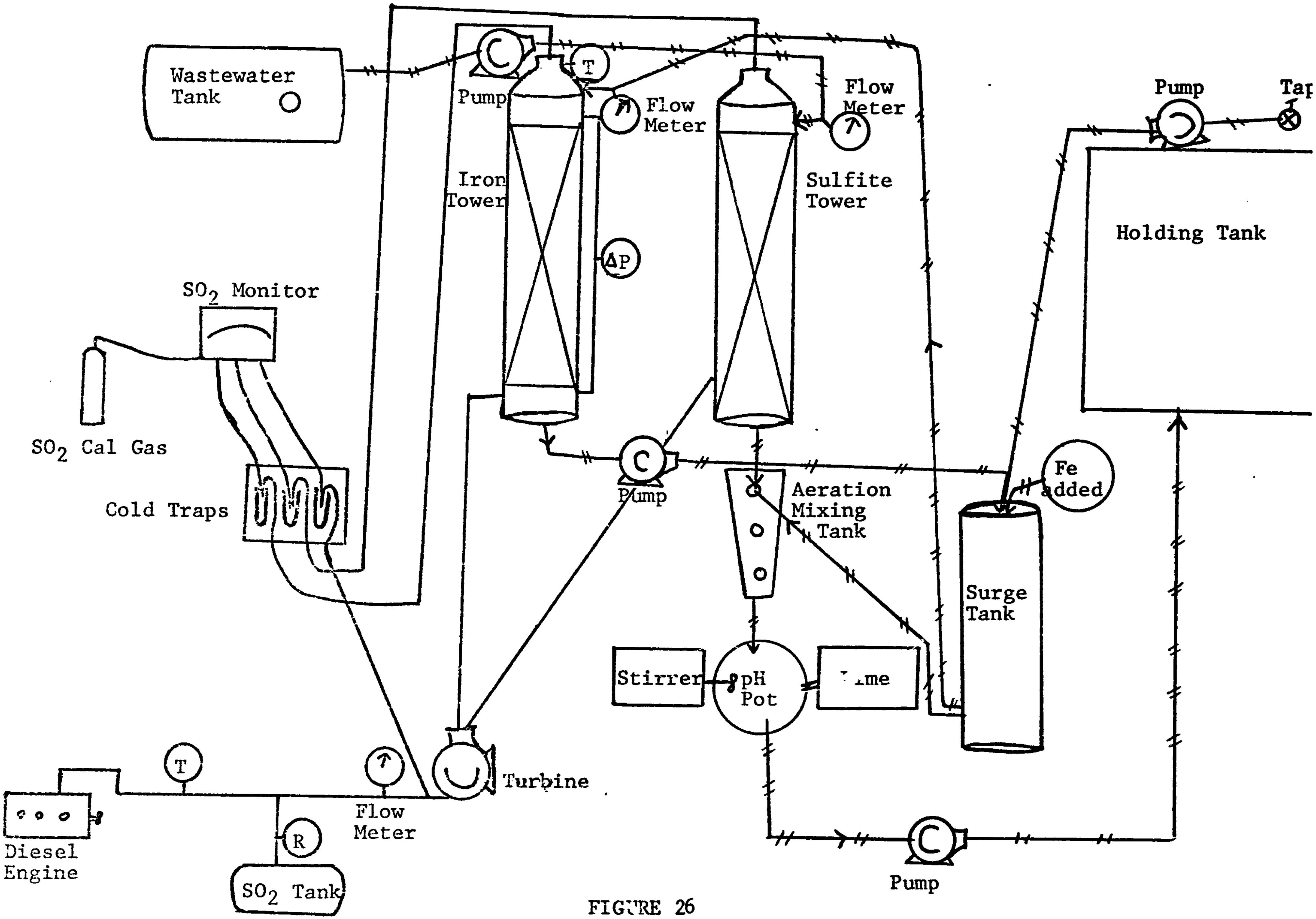


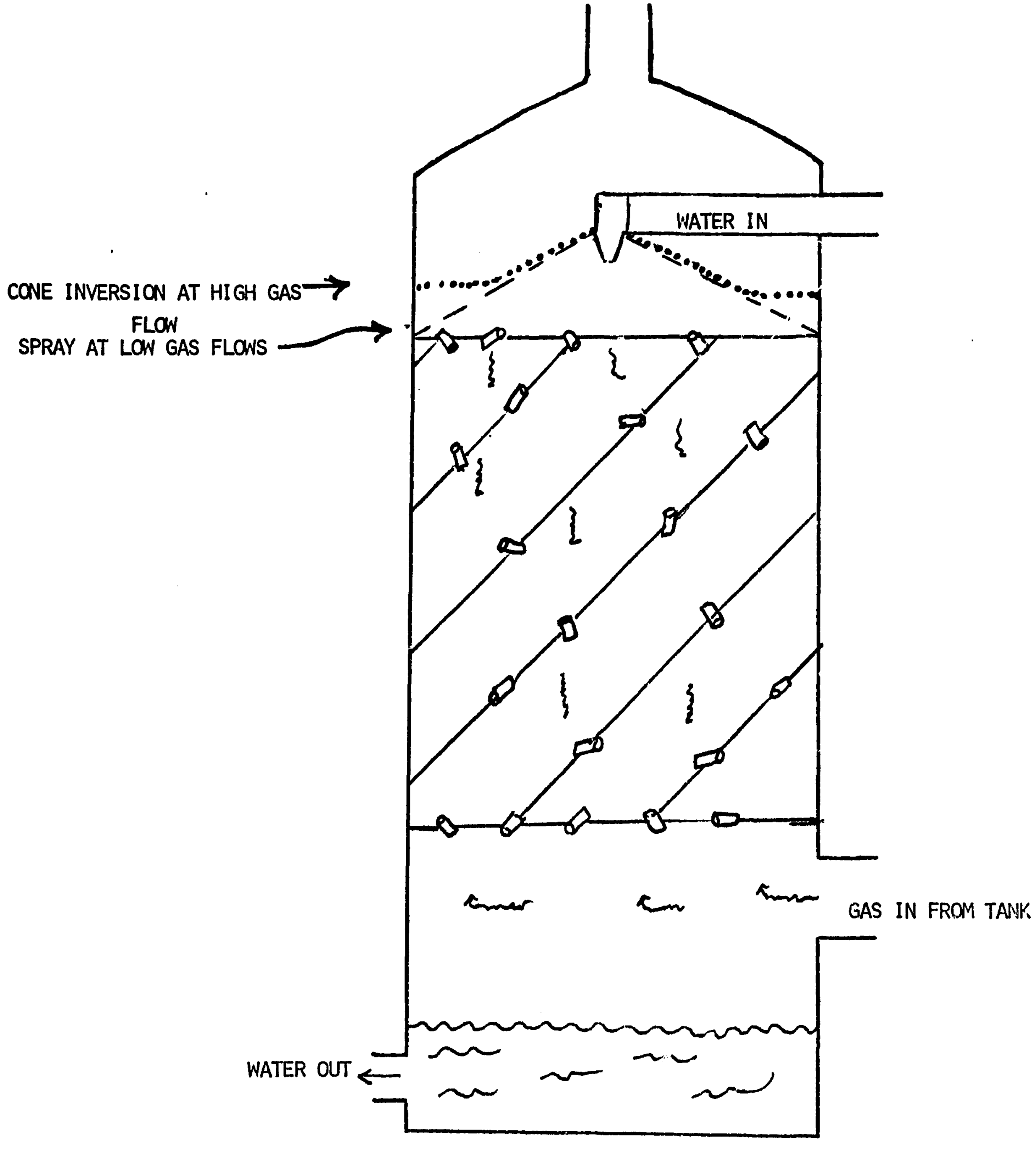
FIGURE 26
Parallel Towers

in incomplete coliform kill.

The morning of the last day there was still no apparent reason for the pH being so high in the sulfite tower. All the equipment was checked, and finally the malfunction was found. Prior to this time when checking flows, and flow patterns, lower gas velocities had been used when checking the sulfite tower and setting the spray head to produce a spray that just covered the packing media. This is shown in Figure 29. However, just prior to reaching the 300 cfm gas flow rate required for the test, the spray cone tended to invert. Thus a great deal of water hit the side of the tower, and went down the side without contacting the packing media. Because a stainless steel tower had been used for the sulfite tower, this particular phenomena was not spotted during the test runs. Flow rates were adjusted downward, and the test was set up to include ozone as required by the contract. However, the test day turned out to be a diaster with the ozone generator failing before measurements could be made; and a number of other malfunctions occurred throughout the day, such as leaking pumps, pump failures, and in the end, no test data could be obtained.

In the wastewater test program five different wastewater runs were made. Eighty-one level "b" tests were performed and one hundred-sixty level "a" were performed with more than three thousand data points gained but with very inconclusive results. However, some conclusions could be reached; a) even though the wastewater treatment facility was very marginal if not inadequate,

FIGURE 29


WATER IN
CONE INVERSION AT HIGH GAS FLOW
SPRAY AT LOW GAS FLOWS
GAS IN FROM TANK
WATER OUT

it was shown that 100 ppm of iron in the final wastewater solution produces a good percipitate, b) the series or parallel systems could be used if proper conditions could be achieved with the equipment, but the parallel system was more versatile, c) the parallel system should achieve lower pH's in the sulfite tower, because the SO_2 concentration entering the tower could be maintained at a higher level, d) the iron tower could be easily operated, and a mixture of sulfite tower water and the iron tower water could be easily maintained.

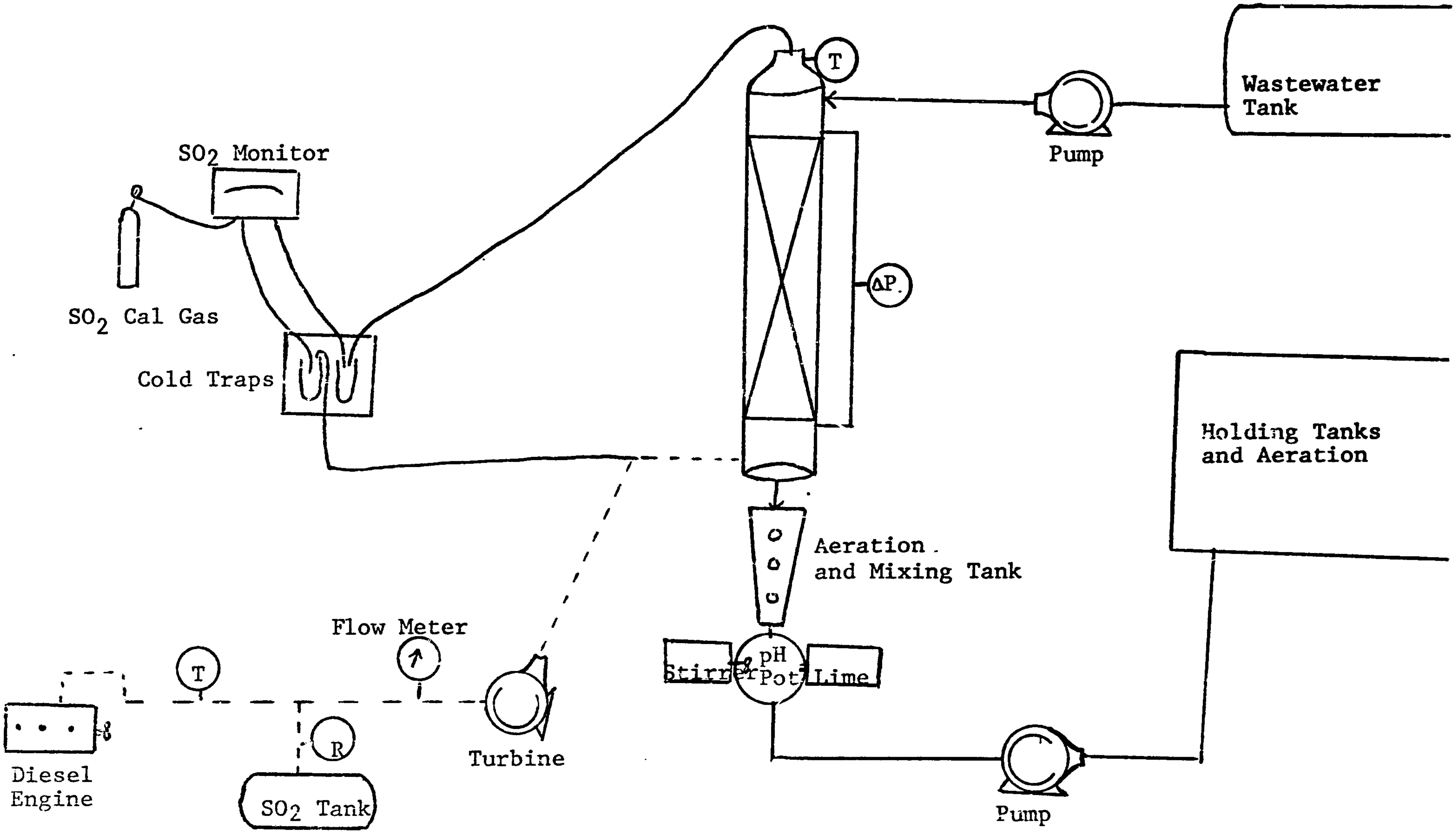
After the completion of the test program and analysis of the data was performed, it was decided in discussions between Chemsoil and the NASA technical monitor that a short series of added tests would be conducted to better identify the ability of the system to produce well-treated wastewater.

Added Wastewater Tests. It was agreed upon that simplified tests could be performed. This was a necessity because the amount of test personel was now extremely limited. The simplified tests would be done with a 100 ppm iron solution in the tower which had previously been the iron tower. The test purpose was to try to achieve increased levels of sulfite scrubbing with a 100 ppm of iron in the solution. This could be done in a full system by adding the 10% water from the iron tower, with a thousand ppm of iron to 90% incoming water before it enters the sulfite tower. This single tower test operation would eliminate the necessity for recycle and all of the manual level controls which had made the previous testing so complex and difficult. The water distribution tray could be used rather than the spray, so that the problem of spray inversion found in the previous test group would not be a problem.

The schematic of these simplified test runs is shown in Figure 30. Investigations would center around the wastewater aspect of scrubbing because it had already been proved that the SO_2 removal was achievable in the tower. Four items in particular were to be pursued; 1) the requirement to lower the pH to 2.5 or less, 2) the coliform kill was to be investigated, 3) aeration prior to adding lime, as well as post-lime aeration was to be investigated to enhance percipitation, 4) the ferrous ion and the sulfite ion removal by a post-aeration was to be more thoroughly investigated.

The first test run was made using just the wastewater without iron addition to be a baseline. The L/G turned out to be 41, about 12% better than tap water which could be expected because more constiuents in the water react with the SO_2 than pure tap water. Additional runs were then made at 50 ppm of iron which yielded an L/G of about 42, a pH of 2.3 was achieved, but no significant improvement in the L/G was seen. Another run was then made using 100 ppm of iron. The L/G at that point dropped to 31, a pH of 2.3 was achieved. This L/G of 31 indicates about 30% more SO_2 could be added to the 100 ppm iron water than to the tap water, and 25% more than with the basic wastewater. Finally a run was made at 1000 ppm, and the L/G came back up to about 40 and the pH achieved was about 2.0.

FIGURE 30



Wastewater Tank
Pump
T
ΔP.
SO_2 Monitor
SO_2 Cal Gas
Cold Traps
Holding Tanks and Aeration
Aeration and Mixing Tank
Stirrer
pH Pot
Lime
Flow Meter
T
R
Turbine
Diesel Engine
SO_2 Tank
Pump

It is obvious that the 1000 ppm didn't particularly help the wastewater's ability to remove SO_2.

Table 11 shows the results of one of the wastewater runs. The wastewater was extremely strong at this point as can be seen by a COD level nearly 3200. Results of treatment were not spectacular, with 40% of COD still remaining in the solution after percipitation. The coliform count of at 9.2 wasn't bad considering the quality of wastewater. It can be seen that ammonia reduction was not outstanding, but phosphate reduction from 85 ppm to .4 ppm was outstanding. Several modes of aeration were investigated and it was found that pre-aeration prior to neutralization appeared to aid in producing a better precipitate.

Thus, the next day run was made with a different wastewater with more normal values and the results of that run can be seen in Table 12. A significant piece of information was found at that point; the soluable COD was approximately 50% of the total COD, which is extremely high in value for soluable COD. Again using pre and post aeration the best aerated sample showed significant reductions in COD, BOD, and phosphate, as well as the coliform count reduced to a value which is considered very good wastewater treatment, less than 2.2.

Correcting for some of the base line measurements that had been made with tap water, Table 13 shows that this final test, produced reductions of 75% in BOD, 78% in COD, 43% in ammonia, and a 98% reduction in the phosphate levels. All of the results were achieved without a good contacting tank design, good aeration

C-2

TABLE XI

	Raw Sewage mg/l	Best Aerated Sample
COD	3160	1440
Ammonia	26	18
Phosphate	85	.4
Coliform	greater than 16	9.2
pH	5.7	8.6
DS	950	1325
SO_4	less than 15	456

TABLE XII

	Raw Sewage mg/1	Best Aerated Sample
BOD	336	104
COD	642	180
Sol. COD	327	
Ammonia	17	9.7
Phosphate	12	.3
Coliform	greater than 16	less than 2.2
pH	6.3	7.8
SO_4	less than 15	

TABLE XIII

Corrected for Baseline

	Raw Wastewater mg/l	Best Aerated Sample	% Reduction
BOD	336	84	75%
COD	642	140	78%
Ammonia	17	9.7	43%
Phosphate	12	.3	98%