NASA CONFERENCE PUBLICATION 2049

National Aeronautics and Space Administration/

Florida Institute of Technology

Conference On

Environmental Engineering

For Nitrogen Tetroxide(N_2O_4)

A CONFERENCE HELD AT
MELBOURNE, FLORIDA
MARCH 30 and 31, 1978

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A conference jointly sponsored by the
National Aeronautics and Space Administration,
John F. Kennedy Space Center and
Florida Institute of Technology, Melbourne, Florida,
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16. Abstract

This document presents the proceedings of a conference held March 30, 31, 1978, at the Florida Institute of Technology, Melbourne, Florida, sponsored by the National Aeronautics and Space Administration and Florida Institute of Technology. The purpose of the conference was to exchange methods of reducing the user hazards of nitrogen tetroxide, a hypergolic oxidizer. Kennedy Space Center developments in N_2O_4 control for the Space Shuttle were featured. Other areas covered were life support equipment and transportation.

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CONTENTS

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iii

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FORWARD

The NASA/Florida Institute of Technology (FIT) Environmental
Engineering Conference on nitrogen tetroxide took place at
the FIT campus in Melbourne, Florida, on March 30/31, 1978.
Sixty-five (65) persons interested in the emerging problems
of nitrogen tetroxide came to exchange information about
methods of handling this oxidizer and protecting personnel
from its deleterious effects.

This publication is a compilation of the papers presented at
the conference. Each paper is published with no change except
for consecutive page numbering. The authors can be contacted
at their respective addresses.

Enough interest was shown that future conferences are under
consideration.

Eric Rhodes
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ACKNOWLEDGMENTS

A PORTABLE HYPERGOLIC OXIDIZER VAPOR SENSOR

FOR NASA'S SPACE SHUTTLE PROGRAM

March 1978

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1

The Space Shuttle, which will begin test flights from Kennedy Space Center in 1979, uses large quantities of hypergolic propellants. The Reaction Control Systems and Orbital Maneuvering Systems engines use monomethylhydrazine fuel and nitrogen tetroxide oxidizer. Inasmuch as the vapors of these propellants are both toxic and flammable, personnel and equipment safety requirements dictate a need to monitor their concentration wherever the propellants are used.

Nitrogen tetroxide (N_2O_4) is monitored in its vapor form as NO_2. Several techniques are available to measure NO_2 in air. In 1975, the National Institute of Occupational Safety and Health evaluated instruments designed to monitor nitrogen oxides (1). This paper will describe the design and performance characteristics of an electrochemical NO_2 sensor selected by NASA for the Space Shuttle Program.

The instrument was developed for NASA by Energetics Science, Inc., and the development is described in their final report (2).

The instrument consists of a sample pump, an electrochemical cell, and control and display electronics (Figure 1). The pump pushes the sample through the electrochemical cell where the vapors are analyzed and an output proportional to the NO_2 concentration is produced. The output is displayed on a panel meter, and is also available at a recorder jack.

The electrochemical cell is made up of a polypropylene chamber covered with teflon membrane faceplates. (Figure 2). Platinum electrodes are bonded to the faceplates, and the sensing and counter electrodes are potentiostatically controlled at -200 mV with respect to the reference electrode. The cell is filled with electrolyte, consisting of 13.5 cc of 23% solution of KOH.

2

Table 1 lists the manufacturer's specifications for the NO_2 sensor. Two prototype instruments were tested to these specifications by the Naval Research Laboratory (3). Zero drift was typically 0.1 ppm/8 hours for one instrument, but as much as 1.0 ppm/8 hours for the other. Random span drift was on the order of 0.7 ppm/8 hours. There was a slow, negative span drift of about 0.5 ppm over four weeks.

Response and recovery times for the NO_2 sensors are very good. Initial response is almost immediate, and 90% of a change is read within 20 seconds. Accuracy is also very good. The instrument read low by 0.02 ppm at a 0.1 ppm concentration, low by 0.2 ppm at a 1.0 ppm concentration, and low by 0.6 ppm at a 10 ppm concentration. Interference tests were run on the instrument for carbon monoxide, hydrogen, krypton, methane, aliphatic and aromatic hydrocarbons, refrigerant gases and methyl alcohol at 500-1000 ppm concentrations in air. The instrument was not subject to interference from any of these gases. A battery test was also performed, and verified that the instrument is capable of operating eight hours on fully charged batteries.

A field test of one instrument has been performed at White Sands Test Facility (4). The NO_2 sensor performed well in this test, both for monitoring at Threshold Limit Value levels (5 ppm), and leak hunting in oxidizer lines. The random zero drift proved annoying, necessitating frequent rezeroing. This was the instrument with 1 ppm/8 hour drift at NRL. It was recommended that the jewel movement panel meter be replaced with a digital readout, to avoid motion sensitivity. Calibration

was found to be easy using permeation tubes, and required only about one hour. The unit held its calibration two weeks, and probably would hold longer.

In conclusion, the NO_2 sensor is considered to be adequate for NASA's needs. There are no plans at present to change the panel meter. It is felt that improved manufacturing processes will improve the zero drift characteristics. The instrument is accurate, sensitive, and easy to use and calibrate. It should make a significant contribution to the safety and reliability of the Space Shuttle program.

5
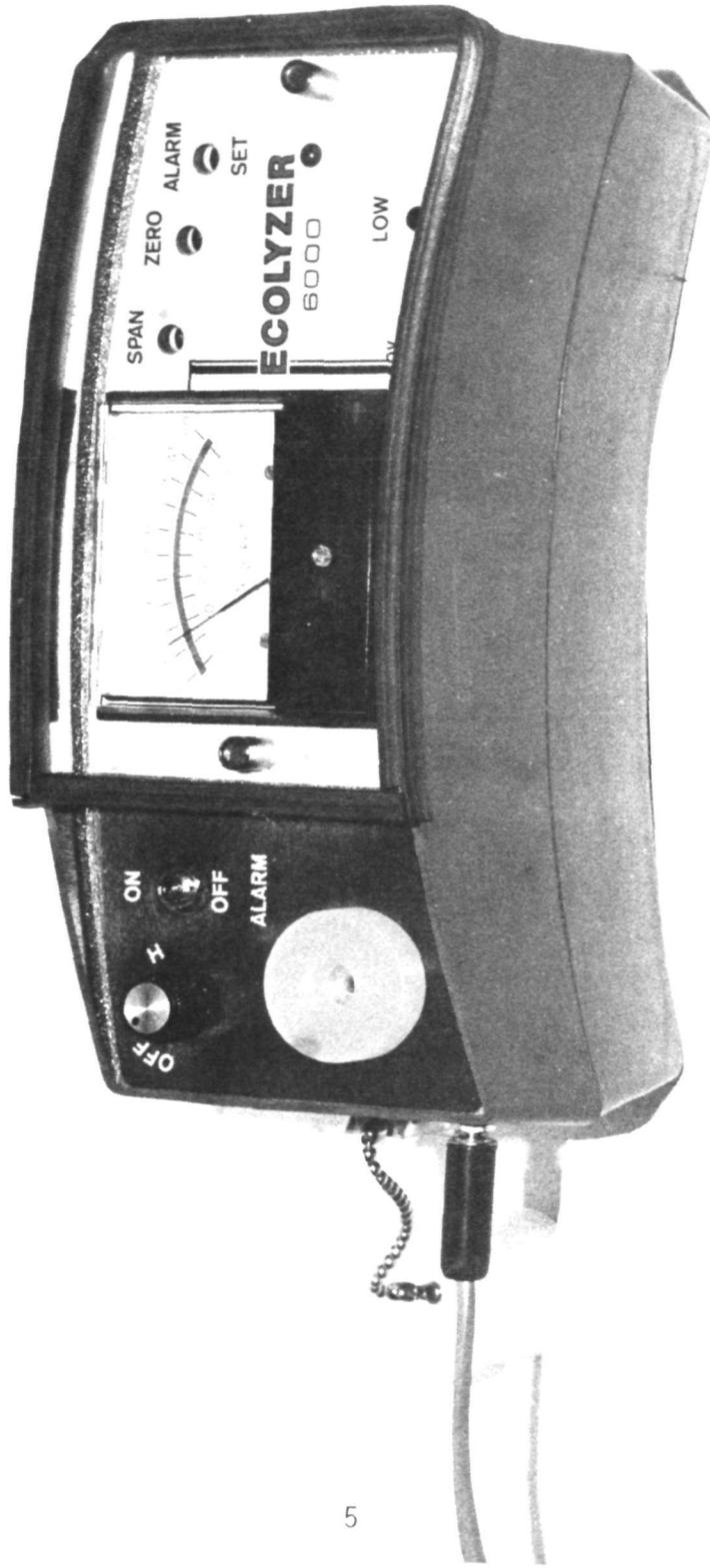
Figure 1

FLOW DIAGRAM OF THE NO_2 HIPSTER

GAS INLET →

REFERENCE → ELECTRODE

← SENSING ELECTRODE

ELECTROLYTE CHAMBER

INSULATOR →

COUNTER → ELECTRODE

GAS EXIT ←
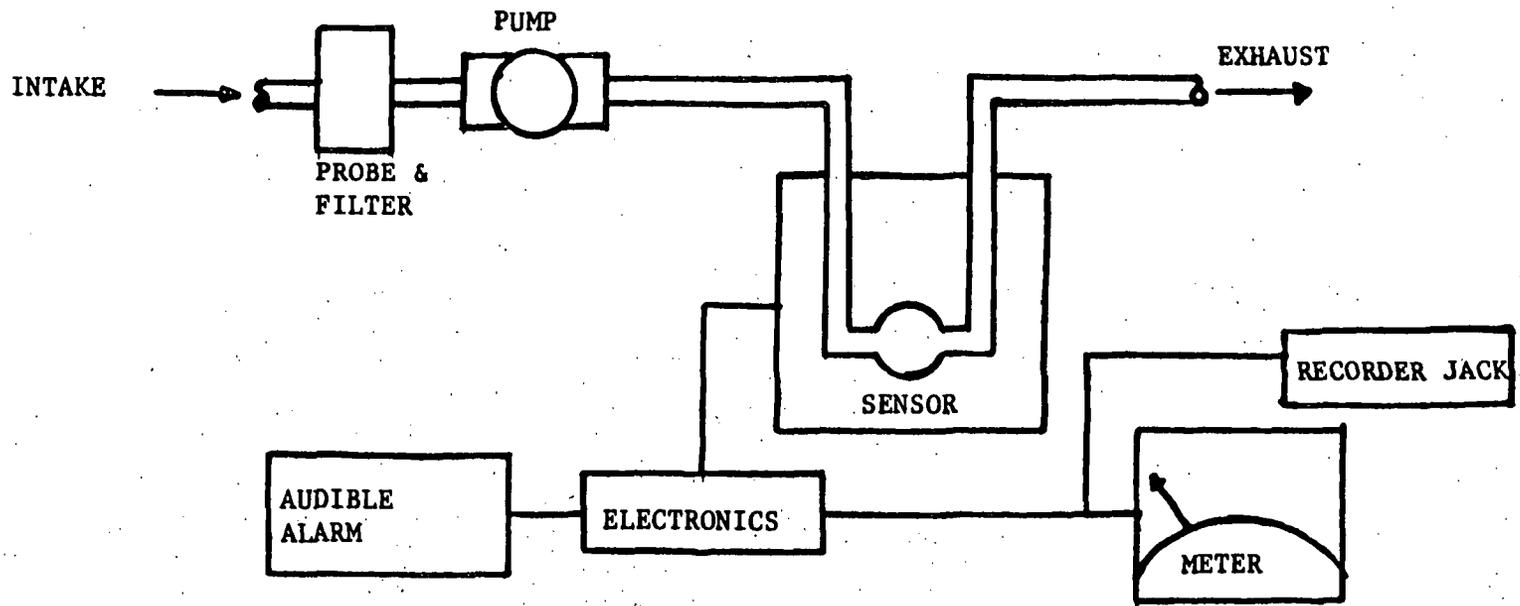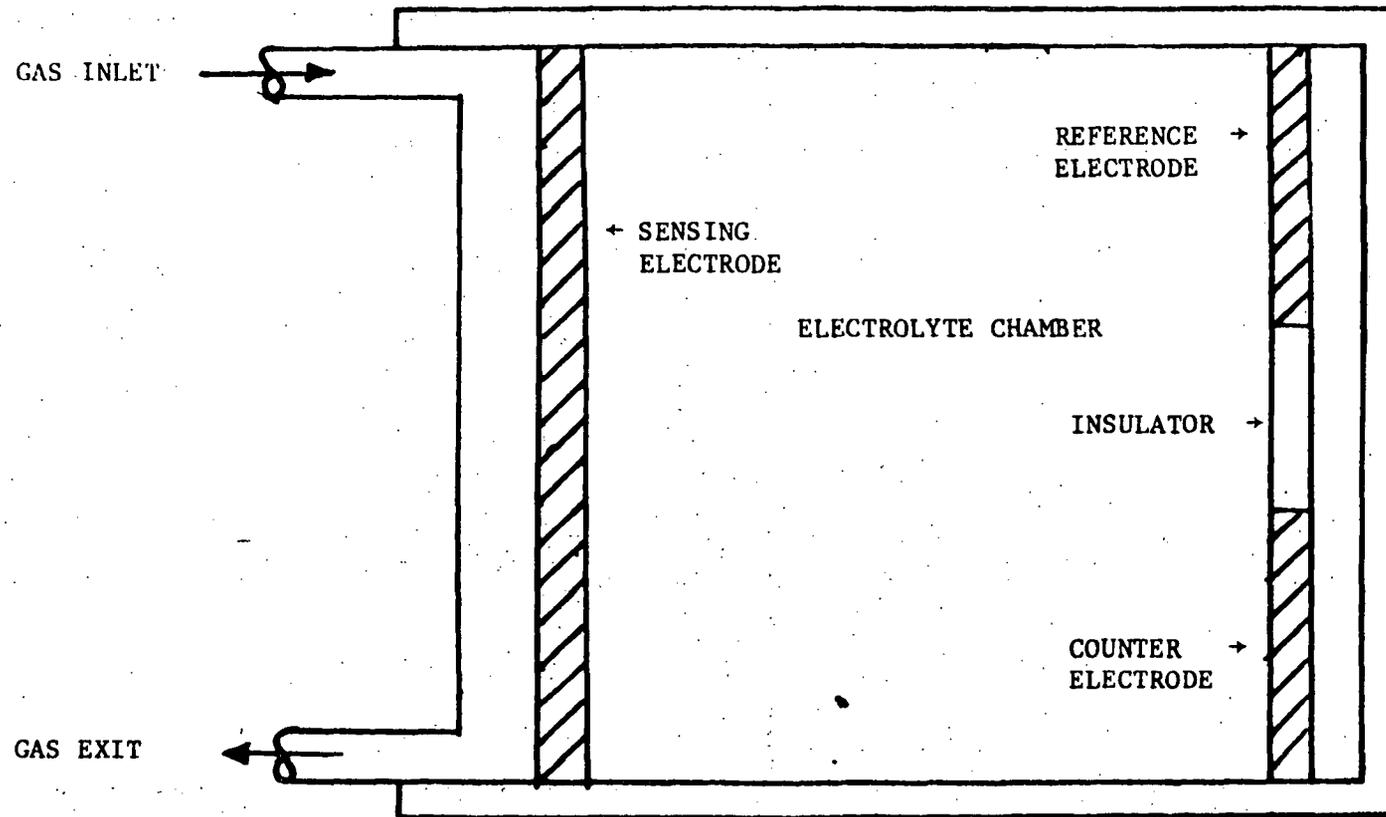
Figure 2   SCHEMATIC OF ELECTROCHEMICAL SENSOR

Table 1

INSTRUMENT SPECIFICATIONS

ITEM	MODEL 6302/NO$_2$ HIPSTER
Charging Power Requirements	110V to 120V AC, 50/60 Hz
Charging Time	Overnight (approx. 16 hours)
Operating Time with full charge	Eight (8) hours of continuous operation
Standby Power Consumption	No more than 48 hours between charge and use
Standard Ranges (Dual)	NO$_2$ 0-5 ppm/0-50 ppm
Response Time	90% of signal within 30 sec.
Accuracy	± 2% of full scale range
Reproducibility	± 2% F.S.
Noise	< 1% F.S.
Stability	
Zero Drift	± 2% of full scale per day
Span or Calibration	± 2% of range per day
Operating Temperature (for full accuracy)	32°F – 104°F
Operating Relative Humidity Range	5% to 95% R.H.
Physical Dimensions	3" x 5" x 8"
Weight	3.5 lbs.

REFERENCES

1) C. D. Parker, "Evaluation of Portable, Direct-reading $NO-NO_x$ Meters, HEW Publication No. (NIOSH) 76-161

2) J. R. Stetter and K. Tellefson, "A Study for Hypergolic Vapor Sensor Development," Final Report, NASA Contract NAS 10-8982, November 1977

3) R. A. Saunders, J. J. DeCorpo, B. J. Stammerjohn, and R. J. Kaulter, "Evaluation of an Electrochemical Detector for Trace Concentrations of Hydrazine Compounds in Air," Preliminary Final Report, NASA Contract CC-45899A, December 1977

4) P. M. Dhooge and T. J. Szydlowski, "Preliminary Report on Evaluation and Field Use of Portable Hypergolic Vapor Detectors (Hipsters), "Lockheed Electronics Co., White Sands Test Facility, N. M. March 1978

POTENTIAL OF A NITROGEN TETROXIDE SPILL OR EMISSION
DURING MOVEMENT FROM SUPPLIER TO USER

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11

POTENTIAL OF A NITROGEN TETROXIDE SPILL OR EMISSION
DURING MOVEMENT FROM SUPPLIER TO USER

INTRODUCTION

As an introduction, (Slide 1), I would like to describe how the Directorate of Energy Management (SF) is involved in nitrogen tetroxide support. SF has the responsibility to supply all DOD and NASA facilities with nitrogen tetroxide. We provide the many services - inventory management, quality control, procurement, transportation, and packaging - to insure that the user receives specification material. SF controls all of the transportation of nitrogen tetroxide between the supplier and DOD or NASA users. There are many potential problems and hazards in shipping nitrogen tetroxide - a Class A poison gas, oxidizer and a very corrosive material if it becomes wet.

TRANSPORT EQUIPMENT

First, let's outline the type of equipment used to transport nitrogen tetroxide. (Slide 2) The Code of Federal Regulations Title 49 and exemption to Title 49 specifies the type of equipment that can be used. Nitrogen tetroxide is moved in carbon steel tank cars, tank trailers and ton containers. This transport equipment is in dedicated service for nitrogen tetroxide. (Slide 3) Our average annual movement of the oxidizer is <u>1.7 million</u> pounds of N_2O_4 (NTO), <u>1 million</u> pounds of N_2O_4 (MON-I) and <u>.4 million</u> pounds of N_2O_4 (MON-III).

SHIPPING

(Slide 3A) Nitrogen tetroxide is moved directly from the supplier to the various using locations. Specific routing instructions are provided to each carrier for each shipment of N_2O_4. When alternate routes are available, trailers are routed around towns. The DOT exemption 1321 provides special requirements for the drivers on parking and safety.

POTENTIAL FOR SPILLS

(Slide 4) During the handling and movement of N_2O_4, there are potential areas for leaks, emissions or spills. These areas include:

a. Accidental spills. Accidental spills can result from vehicle accidents, corrosion, poor housekeeping and human errors.

b. Transfer operations. The greatest potential for spills or leaks is during coupling or uncoupling of the hoses for loading or unloading of tankers.

c. Sampling. Each shipping container requires sampling before it leaves the plant after loading. This can present problems with disposal of the purged liquid and the residual sample.

d. "Empties" - The so-called "empty" trailer is a potential source of emission. Some people tend to forget that the empty trailer contains residual material and they do not handle the vessel as carefully as a full vessel.

(Slide 5) We have been moving nitrogen tetroxide since 1961. Each year we move about 3.1 million pounds of nitrogen tetroxide and the transport equipment logs about 250,000 round trip miles each year. Since

13

we have been moving N_2O_4, the personnel in the Directorate can remember of four incidents involving N_2O_4 trailer while in transit. Only two of the four incidents resulted in the release of N_2O_4 vapors to the environment. There have been no reported incidents of leakage involving tank cars or one ton containers while in transit. There have been problems with leaks at the QD's while unloading at Vandenberg. Occasionally, railcars being used for storage developed gas leaks in the dome area.

(Slide 6) Some of the corrective actions taken to reduce the reoccurrence of the above problems have been:

a. Route trailers around town when possible.

b. Specific load sizes below the maximum loads.

c. Replacing the dome plates with stainless steel and installing new piping and valves.

d. Request contractor to improve their maintenance, testing and housekeeping of the QD's and trailers.

e. Provide check lists for tank car and trailer inspections prior to loading and after unloading.

f. Establish maximum pressure on trailers.

Our accident rate for movement of nitrogen tetroxide by trailer is 1.3 accident per million miles or one per four years.

CONCLUSION

In conclusion, there are many areas that are potential sources of an accidental release of N_2O_4 to the environment. We have taken positive actions to reduce our accident rate and improve our service.

14

POTENTIAL OF A NITROGEN TETROXIDE SPILL OR

EMISSION DURING MOVEMENT FROM SUPPLIER TO USER.

SLIDE 1

TRANSPORT UNITS

	DOT SPEC	METAL	PRESSURE RATING
TANK CARS	105A500W	CARBON STEEL AND LAGGED WITH 4 INCH CORK	500
TRAILERS	MC330 NOVEL	CARBON STEEL	300
TON CONTAINERS	106A500X	CARBON STEEL	500

SLIDE 2

TRANSPORT UNITS (CONT)

	SAFETY	TANK RETEST	CAPACITY
TANK CARS	SAFETY VALVE EQUIPPED WITH FRANGIBLE DISC	10 YEARS SAFETY 5 YEARS	110,000 LBS
TRAILERS	SAFETY VALVE EQUIPPED WITH FRANGIBLE DISC	30 MONTHS	40,000/ 30,000 LBS
TON CONTAINERS	SHALL NOT BE LIQUID FULL AT 130 DEGREES F	5 YEARS	2,000 LBS

ANNUAL MOVEMENT

NTO	1.7 MILLION LBS
MON-I	1 MILLION LBS
MON-III	.4 MILLION LBS

SLIDE 3

LOCATIONS OF NITROGEN TETROXIDE FACILITIES

□ SUPPLIER

○ USERS

SLIDE 3A
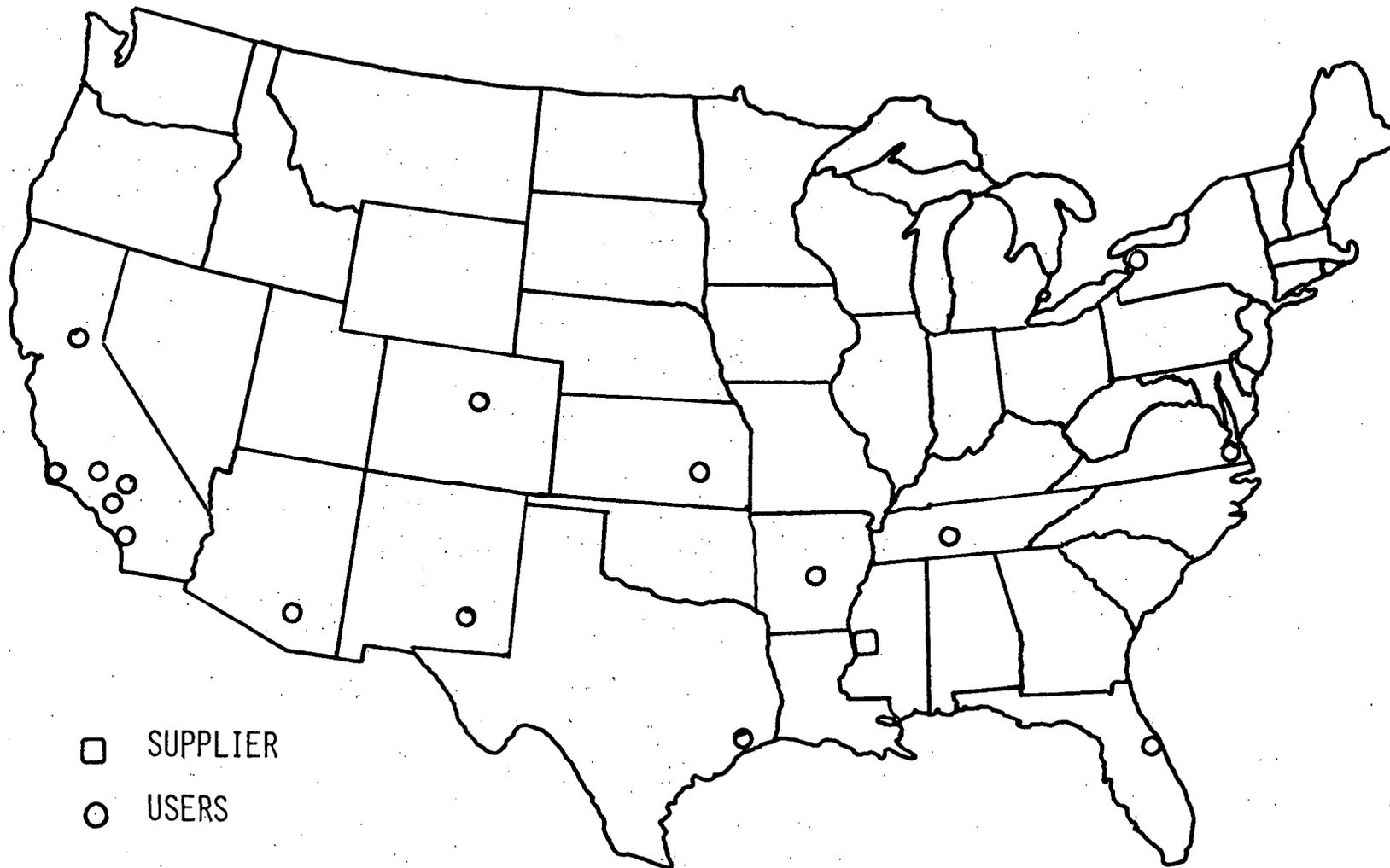
POTENTIAL AREAS

ACCIDENT

LOADING/UNLOADING

SAMPLING

EMPTY TRAILERS

HISTORY

1961

- 3.1 MILLION LBS OF N_2O_4

- 250,000 MILES PER YEAR

- TRAILERS

- TANK CARS

CORRECTIVE ACTION

ROUTES

LOAD SIZE

UPDATING TRAILER DOMES AREA

CHECK LIST

SCRUBBING LIQUORS FOR

NITROGEN TETROXIDE

by

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ABSTRACT

N_2O_4 scrubbing research has a considerable history, if one considers that N_2O_4 is merely a dimer of NO_2. NO_2 is a well-known health hazard and a pollutant of national concern. Once it was determined that the wet scrubbing concept was the most practical solution to the N_2O_4 emission problem, it became important to optimize the composition of the scrubbing liquor. Several reagents were cited in the literature as being advantageous in scrubbing NO_2. Experiments were conducted on a model wet scrubber in order to verify and rank the performances of these scrubbing liquors. The most efficient scrubbing liquor found experimentally was a 10% sodium sulfite solution. This was in agreement with a previous study by Exxon performed under an EPA contract.

Scrubbing Liquors for N_2O_4

Our mission, as originally conceived, was to research and develop design criteria for hardware to prevent discharge to the atmosphere of the hypergolic propellants during the pad loading operations. We were to consider any and all possible methods to accomplish the task. But the final system, of course, had to be safe, effective, economical and simple to operate. Among the concepts considered and researched were the following:

1. Cryogenic trapping of effluent

2. Adsorption towers

3. Wet scrubbers

We quickly found that cryogenic trapping could perhaps be effective, but it was uneconomical and highly dependent upon proper design. We also found that adsorption techniques were very effective on N_2O_4 contaminated effluent present in small concentrations, but the capacity of such systems are poor and regeneration is necessary. Wet scrubbers were quickly found to be overall the most advantageous in all respects. These systems are very simple in design and have large capacity.

Unlike hydrazine scrubbing, N_2O_4 scrubbing research has a considerable history if one considers that N_2O_4 is merely a dimer of nitrogen dioxide (NO_2). Nitrogen dioxide (NO_2) is a well-known health hazard and is a pollutant of national concern. It is one of six compounds for which the EPA has mandated a National Ambient Air Quality Standard. The standard is 100 ug/m^3 (0.05 ppm) annual arithmetic mean. Atmospheric NO_2 is produced by oxidation of nitric oxide (NO) generated by automobiles and power plants. Thus in the last few years there has been a significant effort in the U.S. and a great

effort in Japan to abate NO_2 atmospheric pollution. Catalytic converters perform the task in automobiles, but scrubbing is still a viable option for power plants. The power plant scrubbing problem is made more difficult because the principal oxide of nitrogen emitted is the insoluble nitric oxide (NO), rather than the soluble NO_2. Thus if power plants hope to control NOx emissions by scrubbing they must introduce a step to oxidize the nitric oxide (NO) to nitrogen dioxide (NO_2).

Actually, kinetic data has shown that the soluble NOx species is not NO_2 but N_2O_4 and N_2O_3. As mentioned before N_2O_4 is formed by combining two molecules of NO_2. N_2O_3 is formed by combining NO and NO_2. Thus we are indeed doubly fortunate in the aerospace industry to be faced with the problem of scrubbing N_2O_4 rather than NO. However, NO still presents problems.

When N_2O_3 and N_2O_4 dissolve in water, NO is released according to the equations shown below.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$
$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$
$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$
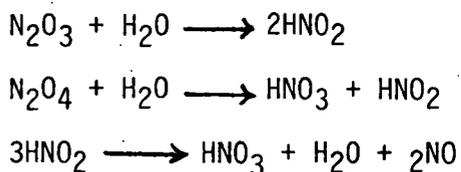
Since this phenomenon is well known, workers in the field have attempted to minimize the NO evolution by adding oxidizing agents to the scrubbing liquor. Some of the agents tested have been potassium permanganate ($KMnO_4$), ozone (O_3), and hydrogen peroxide (H_2O_2). In general these agents were of limited value as far as adding to scrubbing efficiency is concerned.

The history of wet scrubbers for N_2O_4 in aerospace applications goes back to the Gemini program.

Hamilton Standard provided fuel-handling systems for the Gemini and Saturn programs, which included scrubbers for the removal of hypergolic propellants which would otherwise be vented to atmosphere. Gaseous nitrogen-bearing N_2O_4 vapors passed through the scrubbers, which met design specifications for contaminant concentration of less than 5 ppm N_2O_4 or less than 1 ppm MMH at the outlet of the system. This outlet was downstream of a dilution fan/mixing chamber where the scrubber effluent was mixed with fresh air in a 100:1 ratio, thus reducing contaminant concentrations by a factor of one hundred. See Figs. 1 and 2.

The scrubbers were designed to accept from 10 standard cubic feet per minute at 10^6 ppm, up to 60 SCFM at 1500 ppm, of N_2O_4-contaminated nitrogen. The scrubber, operating with a through flow of 60 SCFM, reduced N_2O_4 concentration by at least a factor of 3 (67% efficiency) and MMH concentration by a factor of 15 (93% efficiency).

Scrubbing was accomplished by a cross-flow absorber which moved the gas across sixteen cascaded filters, each with an associated fresh water spray nozzle. The cross-section of the scrubber was about 2/3 ft^2, and of each filter, about 1 ft^2. The filters were of pyrex glass wool supported by stainless steel. The length of the scrubber was about 18 ft., folded once to a "u" form. Water flow rate was 40 GPM. The scrubber and associated

26

Scrubber Diagram

Discharge Air

< 1 ppm MMH
or
< 5 ppm N_2O_4

Dilution Fan – 6060 scfm
P/N GS 6532

6000 scfm
Dilution Air
Inlet

Glass Wool Element (Typ. –16)

H_2O (Typ. –16)

Vent GN_2
with Propellant Fumes

0–10 scfm @ 0–1,000,000
ppm N_2O_4 or MMH

OR
0–60 scfm @ 0–1500 ppm
N_2O_4 or MMH

Scrubber Ass'y P/N GS 6528

H_2O
Drain
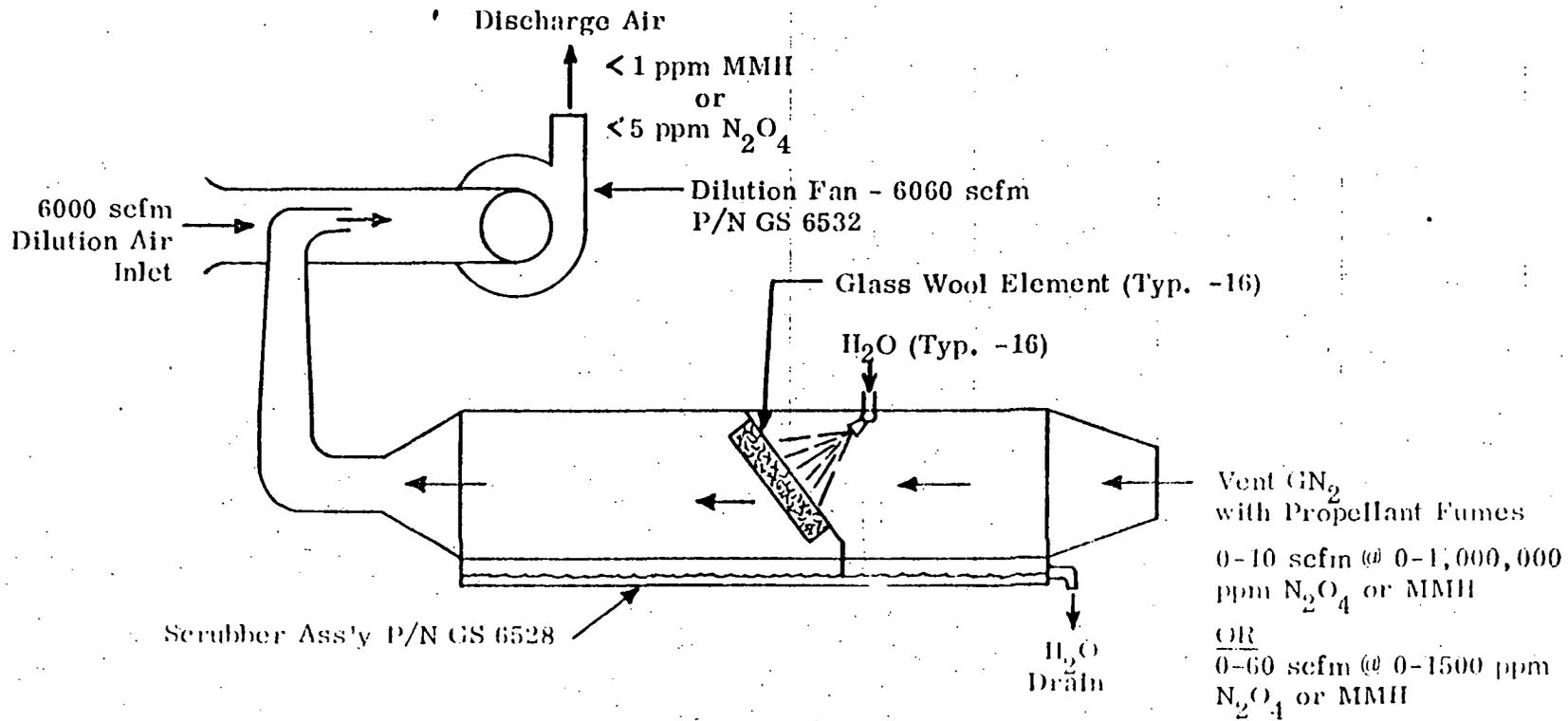
Figure 1.   Side view of the Hamilton Standard (Buffalo Forge) scrubber.

27

Water Manifold: 40 GPM

60 CFM N_2 + 1500 PPM N_2O_4
or MMH max at inlet

Scrubber

Scrubber

500 ppm N_2O_4 or 100 ppm MMH
max at scrubber outlet

6000 CFM Dilution Air

Dilution Blower

6060 CFM Output from System
5 ppm N_2O_4 max, or 1 ppm MMH max.
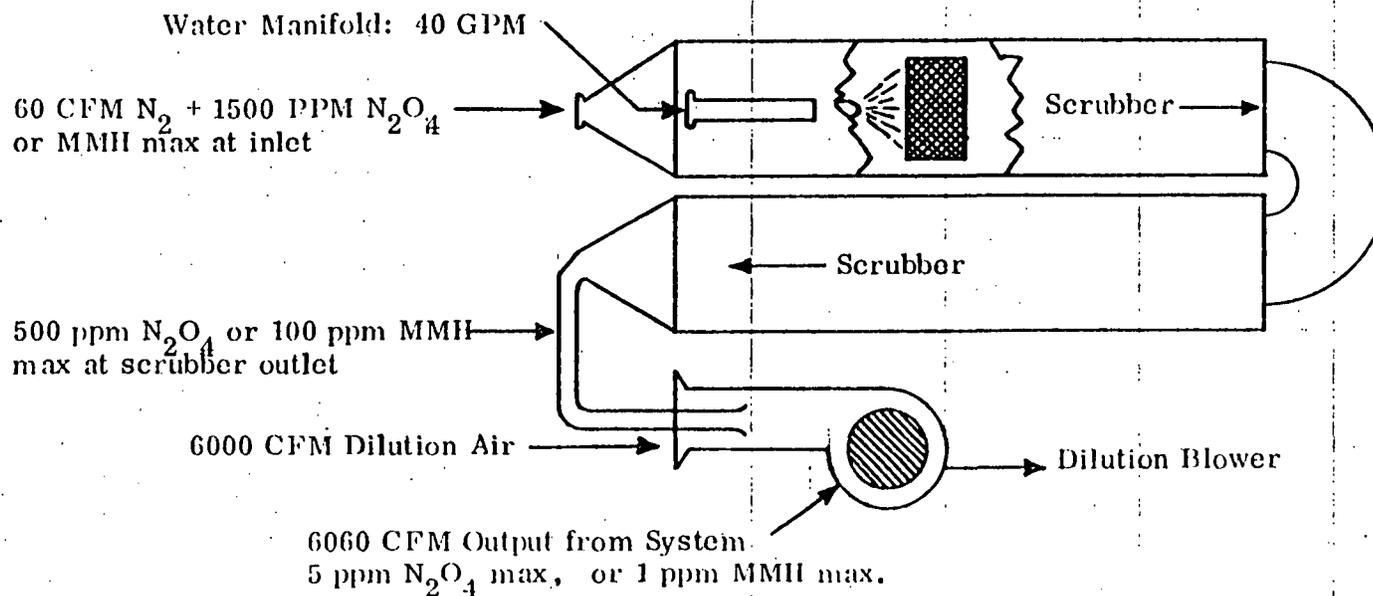
Figure 2. Top View of the Hamilton Standard (Buffalo Forge) Scrubber

28

dilution blower were manufacted by the Buffalo Forge Co. of Buffalo, New York. Thus, previous efforts at wet scrubbing for N_2O_4 in the Gemini program were not eminently successful.

Once it was determined that the wet scrubbing concept was the most practical solution to the N_2O_4 emissions problem, it became important to optimize the composition of the scrubbing liquor. Among the reagents suggested by the literature as being advantageous in scrubbing NO_2 were the following:

Potential Scrubbing Liquors for N_2O_4

Water	H_2O	Ammonium sulfite	$(NH_4)_2SO_3$
Sodium sulfite	Na_2SO_3	Ammonium bisulfite	NH_4HSO_3
Magnesium sulfite	$MgSO_3$	Ammonium nitrate	NH_4NO_3
Ammonium acetate	$CH_3C^O-O^{\ominus}NH_4^{\oplus}$	Calcium oxide	CaO
Ammonium hydroxide	NH_4OH	Magnesium carbonate	$MgCO_3$
Magnesium hydroxide	$Mg(OH)_2$	Aliphatic and aromatic amines	$R-NH_2$
Potassium permanganate	$KMnO_4$	Triethanolamine	$(HOCH_2CH_2)_3N$
Ethanolamine	$HOCH_2CH_2NH_2$	Urea	$H_2N-\overset{O}{C}-NH_2$
Nitric acid	$HNO_3 (20-30\%)$	Ferrous sulfate	$FeSO_4$
Ammonium chloride	NH_4Cl	Sodium chlorite	$NaClO_2$
Ferrous chloride	$FeCl_2$	Ozone	O_3
Sodium hypochlorite	$NaOCl$	Hydrogen peroxide	H_2O_2

Consequently, the essential problem was not to invent a scrubbing liquor but to choose one that actually performed as well as its advocates claimed and one which was truly practical.

After due consideration it was decided that insoluble reagents or reagents which resulted in the formation of a precipitate upon contact with N_2O_4 were impractical. These precipitates would perhaps clog piping and interfere with efficient operation of the recycling pumps. Thus for these reasons we eliminated from consideration calcium oxide, magnesium hydroxide, magnesium carbonate, and potassium permanganate. Reagents containing the nitrate anion were eliminated from consideration because of problems associated with ultimate disposal of the nitrate containing scrubber waste liquor. As most of you know, state regulations concerning discharge of nitrate containing wastes into bodies of water are very strict. Hence, nitric acid and ammonium nitrate were eliminated from consideration.

Although, there are various problems associated with most of the others, it was decided that at least some laboratory trials should be conducted on all the remaining reagents using a wet scrubber model system as shown in Fig. 3.

COMBINATION WET-DRY SCRUBBER SYSTEM

Gas Mixing Chamber
5 cm I.D. x 188 cm

Wet Column
9.5 cm I.D. x 81 cm

Dry Column
9.5 cm I.D. x 60 cm

Tubing
Gases-Flexible plastic 1/4" O.D.
Liquid - Neoprene 1/2" O.D.

Symbols:
≬ - control valve
- pinch clamp

All operations performed under fume hood

Wet Scrubber Solution

Fluid.Vol. 22.7 liter

Gas pump 1 psi

250 cm

220 cm

70 cm

Flow meter 0 to 0.25 gal/min.

100 cm

Dry Column 60 cm

Wet column 90 cm

Gas mixing chamber

190 cm   10 cm   Toxic gas

100 cm

Flow meter   0 - 12 liter/min

GN₂

Wet Scrubber Solution Waste

140 cm

160 cm   Sampling ports

Inlet

170 cm   Wet exit

220 cm   Dry exit

Fig. 3

31
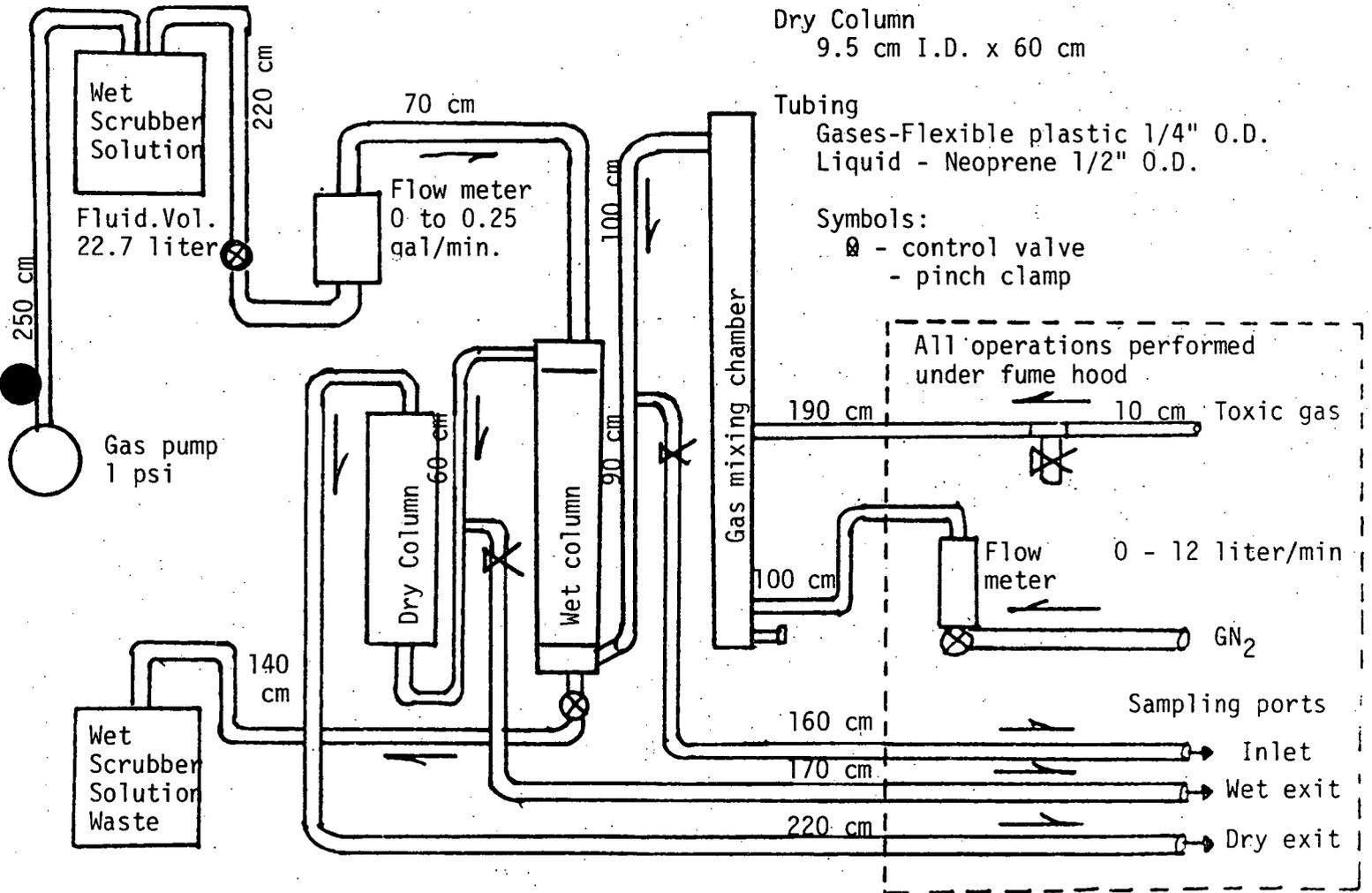
The operation, sampling, and assay techniques for the scrubber system are summarized as follows:

A GN_2 flow of three to five liters per minute was established and a secondary GN_2 flow which was to be merged with N_2O_4 was set at 300 ml/min. The N_2O_4 cylinder was preheated to 20°C prior to the start of the experiment. The scrubbing solution flow is set at 12 to 90 gal/min and the scrubber was wetted down before the N_2O_4 contaminated vapor passed through. The N_2O_4 tank valve was opened and the vapor was merged with the secondary GN_2 flow. The system was allowed to equilibrate for five minutes prior to sampling.

Inlet and outlet samples were taken every five minutes during the experiment. Sampling and analysis methods used were modified methods and procedures of the Standard Analytical Method #04-507, PAA Environmental Health Laboratory for determination of Nitrite in water and nitrogen dioxide in the air. Gas samples were obtained with 10 ml gas sampling syringes at the three sampling ports, which were affixed with gas sampling bulbs. These sampling ports are located as follows:

1) The inlet sample port is located in a position upstream of the wet scrubber.

2) The mid sample port is located between the wet scrubber and the dry scrubber.

3) The outlet port is located downstream from the dry scrubber.

To determine the efficiency of any scrubbing liquor, the following formulae were used:

$$\frac{\text{Inlet ppm-Mid point ppm}}{\text{Inlet ppm}} \times 100 = \text{Efficiency of Wet Scrubber}$$

$$\frac{\text{Inlet ppm - Outlet ppm(Dry scrubber)}}{\text{Inlet ppm}} \times 100 = \text{Total efficiency}$$

32

A sample is taken by inserting the empty syringe's needle through the gas sampling bulb and drawing one ml of gas. This gas sample is then injected into a vial containing 10 ml of NOx absorbing solution which is principally a solution of sulfanilic acid and N-(1-napthyl)-ethylenediamine and allowed to set for 15 minutes prior to reading the absorbance at 540 nm on a spectrophotometer.

The spent liquors, as well as the inlet and outlet gases were also sampled. An assay was conducted on the scrubbing solution prior to the test. As the experiment progressed, the waste liquor assays are taken prior to recycling of the scrubber solution.

Currently, a recycling pump is now used allowing the liquid scrubber waste to be introduced back into the system with fresh solution at a constant rate.

Our first experiments were conducted using plain tap water as the scrubbing liquor. The results are shown in Table 1.

Table 1

Scrubbing N_2O_4 Vapors with H_2O

| | Inlet Gas NO_x ppm | Off Gas, NO_x, ppm | | % Scrubber Efficiency | | Run Duration |
		Wet	Dry	Wet Stage	Total	
Range	3220-2180	32.5-5.0	5.0-0	99.9-98.5	100-99.8	35 min
Average	2787	20.8	2.5	99.1	99.9	

| | Inlet Gas, NO_x ppm | Off Gas, NO_x, ppm | | % Scrubber Efficiency | | Run Duration |
		Wet	Dry	Wet Stage	Total	
Range	6300-4400	163-62	5.5-2.5	98.8.96.9	100-99.2	30 min
Average	5217	84	11	98.4	99.8	

| | Inlet Gas NO_x ppm | Off Gas, NO_x, ppm | | % Scrubber Efficiency | | Run Duration |
		Wet	Dry	Wet STage	Total	
Range	8600-6600	300-100	550-38	98.4-95.5	99.2-95.5	30 min
Average	7300	193	135	97.5	98.2	

As is seen, the results are quite satisfactory using plain water in our system.

Our next series of experiments were conducted with ammonium hydroxide solutions. Ammonium hydroxide solutions have been used experimentally in stack gas scrubbing operations because the ammonium ion converts nitrous acid formed on dissolution of N_2O_4 to environmentally innocuous products as shown. See Fig. 4.

One major problem we envisioned to be associated with use of NH_4OH as a scrubbing liquor was that if for some reason the water in the spent scrubbing liquor evaporated, it would leave potentially highly explosive

organic nitrates and nitrites as residues. Such explosive potential
we believed, would be unacceptable for routine operations.

Also, as we all know, ammonia solutions have very strong pungent odors
which would be repulsive to the operational personnel involved.

Reactions of Ammonium Ion and NO_2

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$HNO_2 + NH_4OH \longrightarrow NH_4NO_2$$

$$HNO_3 + NH_4OH \longrightarrow NH_4NO_3$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$
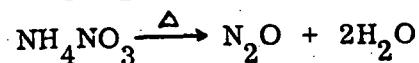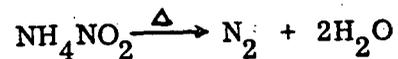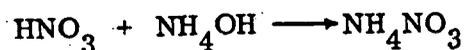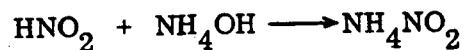
Fig. 4

The results using 3% ammonium hydroxide are shown in Table 2.

Table 2

Scrubbing N_2O_4 vapors with 3% NH_4OH Solution

Inlet Gas NOx, ppm	Off Gas, NOx, ppm		Scrubber Efficiency %		Run Duration	Comments
	Wet	Dry	Wet Stage,	Total		
2800-11,000	22-157	0	99.3-99.4	100%	30 min.	Dry scrubber packed with AL_2O_3 odor at exit. Bottom 1/2 inch of packing has green color from NH_3 complex.
280-7570	16-28	0	99.4-99.6	100%	30 min.	Dry scrubber packed only with act. carbon. Packing emitted NH_3 odor

	Inlet Gas NOx, ppm	Off Gas, NOx,ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	4000-1800	60.0-27.5	10.0-2.5	98.9-98.0	99.9-99.5	30 min.
Average	2800	44.0	3.8	98.5	99.9	
Range	28000-10.0	1200-1.0	2.5-1.0	100.-75.0	100-87.5	120 min.
Average	4830	105	1.5	97.8	100.0	

The efficiencies were so high that further experiments were conducted over several hours in order to determine scrubbing efficiencies of spent scrubbing liquor. Also it was of interest to determine scrubbing efficiencies at differing concentrations of ammonium hydroxide. (See Table 3.)

As is seen, ammonium hydroxide proved to be an extremely efficient scrubbing liquor. But for reasons previously mentioned, the search for a more practical liquor had to continue.

Table 3

Scrubbing N_2O_4 vapors with 3% NH_4OH

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	46000-5.0	1600-1	1	100-50	100-50	240 min
Average	8354	181	1	99.8	100	

Scrubbing N_2O_4 vapors with 10% NH_4OH

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	13,000-44,900	2.5-4250	2.5-14	81-100	0	360 min
Average	18,600	647	4.0	99.9	100	

There is a great deal of literature referring to the use of alkaline scrubbing liquors for NOx. Much of the work indicates that sodium hydroxide is inferior to plain water. In our hands, however, this did not prove to be the case. The results with sodium hydroxide seemed to be roughly equivalent to that of water. Sodium hydroxide solutions would also have the important advantage of being less corrosive to the scrubber than plain water. The results of scrubbing with sodium hydroxide solutions are shown in Table 4.

Table 4
Scrubbing of N_2O_4 vapors with 10% NaOH

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	25000-200	30-2.5	30-1.0	100-81.2	100-96.0	120 min.
Average	6722	18	11	99.6	99.8	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	150-19000	11-225	5-36	63-100	93-100	420 min.
Average	9393	46	13.8	92.2	98.9	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	4000-18000	11-28	2.5-28	63-100	92-100	720 min.
Average	10,537	17.9	11.2	93.9	95.8	

Table 5 shows that the absorption efficiency of scrubber liquor containing $0.1N$ H_2O_2 averages about 90% which is similar to the efficiency of runs made with plain H_2O. The small amount of H_2O_2 apparently was too dilute to rapidly oxidize NO. The efficiency of a run containing $0.25N$ H_2O_2 (Run 3) was approximately 2 percentage points higher. In runs containing alkali plus H_2O_2 (Runs 4 and 5) the efficiency was increased by approximately seven percentage points above the plain H_2O or dilute H_2O_2 values.

Table 5

Scrubbing of N_2O_4 with Hydrogen Peroxide

Scrubber Liquor Composition	Inlet Gas ppm NO_x	Off Gas ppm NO_x	Absorption Efficiency Percent
0.1N H_2O_2	15,700	1450	90.8
0.1N H_2O_2	16,900	1840	89.1
0.25N H_2O_2	18,000	1335	92.6
0.1N NaOH 0.1N H_2O_2	6,700	143	97.8
0.1N NaOH 0.1N H_2O_2	13,700	80	99.2

The wet scrubber system was provided with an apparatus for introducing a gaseous oxidant (O_3 and/or O_2) upstream of the column. The purpose of the oxidant was to oxidize NO (present in the feed stream mostly as a result of reaction of NO_2 with H_2O) to the more water soluble NO_2 form so as to enhance its capture in the column. The results are shown in Table 6.

It is evident from the results that averaging absorption efficiencies from the three set-ups (oxidant introduction in three different ways) the following observations can be made:

1. In plain H_2O runs, O_3/O_2 gives better results than O_2 in alkaline solution, i.e., 99.07 vs. 97.37% respectively.

2. O_3/O_2 in alkaline bath is slightly better than O_2 in alkaline solutions, i.e., 99.52 vs. 99.39% respectively.

3. The absorption efficiencies of set up #1 (O_3/O_2 fed directly to GN_2 line) and set up #2 (O_3/O_2 fed to scrubber liquor) are not significantly different.

Table 6

Scrubbing of H_2O_4 using O_3, O_2, and NaOH

O_3/O_2 Plain H_2O % Abs. Ef.	O_3/O_2 Alkaline Soln. % Abs. Ef.	O_2 Plain H_2O % Abs. Ef.	O_2 Alkaline Soln. % Abs. Ef.
99.15	99.56 (ave. of 5 runs)	98.64	99.48 (ave. of 3 runs)
99.0	99.7	96.1	99.3
----	99.3 (ave. of 3 runs)	----	----
99.07	99.52	97.37	99.39

Our next experimental scrubbing liquor was a 5% NaOCl solution. The rationale was that during the scrubbing operation, chlorine derived from NaOCl would react with the NO evolved upon dissolution of N_2O_4, and form nitrosyl chloride (NOCl) which is soluble in water as well as decomposed by water. The results were encouraging except that a highly noxious gas presumably NOCl was evolved. (See Table 7)

Table 7

Scrubbing N_2O_4 vapors with 5% NaOCl Solution

Inlet Gas NOx, ppm	Off Gas,NOx, ppm	% Scrubber Efficiency
7000	31	99.5
6590	33	99.5
5980	41	99.4

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	68000-13000	34-2.5	17.5-1.5	100-98.8	100-99.2	300 min.
Average	24000	15.5	4.6	99.9	100	

44

As mentioned previously, ammonium hydroxide scrubbing liquors proved
to be very efficient, but one serious disadvantage of these scrubbing
liquors is the strong odor. Ammonium chloride solutions do not have a
significant odor if the pH is neutral or lower but they still possess
the advantageous ammonium ion. Thus, scrubbing experiments with ammonium
chloride solutions were conducted. The results were poor compared to other
liquors. This indicates that key reactions of ammonia and N_2O_4
must take place in the gas phase to produce highly efficient scrubbing.as
shown in Table 8.

Table 8

Scrubbing N_2O_4 vapors with 2% NH_4Cl

Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
	Wet	Dry	Wet Stage	Total	
Range 54000-33000	7000-2500	3500-27.5	95.5-79.0	99.7-91.7	60 min
Average 42333	4833	2176	87.2	94.6	

Scrubbing N_2O_4 vapors with 10% NH_4Cl

Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
	Wet	Dry	Wet Stage	Total	
Range 28000-24000	1000-550	600-0	97.7-96.0	100-97.7	90 min
Average 26000	750	173	97.0	99.3	

$FeCl_2$ and $FeSO_4$ form a nitroso ferrous complex when reacted with nitric oxide. Thus solutions of these entities are reported to be good scrubbing liquors for NO_2. In our hands this did not prove to be the case. The scrubbing liquor turned black and evolved NOx fumes. (See Table 9.

Table 9

Scrubbing N_2O_4 vapors with 5% $FeSO_4$ Solution

Input Gas NOx, ppm	Off Gas, NOx, ppm		Scrubber Effiency %		Run Duration
	Wet Stage	Dry	Wet Stage	Dry Stage	
14,200-25,000	1900-5800	4-8000	84.5-86.7	81-99.98	30 min.

	Input Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	42000-4200	5800-1900	8000-4.25	86.7-84.5	99.98-81.0	30 min
Average	24000	3800	3100	83.8	86.8	

Urea reacts with NO and NO_2 to produce N_2, CO_2, and H_2O. The classical chemistry involved is a reaction between a primary amine and the oxides of nitrogen. Urea also reacts with HNO_3 at room temperature to form an addition compound.

$$N_2O_4 \longrightarrow 2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

$$2HNO_2 + HN_2CONH_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

$$NH_2CONH_2 + HNO_3 \longrightarrow NH_2CONH_2 \cdot HNO_3$$
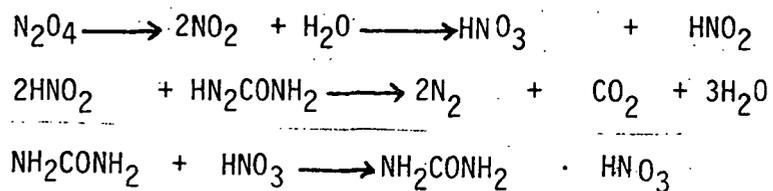
Thus urea solutions have also been reported to be effective scrubbing liquors. In our hands this was not so, presumably because the reactions shown in this slide are favored by higher temperatures. (See Table 10)

Table 10

Scrubbing N_2O_4 vapors with 5% Urea Solution

Inlet Gas NOx, ppm		Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	8300-16000	560-720	1.0-13	92-96.5	99.92-99.99	60 min
Average	2050-10,000	13-130	0	93.7-98.9	100%	60 min

Inlet Gas NOx, ppm		Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	16000-8000	1400-560	13.0-0	96.5-86.5	100-99.9	60 min
Average	12800	796	5.4	93.8	100	

Inlet Gas NOx, ppm		Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	10000-2000	680-13.0	2.5-0	99.8-90.7	100	60 min
Average	5790	193	2.5	96.6	100	

Thus, ferrous sulfate and urea proved far too inefficient to be considered further as scrubbing liquor additives.

Finally, we became aware of an NTIS document entitled, "Development of the Aqueous Processes for Removing NO_x from the Flue Gases" authored by the Esso Research and Engineering Company in September of 1972. This group conducted intensive research on wet scrubbing methods for NO_x. They concluded that the most efficient scrubbing agent for their purpose was sodium sulfite. The only interfering species they found was oxygen which converted SO_3 to SO_4. Since our experimental flows as well as the operational flows contain little oxygen, it was deduced that sodium sulfite should work very well. The experimental data was indeed very encouraging. See Table 11.

Table 11

Scrubbing N_2O_4 vapors with 4% Na_2SO_3

Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
	Wet	Dry	Wet Stage	Total	
Range 100000-19000	800-0	20.0-0	99.9-99.1	100-99.9	75 min
Average 39000	211	5	99.5	100	

Scrubbing NOx vapors with 10% Na_2SO_3

Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
	Wet	Dry	Wet Stage	Total	
Range 160000-500	77.5-10.0	47.5-0	99.5-93.7	100-94.2	360 min.
Average 33063	41.2	23.8	99.9	100	

Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
	Wet	Dry	Wet Stage	Total	
Range 25000-5000	55.0-7.5	5.0-0	100-98.2	100-99.9	360 min.
Average 17,750	21.2	1.3	99.9	100	

At this time we are not able to determine any potential or actual problems concerning the use of sodium sulfite. This material can be handled without the use of any special safety equipment and can be used effectively in concentrations as high as 18%. The material or its reaction products with N_2O_4 are not potentially explosive. The spent liquor can be recycled with little or no decrease in efficiency and there is no sign of SO_2 effluent.

The chemistry of the Na_2SO_3 absorption process is not understood very well at the present time, but we can be reasonably sure that nothing of greater carcinogenicity than $NaNO_2$ is formed. Apparently the sulfite ion has a remarkable capacity to absorb NO_2. It does this over a wide pH range and at temperatures of 125°F (where little N_2O_4 exists). The classical NO_2 absorption equation does not apply since no NO is given off during the absorption process.

The mechanism of this absorption is complex but $SO_3^=$ scrubbing of NO_2 and NO has been reported to involve production of hydroxylamine (NH_2OH) derivatives.

$$N_2O_3 + 4Na_2SO_3 + 3H_2O \longrightarrow 2N(OH)(NaSO_3)_2 + 4NaOH$$

$$1/2N_2O_4 + 2Na_2SO_3 + H_2O \longrightarrow N(OH)(NaSO_3)_2 + 2NaOH$$
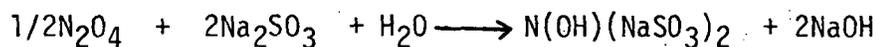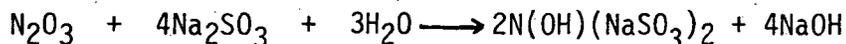
(Ref. Garlet, R., U.S. Patent 3,329,478, Method of Removing Nitrogen Oxides from Gases)

Ammonium sulfite solutions were also reported to be effective scrubbing liquors but in our hands these solutions proved to be unattractive.

See Table 12.

Table 12

Scrubbing N_2O_4 vapors with 2% $(NH_4)_2SO_3$

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	17500-4000	8500-20.	2150-5.0	99.5-45.5	100-74.5	180 min
Average	8100	2474	689	77.0	88.2	

Triethanolamine solutions have also been reported to be effective
scrubbing agents for NO_2 and this was verified in our hands.

However, there is a significant problem associated with the use of TEA.
TEA reacts with N_2O_4 to form tertiary nitrosamines which decompose
readily to secondary nitrosamines which are all highly carcinogenic.

NIOSH has already targeted one of the products, N-nitroso-diethanolamine
as a probable carcinogen.

$$
\begin{array}{c}
\text{(triethanolamine structure)} \quad + \quad 4\text{HONO} \quad \longrightarrow \quad \text{(N-nitroso-diethanolamine structure)} \quad +
\end{array}
$$

$$
\text{O=C-CH}_2\text{-OH} \ + \ N_2O \ + \ 3H_2O
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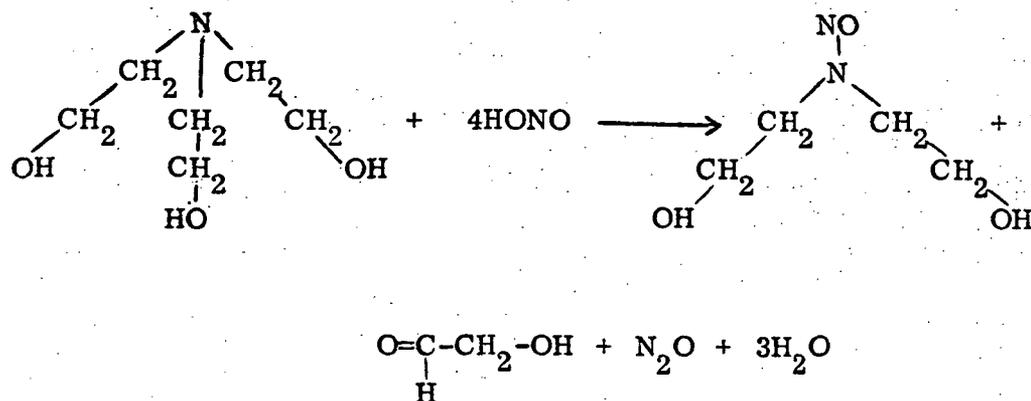
(Ref. Chem. and Engineering News, October 18, 1976, page 12)

This material is present in cutting oil and has been implicated as
causing cancer in machinists.

The results as a scrubbing liquor are shown in Tables 13 and 14.

54

Table 13

Scrubbing N_2O_4 vapors with 6% Triethanolamine (TEA)

2nd Stage Sorbent	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet Stage	Dry	Wet Stage	Dry Stage	
mixture of act. carbon act. Al_2O_3	13,000-14,500	4-40	0	99.81	100	25 min
Al_2O_3	53,000	40-157	5-49	99.70	99.97	30 min
Al_2O_3	8,350-6,400	13-4.5	2.3-0	99.84-99.93	99.97-100	30 min

Table 14

Scrubbing N_2O_4 vapors with 3% TEA

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	24200-18500	3350-0	3050-0	100-85.7	100-96.8	240 min.
Average	20671	971	597	95.9	97.4	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	26000-5000	300-9.0	128-0	99.96-98.1	99.99-99.0	300 min.
Average	14500	99.3	21.6	99.3	99.4	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	12800-770	180-5.0	38.0-0	99.95-76.6	99.99-99.5	420 min.
Average	9117	48.0	8.05	99.5	99.9	

Finally, Table 15 summarizes the top 15 experiments in order of decreasing scrubbing efficiency. Thus we have in the top ranking 10 liquors, sodium hypochlorite, sodium sulfite, ammonium hydroxide, sodium hydroxide, tri-ethanolamine and water.

Table 15

SUMMARY OF N_2O_4 SCRUBBER LIQUOR DATA

	Scrubbing Agent	Average Efficiency W/T	Range W/T	Std. Dev. W/T	Break through time (min)	Run duration (min)
1	5% NaOCl	99.9 100.	0.12 0.08	0.04 0.03	300	300
2	10%NaSO$_3$	99.9 100.0	1.78 0.08	0.65 0.03	360	360
3	10%NaSO$_3$ Waste from #2	99.9 100.	5.8 5.78	2.05 2.04	300(660)	300(720)
4	10%NH$_4$OH	99.9 100.0	19.3 0	6.5 0	360	360
5	3%NH$_4$OH	99.8 100.0	50.0 50.0	17.0 17.0	240	240
6	10%NaOH	99.6 99.9	18.8 6.1	5.3 1.8	120	120
7	4%Na$_2$SO$_3$	99.5 100.0	0.8 0.1	0.32 0.04	75	75
8	6% TEA	99.5 99.9	23.35 0.49	7.7 0.16	120	420
9	20% TEA	99.3 99.4	1.86 0.99	0.7 0.37	60	240
10	H$_2$O	99.1 99.9	1.4 0.2	(0.53*) 0.55 0.08	35	35
11	3% NH$_4$OH	98.5 99.9	0.9 0.5	0.36 0.20	30	30
12	H$_2$O	98.4 99.8	2.0 0.8	0.8 0.32	25	30
13	3%NH$_4$OH	97.8 100.0	25 12.5	7.7 3.8	120	120
14	H$_2$O	97.5 98.2	1.9 3.9	1.15 1.55	30	30
15	10%NH$_4$Cl	97.0 99.3	1.7 2.3	0.85 1.1	75	90

As mentioned previously sodium hypochlorite, ammonium hydroxide, and triethanolamine were dropped from further consideration for various reasons.

Thus it was recommended that the following scrubbing agents for N_2O_4 be evaluated at MMC in a full-flow testing program.

        a.   4-10% Sodium sulfite (Na_2SO_3)

        b.   Plain Water (H_2O)

        c.   3-10% Sodium Hydroxide (NaOH)

ESTIMATED SHUTTLE LOADING EMISSIONS

by

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ABSTRACT

As Space Shuttle tanks are loaded with N_2O_4, pressurization gas is displaced and at the same time N_2O_4 entering the tank evaporates and mixes with the pressurization gas remaining in the tank. Further addition of N_2O_4 to the tank requires venting of this mixture of N_2O_4/NO_2 vapor and pressurization gas, which must be scrubbed prior to atmospheric release.

A computer analysis was performed to estimate concentrations, flow rates, and total quantities vented during the planned fast fill/slow fill cycles of 125 gallon and 640 gallon Space Shuttle tanks. With helium as the pressurization gas, total vent quantities were estimated to be 4.5 and 24 pounds N_2O_4, respectively, for the two tank sizes.

ESTIMATES OF SHUTTLE LOADING EMISSIONS

by

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1. STATEMENT OF THE PROBLEM

The functional parameters pertinent to Space Shuttle hypergol loading operations are given in Table I. Essentially we are concerned with two types of tank for each propellant: 125 gallon tanks that are fast filled at 35 psig and then slow filled at a pressure that rises to 125 psig and stays there, and 640 gallon tanks that are fast filled and slow filled at 35 psig.

TABLE I

Hypergol System Functional Parameters

Orbital System	Propellants On-Board (Gallons)		Flowrate (GPM)		Ullage Pressure (PSIG)	
	MMH	N_2O_4	Fast Fill 0-90%	Slow Fill 90%-100%	Fast Fill	Slow Fill
FRCS	125	125	10	2	35	125
LH ARCS	125	125	10	2	35	125
RH ARCS	125	125	10	2	35	125
LH OMS	640	640	60	10	35	35
RH OMS	640	640	60	10	35	35
PBK	3x640	3x640	60	10	35	35

Assume that we start with a propellant tank full of helium at 35 psig, 70°F, and begin to flow liquid propellant into the tank at a constant rate. As the first propellant enters, evaporation occurs, and liquid continues to evaporate as the tank fills until the gas over the propellant is saturated. At the same time, the vent is open and propellant vapor and pressurization gas are removed from the tank at a rate sufficient to maintain the desired ullage pressure. An estimate of the total quantity of propellant vapor discharged through the vent, as a function of time, is required.

2. FIRST APPROXIMATION

A very simple analysis may be performed by assuming that the mass of propellant vented is simply equal to the mass of saturated propellant vapor that will completely fill the tank minus the amount in the ullage at the end:

$$m_{p.v.} = \frac{p_{sat}(V - V_{ull})}{R_p T}$$

where V is the total tank volume, V_{ull} the final ullage volume, T the temperature of the gas mixture, and R_p and p_{sat} the gas constant and saturation pressure for the propellant in question. This approximation is based on a simplified model in which the tank is assumed to fill instantly with saturated vapor — without any venting being required — and then the saturated vapor is steadily pushed out the vent by the entering propellant. No further evaporation occurs because of the saturation condition.

Saturation pressure of N_2O_4 at 70°F is 14.71 psia, and the molecular weight (corrected for dissociation to NO_2, assuming an equilibrium mixture of $N_2O_4 - NO_2$ at 70°F, 35 psig) is 87.82, giving R_p = 17.597 ft-lbf/lbm - °R. We are concerned with two tank sizes: $(V - V_{ull})$ = 125 gal and 640 gal. The results are:

125 Gallon N_2O_4 Tank:

$$m_{p.v.} = \frac{(14.71)(144)(125)(.1337)}{(17.597)(529.67)} = 3.798 \text{ lbm}$$

640 Gallon N_2O_4 Tank:

63

$$m_{p.v.} = \left(\frac{640}{125}\right)(3.798) = 19.45 \text{ lbm}$$

It should be noted that these calculations do not take account of the increased pressures during the last 10% of fill of the 125 gallon tanks. In the actual fill, the vent would close for a period of time to allow pressure to increase, and hence the quantity vented would be less than that calculated. After compression, the ullage gas still contains the same amount of propellant, but it is less than saturated because of increased temperature. No further evaporation occurs, however, because the liquid propellant is still at 70°F and its vapor pressure is now less than the partial pressure of the propellant in the compressed ullage.

Beyond this consideration, however, it is not possible to ascertain whether this model is conservative or not. It has a conservative aspect, in that the gas being vented always contains the maximum possible concentration of propellant. It also has an anti-conservative aspect, in that the gas flow rate out of the tank is always taken to be its lowest possible value — equal to the volume flow rate of liquid into the tank. Any time evaporation is occurring, the volume flow of gas out of the tank must exceed the liquid volume flow in — a fact not taken into account by this always-saturated approximation.

Because of the fact that evaporation of the propellant in the tank might cause the results found above to be substantially too low, a more careful analysis was undertaken. This analysis is best described as a "second approximation," however, for reasons discussed later. It represents a preliminary estimate of the vent propellant quantities.

3. SECOND APPROXIMATION

   3.1 Formulation

   At any point in time, the volume occupied by gas in the tank is decreasing due to the addition of liquid to the tank, corrected by the amount of liquid that is evaporating:

$$\frac{dV}{dt} = -\left(\dot{Q}_{in} - \frac{\dot{m}_{evap}}{\rho_{liq}}\right) \qquad (1)$$

where

64

$V(t)$ = Tank ullage volume

$\dot{Q}_{in}$ = Volume flow rate of liquid into the tank

$\dot{m}_{evap}$ = Rate at which liquid is evaporating, mass per unit time

ρ_{liq} = Liquid density

The volume flow of gas out the vent is equal to the rate at which the ullage volume is decreasing, plus a term to account for the generation of gas due to evaporation. We assume that the temperature and pressure of the gas mixture remain constant during evaporation, and that both components act as perfect gases. Consider a system composed of the gas molecules near the liquid-gas interface, with new molecules entering the system as liquid evaporates and no molecules leaving the system. This system will therefore be expanding. Its total volume can be treated as the sum of the partial volumes of each component gas because of the perfect gas assumption; the partial volume of the helium is constant (constant mass, temperature, and mixture pressure), while the partial volume of the propellant increases because of mass addition:

$$V_p = M_p R_p T/p$$

$$\frac{dV_p}{dt} = \dot{m}_{evap} R_p T/p$$

where
V_p = partial volume of propellant vapor

m_p = mass of propellant vapor in the system

R_p = gas constant for the propellant vapor

T = mixture temperature

p = mixture pressure

Since the partial volume of the helium is constant, the total volume of this system is increasing at a rate given by dV_p/dt. This term is added to the rate at which the ullage volume is shrinking to give the volume flow of gas out the vent:

$$\dot{Q}_{out} = -\frac{dV}{dt} + \dot{m}_{evap} R_p T/p \qquad (2)$$

The portion of this volume flow that is propellant vapor varies with time because of the non-uniform distribution of propellant vapor in the ullage. Since the vent is the farthest point in the tank from the evaporating liquid surface, the propellant vapor concentration there should always be less than or equal to the average (uniform distribution) concentration, and hence a conservative result will be obtained

65

by assuming a uniform distribution of propellant vapor in the tank at all times. With this assumption, the density of propellant vapor at the vent is

$$\rho_p = \frac{p_p}{R_p T} \tag{3}$$

where the partial pressure of the propellant vapor, which the assumption says is uniform, is given by

$$p_p = m_p R_p T/V \, , \tag{4}$$

m_p being the total mass of propellant vapor contained in the ullage. The mass flow of propellant out the vent is the product of the total volume flow at the vent and the propellant vapor density at the vent:

$$\dot{m}_{p_{out}} = \dot{Q}_{out} \, \rho_p \tag{5}$$

Finally, we have a continuity equation which provides a second relation between $\dot{m}_{p_{out}}$ and $\dot{m}_p$:

$$\frac{dm_p}{dt} = \dot{m}_{evap} - \dot{m}_{p_{out}} \tag{6}$$

Equations (1) through (6) constitute 6 equations – including first order differential equations – for the 6 unknown functions of time, V, $\dot{Q}_{out}$, ρ_p, p_p, m_p, and $\dot{m}_{p_{out}}$, in terms of the parameters $\dot{m}_{evap}$, $\dot{Q}_{in}$, ρ_{liq}, T, p, R_p.

Equations (2) through (6) are readily combined:

$$\frac{dm_p}{dt} = \dot{m}_{evap} - \dot{Q}_{out} \, \rho_p$$

$$= \dot{m}_{evap} - \left(-\frac{dV}{dt} + \dot{m}_{evap} R_p T/p \right) \left(m_p/V \right)$$

$$= \dot{m}_{evap} \left(1 - \frac{m_p}{V} \frac{R_p T}{p} \right) + \frac{m_p}{V} \frac{dV}{dt} \tag{7}$$

Equations (1) and (7) now constitute two first order differential equations for the two unknowns m_p and V; for solution, two initial conditions will also be required.

Before looking at the initial conditions, we should examine $\dot{m}_{evap}$ more closely. Evaporation is expected to be maximum when there is no propellant vapor. For the purpose of this analysis, then, we assumed $\dot{m}_{evap}$ to be given by an equation of the form

66

$$\dot{m}_{evap} = A \left(\frac{p_{sat}(T)}{p_p} - 1 \right)$$

where

$p_{sat}(T) =$ saturation pressure for the propellant

$A \quad =$ "Evaporation rate coefficient" defined by this equation

Substituting this expression into equations (1) and (7), with p_p given by (4), results in

$$\frac{dV}{dt} = - \left(\dot{Q}_{in} - \frac{A}{\rho_{liq}} \left(\frac{p_{sat} V}{m_p R_p T} - 1 \right) \right) \tag{8}$$

$$\frac{dm_p}{dt} = A \left(\frac{p_{sat} V}{m_p R_p T} - 1 \right) \left(1 - \frac{m_p R_p T}{p V} \right) + \frac{m_p}{V} \frac{dV}{dt} \tag{9}$$

3.2 Initial Conditions

Two initial conditions are required. One condition, $V = V_{tank}$ at $t = 0$, is quite straightforward. If we try to apply the condition $m_p = 0$, $t = 0$, however, there is an obvious problem with equation (9). This problem can be resolved by considering that as $t \to 0$, $m_p \to 0$ and $p_p \to 0$, and therefore

$$\dot{m}_{evap} \to A \frac{p_{sat}(T)}{p_p} = A \, p_{sat}(T) / (m_p R_p T / V_{tank})$$

so that with

$\dot{Q}_{out} = 0$ at $t = 0$, we have:

$$\lim_{t \to 0} \left(\frac{dm_p}{dt} \right) = \frac{A \, p_{sat} \, V_{tank}}{m_p R_p T}$$

which can be readily integrated to give

$$\lim_{t \to 0} (m_p) = \left(\frac{2A \, p_{sat} \, V_{tank}}{R_p T} t \right)^{1/2} \tag{10}$$

which can be applied at some small finite time δt, and hence is quite appropriate for the finite difference method of solution that will be applied to obtain the simultaneous solution of equations (8) and (9).

There are two limitations on the initial m_p that must also be considered:

1. The initial m_p cannot exceed the total propellant mass that has entered the tank in the initial time step ζt,

$$m_p \leqslant \dot{Q}_{in} \, \rho_{liq} \, \delta t \qquad (10')$$

2. The initial m_p cannot exceed the mass of propellant present when the tank is full of saturated vapor,

$$m_p \leqslant \frac{p_{sat}(T) \, V}{R_p \, T} \qquad (10'')$$

3.3 Slow Fill Analysis

The slow fill presents no problems in the 640 – gallon tanks, where the fill and outflow rates simply decrease after 90% loading with no change in ullage gas properties. In the 125–gallon tanks, however, the vent closes for a period while the pressure increases.

During the vent-closed period, we assume that the gas undergoes an isentropic compression, with no evaporation or condensation occurring. We further assume that it is a perfect gas with constant specific heats. These assumptions yield the equations

$$V_2 = V_1 \left(\frac{p_1}{p_2} \right)^{1/\gamma} \qquad (11)$$

$$T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{\gamma}} \qquad (12)$$

for final volume and temperature, V_2 and T_2, in terms of volume V_1, temperature T_1, and pressure p_1 at the beginning of the compression, and final pressure p_2. γ is the ratio of specific heats, which for a mixture of perfect gases can be expressed as

$$\gamma = \frac{\sum_i p_i \, \hat{c}_{pi}}{\sum_i p_i \, \hat{c}_{vi}} \qquad (13)$$

where p_i = partial pressure of the ith component

$\hat{c}_{pi}$ = the molal specific heat at constant pressure of the ith component

$\hat{c}_{vi}$ = the molal specific heat at constant volume of the ith component

At standard temperature and low pressure, the specific heats
have the following values:

<u>Helium</u> c_p = 5.00   Btu/lb mole - $^\circ$R

       c_v = 3.000   Btu/lb mole - $^\circ$R

<u>N_2O_4</u> [1] $\hat{c}_p$ = (.2033) (87.82) cal/gmole - $^\circ$K

       $\hat{c}_v$ = $\hat{c}_p$ - R = [(.2033) (87.82) - 1.986] cal/gmole - $^\circ$K

It should be noted that in the case of N_2O_4, the frozen equilibrium
heat capacity was chosen as being the only one consistent with the perfect
gas assumption. The equilibrium molecular weight at 70°F (87.82) was
used in the equations above to obtain the molal heat capacity from Fan
and Mason's value of .2033 cal/gram - $^\circ$C.

Partial pressure of the N_2O_4 vapor is given by equation (4) above.
Helium partial pressure is found by subtracting the appropriate pro-
pellant vapor partial pressure from the tank pressure. The resultant
ratio of specific heats, equation (13), is:

$$\gamma_{N_2O_4 \atop \text{tank} \atop \text{ullage}} = \frac{(.2033) (87.82) p_{N_2O_4} + 5.00 (p - p_{N_2O_4})}{[(.2033) (87.82) - 1.986]p_{N_2O_4} + 3.000(p - p_{N_2O_4})} \quad (13')$$

If we use the saturation pressure at 70° F for the N_2O_4 vapor partial
pressure, we obtain the value

$$\gamma_{N_2O_4 \atop \text{ullage}} = 1.293$$

and substituting this value into equations (11) and (12), with

V_1 = 17.91 ft^3 - (.90) (125 gal) (.1337 ft^3/gal)

  = 2.869 ft^3

T_1 = 70°F = 529.67°R

p_1 = 35 psig = 49.7 psia

p_2 = 125 psig = 139.7 psia

gives the results:

$$V_{2 \atop N_2O_4 \atop \text{ullage}} = 2.869\left(\frac{49.7}{139.7}\right)^{\frac{1}{1.293}} - 1.290 \text{ ft}^3$$

1. Fan, Stephen S. T., and David M. Mason, "Properties of the System $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$." <u>J. of Chem and Eng. Data,</u> Volume 7, pp. 183-186 (April 1962).

$$\begin{matrix} T_2 \\ N_2O_4 \\ \text{ullage} \end{matrix} = 529.67 \left(\frac{139.7}{49.7} \right)^{\frac{.293}{1.293}} = 669.4^{\circ}R = 210^{\circ}F$$

From these results we deduce two important facts:

1.   Since the final ullage volume in the 125 gallon tanks is

$$17.91 - (125)\,(.1337) = 1.20 \text{ ft}^3$$

maximum pressure will be reached before the tank is "full", and the vent will re-open to release some gas at 125 psig.

2.   The saturation pressure of an equilibrium mixture of N_2O_4 and NO_2 calculated for $210^{\circ}F$ is 14,920 mm Hg or 288.4 psia, and since the actual partial pressure of this constituent will increase in proportion to the tank pressure, the final partial pressure is well below saturation, and hence condensation at the relatively cool liquid and solid surfaces, although it will occur, can probably be neglected.

3.4   Numerical Solution

Equations (8) and (9) were written as difference equations:

$$\Delta V = - \left(\dot{Q}_{in} - \frac{A}{\rho_{liq}} \left(\frac{P_{sat}V}{m_p R_p T} - 1 \right) \right) \Delta t \qquad (14)$$

$$\Delta m_p = A \left(\frac{P_{sat}V}{m_p R_p T} - 1 \right) \left(1 - \frac{m_p R_p T}{pV} \right) \Delta t +$$

$$\frac{m_p}{V} \, \Delta V \qquad (15)$$

and solved incrementally; that is, at each time step, the changes in V and m_p were calculated using the values of V and m_p calculated at the preceding time step. Initial values of V and M_p were found as described in Section 3.2.

Values used were the following:

$$p = 7156 \text{ lbf/ft}^2$$
$$T = 529.67^{\circ}R$$
$$\Delta t = 1.0 \text{ sec}$$
$$\rho_{liq} = 90.35 \text{ lbm/ft}^3$$
$$P_{sat} = 2118.24 \text{ lbf/ft}^2$$
$$R_p = 17.597 \text{ ft} - \text{lbf/lbm} - {}^{\circ}R$$
$$\hat{c}_p = 17.85 \text{ cal/mole} - {}^{\circ}K$$

Calculations were performed, in all cases, for five values of the "evaporation rate coefficient" defined on page 9:

$$A = .01, .1, 1.0, 10.0, 100.0 \text{ lbm/sec}$$

(The effect of varying surface area on evaporation rates was not taken into account). The following sets of values were used for the two tank sizes:

	Initial V_{tank}	Final Propellant Volume (liq)	$(\dot{Q}_{in})_{fast}$	$(\dot{Q}_{in})_{slow}$
Small tank	17.91 ft^3	125 gal	10 gal/min	2 gal/min
Large tank	89.5 ft^3	640 gal	60 gal/min	10 gal/min

The procedure was as follows:

1. For the initial time step, an average mass was calculated using equation (10). The average was found in the usual way,

$$(m_p)_{ave} = \frac{1}{\Delta t} \int_0^{\Delta t} m_p(t) \, dt$$

$$= \frac{4}{3} \left(\frac{A \, p_{sat} \, V_{tank}}{R_p T} \Delta t \right)^{1/2}$$

2. The limiting value of m_p from eqn (10') was calculated and compared to the preceding value. If smaller, it replaced it.

3. The limiting value of m_p from eqn (10'') was calculated and compared to the preceding value. If smaller, it replaced it.

4. Outflows for the first time step were calculated using the resultant value of m_p.

5. Volume and mass increments were calculated from equations (14) and (15) using these initial values of V and m_p, and used to find new values of V and m_p.

6. This finite difference procedure was continued until either the ullage was saturated with propellant vapor, or the liquid volume in the tank reached 90% of its final value. Flow rates were calculated at each step using equations (1), (2) and (5), and a running total –

$$\sum \dot{m}_{p_{out}} \Delta t$$

was kept. At each step, a check was made to ensure that the ullage
had not become saturated and that a negative value was not being used
for $\dot{m}_{evap}$.

7. As soon as the ullage became saturated with propellant vapor, the
finite difference procedure was terminated. The remainder of the fast
fill was analyzed using equations (1) through (6) with

$$\dot{m}_{evap} = 0 .$$

In this case the equations are readily solved analytically, and numerical
methods are not required.

8. Following the completion of the fast fill, the slow fill was analyzed.
For the 640 gallon tanks, this simply amounted to changing the value of
$\dot{Q}_{in}$ and preceding as before. For the 125 gallon tanks, an isentropic
portion was calculated using equations (11), (12), (13a) and (13b), after
which the last stage of venting was analyzed as described in steps 6 and 7,
with

$$p = 20116 \text{ lbm/ft}^2$$
$$T = T_2 \text{ (just calculated)}$$
$$\dot{Q}_{in} = 2 \text{ gal/min}$$

and starting with $V = V_2$, the value found for the isentropic compression.

The results for total propellant vent masses are summarized in
Figures 1 and 2. More detailed results, including a listing of the computer
program, are presented in the Appendix.

4. Discussion of Results

No attempt was made to select realistic values of A, which will depend
on the liquid propellant surface area and hence will vary with time, especially in
the case of a spherical tank. The results varied with A throughout the range of
values of A that were investigated. It is likely that realistic values of A will
fall within this range; however, a more thorough study would be required to de-
fine the vent masses with a high degree of certainty.

Two other shortcomings of the analysis should be pointed out:

1. Some discrepancies exist in the way V, m_p, and $\dot{m}_{sat}$ are handled
in the first time step.

2. The slow fill analysis for the 640 gallon tanks does not allow for
the possibility that the ullage might not be saturated.

It should be emphasized that this analysis was intended only as a "second approximation," and was a fast-reaction exercise of very limited duration. We did not have time or funding, at the time this work was done, to refine the analysis beyond the point where consistent and reasonably reliable results were being obtained. Our approach and results, including emphasis on the deficiencies of the analysis, are presented here since we are not aware of the existence of anything better, and for the benefit of anyone who might wish to develop this computer code further.

Figures 1 and 2 are cross-plots of the total amounts vented for each tank versus A. Figure 1 in particular indicates that the propellant mass vented might well grow without bound as the evaporation rate increases. At these high values of propellant vapor mass however, it would be necessary to take account of cooling due to evaporation; this cooling would reduce the vapor pressure and hence the amount evaporated. In addition, we should remember that these high values occur as a result of the very rapid evaporation at early values of time, accompanied by an assumed instantaneous diffusion throughout the tank, with the result that large amounts of propellant are lost out the vent before the gas is saturated. A final consideration: examination of the computer output shows that the curves would stop rising at only slightly higher values of A than those calculated because of the limitations represented by equations (10') and (10'').

With these considerations in mind, it was decided to select the approximate inflection points in the two curves to estimate the total vent quantities:

125 gallon N_2O_4 tank: $m_{p.v.}$ = 4.5 lbm

640 gallon N_2O_4 tank: $m_{p.v.}$ = 24.0 lbm

The 640 gallon figure corresponds to a higher value of A than the 125 gallon figure, which is appropriate since A should be proportional to surface area.

These values are 18.5% and 23.4% greater, respectively, than those obtained with the first approximation. They are also 5 - 10% smaller than the maximum values calculated.

The complete flowrate history (hypergol vapor vent flow rate versus time) calculated by this program is presented in Figure 3.
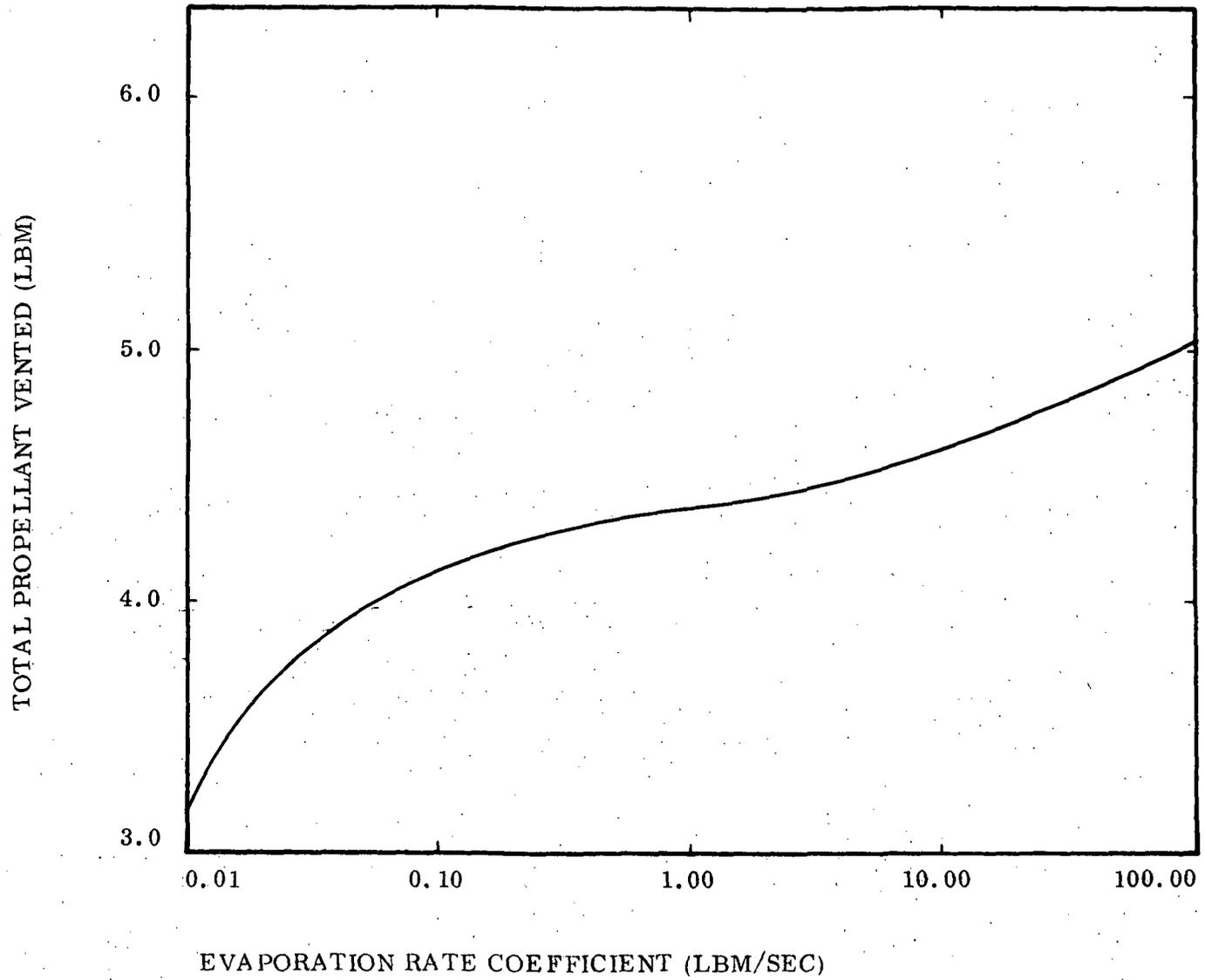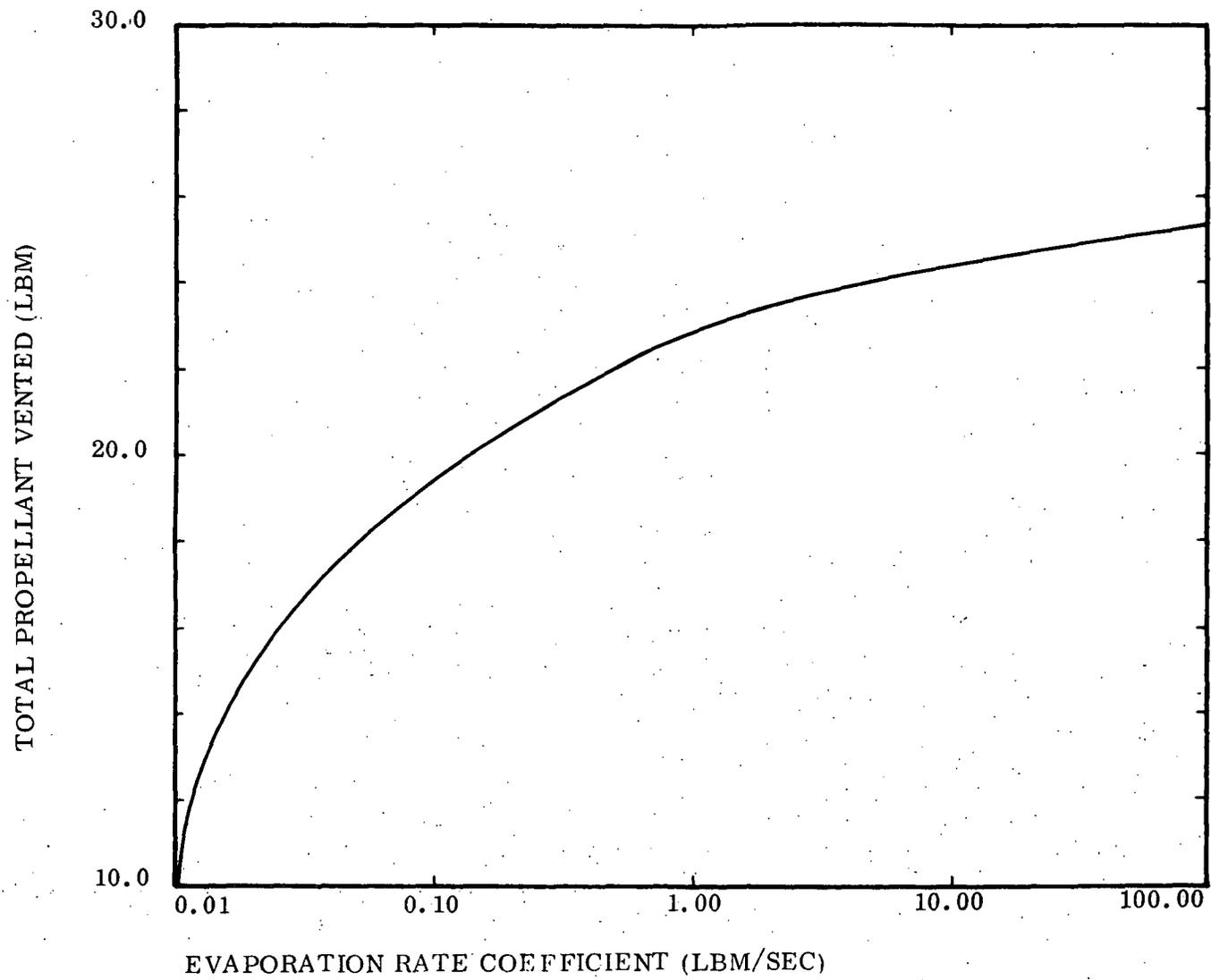
Figure 1: N_2O_4 vent mass, 125 gallon tank

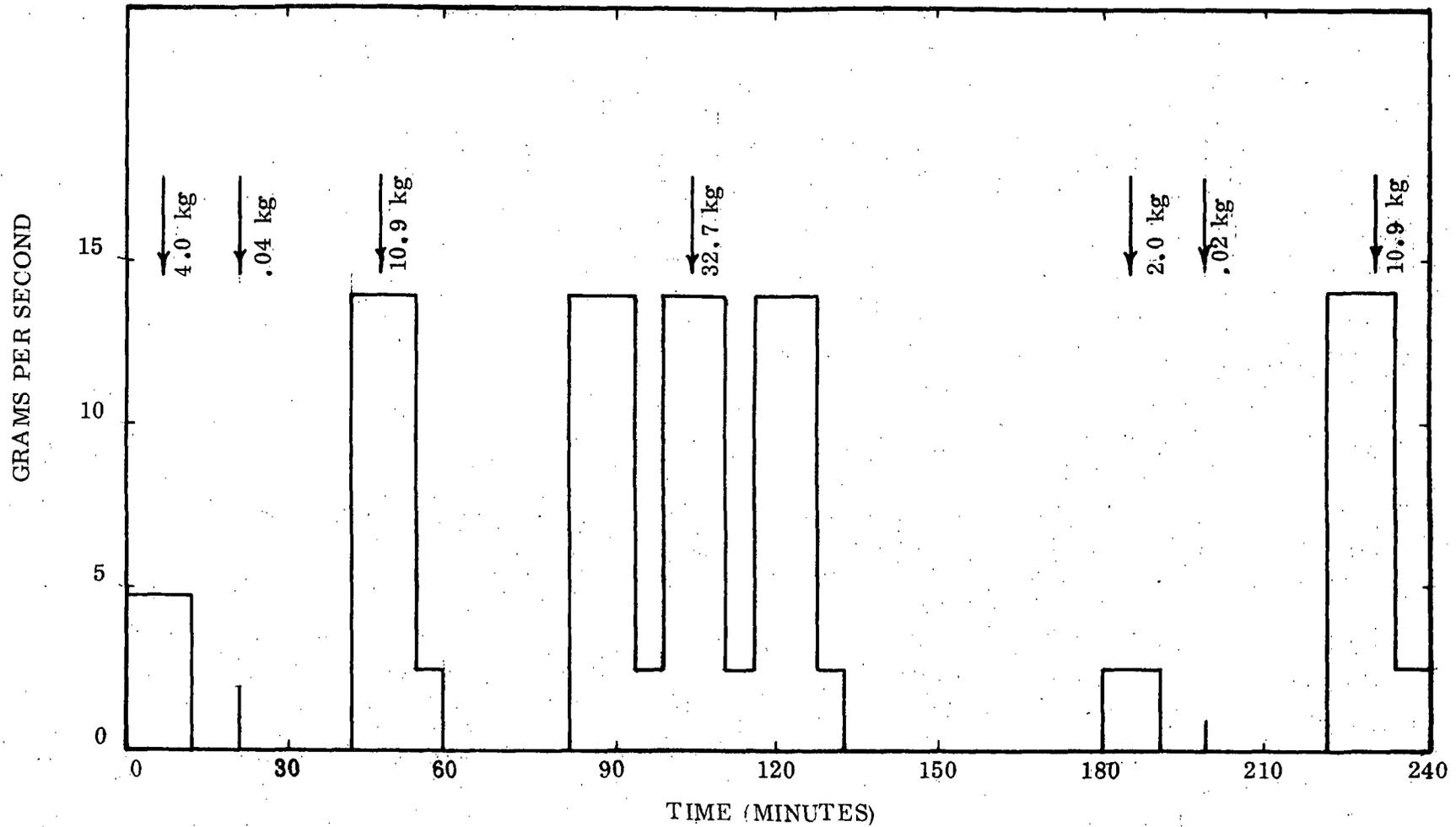Figure 2.: N_2O_4 vent mass, 640 gallon tank

Figure 3: Baseline Flowrate History, N_2O_4 - NO_2 vapors vented during pad servicing operations – does not include helium flow

APPENDIX
VENT FLOW RATE PREDICTIONS FOR LC-39
(NORMAL OPERATING CONDITIONS)

This Appendix includes a listing of the computer program used for these calculations, and results for selected values of the "evaporation rate coefficient," A, defined in Section 3.1.

```
      DIMENSION A(5),VO(4),RHO(2),PSAT(2),R(2),TITLE(10),QDOTJ(4),
     1 VTOT(4),CP(4)
      IN=5
      IOUT=6
      READ (IN,1) (A(I),I=1,5),(VO(J),J=1,2)
      READ (IN,3) (VTOT(J),J=1,2)
      READ (IN,3) (QDOTJ(J),J=1,4)
      READ (IN,3) (CP(K),K=1,2)
    3 FORMAT (8F10.3)
      T=529.67
      PMIX=7156.
      PMIX2=20116
      DELT=1.
      RHO(1)=54.8
      RHO(2)=90.35
      PSAT(1)=111.456
      PSAT(2)=2118.24
      R(1)=33.536
      R(2)=17.597
      DO 100 K=1,2
      READ (IN,2) (TITLE(L),L=1,9)
      WRITE (IOUT,10) (TITLE(J),J=1,9)
      DO 100 J=1,2
      WRITE (IOUT,11) VO(J)
      DO 100 I=1,5
      WRITE (IOUT,12) A(I)
      WRITE (IOUT,14)
      TIME=DELT
      KOUNT=1
      AA=A(I)
      ULLAGE=VTOT(J)-.9*VO(J)*.1337
      QDOT=QDOTJ(J)*.1337/60.
      V=VTOT(J)
      EMM=QDOT*DELT*RHO(K)
      EMM2=SQRT(8./9.*AA*PSAT(K)*V*DELT/R(K)/T)
      IF (EMM2.LT.EMM) EMM=EMM2
      EMM2=PSAT(K)*V/R(K)/T
      IF (EMM2.LT.EMM) EMM=EMM2
      FLOW=QDOT+EMM*(R(K)*T/PMIX-1./RHO(K))/DELT
      FLAW=FLOW/.1337
      EFFLUX=FLOW*EMM/V
      SCRUB=EFFLUX*DELT
   44 PARA=PSAT(K)*V/EMM/R(K)/T
      IF (PARA.LE.1.) GO TO 66
      EVAP=AA*(PARA-1.)
      TEST=QDOT*RHO(K)
      IF (EVAP.GT.TEST) EVAP=TEST
```

```
      DELV=(EVAP/RHC(K)-QCOT)*DELT
      DELM=EVAP*(1.-PSAT(K)/PMIX/PARA)*DELT+EMM/V*DELV
22    TIME=TIME+DELT
      EMM=EMM+DELM
      V=V+DELV
      PP=EMM*R(K)*T/V
      FLOW=QDOT+EVAP*(R(K)*T/PMIX-1./RHC(K))
      FLAW=FLOW/.1337
      EFFLUX=FLOW*EMM/V
      SCRUB=SCRUB+EFFLUX*DELT
      KCUNT=KCUNT+1
      IF (KOUNT.LT.10) GO TO 33
      VOUT=V/.1337
      POUT=PP/144.
      WRITE (IOUT,13) TIME,EMM,VCUT,POUT,FLAW,EFFLUX,SCRUB
      KCUNT=0
33    IF (V.GT.ULLAGE) GO TO 44
      VOUT=V/.1337
      POUT=PP/144.
      GO TO 88
66    EMM=PSAT(K)*V/R(K)/T
      PP=PSAT(K)
      VCUT=V/.1337
      POUT=PSAT(K)/144.
      WRITE (IOUT,13) TIME,EMM,VOUT,POUT,FLAW,EFFLUX,SCRUB
      CHEK1=PSAT(K)*ULLAGE/R(K)/T
      TIDE=(V-ULLAGE)/QDOT
      TIME=TIME+TIDE
      VOUT=ULLAGE/.1337
      POUT=PSAT(K)/144.
      FLAW=QDOT/.1337
      EFFLUX=QDCT*PSAT(K)/R(K)/T
      SCRUB=SCRUB+EFFLUX*TIDE
      CHEK2=EMM-EFFLUX*TIDE
      IF (ABS(CHEK1-CHEK2).GT..01*CHEK1) WRITE (IOUT,15)
      EMM=CHEK1
88    WRITE (IOUT,13) TIME,EMM,VCUT,PCUT,FLAW,EFFLUX,SCRUB
      QDOT=QDOTJ(J+2)*.1337/60.
      ULOLD=ULLAGE
      ULLAGE=VTOT(J)-VO(J)*.1337
      IF (J.EQ.1) GC TO 99
      EMM=PSAT(K)*ULLAGE/R(K)/T
      TIDE=VO(J)*.01337/QCOT
      TIME=TIME+TIDE
      VOUT=ULLAGE/.1337
      FLAW=QDOT/.1337
      EFFLUX=QDOT*PSAT(K)/R(K)/T
      SCRUB=SCRUB+EFFLUX*TIDE
      WRITE (IOUT,13) TIME,EMM,VOUT,POUT,FLAW,EFFLUX,SCRUB
      GO TO 100
99    WRITE (IOUT,16)
      GAMMA=(PP*CP(K)+(PMIX-PP)*5.)/(PP*(CP(K)-1.986)+(PMIX-PP)*3.)
      PCW1=1./GAMMA
      VISEN=ULOLD*(PMIX/PMIX2)**PCW1
      IF (VISEN.LT.ULLAGE) GC TO 100
      TIME=TIME+(ULOLD-VISEN)/QDOT
      VOUT=VISEN/.1337
      PP=PP*PMIX2/PMIX
```

79

```
      POUT=PP/144.
      FLAW=0.
      EFFLUX=0.
      WRITE (IOUT,13) TIME,EMM,VOUT,POUT,FLAW,EFFLUX,SCRUB
      WRITE (IOUT,17)
      POW2=(GAMMA-1.)/GAMMA
      T2=T*(PMIX2/PMIX)**POW2
      TIDE=(VISEN-ULLAGE)/QDOT
      TIME=TIME+TIDE
      VOUT=ULLAGE/.1337
      FLAW=QDOT/.1337
      EFFLUX=QDOT*PP/R(K)/T2
      SCRUB=SCRUB+EFFLUX*TIDE
      EMM=EMM-EFFLUX*TIDE

      WRITE (IOUT,13) TIME,EMM,VOUT,POUT,FLAW,EFFLUX,SCRUB
100   CONTINUE
      STOP
    1 FORMAT (5F10.3/4F10.3)
    2 FORMAT (9A4)
   10 FORMAT (1H1,9A4)
   11 FORMAT (///' FINAL PROPELLANT VOLUME =',F6.0,' GALLONS'/)
   12 FORMAT (/' EVAPORATION RATE COEFFICIENT =',F7.2, 'LBM/SEC'/)
   13 FORMAT (F8.0,F11.3,F11.2,F10.3,F11.3,F12.4,F12.3)
   14 FORMAT (//3X,'TIME    PROPELLANT   ULLAGE    PARTIAL    TOTAL     PR
     1ROPELLANT',6X,'TOTAL'/3X,'(SEC)    VAPOR MASS   VOLUME   PRESSURE
     2 OUTFLOW     OUTFLOW    PROPELLANTS'/14X,'(LBM)     (GAL)     (PSIA
     3A)    (GAL/SEC)   (LBM/SEC)   VENTED(LBM)'/)
   15 FORMAT (' OOPS')
   16 FORMAT (' VENT CLOSES')
   17 FORMAT (' VENT OPENS')
      END
```
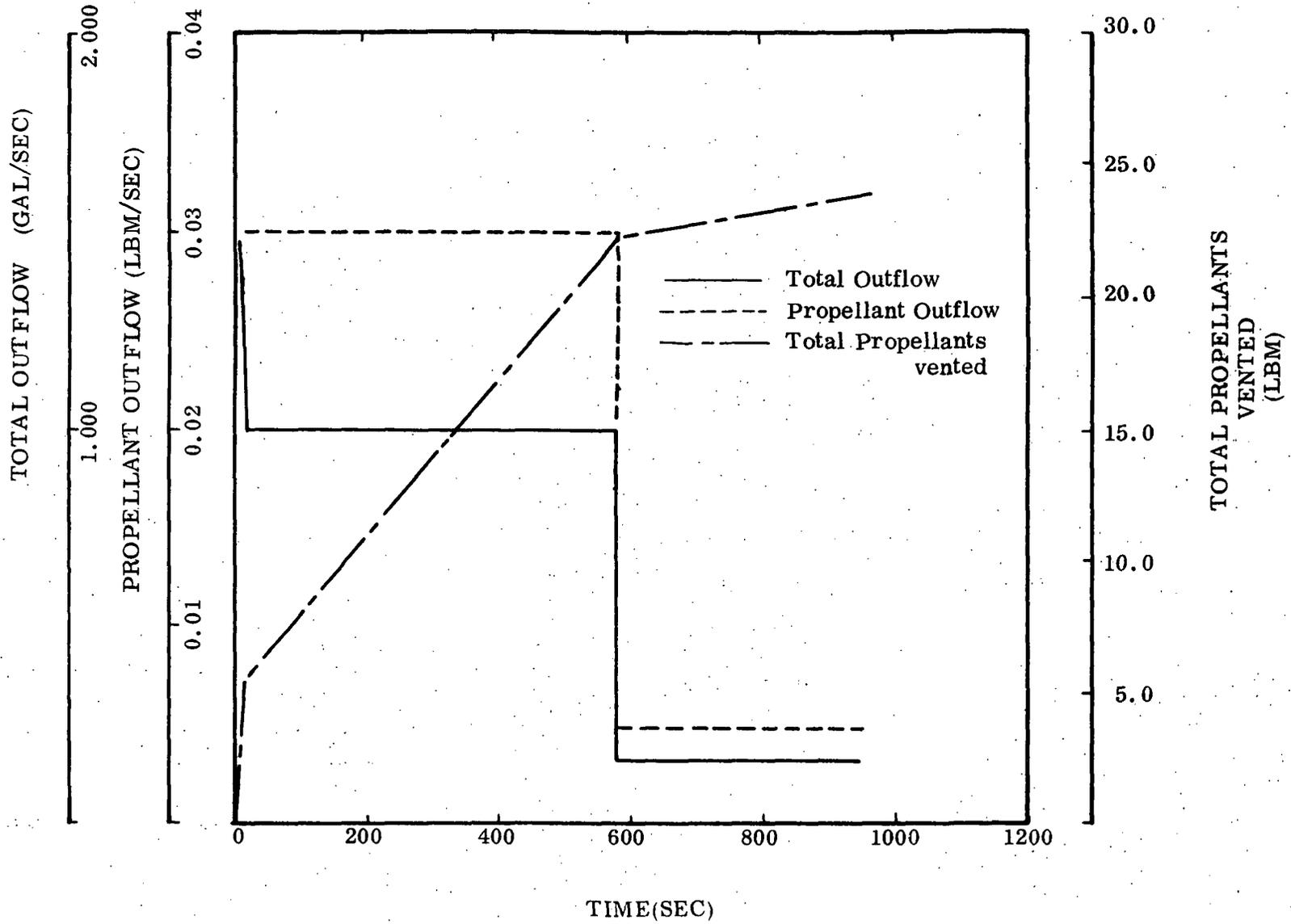
N_2O_4 RESULTS - 125 GALLON TANK

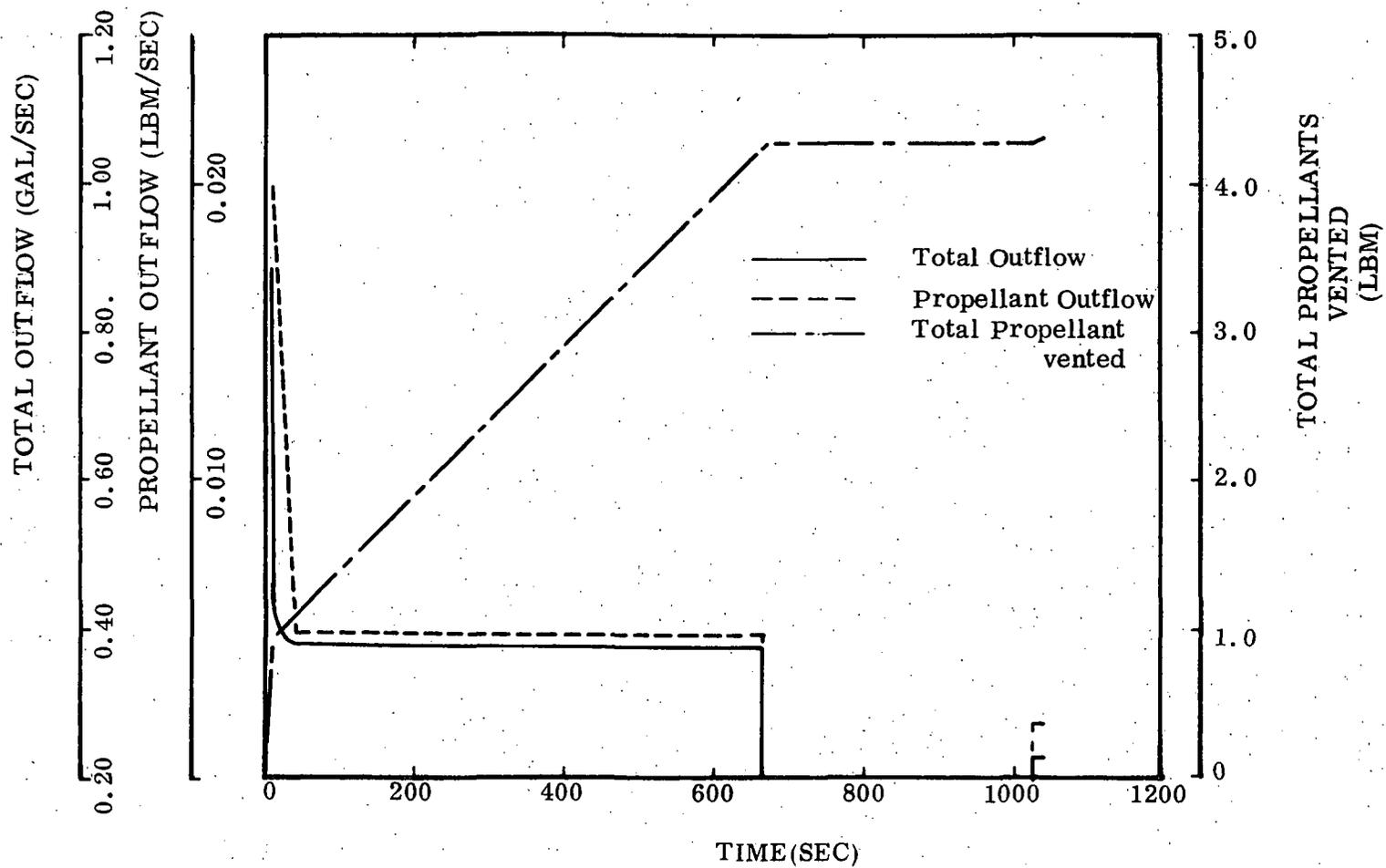EVAPORATION RATE COEFFICIENT =   1.00LBM/SEC

TIME (SEC)	PROPELLANT VAPOR MASS (LBM)	ULLAGE VOLUME (GAL)	PARTIAL PRESSURE (PSIA)	TOTAL OUTFLOW (GAL/SEC)	PROPELLANT OUTFLOW (LBM/SEC)	TOTAL PROPELLANTS VENTED(LBM)
10.	3.862	132.66	14.095	0.691	0.0201	0.876
20.	3.958	131.01	14.626	0.234	0.0071	0.984
30.	3.927	129.35	14.698	0.176	0.0053	1.043
40.	3.879	127.68	14.708	0.168	0.0051	1.094
50.	3.829	126.01	14.710	0.167	0.0051	1.145
58.	3.788	124.68	14.710	0.167	0.0051	1.186
677.	0.652	21.46	14.710	0.167	0.0051	4.322
VENT CLOSES						
1032.	0.652	9.65	41.351	0.000	0.0000	4.322
VENT OPENS						
1052.	0.605	8.96	41.351	0.033	0.0023	4.369

N$_2$O$_4$ RESULTS 640 GALLON TANK

EVAPORATION RATE COEFFICIENT = 10.00LBM/SEC

TIME (SEC)	PROPELLANT VAPOR MASS (LBM)	ULLAGE VOLUME (GAL)	PARTIAL PRESSURE (PSIA)	TOTAL OUTFLOW (GAL/SEC)	PROPELLANT OUTFLOW (LBM/SEC)	TOTAL PROPELLANTS VENTED(LBM)
10.	20.029	661.26	14.663	1.477	0.0447	5.112
20.	19.788	651.27	14.709	1.006	0.0306	5.441
30.	19.485	641.27	14.710	1.000	0.0304	5.746
31.	19.455	640.27	14.710	1.000	0.0304	5.776
578.	2.838	93.41	14.710	1.000	0.0304	22.392
962.	0.894	29.41	14.710	0.167	0.0051	24.337

Slow fill commences at 578 sec, ends at 962 sec.

640 GAL. TANK, N_2O_4, EVAPORATION RATE COEFFICIENT = 10.0 $\frac{lbm}{sec}$

TOTAL OUTFLOW (GAL/SEC)

PROPELLANT OUTFLOW (LBM/SEC)

TOTAL PROPELLANTS VENTED (LBM)

———— Total Outflow

– – – – Propellant Outflow

— · — Total Propellants vented

TIME(SEC)

125 GAL. TANK, N_2O_4, EVAPORATION RATE COEFFICIENT = 1.00 $\frac{lbm}{sec}$

84

MARTIN MARIETTA CORPORATION

DENVER DIVISION

ENGINEERING PROPULSION LABORATORY

NITROGEN TETROXIDE VAPOR SCRUBBER

USING A RECIRCULATING LIQUID

PREPARED BY:

T. D. Reisert, Program Manager
Martin Marietta Corporation

TABLE OF CONTENTS

FOREWORD

The work described herein was conducted by Martin
Marietta Corporation, Denver Divison, under NASA
Contract NAS10-9095, under the management of the
NASA Project Manager, Mr. H. H. Franks, Spacecraft
and Storables Section, NASA-Kennedy Center, Florida.

1.0   INTRODUCTION

The Martin Marietta Corporation was placed on contract by the John F. Kennedy Space Center (KSC) in January 1977, to design, manufacture, test and deliver four (4) Hypergolic Oxidizer Vapor Scrubbers. Delivery of the scrubbers was completed in October 1977.

The scrubbers are required to reduce N_2O_4 contamination of nitrogen vent gas streams to a safe level to preclude health hazard to personnel and to preclude adverse environmental effects. The scrubber principle involved is to absorb and neutralize the N_2O_4 component in a closed circuit circulating water/chemical solution in a vertical counter-flow, packed-tower configuration.

The operational and performance test requirements for the scrubbers are defined in KSC Specification No. 79K08492. Basically, this consists of demonstrating that the exit gas contamination level from the scrubbers does not exceed 150 ppm oxidizer under any flow conditions up to 400 scfm with inlet concentrations of up to 100,000 ppm oxidizer.

Early developmental work involving chemical analysis and scrubber liquor selection was performed by the Florida Institute of Technology (FIT). Some of this work consisting of prototype testing was done by Martin Marietta under contract to the FIT.

The basic scrubber concept design was developed by the Planning Research Corporation (PRC) for KSC. This design was identified in KSC Specification No. 79K08492, which specified the functional and physical characteristics of the scrubbers, including: scrubber liquors and concentrations, sump liquor flow rates, scrubber capacity, physical size and shape, construction material, environmental conditions, and quality conformance inspections involving the use of Drager tubes for concentration measurements. This specification provided the design criteria for the detail design produced by Martin Marietta.

During the detail design development, it was evident that several concept changes were required. These were coordinated with KSC and incorporated.

Several problems were encountered during the performance testing that led to a series of investigations and supplementary testing. It was finally necessary to change the scrubber liquors in oxidizer scrubber to successfully achieve performance requirements.

This report provides a description of the scrubbers, the test configuration, and the various tests performed. Schedule limitations precluded performing the complete test matrix using the final scrubber liquor. Sufficient testing was accomplished, however, to demonstrate that the oxidizer scrubbers fully comply with the performance specification.

2.0   SUMMARY

An Oxidizer Hypergolic Toxic Vapor (HTV) Scrubber has been developed at the Martin Marietta Engineering Propulsion Laboratory in Denver, Colorado. Performance testing was conducted during May through July 1977.

The purpose of the test program was to operate the scrubber with varying inlet propellant concentrations and flow rates and demonstrate that exit gas concentrations were reduced to less than 150 ppm for oxidizer. The oxidizer scrubber inlet concentrations were varied over a range of 440 to 259,000 ppm with flow rates varying from 50 to 400 scfm. In addition, worst case conditions were testing consisting of high and low flow rates with high propellant vapor concentrations.

Several problems were encountered during the performance testing of the scrubber. It was evident from the first series of tests that the performance requirements were not being met. This led to a series of investigations and supplementary testing to determine the cause of below specification performance. This activity included:

1. Upgrading the sump liquor flow rates by adjusting the pump clearances.

2. Incorporating a viewport in three of the packed towers to observe the uniformity of liquor spray over the packed beds.

3. Evaluating the mixing of the N_2 and N_2O_4 inlet gases.

4. Inspecting the tower nozzles to determine if any clogging of the nozzles had occurred.

5. Evaluating the nozzle spray patterns to determine the spray distribution.

6. Conducting smoke tests to evaluate gas flow through the packed towers.

7. Conducting tests to determine if the packed towers were flooding.

8. Consulting with the packing material manufacturer to determine if application of the packing was proper.

9. A thorough evaluation of the gas sampling techniques.

While these investigations improved the knowledge and understanding of the scrubber operation, the scrubber performance was not significantly improved and it was still not per specification.

2.0 SUMMARY (cont'd)

Consultation with the Florida Institute of Technology revealed that a 10-percent solution of sodium sulfite (Na_2SO_3) may be a better scrubber liquor. The scrubber liquor was changed from sodium hydroxide to sodium sulfite and additional testing was performed. The scrubber performance was within specification under all conditions tested. The use of sodium sulfite, however, presented additional problems:

1. The scrubber did not have the capacity to scrub 600 pounds of N_2O_4 as required; and

2. After extended running, a solid precipitate was noted in the bottom of the sump.

Chemical analysis revealed that both of these problems could be eliminated by using a sump liquor consisting of a mixture of sodium sulfite and sodium hydroxide. Additional testing was performed with successful results, i.e., the capacity was adequate, there was no precipitate formed and the scrubber performance was within specification.

The scrubber performance was determined by analyzing scrubber exit gas samples using detector tubes (Kitagawa and Drager) as required by specification. It was necessary to measure the inlet gas concentrations using a wet chemistry method because of the high concentrations. The wet chemistry method was also used for exit gas analysis as a backup to the detector tube method and to obtain quantitative data. Throughout the test program, good correlation between the two analysis methods was not achieved. The discrepancy is academic, however, because the performance was within specification for both methods of analysis.

3.0 HARDWARE DESCRIPTION

3.1 Scrubber Description

The scrubber contains wet packed bed scrubbing towers, a storage (sump) tank for the chemical solution (liquor) and pneumatic and electrical systems. The scrubber is approximately 8 feet by 8 feet by 11 feet high and weighs approximately 7,000 pounds empty, 10,500 pounds with stoneware loaded, and 18,500 pounds with stoneware and 750 gallons of 18% sodium sulfite and 5% sodium hydroxide solution loaded in the storage tank. The scrubber is shown schematically in Figure 1. It has 4 towers connected in series to minimize the total height and insure good gas/liquid contact. Tower bed packing materials are commerical grade chemical stoneware intalox saddles. The nominal sizes of saddles utilized are 1/2 inch, 3/4 inch and 1 inch. A polypropylene mesh demister is located in the top of twoer #4 to remove liquid droplets from the existing gas stream. The chemical solution is held in the storage tank in the base of the scrubber. When the pump is started, the solution is pumped to a 125 degree teflon spray nozzle at the top of each tower. The chemical solution then counterflows the exhaust gas stream and gravity drains back to the sump.

There are two modes of operation for the scrubber. In the first mode, designated the operative mode, the exhaust gas to be scrubbed flows through the scrubber 6-inch inlet line to the towers. In the second mode, designated the inoperative mode, pneumatic valves are positioned to close the 6-inch inlet line and open the 3-inch line. The exhaust gas then enters the storage tank below the chemical solution liquid leve, bubbles through the solution and exits out the last tower.

3.2 Performance Test Setup

The schematic for the oxidizer scrubber test setup is in Figure 2. A photograph of the test setup used for these tests is shown in Figure 3.

Input N_2O_4 vapors to the scrubber were generated in a water jacketed tank that held liquid N_2O_4. The water was heated to approximately 130°F for the N_2O_4 to get the liquid propellant above its boiling point at the necessary pressure for transfer. The vapors flowed through tubing (which had been warpped with heater tape and insulated) to a mixing pipe where the vapors were mixed with heated nitrogen gas at selected flow rates. A hand valve in the propellant flow line was used to throttle the amount of vapor reaching the scrubber.
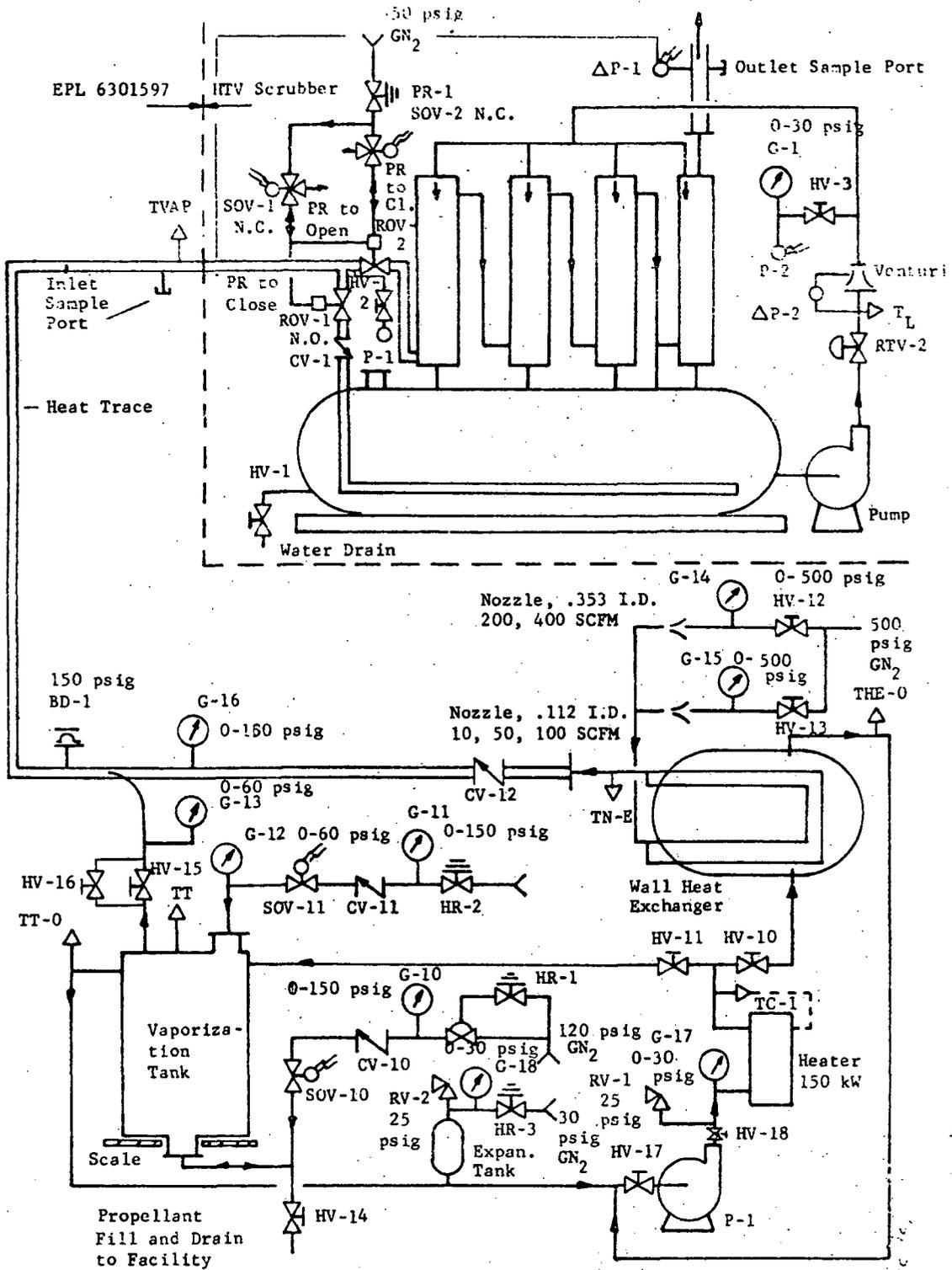
FIGURE 1   SCHEMATIC - OXIDIZER TOXIC VAPOR SCRUBBER

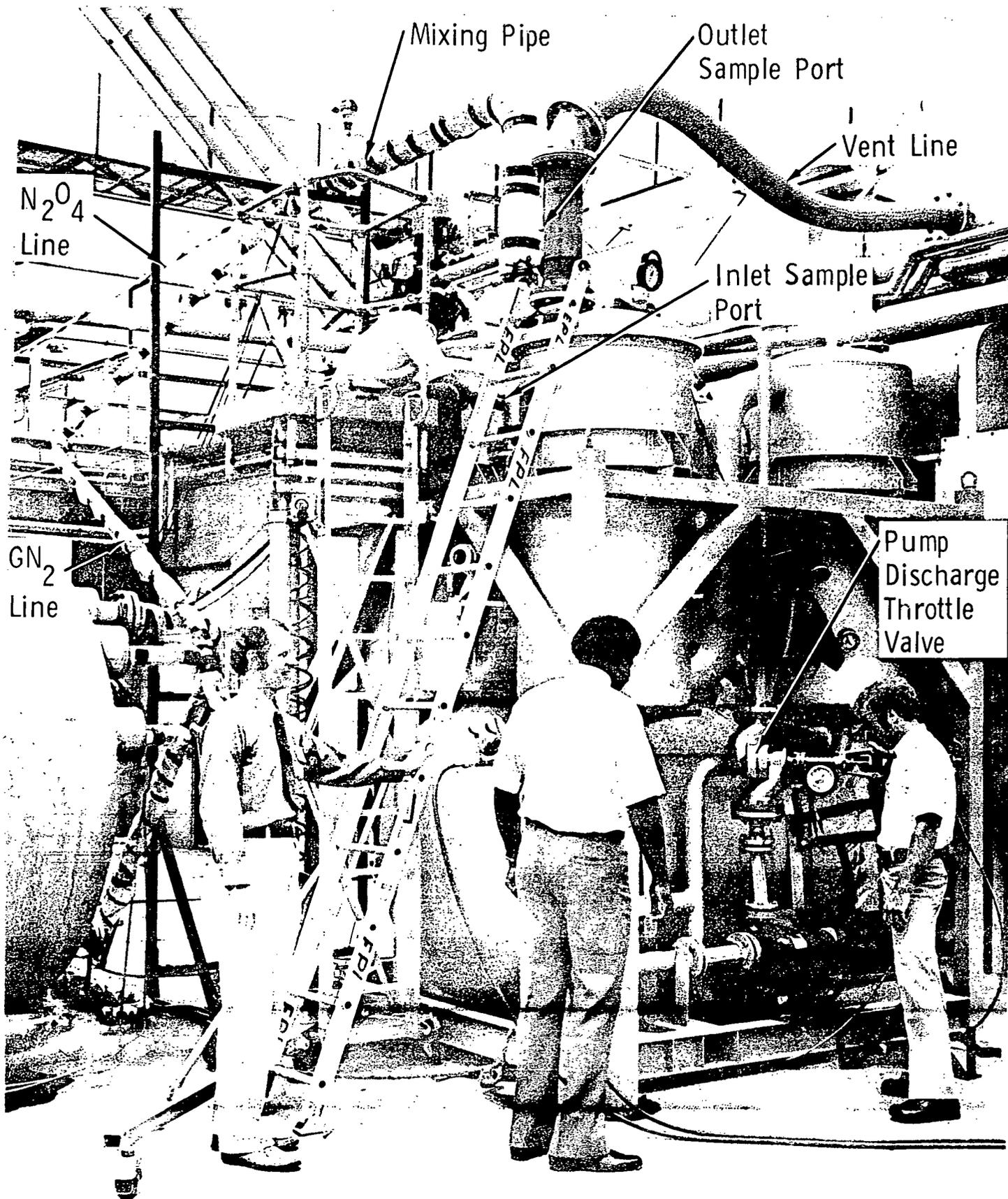Figure 2   Scrubber Performance Test Fixture Setup

FIGURE 3 N_2O_4 Scrubber Test Setup

94

3.0   HARDWARE DESCRIPTION (cont'd)

3.2   Performance Test Setup (cont'd)

Input gas samples for the wet chemistry analysis were taken with a
gas sample syringe inserted through a rubber septum into the input
gas flow approximately 1-12/ feet upstream of the scrubber inlet
port. Output gas samples were taken with a separate syringe inserted
through a rubber septum into the vent gas flow approximately 2 feet
downstream of the scrubber outlet port. The sampling approach was
to take three samples of the inlet and outlet gas concentrations for
one steady state condition. The samples were taken in the same
manner by the same person for each data point with a time of two to
five minutes between each of the three points. The gas concentra-
tions were then analyzed by the wet chemistry methods described in
Reference 1.

Gas detector tube measurements were made in the outlet gas flow
stream through a 3/8-inch AN port at the same elevation as the wet
chemistry sample port.

The sump liquor flow was varied by adjusting the remotely controlled
throttle valve on the scrubber pump discharge line. This valve was
installed for test purposes only.

The performance test matrix for the N_2O_4 scrubber is defined in
Table 1.

Table 1. Test Matrix - N_2O_4 Performance Tests

N_2O_4 Input Vapor Concentrations, ppm	Nitrogen Gas Flow Rate, scfm			
	50	100	200	400
500	X	X	X	X
	X	X	X	X
	X	X	X	
	X	X		
	X	X		
	X	X		
	X			
100,000	X			

X = 100, 150 and 200 gpm liquid flow rates.

Worst Case Condition No. 1

Nitrogen Flow Rate: 10 scfm

N_2O_4 Input Vapor Concentration: 900,000 ppm

Liquid Flow Rate: Maximum

Worst Case Condition No. 2

Nitrogen Flow Rate: 400 scfm

N_2O_4 Input Vapor Concentration: 100,000 ppm

Liquid Flow Rate: Maximum

4.0 TEST DESCRIPTION FOR N_2O_4 SCRUBBER

The testing of the N_2O_4 scrubbers consisted of three separate phases. These phases were test runs made to evaluate the scrubber using three different sump liquors: sodium hydroxide (NaOH), sodium sulfite (Na_2SO_3) and a mixture of NaOH and Na_2SO_3.

4.1 Sodium Hydroxide (NaOH)

Forty-seven runs were made during the period from 04/27/77 through 06/16/77. During the forty-seven runs, the sump liquor flow rate was varied from 85 gpm to 181 gpm. The strength of the sump liquor varied from 7.95% NaOH to 2.16% NaOH. The scrubber was run in the operative and in the inoperative modes. Summaries of the test results for the NaOH sump liquor operative and inoperative mode test runs are found in Tables 2 and 3.

4.1.1 Post Test Inspection

- After run 47 was completed, the NaOH sump liquor was drained. The towers were inspected and it was noted that the stoneware had settled 1 to 1-1/2 inches in all four towers. There was no caking of precipitates on the stoneware or the nozzles. Liquid was detected in the test setup vent line and identified as nitric acid. The scrubber pump was disassembled. Stoneware chips had been circulated by the pump and scoring of the impeller, impeller housing and pump shaft was noted.

4.1.2 Conclusions: NaOH Sump Liquor Test Series

1. The desired outlet gas concentration of 150 ppm NO_2 or less could not be obtained with the NaOH solution.

2. Higher pump flow rate gives a lower outlet gas concentration.

3. Higher inlet gas concentration gives a higher outlet gas concentration.

4. Higher nitrogen flow rate gives a higher outlet gas concentration.

5. Proper circulation is occurring in the sump as designed.

6. Inoperative mode scrubs less efficiently than operative mode.

7. When scrubber pump is shut off, scrubber bed will contain enough sump liquor to scrub for a minimum of four minutes at selected flow rates of nitrogen and inlet gas concentrations.

8. Best scrubbing performance is with low sump strength (2 to 3% NaOH) rather than high sump strength (6 to 8% NaOH).

9. Majority of scrubbing is performed in the first tower.

Table 2   Test Data Summary, N_2O_4 Scrubber with
NaOH Sump Liquor, Operative Mode

GN Flowrate, scfm	Date	Run	Wet Chemistry		Average Liquor Flowrate, gpm	Outlet Gas Detector Tube, ppm		Liquor Strength	
			Average Inlet Gas, ppm	Average Outlet Gas, ppm		Drager	Kitagawa	pH	% Conc.
10	5-27-77	3	91,200	280	133		750		
	5-27-77	2	95,500	443	171		500		
	5-27-77	4	98,100	107	95		850		3.96
	5-27-77	1	217,000	3,330	172		500		7.88
	6-6-77	31	484,000	636	160				
50	6-1-77	13	1,960	398	128				
	6-1-77	12	2,350	299	144				
	6-1-77	7	5,310	275	135				
	6-1-77	6	6,680	342	149				
	6-1-77	5	7,990	301	181				6.64
	6-1-77	11	34,200	276	181				
	6-7-77	33	34,900	258	157				6.48
	6-16-77	46	47,200	179	165				2.88
	6-6-77	26	54,700	304	154				7.92
	6-8-77	37	58,500	199	172				5.04
	6-3-77	23	229,000	107	178	500			
	6-3-77	25	249,000	65	115	1,000			2.76
	6-3-77	24	259,000	32	145	1,000			
100	6-1-77	10	6,440	454	172	50			
	6-1-77	9	7,080	504	148	100-150			
	6-1-77	8	7,600	501	110				
	6-16-77	47	18,800	504	167				2.16
	6-7-77	34	22,200	634	157				6.1
	6-1-77	16	23,800	951	129	500			
	6-1-77	14	24,400	693	181	500			
	6-1-77	15	26,800	957	154	500			
	6-6-77	27	30,900	653	157				
	6-8-77	38	31,100	538	176				
150	6-6-77	29	22,600	1,100	160				
200	6-7-77	35	12,800	1,040	157				
	6-8-77	39	17,000	951	181				
	6-6-77	28	17,700	1,070	159				
	6-3-77	17	20,100	928	158				
	6-3-77	18	20,700	1,130	131				
	6-3-77	19	22,500	1,040	102				
400	6-3-77	20	4,910	1,680	72				
	6-3-77	21	5,530	1,390	128	1,000+			
	6-3-77	22	6,470	1,570	167				
	6-7-77	36	7,100	1,140	159				
	6-6-77	30	12,000	903	160				6.38
	6-6-77	32	80,000	2,400	160				

Table 3   Test Data Summary, N_2O_4 Scrubber with
NaOH Sump Liquor, Inoperative Mode

GN$_2$ Flowrate, scfm	Date	Run	Wet Chemistry		Outlet Gas Detector Tube, ppm		Liquor Strength	
			Average Inlet Gas, ppm	Average Outlet Gas, ppm	Drager	Kitagawa	pH	% Conc.
10	6-9-77	44	922,000	3,720				
50	6-9-77	40	42,500	538				4.56
100	6-9-77	45	22,100	400				
	6-9-77	41	24,700	1,760				3.72
200	6-9-77	42	12,300	2,810				
400	6-9-77	43	74,400	9,100				

4.0   TEST DESCRIPTION FOR N$_2$O$_4$ SCRUBBER (cont'd)

4.2   Scrubber Tower Operation Tests

The desired output of 150 ppm NO$_2$ or less was not obtained with the NaOH sump liquor. Several possibilities were investigated to evaluate if the scrubber towers were flooding at certain test conditions or if the gas was channeling in the towers so that maximum scrubbing would not be achieved. It was hoped that these tests could help explain the high outlet gas concentrations.

A dry bed smoke test was performed to observe the gas flow in a dry tower. With the pump off and the valves in the operative mode position, nitrogen was flowed at 10 to 400 scfm through the scrubber. A smoke candle was moved across the diameter of the tower along the surface of the packed bed and the gas flow observed. At 10 scfm, a smoke candle indicated that the flow at the edges of the tower was more pronounced than in the center. At 400 scfm, the flow dispersion in the tower was nearly uniform.

A wet bed smoke test was also performed to determine the gas flow characteristics in an operational or wet bed tower. With the lid and demister of tower #4 removed, a nozzle was installed to spray at approximately the same height as the nozzle in tower #4 when the lid is installed. The pump was turned on and tower #4 was thoroughly soaked, the pump shut off and GN$_2$ flow measurements were made with a smoke candle for 1 to 2 min utes as the water gravity drained through the tower. This technique was repeated for GN$_2$ flows of 10, 50, 100, 200 and 400 scfm. At 10 scfm, the GN$_2$ flow was uniform over the bed surface as measured by a smoke candle. At 50 and 100 scfm, the flow around the edges of the tower was slightly less than the flow in the center. At 200 and 400 scfm, the flow pattern seemed uniform as measured by the smoke candle.

Another test was performed to determine if flooding had occurred in tower #1. In order to increase the liquid flow rate to Tower 1, the nozzles in towers #3 and #4 were removed and the supply line capped. The scrubber pump was turned on and 60 gpm was flowed through tower #1 spray nozzle. Nitrogen flow was varied from 10 scfm to 400 scfm. No flooding of the tower was observed under these conditions.

A test to evaluate the spray pattern of the scrubber teflon nozzles was conducted to determine the distribution of liquor to the packed bed surface during scrubber operation. The 2-piece nozzle was tested with the inner diffuser vane pinned and with it free to rotate. A series of plastic cups were arranged along a line representing the diameter of the tower. A teflon spray nozzle was positioned at a height above the cups that approximated the nozzle height above the scrubber bed. The nozzle was connected to a water line with a flow capacity of 40 gallons per minute. The water was turned on for a brief period to partially fill the cups. From the amount of liquid in the cups, a distribution was determined. The results obtained indicated that the center portion of the tower packed bed surface received about 1/3 more water than the outer portions of the surface with inner diffuser vane pinned and with the diffuser vane free to rotate.

4.0   TEST DESCRIPTION FOR N$_2$O$_4$ SCRUBBER (cont'd)

4.2 '   Scrubber Tower Operation Tests (cont'd)

It was concluded from these tests that the gas and liquid flow distribution in the towers was good for the conditions tested and no changes to the tower configuration needed to be made. The spray nozzles in the towers are satisfactory and should continue to be used in the scrubbers.

4.3   Sodium Sulfite (Na$_2$SO$_3$) Sump Liquor

The initial tests of the oxidizer scrubber were performed utilizing a solution of sodium hydroxide as the sump liquor. This test series indicated that the desired output of 150 ppm NO$_2$ or less could not be obtained with the NaOH solution. References[2] in the report, "Hypergolic Propellant Vapor Disposal", Florida Institute of Technology, Contract NAS10-8399, indicated good results could be obtained by use of sodium sulfite solution as the scrubbing liquor.

Thirty-eight (38) test runs using sodium sulfite as the sump liquor were made during the period from 06/23/77 through 07/06/77. Tests were made with sump liquor concentrations at 10% and 25% Na$_2$SO$_3$. The actual concentration of the Na$_2$SO$_3$ could not be easily measured so pH readings were used as an indication of sump liquor strength. Na$_2$SO$_3$ was also added to partially depleted sump solution to determine if liquor strength could be increased during usage without a complete drain and refill operation. Summaries of the test data for the Na$_2$SO$_3$ sump liquor operative and inoperative mode test runs are presented in Tables 4 and 5.

Conclusions: Na$_2$SO$_3$ Sump Liquor Test Series

As a result of the tests conducted, the following conclusions were reached:

1. Sodium sulfite gave much better overall performance than sodium hydroxide as a sump liquor and met the scrubber specification requirement that the output gas concentration be less than 150 ppm of NO$_2$.

2. Sodium sulfite formed a one-inch layer of precipitate in the bottom of the sump tank during the capacity test.

3. Higher pump flow rate gives a lower outlet gas concentration.

4. Higher inlet gas concentration gives a higher outlet gas concentration.

5. Higher nitrogen flow rate gives a higher outlet gas concentration.

6. Inoperative mode scrubs less efficiently than operative mode.

Table 4   Test Data Summary N_2O_4 Scrubber with Na_2SO_3 Sump Liquor, Operative Mode

GN₂ Flowrate, scfm	Date	Run	Wet Chemistry Average Inlet Gas, ppm	Average Outlet Gas, ppm	Average Liquor Flowrate, gpm	Outlet Gas Detector Tube, ppm Drager	Kitagawa	Liquor Strength pH	% Conc.
10	6-25-77	15	606,000	0	150		0	7	
50	6-25-77	11	634	0	148		0	9	
	6-24-77	5	1,490	0	151		0	8-9	
	6-29-77	17	9,570	0	150			10	
	6-24-77	9	11,300	0	151		0	8-9	
	6-23-77	3	16,800	2.0	147	<5	0	8	
	6-23-77	1	21,200	3.1	150			9-10	
	7-1-77	28	22,000	413*	127				
	6-23-77	4	22,400	6.1	154	0	0	8-9	
	7-1-77	30	28,900	453*	146			7	
	7-6-77	31	29,300	0	147			10	
	6-29-77	18	25,500	0	153			8-9	
	7-1-77	27	30,200	377*	154				
	7-1-77	25	30,700	187	154				
	6-23-77	2	30,700	6.1	154	<5	<10	8	
	7-1-77	26	31,300	377*	154				
	7-1-77	29	31,700	893*	103			7-8	
	7-6-77	33	147,000	417	148				
100	6-24-77	6	442	5.3	154		0	8	
	6-25-77	12	6,950	0	154		0		
	6-24-77	10	7,050	0	146		0	8-9	
	6-29-77	19	12,400 / 24,600	46 / 0	98 / 153				
	7-6-77	36	24,800	183	113		10	9-10	
	7-6-77	37	29,500	193	146			8-9	
200	6-24-77	7	683	0	151		0	8	
	6-25-77	13	4,770	0	154		0	8	
	6-29-77	20	5,230 / 5,720 / 5,550	30 / 44 / 48	148 / 127 / 106			8-9	
400	6-24-77	8	561	1.2	154		0	8-9	
	6-25-77	14	3,110	0	151		0	8	
	6-30-77	21	4,360 / 4,000 / 3,880	0	149 / 128 / 98			9-10	
	6-25-77	16	41,600	0.7	149		0	7-8	

*Made during latter part of capacity run with sump liquor partially depleted..

Table 5   Test Data Summary, N_2O_4 Scrubber with
Na_2SO_3 Sump Liquor, Inoperative Mode

GN₂ Flowrate, scfm	Date	Run	Wet Chemistry		Outlet Gas Detector Tube, ppm		Liquor Strength	
			Average Inlet Gas, ppm	Average Outlet Gas, ppm	Drager	Kitagawa	pH	% Conc.
10	7-6-77	35	565,000	680				
50	6-30-77	22	14,900	0			9	
100	6-30-77	23	18,400	15				
200	6-30-77	24	10,200	54				
400	7-6-77	34	51,100	53				

103

4.0 <u>TEST DESCRIPTION FOR N$_2$O$_4$ SCRUBBER</u> (cont'd)

4.3 <u>Sodium Sulfite (Na$_2$SO$_3$) Sump Liquor</u>

7. A sharp breaking point of reduced scrubber efficiency did not occur as the 600 lb N$_2$O$_4$ goal was reached in the capacity run.

8. When the scrubber pump is shut off, the scrubber bed will contain enough sump liquor to scrub for a minimum of five minutes at selected flow rates of nitrogen and inlet gas concentrations.

4.4 <u>Sodium Hydroxide (NaOH)/Sodium Sulfite (Na$_2$SO$_3$) Sump Liquor</u>

A mixture of Na$_2$SO$_3$ and NaOH was made in the sump to determine if capacity could be increased and the precipitate from the sodium sulfite kept in solution. Twenty runs were made during the period from 07/07/77 through 07/09/77. One sump solution mixture was used for the entire series. The sump pH remained at 10 for the twenty runs. The scrubber was run in the operative and inoperative mode. Summaries of the test results for the NaOH/Na$_2$SO$_3$ sump liquor operative and inoperative mode test runs are found in Tables 6 and 7.

<u>Post Test Inspection</u> - The sump liquor was drained and no salts were noted. The drop in sump liquor flow rate from 172 gpm to 139 gpm between run 8 and previous runs could be explained by partially plugged tower spray nozzles. An examination of the tower spray nozzles were made and whole 1/2-inch saddles from the packed bed were found in the following quantities: Tower 1, 4 saddles; tower 2, 16 saddles; tower 3, 3 saddles; tower 4, 1 saddle. Apparently, 1/2-inch saddles had migrated downward through the 1-inch saddles and holding screen into the sump storage tank. During the inoperative mode, runs 5, 6 and 7, the saddles were suspended in the sump solution by the agitation in the sump from the inlet nitrogen bubbling through the inlet diffuser in the sump storage tank bottom. When run 8 was performed and the scrubber pump turned on, the saddles were passed through the pump and into the tower spray nozzles. Runs 8 through 20 were performed at reduced sump liquor flow rate.

5.0   CONCLUSIONS: NaOH/Na$_2$SO$_3$ SUMP LIQUOR

As a result of the tests conducted, the following conclusions were reached:

1. The sump liquor was as efficient as Na$_2$SO$_3$ for scrubbing in the inoperative mode.

2. NaOH/Na$_2$SO$_3$ did not precipitate a solid.

3. Half inch saddles appeared in the sump tank during the test and were ingested through the pump and lodged in the nozzles. This indicated the need to prevent the pump from ingesting the saddles, either by filtering the pump suction line or by insuring that the half inch saddles would not migrate through the one inch saddles and support plates in the towers.

4. Six hundred sixteen pounds of N$_2$O$_4$ can be absorbed by the sump liquor although the efficiency drops after 560 pounds of N$_2$O$_4$ is absorbed.

5. The operative mode test results for the NaOH/Na$_2$SO$_3$ mixture were generally not as good as for the Na$_2$SO$_3$ by itself.

6. Early in the test (after run 7), the nozzles became partially clogged with whole stoneware saddles which had been ingested through the pump. This reduced the sump liquor flow rate and probably distorted the spray patterns in the towers. It this problem had not existed, results probably would have been better. Test results show that after 560 pounds of oxidizer had been reacted in the unit, the measured concentration of the outlet gas was 124 ppm for an input concentration of 137,000 ppm. Not until 600 pounds had been reacted, did the outlet concentration indicate that the specification of less than 150 ppm had been exceeded. Visual observations of the vent stack during all of these tests was made by the entire test crew and no brown vapors were observed at any time. On the basis of these results, it is believed that with full liquor flow and unclogged tower nozzles, that the mixture of sodium sulfite and sodium hydroxide would scrub as well as the sodium sulfite by itself and that the capacity to react 600 pounds of oxidizer could be achieved.

7. A mixture of 5% NaOH and 18% Na$_2$SO$_3$ in water is recommended as the sump liquor to be used in the oxidizer scrubber.

Table 6   Test Data Summary, N_2O_4 Scrubber with
NaOH/Na$_2$SO$_3$ Sump Liquor, Operative Mode

GN$_2$ Flowrate, scfm	Date	Run	Wet Chemistry		Average Liquor Flowrate, gpm	Outlet Gas Detector Tube, ppm		Liquor Strength	
			Average Inlet Gas, ppm	Average Outlet Gas, ppm		Drager	Kitagawa	pH	% Conc.
10	7-9-77	12	489,000	258	133				
50	7-9-77	16	1,070	14	133				
	7-7-77	1	4,230	5	172			10	
	7-9-77	20	117,000	752	133				
	7-9-77	19	132,000	825	135				
	7-9-77	18	137,000	124	133				
	7-9-77	17	176,000	949	133				
100	7-9-77	15	6,170	39	133				
	7-7-77	9	12,900	36	133			10	
	7-9-77	10	22,400	153	139				
200	7-7-77	8	3,270	0	139				
	7-9-77	14	4,770	23	133				
400	7-9-77	13	3,900	38	132				
	7-9-77	11	27,500	546	139				

Table 7   Test Data Summary, N_2O_4 Scrubber with
NaOH/Na$_2$SO$_3$ Sump Liquor, Inoperative Mode

GN$_2$ Flowrate, scfm	Date	Run	Wet Chemistry		Outlet Gas Detector Tube ppm		Liquor Strength	
			Average Inlet Gas, ppm	Average Outlet Gas, ppm	Drager	Kitagawa	pH	% Conc.
10	7-7-77	3	737,000	61				
50	7-8-77	5	11,600	0			10	
	7-7-77	4	49,900	–			10	
100	7-8-77	6	10,800	0				
200	7-8-77	7	5,830	0				
400	7-7-77	2	49,900	60				

REFERENCES:

1. Test Report for Performance Test of Hypergolic Propellant Vapor Scrubbers, T. A. Murdock, October 1977.

APPENDIX A - ABBREVIATIONS

cc	Cubic centimeter
DR	Drager Gas Detector Tube
EPL	Engineering Propulsion Laboratory Martin Marietta Corporation Denver, Colorado
FIT	Florida Institute of Technology Melbourne, Florida
gal.	Gallon
GN_2	Gaseous nitrogen
gpm	Gallons per minute
HTV	Hypergolic Toxic Vapor
KIT	Kitagawa Gas Detector Tube
KSC	Kennedy Space Center
LN_2	Liquid Nitrogen
ml	Milliliter
MMC	Martin Marietta Corporation
N_2O_4	Nitrogen tetroxide
NaOH	Sodium Hydroxide
Na_2SO_3	Sodium sulfite
NO_2	Nitrogen dioxide
pH	Measure of acidity and alkalinity
psid	Pounds per square inch, differential
psig	Pounds per square inch, gage
P/N	Part number
ppm	Parts per million
scfm	Standard cubic feet per minute
	Microns

Symbol	Designator	Meaning
	BD	Burst Disc
	CV	Check Valve
	G	Gage
	HV	Hand Valve
	P	Pressure Transducer
	ΔP	Differential Pressure Transducer
	PR	Pressure Regulator
	ROV	Remote Operated Valve
	RTV	Remote Throttle Valve
	RV	Relief Valve
	SOV	Solenoid Valve
	TC	Thermocouple
	THE-0	Temperature, Heat Exchanger
	TL	Temperature, Line
	TT	Temperature, Tank
	T_{VAP}	Temperature, Vapor

NITROGEN TETROXIDE SCRUBBER

DATA ANALYSIS

BY

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ABSTRACT

A major difficulty in the analysis of scrubber data is that of separating the physical effects, such as mass transfer, from the physico-chemical effects, such as reaction rates. This is especially true for the absorbtion of nitrogen tetroxide in the various liquids that were tested in the NASA-Kennedy Space Center Hypergolic Toxic Vapor Scrubber Program. A fruitful approach to correlating the data for outlet concentrations was to treat the overall absorbtion as a pseudo first-order absorbtion equation. This approach provided a method for normalizing the data to constant inlet concentration, constant sump liquor condition, and constant scrubbing time, and permitted evaluation of the test and fluid parameters that affected both absorbtion rate and scrubbing time. The analysis indicated that scrubber performance may be improved by optimizing liquor concentrations and liquor flowrate distributions.

1.0   INTRODUCTION

The absorbtion of gases in liquids with which they react can be extremely complex with regard to the chemical reactions in the liquid. This is especially true for the absorbtion of nitrogen tetroxide in the various liquids that we tested (References 1 and 2).

A schematic diagram of the scrubber is shown in Figure 1. Nitrogen tetroxide vapor mixed with nitrogen gas enters the inlet vent on the right. Two modes of scrubbing were tested.

The operative mode is counter-flow scrubbing of the vapor with circulating liquid in packed towers. The inoperative mode scrubbing is vapor bubbling through a liquid.

In the operative mode, the gas-vapor mixture sequentially enters the bottom of the towers and flows out the top, finally exiting from tower 4 outlet vent. During this mode of operation, liquor from the storage tank is pumped to the top of each tower to wet the packing (ceramic saddles); the liquor then drains back into the storage tank.

In the inoperative mode, the gas-vapor mixture enters the diffuser pipe in the bottom of the storage tank, bubbles up through the liquor to flow through tower 4 and exits from the outlet vent. Liquor is not pumped to wet the towers for inoperative mode scrubbing.

Test data were obtained for nitrogen flow rates of 10, 50, 100, 200 and 400 standard cubic feet per minute. The nitrogen was mixed with nitrogen tetroxide vapors to produce inlet vapor concentrations ranging from hundreds to hundreds of thousands parts per million. Three different sump liquors were tested; sodium hydroxide in water, sodium sulfite in water, and a mixture of sodium hydroxide and sodium sulfite in water. The tests are described in detail in Reference 2.

2.0 ANALYSIS

A fruitful and apparently uncommon approach to correlating the data for outlet concentrations was to treat the overall absorbtion as a pseudo first order absorbtion equation,

$$\frac{dc}{dt} = -kc$$

The integrated form of the pseudo first-order absorbtion equation is

$$\log C_{out} = \log C_{in} - kt$$

where

$$C_{out} = \text{outlet concentration}$$

$$C_{in} = \text{inlet concentration}$$

$$k = \text{average absorbtion rate}$$

$$t = \text{scrubbing time}$$

If the reaction is truly a first-order reaction, the absorbtion rate k will not vary with species concentrations (Reference 3). If the reaction is not first order, k will vary with concentration of the scrubbed species or of other species. It is also possible for k to vary with the condition of the tower packed bed and with flowrate of the gases through the tower packed bed. This could result from poor wetting of the packed bed, either because of a too low liquid flowrate or because of poor liquid distribution within the packed bed (Reference 4).

Plotting outlet concentrations versus inlet concentrations on log-log graph paper permits evaluation of the test and/or fluid parameters that affect either absorbtion rate k or scrubbing time t. Such a plot provides a method for normalizing the data to constant inlet concentration, constant sump liquor condition or constant scrubbing time. Examples will be given in the data that follows.

The gas concentrations that will be shown in the figures are determined by the wet chemistry method (Reference 2). No estimates of the uncertainty of the measurements were made in this analysis. The individual shaded areas represent a sequential set of runs for which the flow control valve settings were constant. The numbers next to the shaded areas are run numbers as described in the test report (Reference 2). Test data from each of the three sump liquors will be discussed.

2.1 Sodium Hydroxide in Water

Figure 2-1 shows the performance of the N_2O_4 scrubber with sodium hydroxide (NaOH) in water as the sump liquor. Scrubbing performance ranges from good (runs 23, 24 and 25) to poor (all runs near the $kt = 0$ line). The

inoperative data correlate with nitrogen flowrate. The operative data imply poor or marginal tower wetting and/or saturated liquid in the towers.

An example of normalizing the inoperative data to explicitly show the correlation of outlet concentration with nitrogen flowrate is given in Figure 2-2. The data were normalized to an inlet concentration of 10,000 PPM by translating the inoperative data points parallel to lines of constant kt in Figure 2-1. The added scrubbing obtained by wetting tower 4 is also shown.

Figure 2-3 shows the relative contributions of each tower to overall scrubbing. The data were normalized to an inlet concentration of 10,000 PPM. Note the larger amount of scrubbing in tower 1 and the nearly uniform scrubbing contributions of the remaining towers. A possible explanation is that tower 1 scrubs the easily absorbed N_2O_4 while the remaining towers are scrubbing the more difficult NO_2.

Figure 2-4 shows the product of absorbtion rate times scrubbing time for the tower data and the inoperative mode data. Note that tower 1 scrubs twice as well for the nitrogen flowrate of 50 scfm than for the 100 scfm flowrate. This implies that the absorbtion rate is the same for both flowrates since the scrubbing time of the 50 scfm flowrate is twice that of the 100 scfm flowrate. Towers 2, 3 and 4 scrub equally well at both flowrates. The average of absorbtion rate times dwell time for the inoperative mode data were normalized to an inlet concentration of 10,000 PPM and then normalized again to k t = 1.0 for a nitrogen flowrate of 50 scfm. Since this is data for gas-vapor diffusion through a given depth of liquid, the product k t may also be proportional to a gas-liquid surface area to volume ratio for diffusion. As the flowrate increases from 10 to 200, the ratio decreases. At higher flowrates, the increased agitation in the liquid may cause the ratio to increase. The added contribution to scrubbing with tower 4 wet is also shown. This increment corresponds to the scrubbing of NO_2 in a single tower for operative mode.

The effect of liquor flowrate to the towers is shown in Figure 2-5. Scrubbing improves with higher liquid flowrate to the towers and with increased dwell time, i.e., lower gas flowrate.

2.2 Sodium Sulfite in Water

Figure 3-1 shows the performance of the N_2O_4 scrubber with sodium sulfite (Na_2SO_3) in water as the sump liquor. These data show outlet concentrations ranging from complete scrubbing (0 PPM) to little scrubbing (outlet concentration nearly equal to inlet concentration). Outlet concentrations of from 0 to 0.1 PPM are shown on Figure 3-1 as 0.1 PPM. The data show the effects of probable poor tower wetting and saturated liquid. Runs 25 through 30 show scrubbing performance for the 25% sodium sulfite liquor as the total amount of N_2O_4 absorbed approaches 600 lbs. Run 31 shows the outlet concentration return to 0 PPM for a fresh sump liquor of 10% sodium sulfite. These data do not permit determination of optimum sump liquor concentrations. Runs 36 and 37 show nearly the same scrubbing performance even though tower 4 was not wetted for run 36. The liquor flowrate through the wetted towers was the same, i.e., total liquor flow for run 36 was 3/4 of the flow for run 37. This shows that tower 4 did not contribute to scrubbing. The lack of scrubbing could be due to an improper distribution of liquor to the towers.

Run 32 demonstrates the dramatic effect of poor tower wetting and/or saturated liquid. The scrubber was set in the operative mode at a nitrogen flowrate of 50 scfm and a nominal inlet concentration of 27,000 PPM. Outlet concentration was 0 PPM. Then the sump liquor pump was shut off. The outlet concentration rose to 30 PPM at 5 minutes, 9,100 PPM at 10 minutes, 10,600 PPM at 15 minutes and 10,900 PPM at 20 minutes. Thus, the low outlet concentrations on the order of 0 PPM are representative of good scrubbing, i.e., well-wetted towers, sufficient dwell time and an unsaturated liquor. The higher outlet concentrations that occurred with the pump off are the result of poor tower wetting and/or saturated liquor.

Figure 3-2 shows the time history of scrubbing for run 32. The data is normalized to an inlet concentration of 10,000 PPM. Note the initial rapid decrease in scrubbing. This indicates that a relatively small change in liquor flowrate could affect scrubbing. The nominal liquor flowrate is 160 GPM.

Figure 3-3 shows the effect of liquor flowrate on scrubbing performance.

2.3   Mixture of Sodium Hydroxide and Sodium Sulfite in Water

Figure 4-1 shows the performance of the N_2O_4 scrubber with water and a mixture of 18% sodium sulfite - 5% sodium hydroxide as the sump liquor. These data show the effects of poorly wetted towers and/or insufficient dwell times for pump-off data, high flowrate data and for runs 10 through 20 with the exception of the low nitrogen flowrate runs 12 and 18. Post test examination revealed that for these runs (10 through 20), ceramic saddles had been conveyed in the sump liquor flow to deposit at the shower heads in the towers which probably caused flow distortion and poorly wetted towers. The data show no effects of sump temperature changes from 83 to 135°F. Since pH was constant and no species concentrations in the sump liquor were measured, the data could not be normalized to show optimum liquor concentration.

Figure 4-2 shows the pump-off data of run 4. Since the degradation in scrubbing performance with time is even more rapid than the previous pump-off data with sodium sulfite alone in the sump liquor, it is expected that the sensitivity of scrubbing performance to liquor flowrate and distribution should also be greater. This is partially confirmed by the impaired spray nozzles of runs 9-20.

Figure 4-3 summarizes the effects of tower wetting and/or saturated liquor. The data do not permit separating the two effects.

3.0   CONCLUSIONS

Analysis of the scrubber test data in terms of a pseudo first-order absorbtion equation provides a powerful method for separating physical

116

effects from physico-chemical effects. Analysis of chemical reactions in terms of a pseudo first-order reaction equation is a common approach in theoretical chemical kinetics but apparently has not been applied previously to the analysis and correlation of absorbtion data.

The wide variations of outlet concentrations for the same nominal run conditions suggests that the tower conditions of wetting and/or liquid saturation are marginal. This is supported by the pump-off data which show outlet concentrations increasing greater than 3 orders of magnitude when the liquid flow was stopped.

The upper limit for the scrubbing capacity of the sodium hydroxide/ sodium sulfite sump liquor was not determined. The reduced performance of the later capacity runs may be due only to impaired liquid distribution in the towers resulting from the ceramic saddles that migrated to the shower heads.

Although this scrubber was designed to reduce outlet concentrations to 150 or less PPM N_2O_4, maximum permissible outlet concentrations will likely be reduced in the future. Optimization of the scrubber will permit more stringent outlet concentations to be met. The optimization of liquor concentrations requires detail species concentration measurements rather than simply pH determinations.

4.0   RECOMMENDATIONS

It is recommended that additional analyses and tests be conducted to extend and/or verify the conclusions of this report. This would develop additional information on the order and sensitivities of the chemical reactions and produce suggestions for optimum operation of the scrubber system such as feedback control of the sump liquor, corrections of liquid and gas flow patterns and distribution schedules, and dwell times. The tests would include the effect of geometry changes on flow patterns and distributions, measurements of performance in regions not covered by present tests, use of feedback control and finally, confirmation of performance predictions when operated in a predicted optimum configuration.

5.0 REFERENCES

1. Bowman, T. E., et al: "Disposal of Hypergolic Propellants, Final Report", Florida Institute of Technology, Melbourne, Florida 32901, 1974.

2. Murdock, T.A.: "Performance Test of Hypergolic Propellant Vapor Scrubbers", Test Report Test Number T-77-37-4, Martin Marietta Corporation, Denver Division, Engineering Propulsion Laboratory, Denver, Colorado, October 1977.

3. Laidler, K.J.: Chemical Kinetics, McGraw-Hill Book Company, Inc., 1950.

4. Danckwerts, P.V.: Gas-Liquid Reactions, McGraw-Hill Book Company, 1970.

ACKNOWLEDGEMENT

FIGURE 1   SCHEMATIC - OXIDIZER TOXIC VAPOR SCRUBBER

119
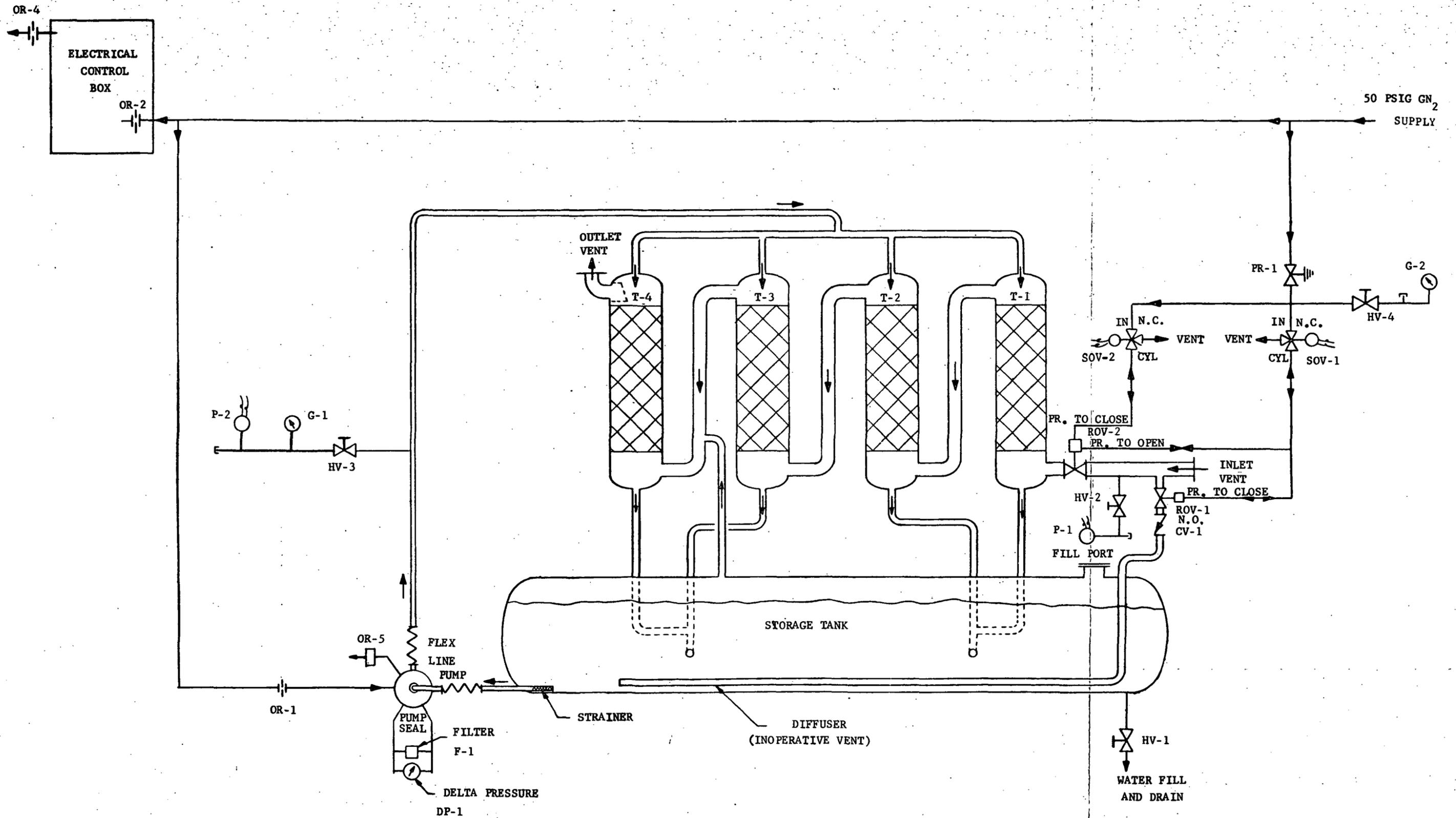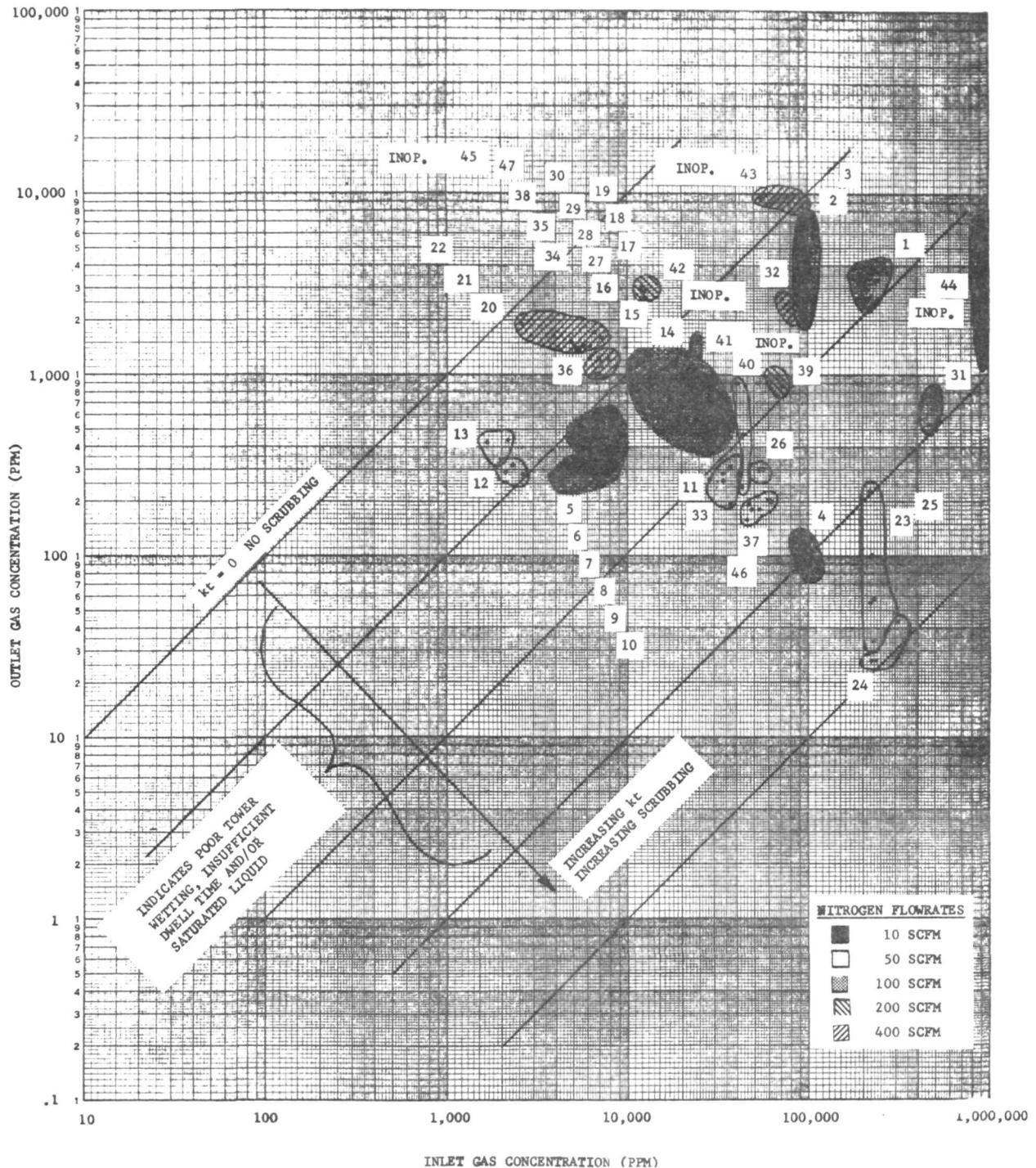
Figure 2-1
N_2O_4 Scrubber with NaOH Sump Solution Inlet Gas Concentration (PPM)
vs Outlet Gas Concentration (PPM) for Various Nitrogen Flowrates

FIGURE 2-2: EFFECT OF NITROGEN
FLOWRATE ON OUTLET
CONCENTRATION

FIGURE 2-3: EFFECT OF NUMBER OF
TOWERS ON OUTLET
CONCENTRATION

NOTES:
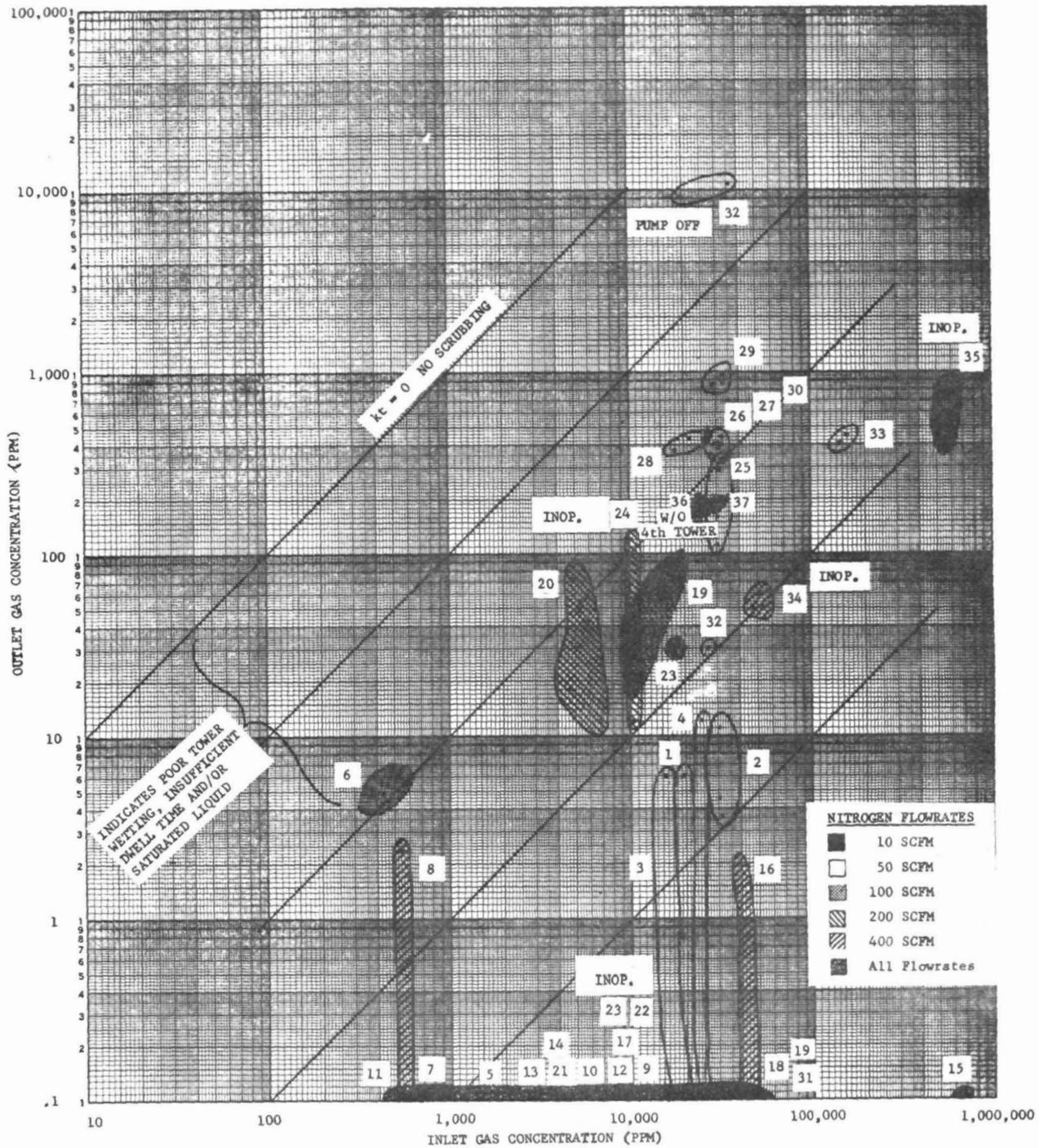1. LIQUOR FLOWRATE = 145-147 GPM
2. NaOH CONCENTRATION = 2.16-2.80 %
3. OPERATIVE MODE
   O $\dot{Q}_{N_2}$ = 50 SCFM
   △ $\dot{Q}_{N_2}$ = 100 SCFM
4. DATA NORMALIZED TO C_{IN} = 10000 PPM

OUTLET CONCENTRATION ~ PPM
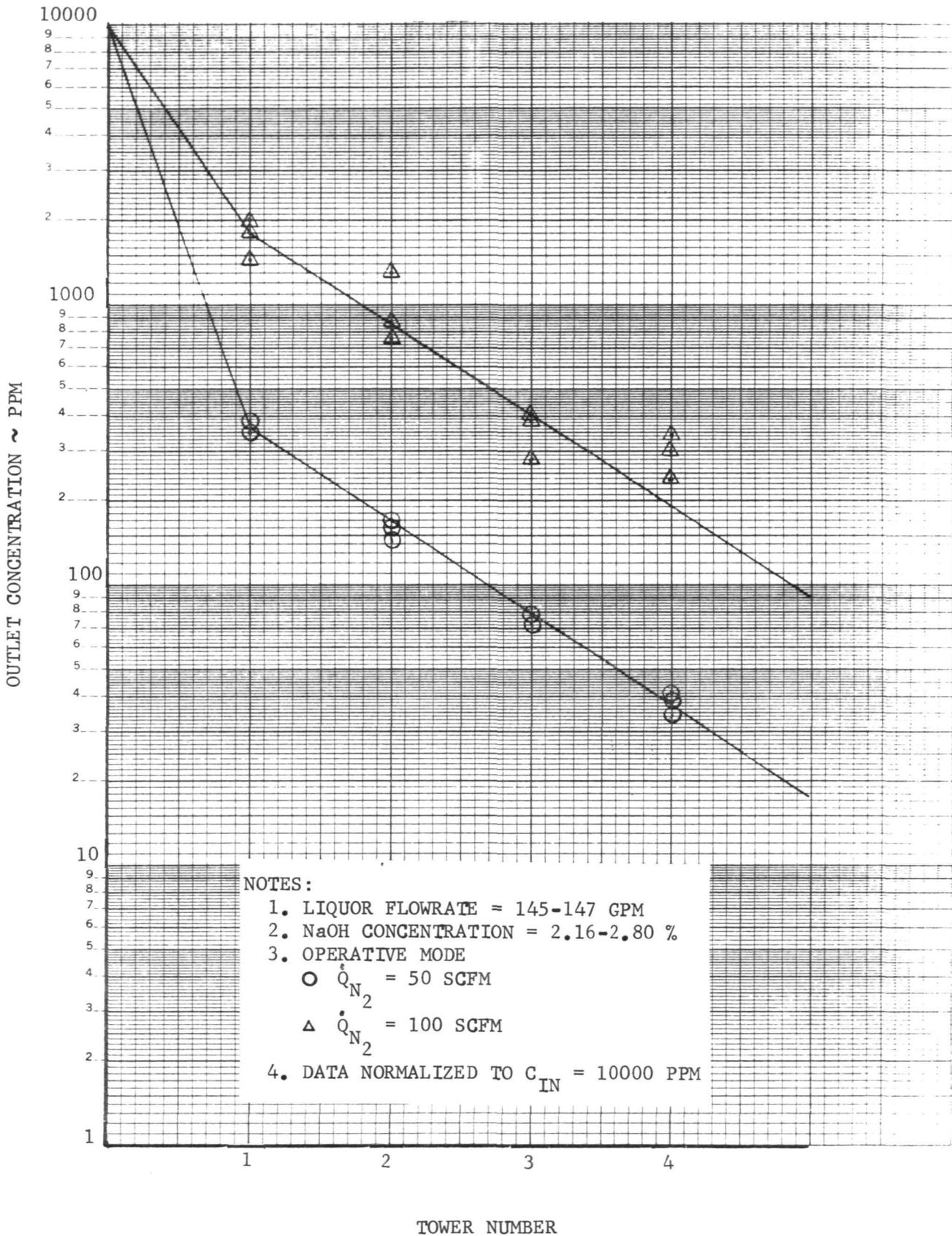
TOWER NUMBER

FIGURE 2-4: EFFECT OF NUMBER OF
TOWERS AND GAS FLOWRATE
ON EFFECTIVE ABSORBTION

NOTES:
  1. OPERATIVE MODE
     $\bigcirc$ $\dot{Q}_{N_2}$ = 50 SCFM

     $\triangle$ $\dot{Q}_{N_2}$ = 100 SCFM

NOTES:
  1. INOPERATIVE MODE

TOWER 4 IS WET

123
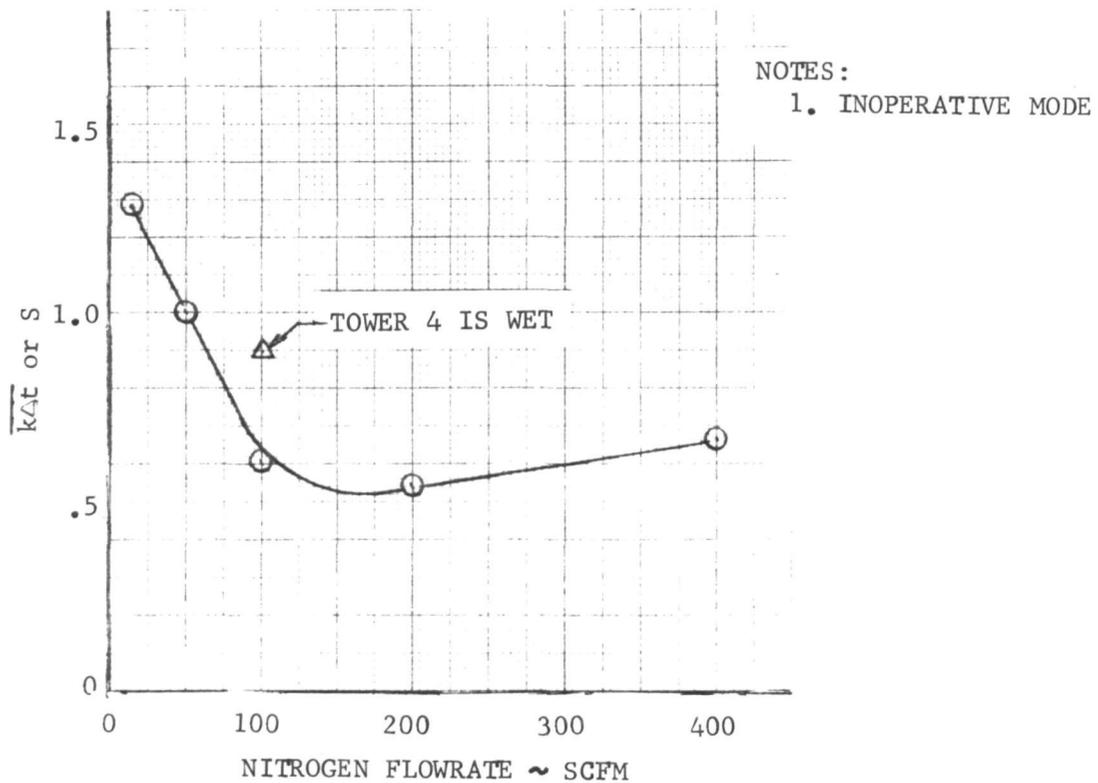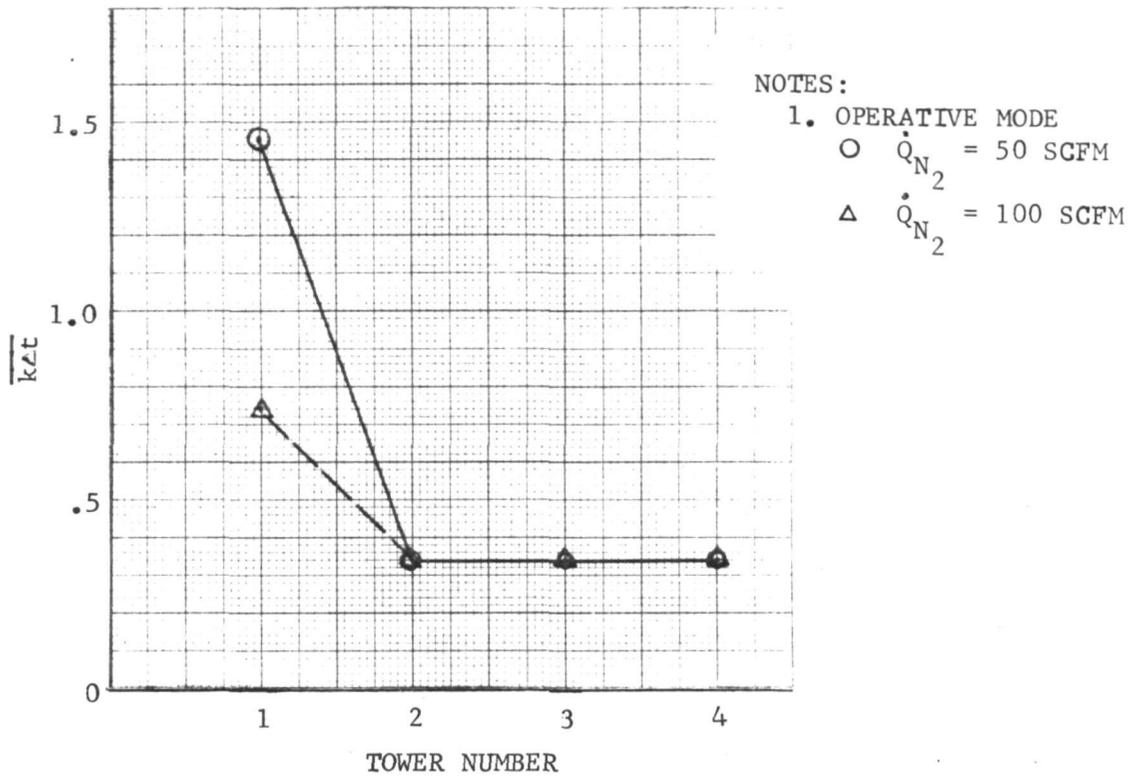
FIGURE 2-5: EFFECT OF LIQUOR
FLOWRATE ON OUTLET
CONCENTRATION

OUTLET CONCENTRATION ~ PPM

NOTES:
1. OPERATIVE MODE
   ◇ Q_{N_2} = 200 SCFM
   □ Q_{N_2} = 400 SCFM
2. NaOH CONCENTRATION = 5.5-6.8 %
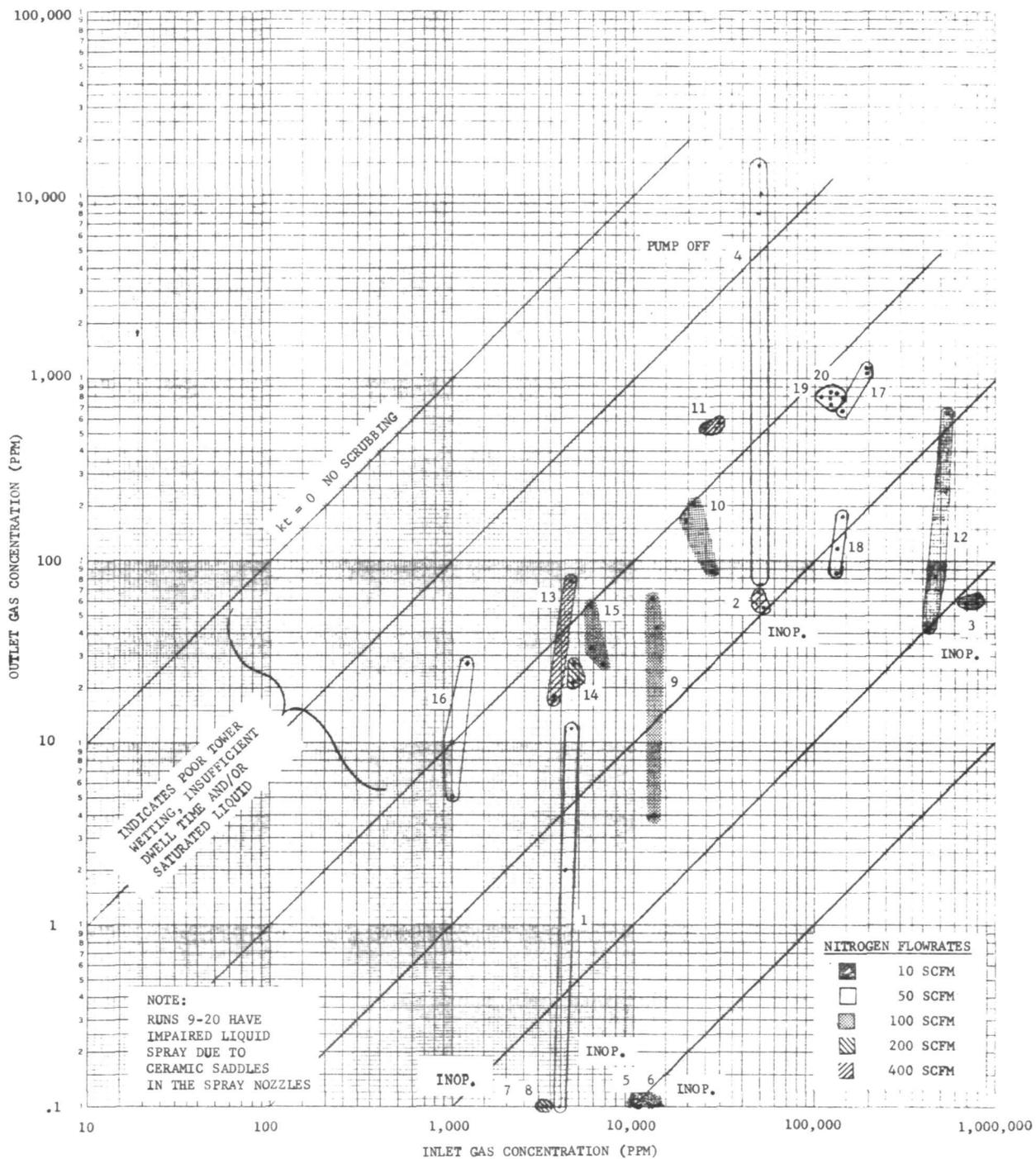3. DATA NORMALIZED TO C_{IN} = 10000 PPM

LIQUOR FLOWRATE, Q_L ~ GPM

124
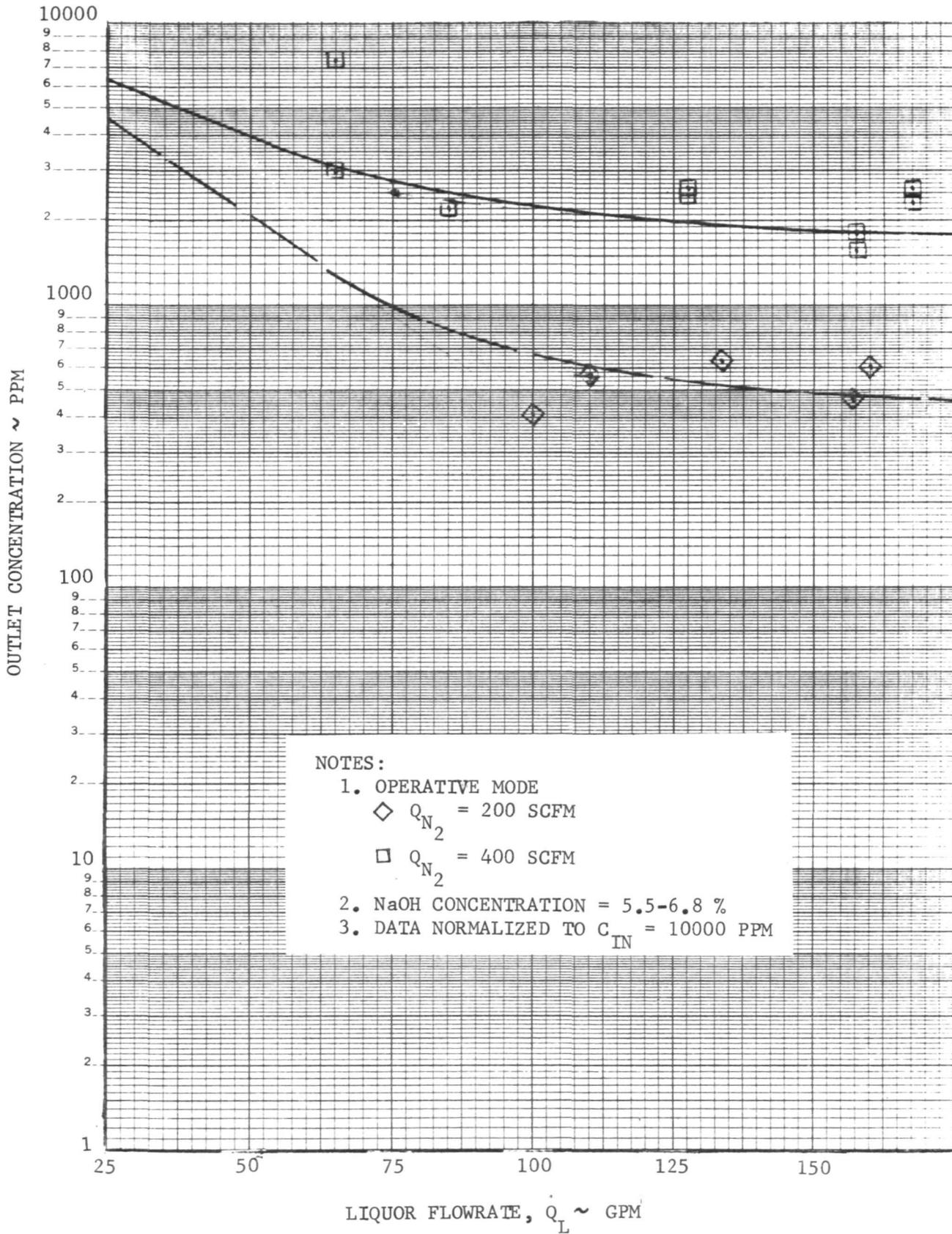
Figure 3-1
N_2O_4 Scrubber with Na_2SO_3 Sump Solution Inlet Gas Concentration vs
Outlet Gas Concentration for Various Nitrogen Flowrates

FIGURE 3-2: EFFECT OF TOWER
DRYING TIME ON OUTLET
CONCENTRATION

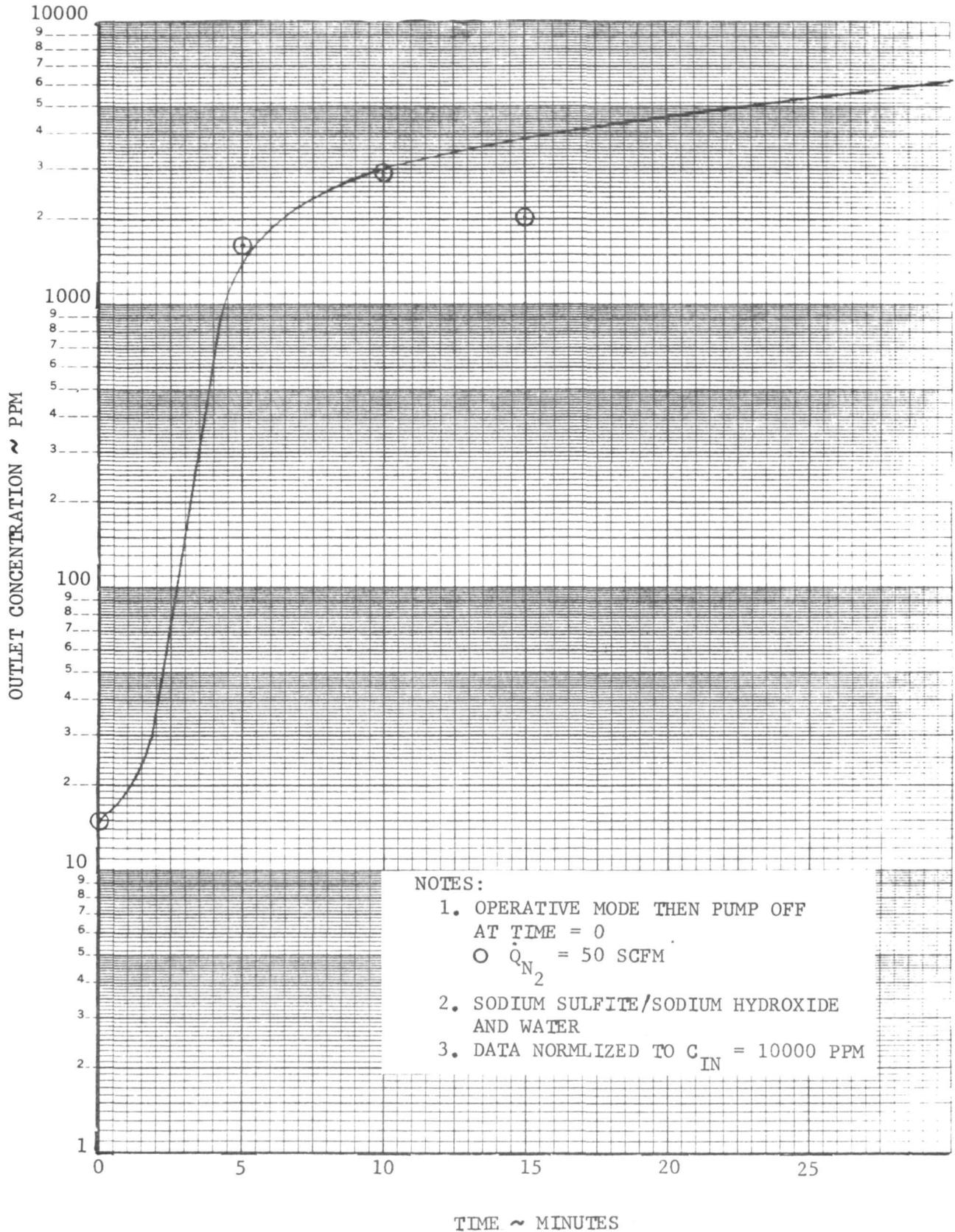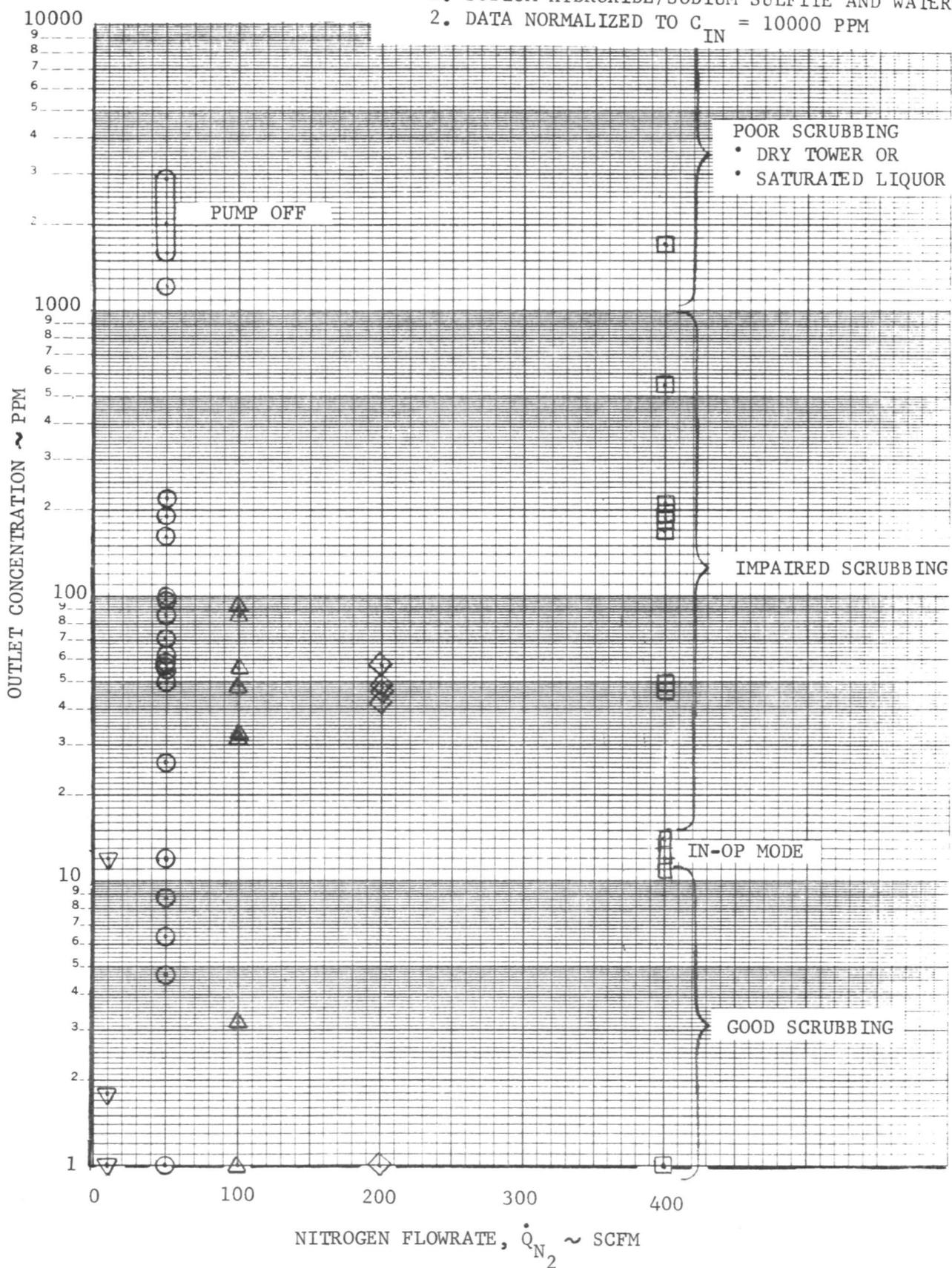OUTLET CONCENTRATION ~ PPM

NOTE:
1. OPERATIVE MODE THEN PUMP OFF
   AT TIME = 0
   O $\dot{Q}_{N_2}$ = 50 SCFM

2. SODIUM SULFITE AND WATER
3. DATA NORMALIZED TO C_{IN} = 10000 PPM

TIME ~ MINUTES

126
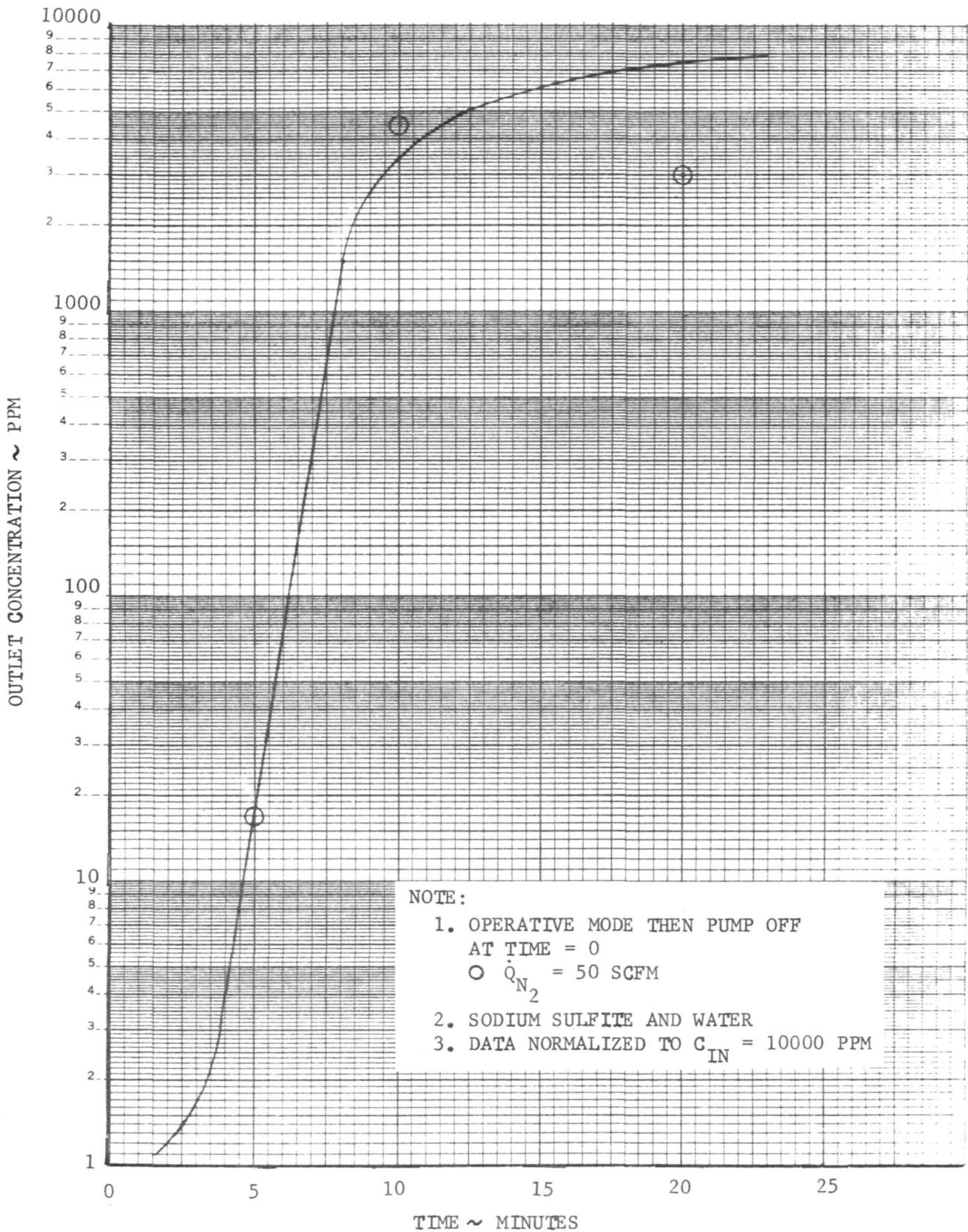
FIGURE 3-3: EFFECT OF LIQUOR
FLOWRATE ON OUTLET
CONCENTRATION

NOTES:
1. OPERATIVE MODE
   O $\dot{Q}_{N_2}$ = 50 SCFM
2. SODIUM SULFITE AND WATER
3. DATA NORMALIZED TO C_{IN} = 10000 PPM

OUTLET CONCENTRATION ~ PPM

LIQUOR FLOWRATE, $\dot{Q}_L$ ~ GPM

127
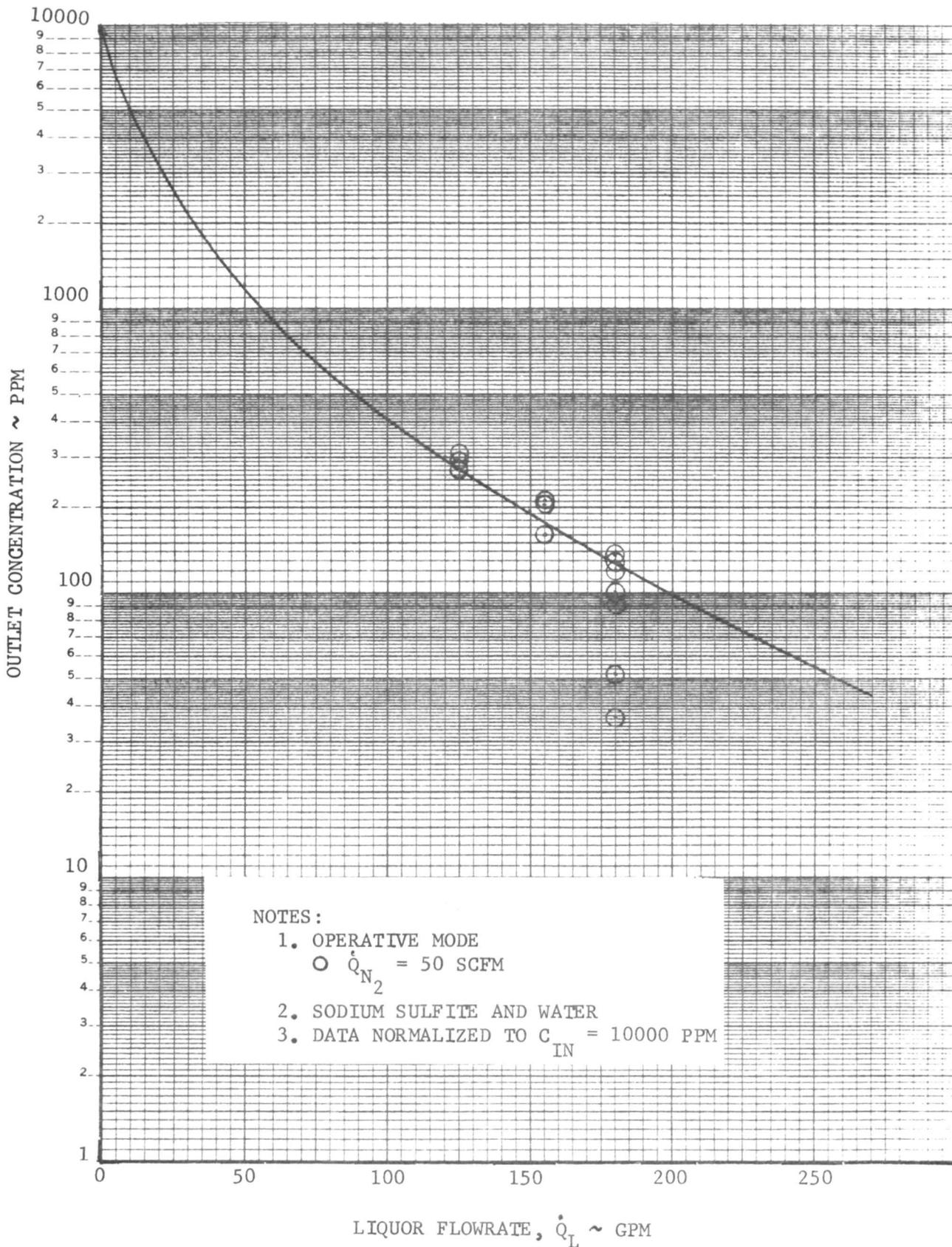
Figure 4-1
N_2O_4 Scrubber with $NaOH/Na_2SO_3$ Sump Solution Inlet Gas Concentration
(PPM) vs Outlet Gas Concentration (ppm) for Various Nitrogen Flowrates

128

FIGURE 4-2: EFFECT OF TOWER
         DRYING TIME ON OUTLET
         CONCENTRATION

NOTES:
1. OPERATIVE MODE THEN PUMP OFF
   AT TIME = 0
   O $\dot{Q}_{N_2}$ = 50 SCFM

2. SODIUM SULFITE/SODIUM HYDROXIDE
   AND WATER
3. DATA NORMLIZED TO C_{IN} = 10000 PPM

OUTLET CONCENTRATION ~ PPM

TIME ~ MINUTES

129

FIGURE 4-3: EFFECT OF TOWER/LIQUOR
CONDITION ON OUTLET
CONCENTRATION

NOTES:
1. SODIUM HYDROXIDE/SODIUM SULFITE AND WATER
2. DATA NORMALIZED TO C_{IN} = 10000 PPM

POOR SCRUBBING
• DRY TOWER OR
• SATURATED LIQUOR

PUMP OFF

IMPAIRED SCRUBBING

IN-OP MODE

GOOD SCRUBBING

OUTLET CONCENTRATION ～ PPM

NITROGEN FLOWRATE, $\dot{Q}_{N_2}$ ～ SCFM

ULTIMATE DISPOSAL OF SCRUBBER WASTES

by

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ABSTRACT

Part of the initial concern with using the wet scrubbers on the hypergolic propellants was the subsequential disposal of the liquid wastes. To do this, consideration was given of all possible methods to reduce the volume of the wastes and stay within the guidelines established by the state and federal environmental protection agencies.

One method that was proposed was the use of water hyacinths in disposal ponds to reduce the waste concentration in the effluent to less than EPA tolerable levels. This method was under consideration and even in use by private industry, municipal governments, and NASA for upgrading existing wastewater treatment facilities to a tertiary system.

At the present, Battelle Memorial Institute, National Space Technology Laboratories/NASA, and Florida Institute of Technology feel the use of water hyacinths in disposal ponds appears to be a very cost-effective method for reduction and disposal of hypergolic propellants.

ULTIMATE DISPOSAL OF SCRUBBER WASTES

Part of the initial problem with using the wet scrubbers on vented hypergolic propellants was the ultimate disposal of the liquid scrubber wastes. Hence, consideration was given to all possible methods of reducing the amounts of nitrogen in the wastes to stay within the guidelines established by the state and federal agencies. These guidelines require that the total Nitrogen discharged to any body of water be no more than 5.0 ppm.

One proposed method was the use of water hyacinths in disposal ponds to reduce the waste concentration in the effluent to acceptable levels. It was postulated that hyacinths may absorb NO_3^-/NO_2^- from N_2O_4 scrubber wastes.

A literature search was made preliminary to initiation of test runs in the Prototype Disposal Pond at KSC or at FIT to acquire a better background on the bioassimilation method for removal of pollutants from water.

At the present, operational waste water treatment plants utilizing water hyacinths as part of a functional design are in use by private industry, municipal governments, and NASA. These uses include new facilities and the upgrading of existing waste water treatment plants to a tertiary system. Examples are: General Development Corporation, Palm Bay, Fl, Disneyworld, Lake Buena Vista, Fl., and NASA, National Space Technology Laboratories, Bay St. Louis, Miss.

This is, in fact, not a new concept. Suggestions for this application date back at least to the 1940's, but recent emphasis on

132

on improved water quality has created a situation in which the hyacinth's capabilities have great potential value.

The approach to utilizing water hyacinth for absorption of oxidizer and fuel wastes is to introduce the diluted wastes into PVC-lined ponds, of proper size and depth, the surface of which is covered with a mat of hyacinth plants. Several favorable characteristics of the hyacinth exist which make it attractive for this purpose. For example, the high absorption capability for nitrogen-containing compounds for rapid depletion of pollutants, its rapid growth rate, the ability to withstand relatively high concentrations of the toxic materials, the ability to service a wide pH range of 4 to 10, together with the relative ease of harvesting the large, free-floating plants have made the water hyacinth an attractive plant choice for this purpose.

To understand the use of hyacinths, one must know about the plants and its characteristics.

The water hyacinth (Eichornia crassipes) is a flowering aquatic plant found in waterways of tropical and semitropical areas around the world. It currently grows throughout Florida, in southern Georgia, Alabama Mississippi, Louisiana, and in parts of Texas and California. The plant is sometimes found rooted in soil, but more commonly is free-floating, drawing nutrients from the water. The individual plants are of moderate size, measuring perhaps 50 cm from root tip to the top of the flower cluster. Typical weight is 1 kg, of which 95 percent is water.

The hyacinths have been designated a noxious weed by the federal government because of the plant's tendency to form dense mats. which interfere with most waterway uses. Under favorable growth conditions, spreading of hyacinths mats can be extremely rapid, doubling total plant mass in periods of a few weeks.

The disposal pond size requirement is dependent on several factors. The first factor is the quantity of each pollutant to be disposed of per unit time. The pond size will be directly proportional to the total amount of hypergolic wastes generated at KSC which have to be treated. The pond size will further depend on maintaining the concentrations of the wastes in the pond water to below the harmful limits of each waste. The "safe" limits for both N_2O_4 and MMH wastes were established by trial runs in 50 gal. tanks. An advantage arising by simultaneous treatment of both wastes is one of economy. Less chemicals for pH adjustment is required as a result of the self-neutralizing feature. In very dilute solution no odor problems were observed nor are other problems, as chemical burns, animal deaths, etc., expected.

The second factor, the degree of pollutant removal required, may have a significant effect on pond size. The more stringent the liquid effluent requirement adopted, the larger the pond area or the longer detention time will be necessary for reducing pollutant concentration to acceptable limits prior to discharging the pond water to surface water or to ground disposal.

The third factor, hyacinth growth rate was obtained from literature for central Florida estimating a minimum of 10 to a high of 80 tons dry weight per hectare year. Hyacinth growth rate is not uniform the year round. In central Florida a short period during winter may occur in which

134

growth is slow due to freezing air temperature.

Temperature is of paramount importance in the design of a pond system. It affects photosynthetic O_2 production, hyacinth growth rate, as well as other biological reactions. The optimum temperature range for maximum hyacinth growth rate is 22-27°C. Limiting lower and upper values were reported to be 2°C and 35°C, respectively.

When the water temperature decreased to freezing, the hyacinths are highly susceptable to damage or death. A similar situation occurs when water temperatures approach 35°C. At that point, the beneficial algal population will be severely curtailed. Such high temperatures were not observed at the disposal pond during the time of testing.

Light intensities are relatively high in mid-Florida, even during winter months. Hyacinth growth or development is slowed during winter months, consequently reducing the permissible loading per unit pond surface area at this time. If pond loadings are maintained below critical levels so that hyacinth development and the resultant photo- synthetic activity maintains aerobic conditions, then water stabiliza- tion and nitrate removal can be still effective in winter. The amount of stabilization achieved in winter is 1/3 or less the summer rate in central Florida.

Except for a period of approximately four months in winter, when activity is at its lowest, hyacinth activity is both directly and indirectly responsible for other changes besides oxygenation. The photosynthetic plants are responsible for elevating the pH of the water permitting nitrification with the escape of NH_3. All pond systems have an excellent buffering capacity for balancing out excessive peak loads and extreme pH variations. Various nutrients such as phosphates and trace metallic elements are simultaneously embodied in the plant cells.

135

Thus, if the hyacinths are periodically harvested, the NO_3^-/NO_2^- content, metallic constituents and nutrients of the water are accordingly reduced. It appears, therefore, that as long as a pond remains aerobic, climatic changes have an effect on water purification.

In addition to seasonal changes, the nutrient content of hyacinth varies with location and water quality. The Kjeldahl N_2 of hyacinth plant from the disposal pond vs a natural plant as a control were found to be 1.96% vs 1.53%, respectively, based on air dried plants.

The essential role of the hyacinth is its ability to assimilate the nitrogen compounds. Previous research demonstrated a high removal of NH_4^+ and NO_3^--nitrogen from waters in which the hyacinths were growing in the laboratory and in farm ponds. The rate of NO_3^- ion uptake was shown to be slower than NH_4^+ ion.

The mineral content of water hyacinth varies with location. Significantly, considerable absorption of some heavy metals, as Fe, Pb, Cr and Cu occurs during the growth of the plant. At NSTL, with the addition of Cadmium to their disposal ponds, there was a reduction of 60% within the first day. This fact can be of interest from the standpoint of providing an alternative means for disposing of the unwanted metallic constituents in plating wastes or miscellaneous chemical wastes. Further, it is believed that simultaneous treatment of hypergolic wastes and heavy-metal containing wastes in a common pond is feasible after suitable dilution.

As will be discussed later, the total nitrogen content at the end of one experimental run was reduced from 118 ppm to 2.68 ppm. This value is below the Florida Department of Pollution Control Regulation, Chapter 17-3

136

criterion for an advanced waste water treatment effluent. Thus, it would be permissable to discharge the pond effluent directly to the ground or a receiving body of water.

The effect of the residual nitrogen on the receiving body of water would be minimal and no worse than the effect from the discharge of secondary effluent now permitted into streams from typical sewage treatment plants.

The estimated costs of these systems can be expected to vary over a wide range, depending on a number of local and particular circumstances. In same cases, lagoons may already be available. In others, adequate land may already be owned by the operating authority. Also, it may be that lagoon construction costs might be cut substantially by use of a labor force from various municipal organizations.

For cost comparison purposes, it was decided to assume that completely new facilities were to be engineered and constructed, with full market prices to be paid for land, equipment, and services. The cost estimates included both operating costs and annualized capital costs. The principal elements are:

     a. Land acquisition

     b. Engineering

     c. Construction

     d. Interest

     e. Labor costs, both direct and indirect

     f. Maintenance and administrative costs, and materials and
        supplies

A cost comparison was made between the construction of hyacinth-based and other waste water treatment systems.

In central Florida, where the hyacinth system can operate year-round, it offers the possibility of meeting all the effluent requirements at a cost of about $.50/1000 gallons. Whereas the hybrid design system will meet all the effluents requirements at a cost of about $.89/1000 gallons. This suggests that the hyacinth system has an appreciable cost advantage, even using full costs.

If land is already owned, or if lagoons are already in existence, hyacinth system costs can be further reduced. In the case of the hyacinth design, if the capital cost can be reduced to a nominal amount the overall cost would be reduced some 20 percent, bringing the cost per 1000 gallons to approximately $.40 in central Florida. This is less than half the cost of the conventional system.

These cost estimates are from reports by NASA's National Space Technology Laboratories and Battelle Memorial Institute.

To prepare the experimental disposal pond, a site was chosen away from any flood areas. The bottom of the pond pit was sloped to allow for draining. The ground was chemically treated to prevent growth of trees or other vegetation. In the graded excavated pit, a hypalon unreinforced liner was installed. This liner was to prevent leaching out of pollutants from the system. Refer to Figure 1.
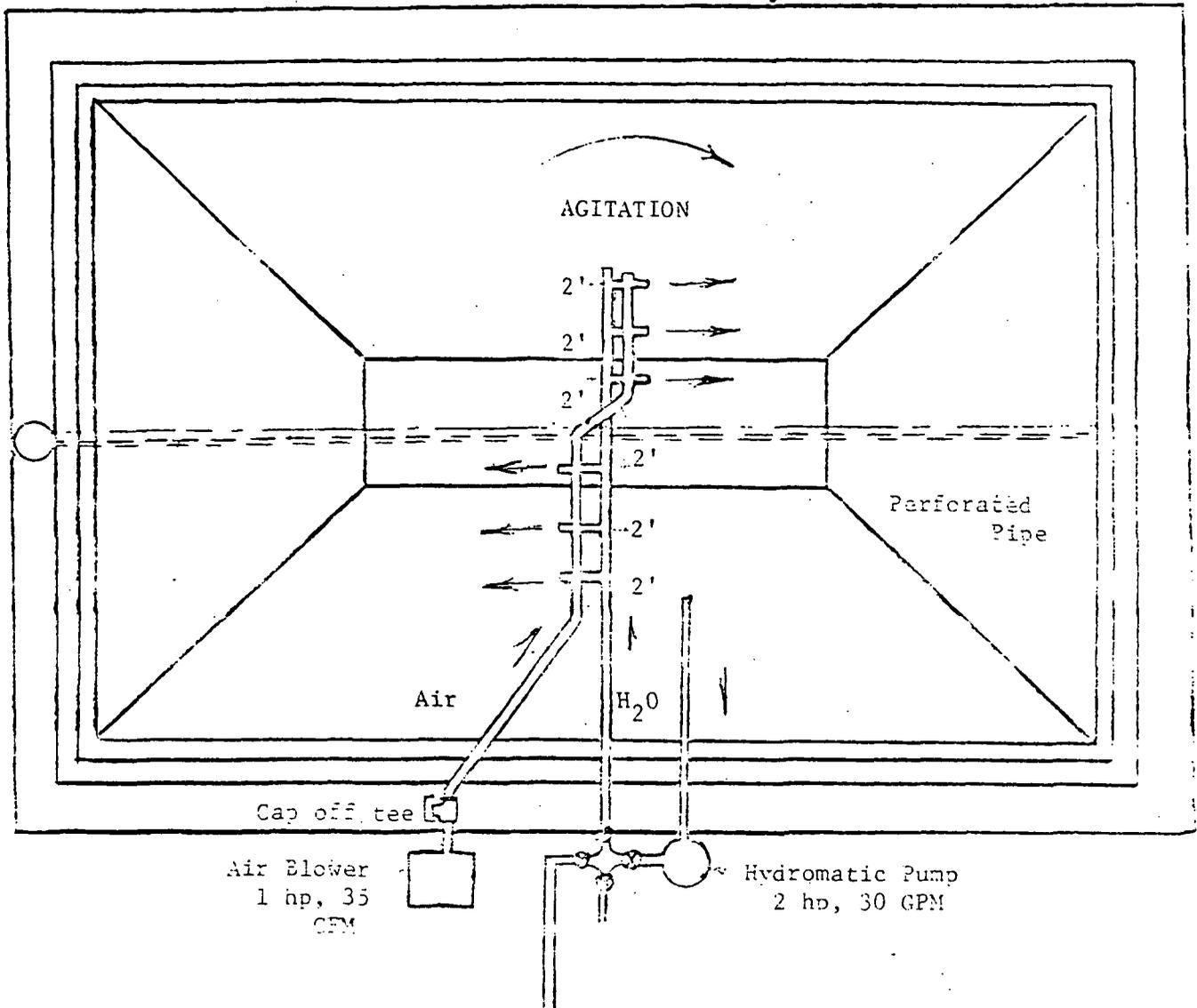
Figure 1.   Schematic of Pond.

The pond was situated conveniently with respect to a supply of water and electrical power for operating pumps and air blowers. The water circulation pump was designed to prevent an anaerobic condition from developing by an occasional turnover of the bottom water layer so as to keep the organic debris in suspension or accessible to dissolved oxygen.   The air blower was installed to provide supplemental oxygen to the system.   The dimension of the pond is 24 x 36 feet with an operating liquid volume of 9000 gallons.   Refer to Figure 2.
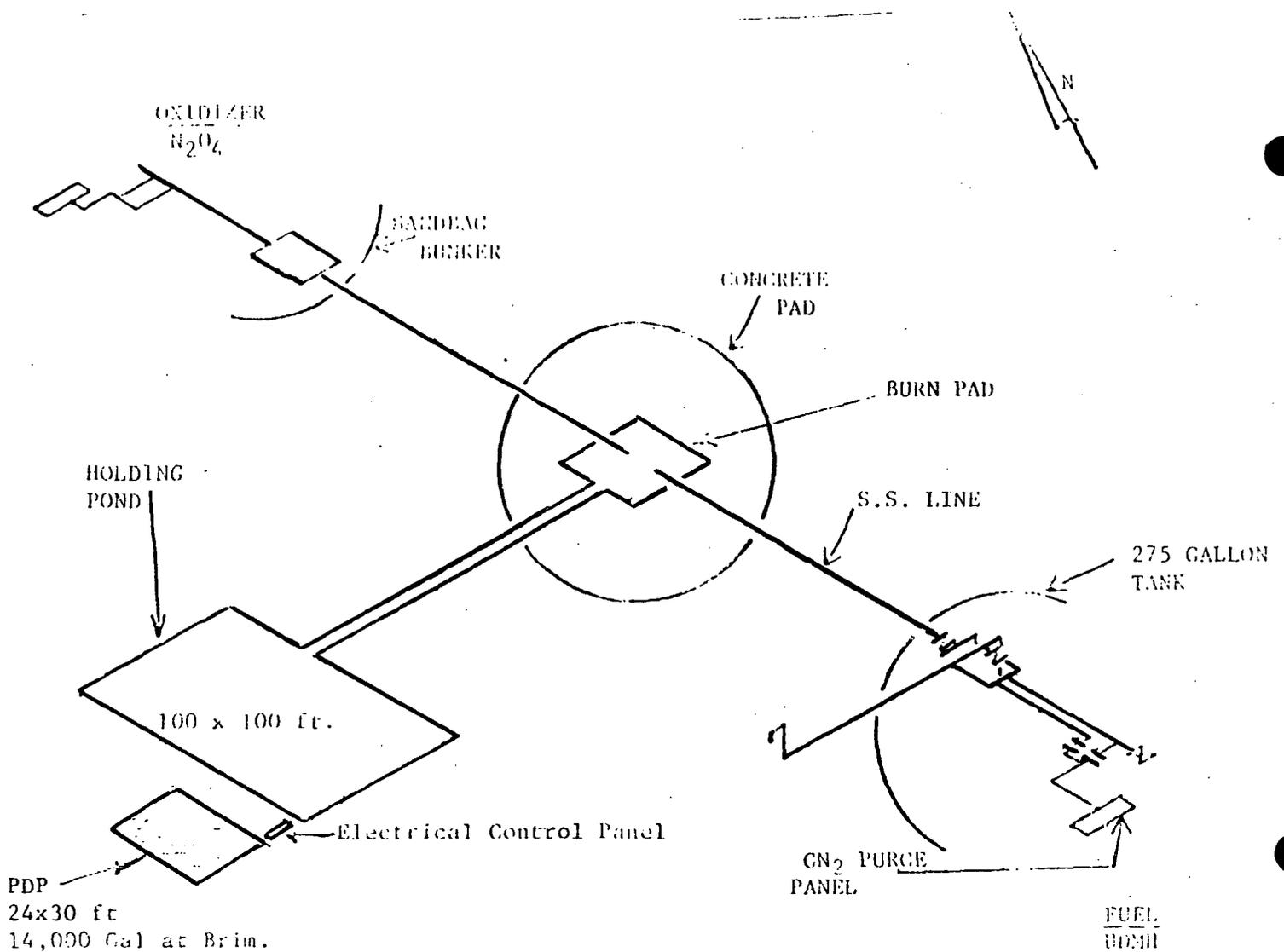
Figure 2. Pond Layout in Fire Suppression
Training Area.

Prior to conducting any experimental runs, it was necessary

to provide a suitable chemical and biological environment to ensure

adequate growth and health for the hyacinths. The following describes

the preparation.

To 8600 gallons of water in the disposal pond, algae inoculum

nutrients, and trace elements were added. The algae inoculum consisted

of two gallons of fresh aerobic digestor sludge from a sewage water

treatment plant. In addition to the algae, the sludge contained the

biota usually found in this material which was necessary for establishing

a balanced ecological system.

In addition to these elements, trace quantities of other elements may be expected to occur from the impurities of the chemicals as well as from the dissolved and suspended materials naturally present in the water used to fill the pond.

Four days were allowed for the pond to come to chemical and biological equilibrium prior to stocking with hyacinths. After stocking, two days were allowed to acclimate the plants to the new surroundings.

The objectives of Run #1 (N_2O_4/hyacinth) are:

(1) to determine the fall-winter NO_3^-/NO_2^- uptake rate of water hyacinths.

(2) to discover potential problem areas in operating such a pond

(3) to observe the feasibility of utilizing hyacinth as a method for destroying N_2O_4 wastes.

After preparing the pond as described in the previous section, Run #1 was started on November 11, 1976, which was 0-day for timing purposes. On this day, first a circulatory motion was established in the pond by means of the jet eductors. Then four liters of pure N_2O_4 were slowly introduced over a two hour period to minimize local pockets of high NO_3/NO_2 concentrations which could seriously damage the plants.

Prior to adding the N_2O_4, pH was 9.9 on Nov. 11, 1976. After addition the pH dropped drastically to 3.6. As a result of this low pH the algae in the pond were severely damaged and practically disappeared in all but isolated pockets. The hyacinth survived this treatment without any visible damage. At the next sampling date a week later, however, the pH had risen to 6.0 as a result of the natural buffering action of the plants in the pond. The algae population started to multiply rapidly. After another week pH had risen to 9.4. At this time a pH adjustment was made by addition of Na_2HPO_4 and H_3PO_4 for two purposes.

141

One, to decrease pH to the more favorable natural level and two, to increase phosphate to approximately the 20 ppm level. Henceforth, pH changes were within several tenths of the neutral point (the pH preferred by hyacinth).

Water samples were taken at weekly intervals or more frequently for the duration of the run to follow the progress of nitrogen uptake and other changes. The sample consisted of an integrated 1 gallon of water collected from 10 equidistant points around the perimeter of the pond, 6 or more inches below the water surface. On the spot analysis of dissolved oxygen was performed on a top and bottom water sample. These data were used in interpreting the results. Analyses on the collected sample were performed at FIT on the same day or samples were stored in a refrigerator at $4^{\circ}C$ for the next day. The test methods used were as given in "Standard Methods, Water and Waste Water" 13th edition. Refer to Chart 1.

Chart 1.   Analytical Data for Run #1 PDP

Days	NO_3^- (ppm)	NO_2^- (ppm)	NH_4^+ (ppm)	Total Nitrogen	$0-PO_4$ (ppm)	D.O. (mg/l)	pH	Turbidity F.T.U.	True Color
0	462	41.25	0.67	118.05	2.9	----	3.6	25	50
+12	392	24.75	4.45	100.15	4.0	T:6.0 B:3.5	9.4	35	51
+20	348	18.98	2.60	86.90	21.3	9.5	7.6	30	5
+27	312	16.50	1.50	77.20	20.5	T:7.6 B:7.2	7.3	40	20
+40	255	0.12	0.44	58.40	18.50	T:8.4 B:6.2	6.9	20	20
+50	275	0.83	4.60	66.50	17.50	T:9.4 B:4.2	6.9	15	35
+57	9	0.03	0.32	2.27	15.50	T:11.4 B:8.6	7.5	25	5

The NO_3^- uptake by hacinth in the disposal pond during the winter period of mid-Nov. 76 to mid-Jan. 77. The results show an initial slow decrease in NO_3^- from the 462 ppm peak level to approximately the 280 ppm level in a 50 day period, then a rapid decrease to the 10 ppm level in the succeeding 8 day period, and finally a very slow drop to the 6 ppm level occurring in the next 16 days. At this point the run was terminated. The 10 ppm level was arbitrarily selected as a target to indicate completion

of a run. Fluctuations of the NO_3^- in or about this level will occur naturally due to the decomposition of proteinaceous materials in teh organic detritus. The rapid NO_3^- uptake occurring in the 8 day period was partly attributed to the observed algal bloom. The very slow uptake occurring in the last stage can be accounted for by the after effects of the near freeze and the freeze which caused a die back of the hyacinth plants. The subsequent decomposition of dead plant tissues releases a small amount of NO_3 salts into the pond water.

The rate of NO_3 absorption during the winter months in Run #1 was found to be 64.4 lbs. NO_3 per acre day in a pond containing approximately 3-1/2 feet of water with an average 70% hyacinth coverage.

It is evident that the NO_2^- was reduced from a peak of 41 ppm to below 1 ppm then rose to 4.5 and dropped to below 1 ppm after 57 days. The NO_2^- was reduced to the low level at about the same time as NO_3^-.

A second $o\text{-}PO_4$ addition was made to the pond on 12-2-76 in order to increase the concentration to a preferred level. A slow decrease in $o\text{-}PO_4$ is shown for the duration of the run.

The amount of NH_4^+ was increased from almost nil up to the 4.5 ppm level in about a 6-day period then dropped to below 1 ppm and finally increased to about 12 ppm at the 57th day. This increase is related to the die-back of the hyacinth as a consequence of the cold snap occurring at the same time.

A near kill of the algal population resulted after the introduction of 4 1 N_2O_4 into the pond in order to increase the NO_3^-/NO_2^- concentrations desired from the existing temporary levels of 228 ppm/0.27 ppm to the final

144

desired levels of 462 ppm/41 ppm respectively. The hyacinth survived this shock addition with minimal visible effect. After one or two weeks the algal population reappeared in large numbers.

At the start of Run #1 the pond was initially filled to contain approximately 8,600 gallons of water. Chloride (Cl^-) picked up by hyacinth is considered to be minimal. Therefore, the Cl^- concentration in the pond water was used to monitor the water level. The Cl^- remained essentially the same from start to finish of the run. The small variation shown is considered an experimental error with our method of analysis. Thus, the Cl^- concentration does not show either a dilution effect that can be attributed to rain or an evaporation effect, i.e. the volume of water was fairly constant during the run.

The NO_3^- was increased to 462 ppm; the apparent free Cl_2 rose to above .6 ppm. Then, as NO_3^- decreased to 253 ppm, the apparent Cl_2 decreased to .02 ppm. For this reason the tests for free Cl_2 were discontinued since they have no significance. Two hyacinth stockings were made, first on Nov. 14, 1977, second on Nov. 18, 1976, resulting in 60% coverage. Due to plant growth and a small increase in the number of plants the coverage increased to approximately 85% near the end of the run.

The occurrence of freezing weather in the 2nd week of January resulted in severe damage. Approximately 90-95% of the exposed parts of the plants turned brown. Patches of ice were observed on the pond surface

145

and the water temperature was at the freezing point. The cold snap coincided roughly with the end of the run on the 57th day. However, data collection was continued until January 21. Hyacinth coverage was difficult to judge but estimated at about 10%.

The turbidity in water is caused by the presence of suspended matter, such as clay or inorganic or organic matter. The increase in turbidity was due almost entirely to the increase in the population of algae rather than from suspended solids. Turbidity increased from 18 FTU to a high of 52 then decreased to 19 on the 57th day. As the nitrogenous compounds were used up, turbidity dropped to about the original level. Color in water may result from the presence of humus, plankton, weeks, etc. True color, as used herein is the measurement obtained from the sample from which turbidity has been removed by means of centrifugation. Apparent color is determined on the original sample without any pretreatment. True color fluctuated rather widely. Apparent color reached a peak coinciding with that of turbidity, which then decreased. Both measures decreased toward the end of the run.

The analysis of dissolved oxygen (DO) is a key test in water pollution control activities. The samples taken either from four inches below the water surface or from the bottom of the pond. The latter samples were obtained by means of a sampler assembly used for this purpose.

Measurements were made on site because of the instability
of the samples on storage. Both D.O.'s roughly parallel each other.
The water temperatures were taken for certain samples. The lowest
bottom reading obtained was 3.5 ppm, the highest top sample reading
was 12.1 ppm obtained on Nov. 16, 1976. The lower than normal air
temperature during Run #1 probably explains the higher than expected
D.O. level found in the pond containing a mat coverage of up to 80%.

The D.O. level is an important consideration in maintaining
the desired aerobic conditions in the pond.

The Nitrogen-Phosphorus Ratio (N/P) was 125 immediately
after adding N_2O_4 to the pond, but within 6 days decreased to 69. An
addition of $NaHPO_4$ and H_3PO_4 was made on the 12th day. From the 14th
to the 50th day the ratio did not vary greatly. However, the ratio was
sharply reduced during the algal bloom period and was decreased to about
the .5 level for the duration of the run which extended to the 72nd day.
During the algal bloom period the NO_3 was reduced to the 10 ppm or lower
level by the hyacinth-algae.

Chart 2.   COD Results on Filtered Sample
From PDP

Days	COD mg/l	Agit/n.Agit	Comments
0	69.5	AGIT	
6	44.4	NA	
6	46.3	AGIT	
6	24.3	NA	Large KSC Pond
6	19.3	-	KSC Tap H_2O
12	38.6	SHORT AGIT	
14	42.4	AGIT	
20	38.6	NA	
23	Not tested	AGIT	

147

The Chemical Oxygen Demand (COD) determination provides a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. It is an important parameter in stream and industrial waste studies. Refer to Chart 2.

The change in COD is a slow decrease from about 89 mg/l to 42 mg/l over a 10 week period. Filtered samples were used in the test to remove the large amount of algae present in the pond water. Therefore, the results reflect only that portion of soluble organic or oxidizing matter that was present in the filtrate. Interpretation of these data is inconclusive since a correlation with uptake of any nutrient, hyacinth coverage or other easily observable relationship could not be found. Consequently, COD testing was curtailed after the 12th water sample.

This run showed that various forms of soluble nitrogen-containing material in the pond water were bioassimilated by the aquatic biota. The major TN absorbed was attributed to the hyacinth because of their larger biomass. The fall uptake rate was 16.4 lbs TN/acre-day.

Of great importance, it was shown the feasibility of the moving soluble N_2 compounds (up to 460 ppm NO_3) from water by hyacinths existed.

It was estimated that the disposal pond had a maximum resident population of approximately 3760 hyacinth plants at the end of Run #1. The increase from the initial 50% mat coverage to the final 75% coverage after a 6 weeks period was attributed mostly to increase in plant size rather than any substantial increase in the number of new plants.

Run #4 was set up and performed with objectives similar to Run #1 except the ratio of NO_2^- to NO_3^- was considerably higher than in Run #1, and the volume of water was greater. Again, upon the addition of pure N_2O_4 it was not neutralized. The sampling and analytical procedures utilized were similar to those described for Run #1. The purpose of Run #4 was to determine the results for winter. A second purpose was to observe the effect of a high NO_2^- concentration on hyacinths. The pH was maintained above 6.0 during addition of the N_2O_4 by adjustment with NaOH solution.

The condition of the hyacinth in the pond at initiation of Run #4 was fair to poor. The plants were recovering from the effects of the freeze which occurred a few weeks previously.

A freeze or near freeze occurred on February 17, 1977, causing severe damage to the hyacinth.

Chart 3. Analytical Data for Run #4 PDP

Days	NO_3^- (ppm)	NO_2^- (ppm)	NH_4^+ (ppm)	Total Nitrogen	$O-PO_4$ (ppm)	D.O. (mg/1)	pH	Turbidity F.T.U.	True Color
0	135	33.00	1.16	40.7	19.3	---	6.3	28	30
5	121	13.20	1.34	31.5	18.5	T:12.6 B:4.2	6.7	32	75
13	37	0.17	1.34	8.6	18.5	T:7.4 B:4.0	6.5	40	75
27	16	0.40	1.65	4.2	16.5	T:6.4 B:2.5	6.8	30	100
33	16	0.15	2.20	3.8	18.0	T:11.4 B:2.8	7.2	28	100
40	17	0.11	1.71	3.6	---	T:9.25 B:4.75	7.0	--	---

Six water samples were taken during the run. For purposes of calculating the nitrogen uptake rate, run duration was set at 35 days though data was collected for 40 days. The NO_3/NO_2 were reduced from the 135/33 ppm to the 17/.11 ppm levels, respectively. Refer to Chart 3.

The TN was reduced from 40.7 to the 3.6 ppm level; $O-PO_4$ decreases slowly with time. Turbidity increases from 28 to 40 then decreases to 28 FTU.

The coverage of live plants was reduced to about 10% after the freeze of Feb. 17 due to the poor initial condition of the plants combined with adverse cold weather periods. The rate of nitrogen absorption from the pond was greatly reduced.

The comments made in Run #1 apply as well to Run #4 for the following tests: pH, Cl^-, MMH, color, and D.O. The differences are those of degree and of not too much consequence.

The NO_2 concentration in Run #4 was 33 ppm compared to 41 ppm in run #1. No pronounced toxicity effects, at least easily observable effects, were noted on the hyacinth due to the high NO_2/NO_3 ratio. The algae may have suffered a slight decrease immediately after N_2O_4 addition, but at the next sampling period, a week later, the algae appeared to be unaffected.

Due to the cold temperature during Run #4, damage occurred in the 3d week into the run, resulting in low nitrogen uptake. The TN uptake rate was calculated to be 9.76 lbs/acre-day.

Thus, the TN uptake rate was lower in run #4 than in run #1 in which a rate of 16.6 lbs/acre-day was obtained.

The experiences with Runs #1 and 4 provides useful design information. Also, one is able to predict that a hyacinth recovery period of several weeks may be necessary for new growth and damage repair in winter

150

months. In the event of a hard freeze in central Florida, which is unlikely, it is conceivable for extensive irreparable damage to occur, h-cessitating hyacinth restocking.

The winter rate of TN uptake is strongly dependent on air temperature. A rate of about 10 lbs/acre-day may be expected in the event of a mild freeze that damages the leaves of the hyacinth; or considerably less if both leaves and roots are damaged.

If a freeze factor is incorporated into the design equations for the hyacinth pond-disposal system, the TN uptake would be increased.

Run #A-3 was set up and operated with objectives similar to Runs #1 and 4, primarily to determine the spring NO_3^-/NO_2^- uptake rate of water hyacinth. The N_2O_4 was added and again not neutralized.

The general condition of the weather had improved with a warming trend. The hyacinths were in good shape at the initiation of Run #A-3.

During the run, a total of five samples were taken over a duration of 19 days. Refer to Chart 4.

Chart 4. Analytical Data for Run A-3 (N_2O_4/Hyacinths)

Days	NO_3^- (ppm)	NO_2^- (ppm)	NH_4^+ (ppm)	Total Nitrogen	$O-PO_4$ (ppm)	D.O (mg/l)	pH	Turbidity F.T.U.	True Color
0	282.	116	--	97	28.0	--	5.4	120	70
1	262.	114	--	95	27.2	--	5.6	--	--
7	142.	56	--	51	22.5	--	7.3	120	74
13	43.	23	--	18	17.0	--	7.1	150	100
19	0.13	0.02	--	1	20.8	--	6.8	85	96

The NO_3^-/NO_2^- were reduced from 282 to 0.13 ppm and 116 to 0.02 ppm, respectively.

The TN was reduced from 97 to 1 ppm, and the $O-PO_4$ decreased at a slow rate compared to TN rate.

The turbidity and true color increased with the algal growth present and decreased as the NO_3^-/NO_2^- were utilized.

The plants were maintained at approximately 80% coverage. As the rapid uptake of NO_3^-/NO_2^- occurred, an extreme rate of growth required weekly harvesting of the hyacinths which displayed a rich, green, healthy color. The weekly harvest reduced the coverage from 90-95% back to 80%.

The spring TN uptake rate was calculated to be 41.5 lbs/acre-day.

Run #C-1 was set-up and performed primarily with the objective of determining the summer NO_3^-/NO_2^- uptake rate of water hyacinths. Similar to previous runs, the objectives included the continuation of the feasibility study of utilizing hyacinths as a method for destroying N_2O_4 wastes and observing for potential problem areas in operating such a pond.

Setting up the pond of 10,000 gallons required that six liters of pure N_2O_4 be added to the pond. A critical point was made in keeping the pH within tolerable limits for the hyacinths. This was accomplished by adding two gallons of 5% NaOH for a pH of 9.2. This pH was lowered to 4.4 with the addition of 6 liters of pure N_2O_4. The final pH of 5.4 was established by adding one more gallon of 5% NaOH. Refer to Chart 5.

152

Chart 5.   Analytical Data for Run C-1 PDP

Days	NO_3^- (ppm)	NO_2^- (ppm)	NH_4^+ (ppm)	Total Nitrogen	$O-PO_4$ (ppm)	D.O. (mg/l)	pH	Turbidity F.T.U.	True Color
0	268.4	108.9	1.63	95.38	28.0		5.4	120	500$^{\pm}$
+1	281.6	111.4	1.46	98.95	27.25		5.55	35	
+7	140.8	56.1		50.34	22.50		7.3	120	325
+13	44.0	23.9	1.65	18.60	17.00		7.1	150	400
+19	0.13	0.33	1.16	1.08	20.75		6.8	260	85
+28	0.88	0.007	1.57	1.49	18.00		6.6	245	60

The run required a duration of 28 days during which the NO_3^- was reduced from 268.4 to 0.88 and the NO_2^- from 108.9 to 0.007. The NH_4^+ fluctuated from 1.6 at the start to 1.57 at the end. The TN decreased from 95.38 to 1.49 ppm, and the $O-PO_4$ was appreciably slow in uptake with a starting concentration of 28.0 and final of 18.00 ppm.

The turbidity and true color were initially high due to a very dense population of algae amongst the hyacinths. These values dropped with decrease of algae due to the high concentration of N_2O_4 added to the pond. The turbidity and true color increased as the algae started to reflourish.

Hyacinth coverage was initially 45% and steadily increased to 99% at the end of the run.

If allowed to grow without harvesting, the hyacinths soon out grow their containment (100%+ coverage).

Run #C-3 was organized and operated with these objectives:

1) To observe the feasibility of utilizing hyacinths as a
   method for destroying possible scrubber waste.

2) For determining the NO_3^-/NO_2^- levels of this possible waste
   and its subsequential summer rate of uptake by water
   hyacinths.

The run was started with addition of 50 gallons of 5% NaOH solution
which has been reacted with six liters of N_2O_4 to 8600 gals. water in
the pond. This simulated the addition of N_2O_4/NaOH vapor scrubber liquor
waste to a hyacinth pond under the "worst condition," i.e. high NO_3^-,
high NO_2^-, and high pH. It was noted that the hyacinth survived the
shock of the high NO_3^-/NO_2^- but the algae and pond fauna (insects, snails,
and tadpoles) did not. Refer to Chart 6.

Chart 6.   Analytical Data for Run C-3 PDP

Days	NO_3^- (ppm)	NO_2^- (ppm)	NH_4^+ (ppm)	Total Nitrogen	$O-PO_4$ (ppm)	D.O. (mg/1)	pH	Turbidity F.T.U.	True Color
0	237.6	83.3	3.54	82.15	4.33	T 8.0 B 2.0	10.2	115	305
+3	220.0	85.8	4.15	79.4	6.7	T 3.8 B 0.4	9.2	105	345
+10	213.4	72.6	4.03	73.8	7.7	T 4.0 B 0.0	7.95	67	210
+17	37.0	21.5	1.22	15.9	5.3	T 9.0 B 9.0	8.4	85	220
+24	30.8	0.264	2.68	33.7	3.9	T 4.0 B 0.4	7.9	85	280
+31	31.7	0.237	3.48	10.1	3.83	T 10.0 B 9.0	7.8	108	345
+35	6.6	0.554	3.29	4.4	0.58	T 4.0 B 0.0	7.8	90	340
+38	3.96	0.244	4.88	5.0	0.40	T 3.0 B 0.0	8.3	90	300

This run was completed in 35 days. The NO_3^- was reduced from 237.6 to 3.96 ppm, the NO_2^- was reduced from 83.3 to 0.554 ppm, and the NH_4^+ fluctuated starting at 3.54 and ending with 4.88. There was a drastic reduction at 17 days into the run when the NO_3^-/NO_2^- dropped from 213.4/72.6 to 37.0/21.5 ppm, respectively.

The initial $O-PO_4$ reading of 4.33 was established by the addition of 500 ml of H_3PO_4 to the $N_2O_4/NaOH$ solution. This was reduced to 0.58 ppm.

The pH of 10.2 was high due to the excess of NaOH in the solution. This was lowered by the natural buffering action of the hyacinths.

The turbidity and true color remained about their initial levels due to the large quantity noted in the pond waters.

There was a substantial reduction of TN from 82.15 to 5.0 This calculates to a summer uptake rate of 20.5 lbs TN per acre-day.

The hyacinths grew well on the $N_2O_4/NaOH$ solution with a minimum of supervision, which was primarily for harvesting and sample collection.

At the present, Run B-5 is under progress. This run is to evaluate the reduction of NO_3/NO_2 when a scrubber solution of 5% NaOH/ 18% Na_2SO_3 reacted with N_2O_4 is added to the pond. This material is more than likely to be the actual composition of the oxidizer scrubber waste during the Shuttle era. Since sodium sulfite is a strong reducing agent, a considerable COD problem comes about when the scrubber liquor is discharged to the pond. It is hoped that aeration aids the hyacinths absorption of this oxidizer scrubber wastes.

Based on this study the following overall conclusions were drawn:

(1) Water hyacinth readily assimilate from a dilute solution soluble nitrogen - containing compounds, including N_2O_4, MMH and/or their hydrolysis and/or other reactions products.

(2) The feasibility of the hyacinth pond concept as the ultimate method for destroying N_2O_4 or MMH wastes was fully demonstrated by this investigation.

(3) Nitrogen compound absorption by hyacinth in a pond provides a low cost and efficient means for disposing of N_2O_4 wastes generated at KSC. The hyacinth mats are ultimately disposed of by the low cost sanitary landfilling method rather than harvesting for use as a proteinaceous animal additive. This in large part being due to the very low volume of hyacinth produced in a one, or at most a few, acres of pond surface.

(4) The seasonal influence of temperature does affect the TN uptake rate. Spring has the best growth with a TN uptake rate of 41.5 lbs/day-acre, followed by the summer and fall with 20.5 lbs/day-acre and 16.4 lbs/day-acre. Last is the TN uptake rate of 9.8 lbs/day-acre for winter in spite of the freezing problems encountered. Refer to Chart 7.

Chart 7.   UPTAKE RATES

Season	Lbs Total Nitrogen Per Day – Acre	Comments
Winter	9.8	Freeze Damage to Hyacinth.
Spring	41.5	Period of Greatest Growth
Summer	20.5	
Fall	16.4	

(5) Follow up work is necessary to optimize the operating procedures for both N_2O_4 and MMH for application at NASA and for environmental concerns.

ADVANCED LIFE SUPPORT EQUIPMENT

FOR

NITROGEN TETROXIDE ENVIRONMENTS

March 31, 1978

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Florida 32899

The present life support device for operating in NO_2 environments is the SCAPE (Self-Contained Atmospheric Protective Ensemble), used by both NASA and the Air Force, and also the French in French Guinea. The present suit material is butyl boated nomex per MIL-C-38149. Faceplates are either PVC or acrylic. Boots, gloves, faceplate seal, and cuffs are butyl. To date, there have been no documented exposures to concentrations exceeding TLVs in SCAPE at KSC. Of course, suits are not instrumented and occasionally workers have reported smelling propellants.

From references 4 and 5, tests show that 2/3 of subjects (N=42) tested can detect MMH at .2 ppm (TLV=.2 ppm) and 1/4 of subjects (N=59) tested can detect NO_2 at .9 ppm (TLV=5 ppm). With NO_2, 8 of 59 (13.6%) subjects experienced irritation of the nasal mucosa. Figures 1 and 2 show the effects of breathing NO_2 at .9 ppm or 18% of the present TLV. (So while 5 ppm is the present legal limit, NIOSH has recommended 1 ppm, and this should be the design goal of any SCAPE system.)

Figure 3 shows the locations on the Orbiter of the various fluid commodities. One (1) is N_2O_4; 123 gallons in the forward RCS tank, and in both aft RCS tanks, two 640 gallon OMS tanks for a total of 1650 gallons of N_2O_4. Seven (7) is MMH; 127 gallons in the forward RCS tank and in both aft RCS tanks, two 640 gallon OMS tanks for a total of 1661 gallons of MMH. Two (2) is hydrazine; three tanks for a total of 291 pounds. Three (3) is ammonia; 97.6 pounds, two tanks in the aft.

From the same source document, see Appendix 1, the hazards that personnel engaged in Orbiter crash/rescue operations may be exposed to are:

Unexpended pyrotechnic devices

Toxic fumes

Raw propellants (hydrazine., MMH, and N_2O_4)

Flash fires

High pressures

Hot brakes/wheels (fire/explosion)

Static discharge

Steam/hot water

Propellant (fuel/oxidizer) fires

The first personnel to approach the Orbiter after it has landed, provided it is not on fire, will be in SCAPE (see Figures 4 and 5). The present SCAPE was not designed as a body armor, nor a fire proximity suit, nor is the proposed SCAPE. SCAPE's primary function is to provide a protective envelope about its user that will prevent intrusion of toxic propellants, and maintain the suit interior at or below TLVs with as little inconvenience to the wearer as possible.

The problems of maintaining suit integrity are as follows:

1. Suit material permeability.

2. Sealing of all suit penetrations.

3. Maintaining a positive pressure within the suit, 14" H_2O for SCAPE.

The positive pressure is maintained by a two hour cryogenic backpack worn under the suit (Figure 6), that maintains a purge of approximately 1.4 scfm through three relief valves while recirculating the suit air at 12.7 scfm. The SCAPE leakage spec is 10,000 sccm at .4" H_2O with the relief valves taped off. The Apollo Space Suit leakage spec was 180 sccm at 3.75 psig. A good tight SCAPE has approximately a 2000 sccm leak rate. The reason for the disparity in leak rates is that the zipper (pressure sealing closure) is installed backwards, such that increasing pressure in the suit does not tend to tighten the sealing surfaces but to part them. The reason for the reversed installation was that of the zipper materials, those externally exposed parts, were nylon and brass, not hyper compatible. This fact has been brought out because, upstream diffusion studies (references 2 and 3) have shown that, depending on the flow rate, upstream diffusion is probable.

The problem of suit material permeability can best be illustrated by discussing a computer simulation based on the suit material permeability specification (.01 mg/in^2/hr), and a 100% NO_2 outside concentration. Ball park figures for suit area, 15.5 sq. ft., which represents 1/2 the surface area of a suit and assuming a spill only on one side of the worker, and suit free volume, 3 ft^3, have been used before. Flow rate out of the suit is 1.4 scfm. In this simulation, NO_2 exceeded TLV in four minutes, 10 seconds. Now, 100% NO_2 concentrations do not occur operationally. There is also a period of time where no permeation takes place. Estimated worst case concentra-

162

tion is 26% for eight minutes. However, the present material does not meet the permeability spec and is severely attacked by N_2O_4. The material permeates at 140-700 times the spec rate, depending on whether or not the material has been exposed to N_2O_4 before (see Figures 7 and 8). Additionally, the butyl coated nomex has such an electrostatic problem that prior to use, all suits have to be sprayed with Statikill. Statikill is a humectant, that is, it accumulates moisture, so that static charges will decay through the moisture. Moisture however, seriously increases the rate of chemical attack of N_2O_4 on the butyl coated nomex.

NASA is presently preparing to test the whole suit in a test chamber with a 26% NO_2 concentration. This type of test has not been performed before on the SCAPE suit.

In considering candidates for a less permeable material, additional design constraints are:

1. Chemical inertness to rocket propellants.

2. Impermeability (or less than .005 mg/in^2/hr for 1/2 hr).

3. Tear resistance.

4. Inflammability or flame retardant material.

5. Abrasion resistance.

6. Resistivity less than 10" 's per square, or induced charge decay of at least 90% in one second.

7. Light in color (preferably white).

163

8. Flexibility, suppleness, or in the cant of the garment
   industry, "a good hand."

9. Bondable, either by heat sealing or with a adhesive that
   does not degrade in rocket propellants.

Chemical inertness is important for the life of the garment
and is a necessary property as any type of chemical attack seriously
increases permeability.

To achieve adequate tear resistance, a coating is generally
applied to a fabric. Fabrics under consideration and in use in
protective clothing are:

1. Cotton (Standard Safety Equipment Co.), PVC coated,used
   at WSTF.

2. Nomex (Arrowhead Products), butyl coated, SCAPE.

3. Teflon (DuPont), viton coated with FEP laminate, Boeing
   fluorine suit.

4. Beta Glass (Dodge Fluoroglass), teflon coated, JPL fluorine
   suit.

5. Kevlar (DuPont), citon coated, AF proximity suit.

To make an environmental barrier of a material found to have
satisfactory chemical, mechanical, and permeability properties, it
must be bondable to itself either through heat sealing, thermowelding
(the preferred methods, since they are cheaper, labor wise) or with
a chemically compatible adhesive.

164

Materials that have good chemical resistance to N_2O_4 are Kalrez, Teflon, PNF (Phosphonitrilic Fluoroelastomer), CR-39 for faceplates, Kydex for helmets. Kalrez cannot be bonded to itself, teflon coated on beta glass can be heat sealed with a teflon FEP film, but to get enough teflon onto a substrate to give sufficient impermeability it becomes too stiff. CR-39 is PPGs new allyl diglycol carbonate and is inert to rocket fuels and oxidizer and the present PVC and acrylic faceplates are not and it has higher impact and abrasion resistance. Kydex made by Rohm and Hass is an alloy of PVC and acrylic and an excellent helmet material. PNF, made by Firestone Rubber Company, is inert to N_2O_4 and rocket fuels, is coatable onto nomex, comes in any color, is bondable and will decay an induced charge to less than 10% in one second, so it will not hold a static charge like teflon, or the present SCAPE material.

From our present state of knowledge, of compatibility, permeability, and electrostatic testing, Firestone's PNF (phospho-nitrilic fluoroelastomer) looks like a very good candidate for the material for the next generation of SCAPE suits, that is coated onto nomex for the suit material, molded into gloves, boots, cuffs, and faceplate seals and for relief valve seals. For the faceplate, CR-39 is much better than the present materials.

The pressure sealing closure problem is unclosed at present. There is an OEB (omni environmental barrier) zipper manufactured by Talon Division of Textron that seals better than the present one, yet still has exterior metals; 12% nickle brass, that will have to

165

be tested to determine if it represents a serious problem. Alternate closure methods are a waist roll cuff as is now used for the boots and gloves or a zip lock type closure. Resolution of the closure method should reduce suit leakage to less than 100 sccm.

Additional problems with the present SCAPE are as follows:

1. Reduced forward visual field due to the relief valve.

2. Inadequate ventilation.

3. Danger of frostbite from a cryo leak.

The relief valve can be moved to the side of the helmet, improving the visual field. This mod is still awaiting prototype testing to measure the effect of CO_2 concentration in the suit caused by repositioning the relief valve.

Per MIL-STD-1472B, recommended air flow into any personal enclosure is 30 scfm minimum, approximately 2/3 should be outside air. Total SCAPE flow is 12.7 scfm (41% of spec), with outside (fresh) air 1.54 scfm (7.7% of spec). If SCAPE had 30 scfm flow, it would be too noisy, and would increase backpack weight prohibitively. While some improvement is desired, by judicious conservation of energy, workers may avoid overheating their enclosures (See Appendix II).

With the present SCAPE the hazard exists of a failure in a cryo line in the backpack, from which the worker has no escape. The backpack can, itself, be self-contained and attached by umbilicals to the personal enclosure. This concept exists with the space suits and

166

with Arrowhead Modular, Omni Environmental Protective Suit (See Appendix III).

In summary, pending NASA funding, suit improvements are:

1. PNF instead of Butyl for suit material, boots, gloves, cuffs, and faceplate seal.

2. CR-39 instead of PVC or acrylic for faceplate material.

3. OEB waist roll cuff or zip lock pressure sealing closure.

4. Relief valves with elastomeric, PNF, seals reducing back flow from 6.54 sccm to less than .10 sccm and longer vent ducts.

5. Improved visual field, by moving relief valve to the side of the helmet.

6. Reduced suit leakage.

7. No static charge problem.

8. Detachable backpack.

If NASA accepts all of these changes, we really ought to have a SCAPE suit that protects the worker in the spirit as well as the letter of the law for the first time.

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5. "Olfactory Response to 0.2 ppm by Volume MMH," TR-WSTF-140,
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    Rockwell International Space Division, August 1, 1977

7. MIL-STD-1472B, Military Standard Human Engineering Design
    Criteria for Military Systems, Equipment, and Facilities,
    December 31, 1974

Subj.# 2
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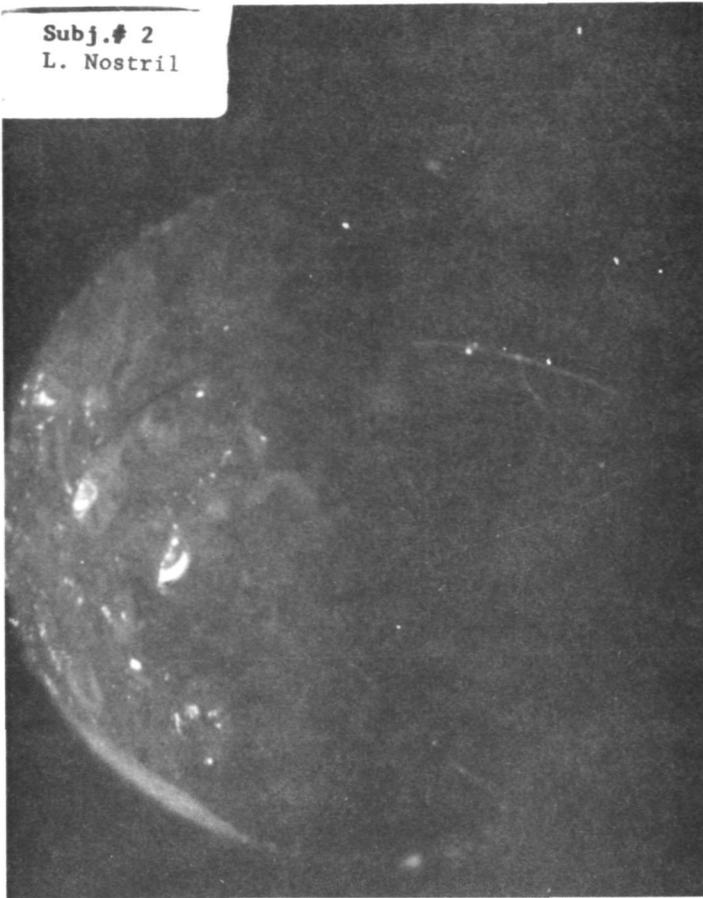
PRETEST

NORMAL NASAL MUCOSA

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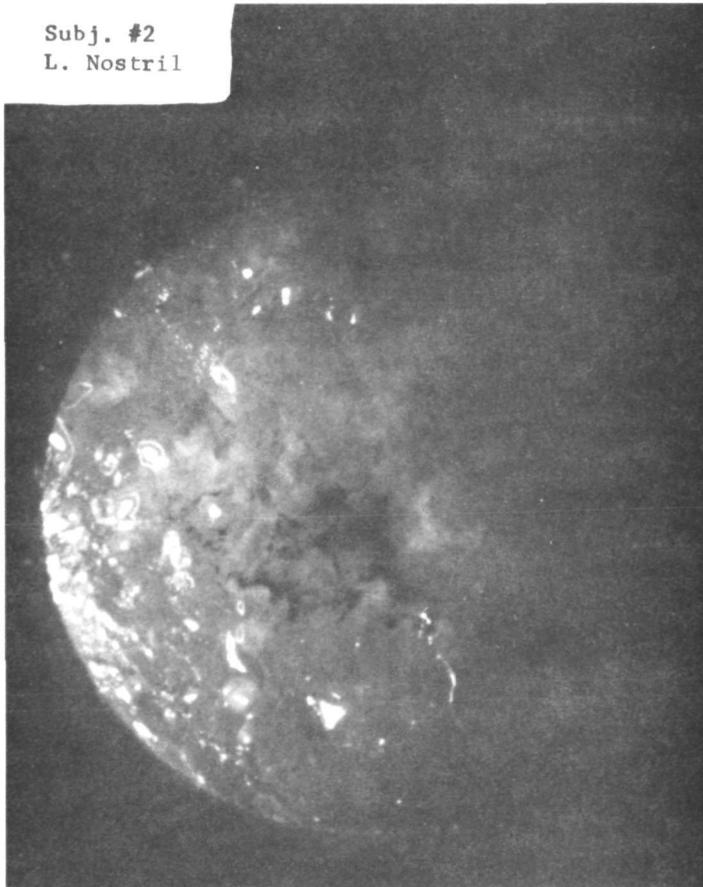
POST TEST

HEMORRHAGENOUS AREAS
AND BLISTERING

Figure 1

169
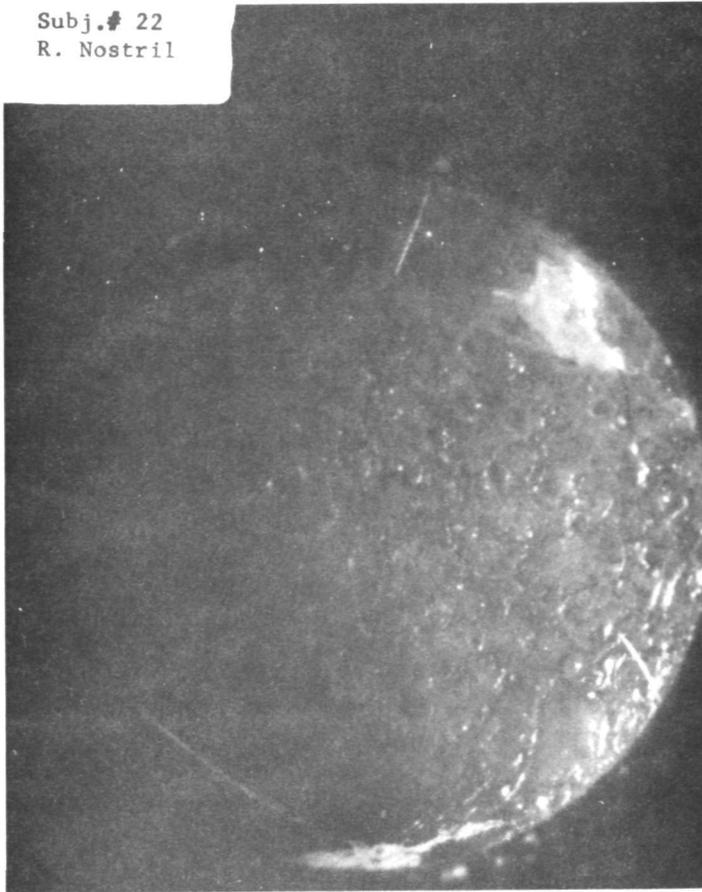
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R. Nostril

PRETEST

NORMAL NASAL MUCOSA

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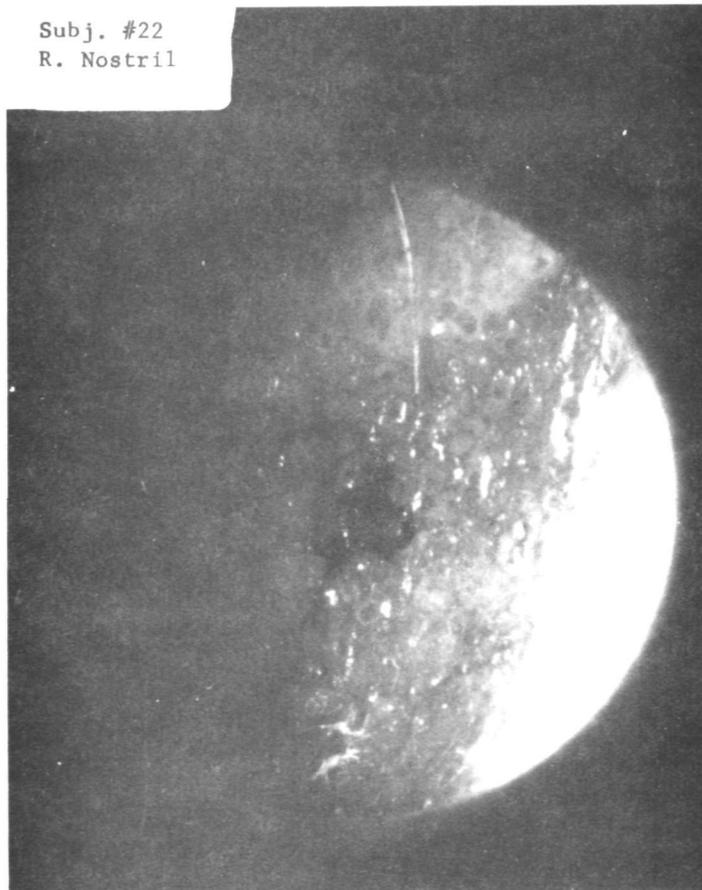
POST TEST

HEMORRHAGENOUS AREAS

AND BLISTERING

Figure 2

170

1	N_2O_4	6	HYDRAULIC FLUID
2	N_2H_4	7	$N_2H_3CH_3$
3	NH_3	8	H_2
4	O_2	9	N_2
5	$C BR F_3$	10	He
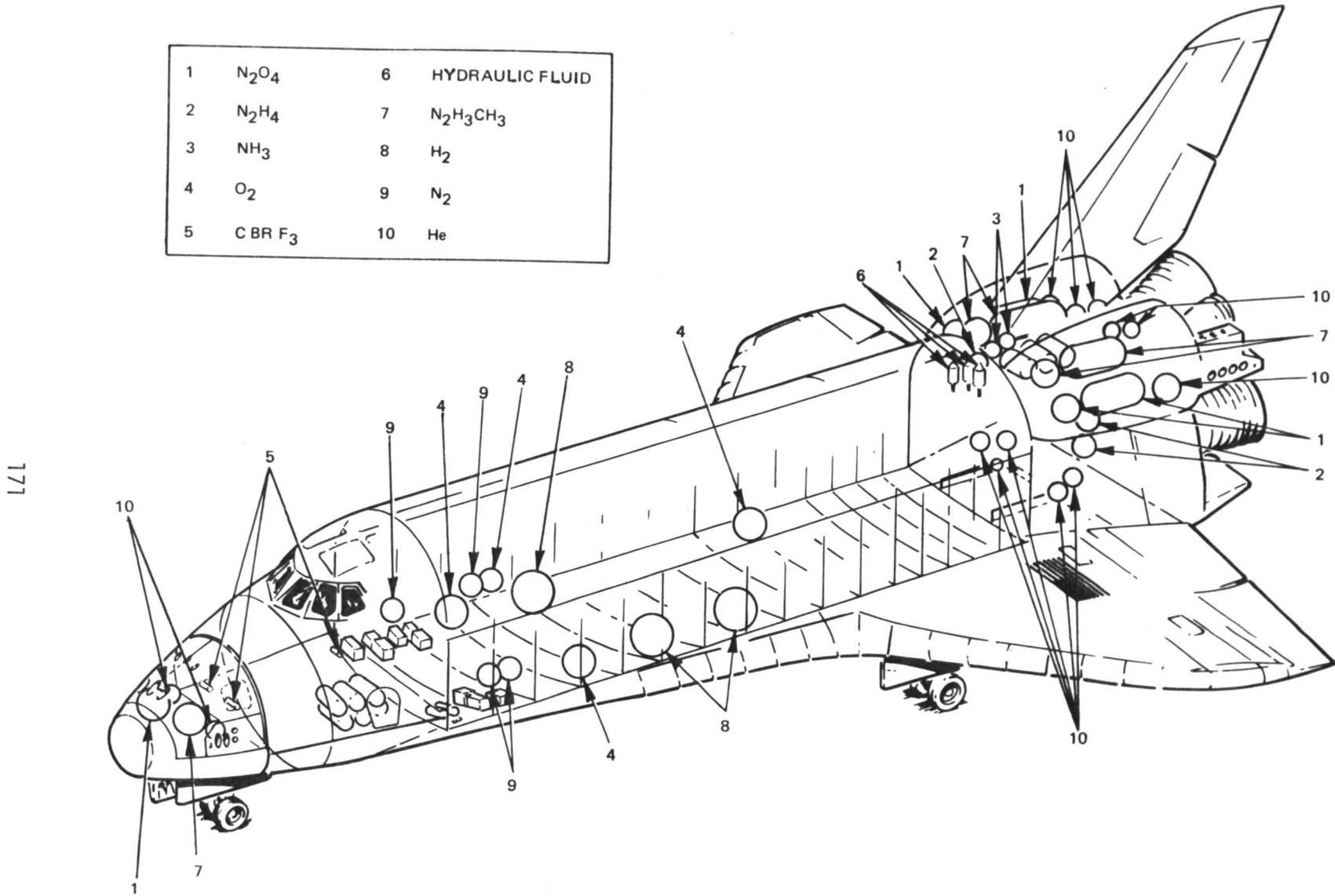
Fluids and Gases--Location

FIGURE 3
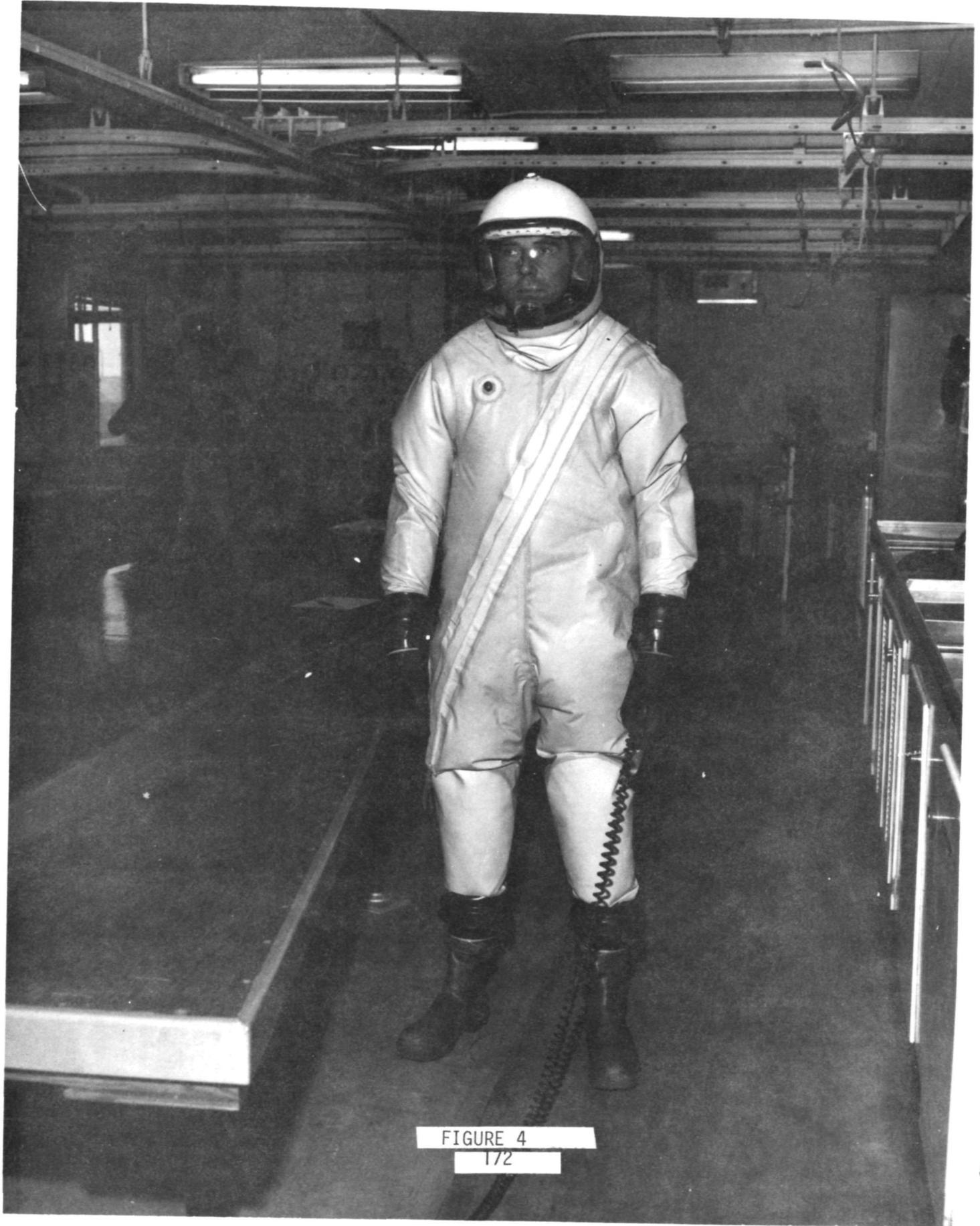
FIGURE 4

172

FIGURE 5

173
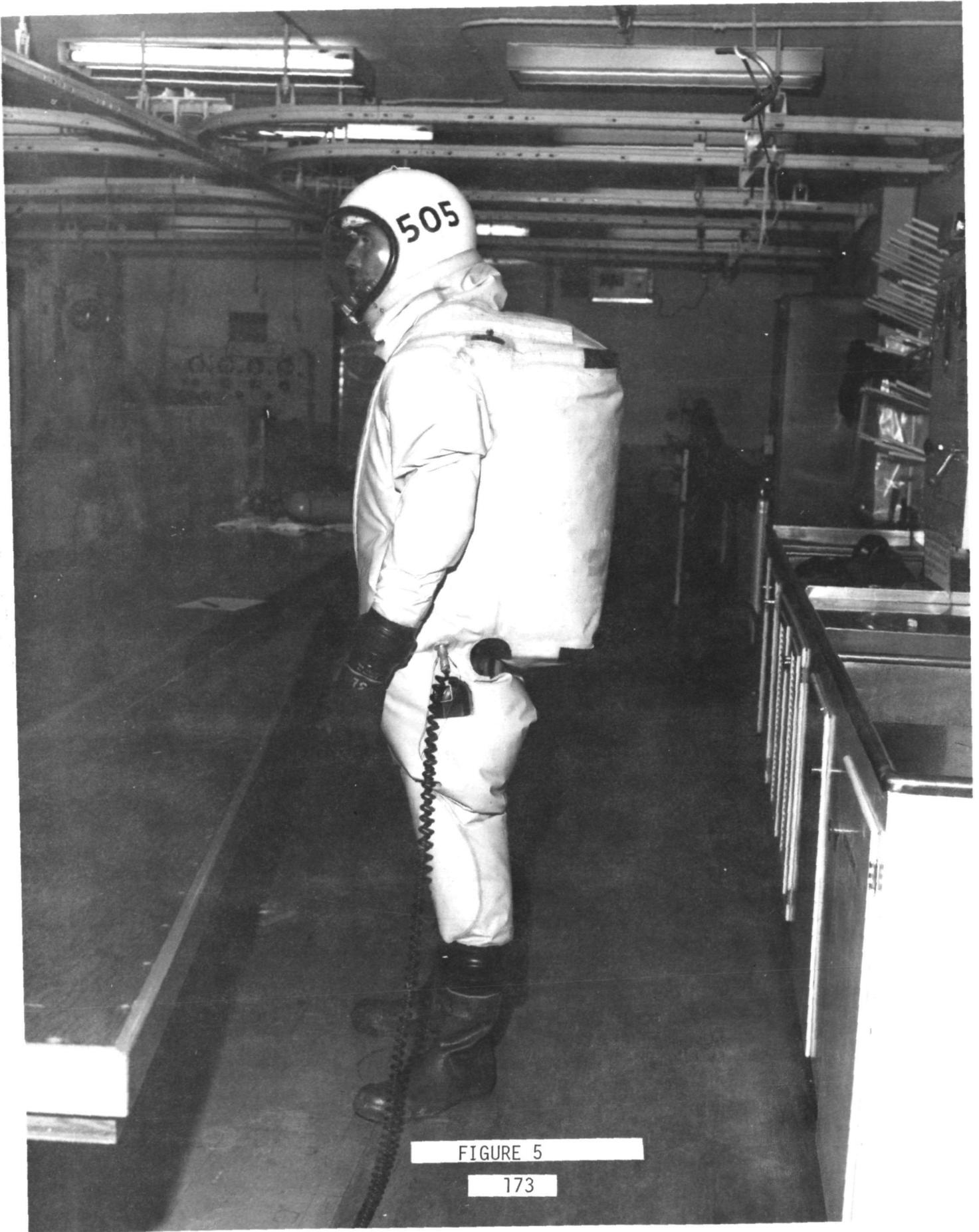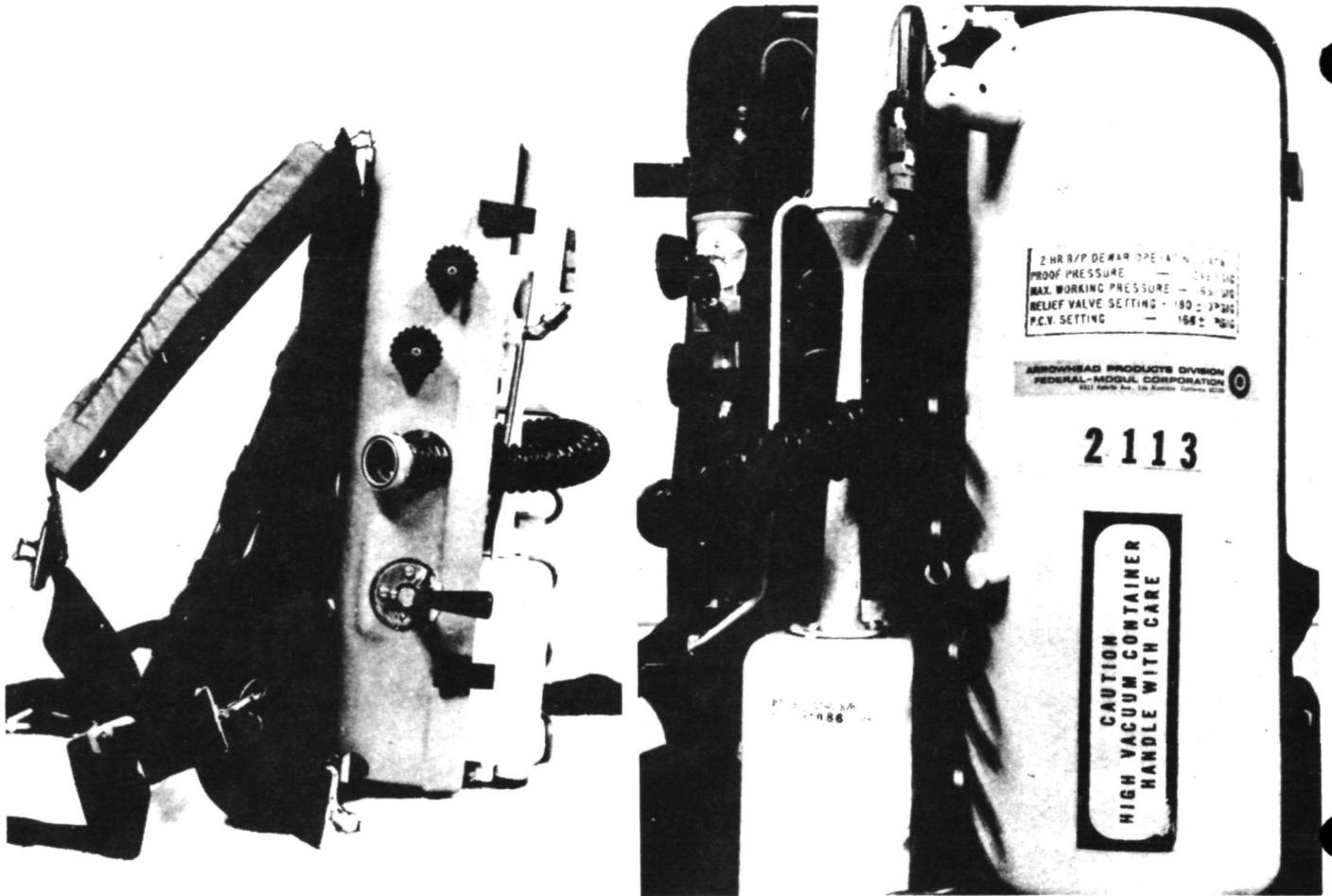
TWO-HOUR ENVIRONMENTAL CONTROL UNIT

DRAWING: 79K00962

USE: To provide air for breathing and ventilation for wearers
                of toxic fuel handlers' coveralls.

MEDIUM: Liquid air (7 liters).

DURATION: 2 hours at 11.7 scfm and 700 to 900 Btu/hr normal cooling.

WEIGHT: 34 lb (15.4 kg) fully charged;
                18.8 lb (8.5 kg) empty.

FEATURE: 90 percent of the air output is recirculated air used in
                cooling the suit; approximately 10 percent is used for
                breathing.

This unit converts liquid air to gaseous air for breathing and ventilating
when used with the coveralls (commonly called SCAPE SUIT) for toxic fuel
handlers. It has a shelf life (standby time) of 16 hours when fully charged.
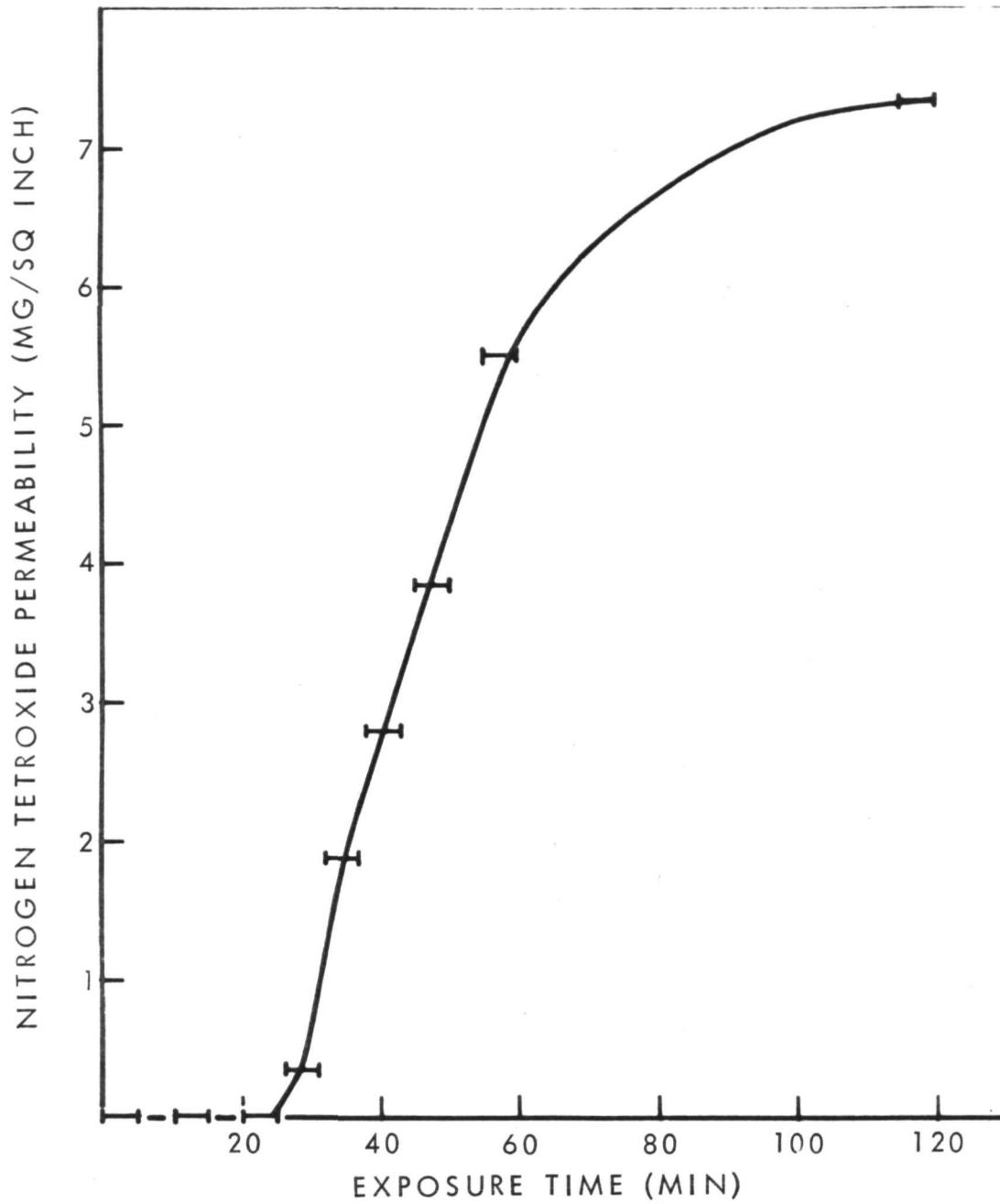
Figure 6
174

Figure 4: SAMPLE 5 PERMEABILITY CURVE
Preconditioned Plain (Unseamed)
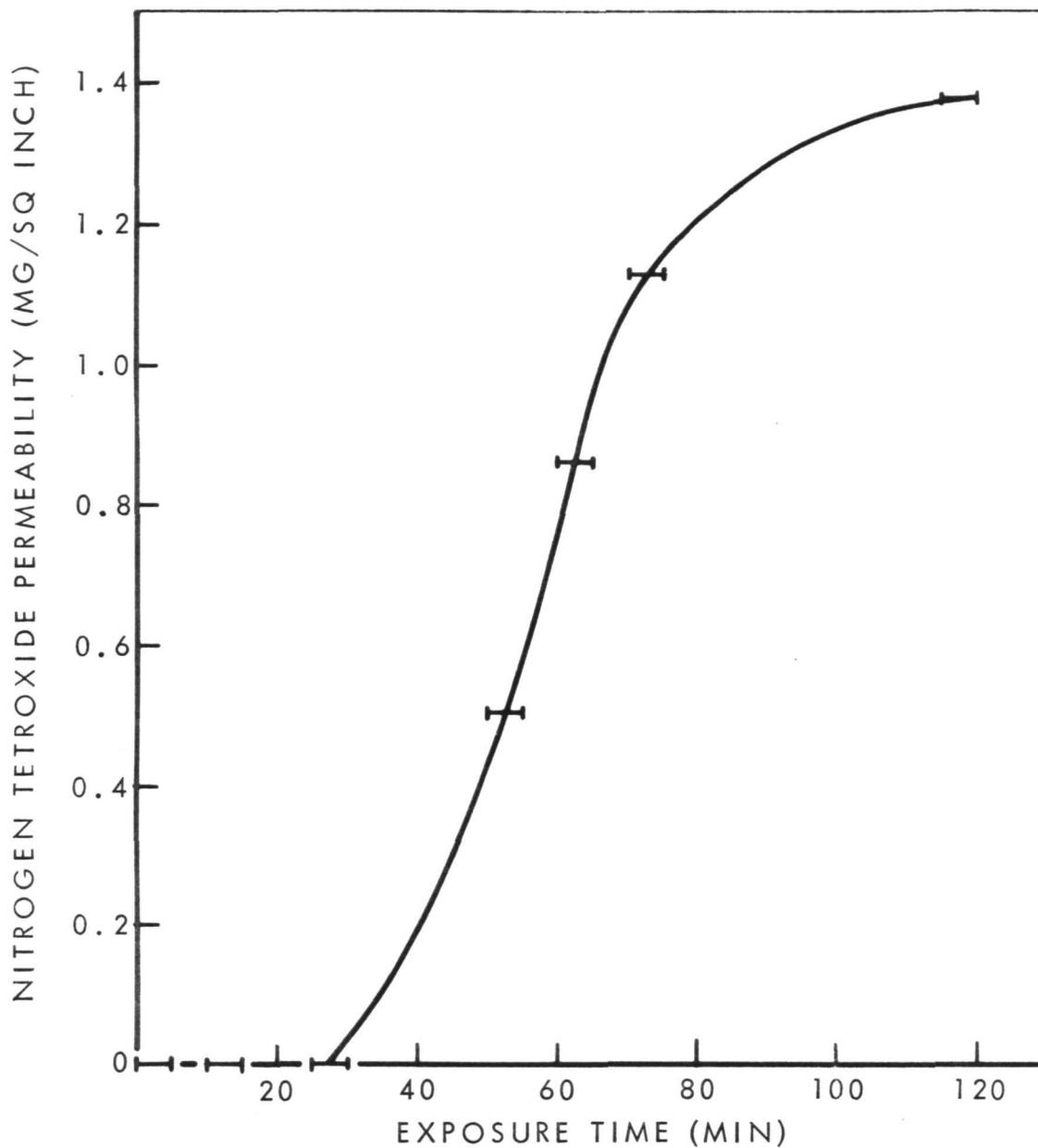
FIGURE 7

Figure 5: SAMPLE 6 PERMEABILITY CURVE
Unconditioned Plain (Unseamed)

FIGURE 8

176

SECTION II

2.0 HAZARDS AND SAFETY PRECAUTIONS

2.1 GENERAL. This section provides information on Orbiter hazards, their location, and first aid. Figure 2-1 shows the location of all the fluid and gas storage tanks. The quantities of fluid/gas listed in Table 2-1 will vary depending on whether the Orbiter completed the mission or the flight was aborted during launch. The quantities listed are with storage tanks full.

2.2 HAZARDS. Personnel engaged in Orbiter crash/rescue operations may be exposed to the following hazards:

- Unexpended pyrotechnic devices
- Toxic fumes
- Raw propellants (hydrazine and nitrogen tetroxide)
- Flash fires
- High pressures
- Hot brakes/wheels (fire/explosion)
- Static discharge
- Steam/hot water
- Propellant (fuel/oxidizer) fires

2.3 PROTECTIVE CLOTHING/BREATHING EQUIPMENT. Protective clothing and breathing equipment must be available for firefighter/rescue personnel. The chief officer shall determine the acceptable level of protection for his personnel after considering the hazards involved. Minimal levels of protection, for each hazard, will be described in this section when applicable.

2.4 MARKINGS, ACCESS PROVISIONS, AND EQUIPMENT LOCATION. Figures 2-2 through 2-15 illustrate the various access panels and doors, Orbiter structure, and components. The intent of these illustrations is to allow personnel to become familiar with the vehicle, its exterior markings, and equipment/component location.

2.5 PYROTECHNIC DEVICES. Pyrotechnic devices are provided for activation of the fire extinguisher system, emergency landing gear release system, and crew emergency escape system. With the exception of the ejection seats, the pyrotechnic devices will normally be disarmed by Contractor/NASA personnel. However, firefighter/rescue personnel must know their location. These devices are shown on Figures 2-16 through 2-18.

NOTE

For additional information on health, flammability, and reactivity codes used within this manual, refer to NFPA Manual, National Fire Codes, Volume 15, Standard 704M.

APPENDIX I

ECU DEFICIENCIES

"MIL-STD-1472B, Military Standard Human Engineering Design Criteria for Military Systems, Equipment and Facilities", page 137 recommends "a minimum of 30 cubic feet per minute per man into any personnel enclosure approximately two-thirds should be outside air".

In SCAPE on maximum flow there is 12.3 SCFM (41% of optimum design). Fresh air is 1/8 of total ECU flow or 1.54 SCFM (7.7% of optimum design).

	MIL-STD-1472B	SCAPE ECU	PERCENT
Recommended flow	30 SCFM	12.7 SCFM max.	41%
Percent outside (fresh)	20 SCFM	1.54 SCFM max.	7.7%

Too much flow creates noise which interferes with communications. Tests could be run with a CAT IV suit to determine how many SCFM are an optimum compromise between recommended air flow and the maximum tolerable noise. Helmet modifications could be considered for noise reduction if the flow could be increased towards optimum design without reducing operating time.

ARROWHEAD PRODUCTS

Modular, Omni-Environmental
Protective Suit

Modular, Omni-Environmental Protective Suit

■ MODULAR DESIGN ■ ALTERNATE AIR SYSTEMS ■ COMPLETE ISOLATION ■ IMPERMEABLE CONSTRUCTION ■ IMPACT, ABRASION RESISTANT ■ HIGH MOBILITY ■ INTEGRAL COMMUNICATIONS

General Description

The multi-hazard protective suit is designed to completely isolate a man from a variety of toxic or hazardous environments. The basic suit — consisting of coveralls, boots, gloves, and a helmet — is fabricated from a variety of impermeable and chemically resistant materials. These materials include coated fabric, stainless steel, laminated reinforced plastics, and special coatings of Teflon and Kynar.

All materials meet rigid permeability requirements and are effective against chemical and biological agents, nitrogen tetroxide, UDMH, hydrazine and other storable propellants.

Through integral connections, environmental control equipment, electronic detection and communications equipment, or emergency equipment may be introduced into the suit. Unique environmental hazards faced in various military and industrial operations can be met through appropriate component selection.

Coverall Design

The coveralls are two-piece, all bonded, with a sealed parting line at the waist. Knee and elbow areas feature external replaceable scuff pads and internal replaceable cushioning. A relief valve with a high dumping capacity is located under a cover on the chest. It is designed to maintain a positive pressure within the suit.

The ventilation system disconnect, mounted in the upper torso section of the suit, also functions as the gas distribution manifold and forms the upper structure of the environmental control unit (ECU) carrying frame. Ducts from this manifold carry air to the helmet and to the gloves and boots.

The ECU frame is fully adjustable for maximum wearer comfort. The entire assembly is readily decontaminated and resists decontamination agents. Acceptance testing includes soap bubble tests at 12-inches of water pressure to verify zero leakage through the seams of the suit or component materials.

Helmet Design

The helmet is of rigid shell construction with a replaceable visor. The size of the visor assures virtually unrestricted visibility. In the normal configuration soft foam earpads carry earphones and serve to stabilize the helmet. In addition to earphones, either a boom-type or a directly mounted microphone may be installed. Radio antennae may be built into the helmet for transceivers. Connections are available for radiac or electronic stethoscopes or for hardwire communications.

Helmet mounted filters with internal ducts and mouthpieces are available as emergency equipment. In cold weather, anti-fog agents or an exhaust deflecting mask may be used to reduce visor fogging. Glasses can be worn inside the helmet.

Component Attachment

All removable components of the suit are automatically sealed when connected. The molded butyl boot disconnect is bonded to the boot. Boots have non-skid sole treads and steel safety toes.

Two types of gloves are provided; inner and outer. The inner glove is very light weight and provides the dexterity required to manipulate small tools and make fine adjustments. The outer glove

may be used alone when fine dexterity is not required. When both gloves are used, the outer one is removable without disturbing the inner glove seal.

The helmet disconnect consists of an aluminum ring and a butyl seal bonded to the helmet and a second aluminum ring bonded to the torso neck.

Air Supply Systems

Air supply systems provide disconnects that allow attachment or removal, even in a contaminated atmosphere, without allowing contaminants to enter the system. The primary air supply for breathing and ventilation is connected to the suit in the area between the shoulder blades.

For optimum cooling with complete mobility, liquid air evaporating packs are used. These may be back mounted or hand carried and connected to the suit via a double duct umbilical or even cart mounted for extended use. Fig. A.

When compressed air is available, simple ventilation or heating and cooling through the use of a vortex tube can be accomplished. Either portable compressors with appropriate filters or facility installed air lines may be used as the supply. Figure B.

Two-gas systems may also be used with the suit. For example: respiratory needs may be met by using a mask and a demand or closed loop oxygen system while cooling is provided by an evaporating liquid refrigerant.

AIR TO HELMET

ADJUSTABLE CHEST HARNESS AND PADDING

AIR TO ARMS AND LEGS

FILTER HOUSING AND DISTRIBUTION CHAMBER

ECU SUPPORT FRAME

VENTILATION DUCTING

FLOW CONTROL CENTER AND AUXILIARY AIR INLET VALVE

ELBOW FOAM PAD

WAIST HARNESS AND PAD
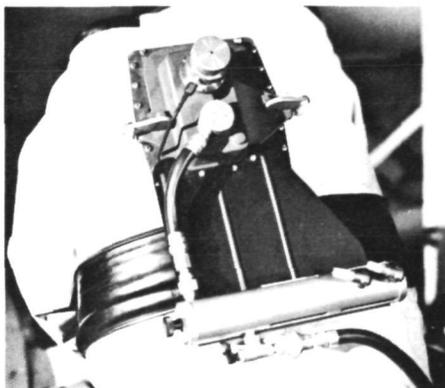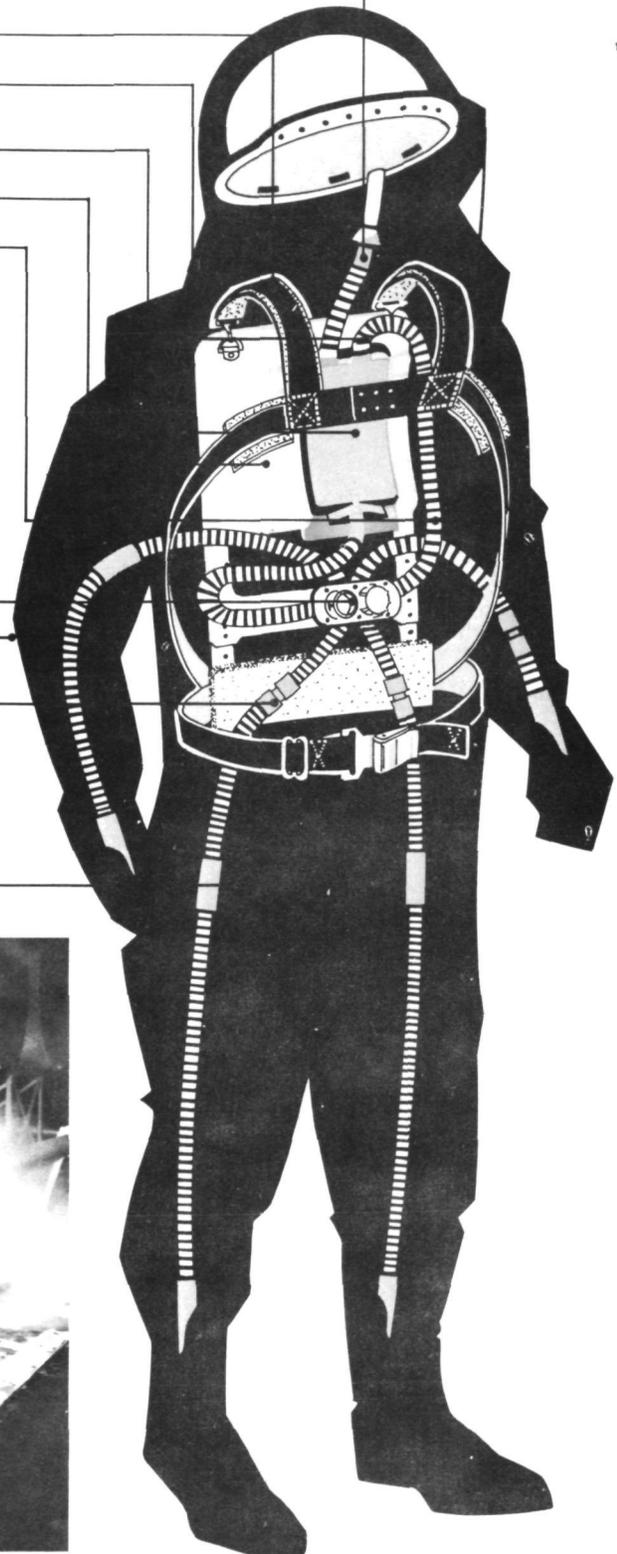
LEG VENTILATION DUCT QUICK DISCONNECTS

KNEE FOAM PAD

FIGURE B. COMPRESSED AIR WITH VORTEX TUBE

FIGURE A. LIQUID AIR PACK WITH UMBILICAL
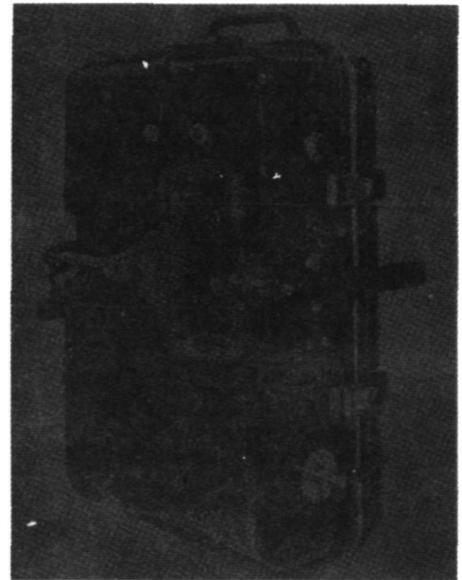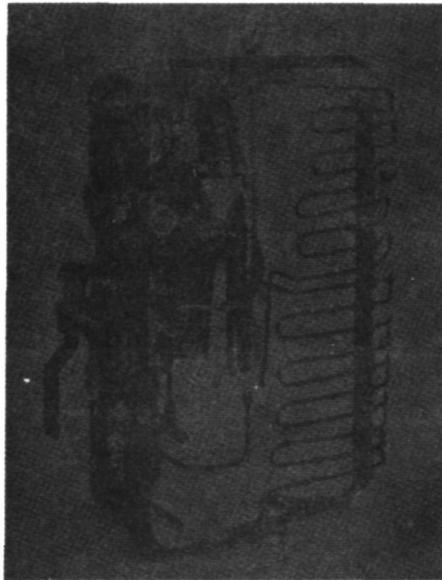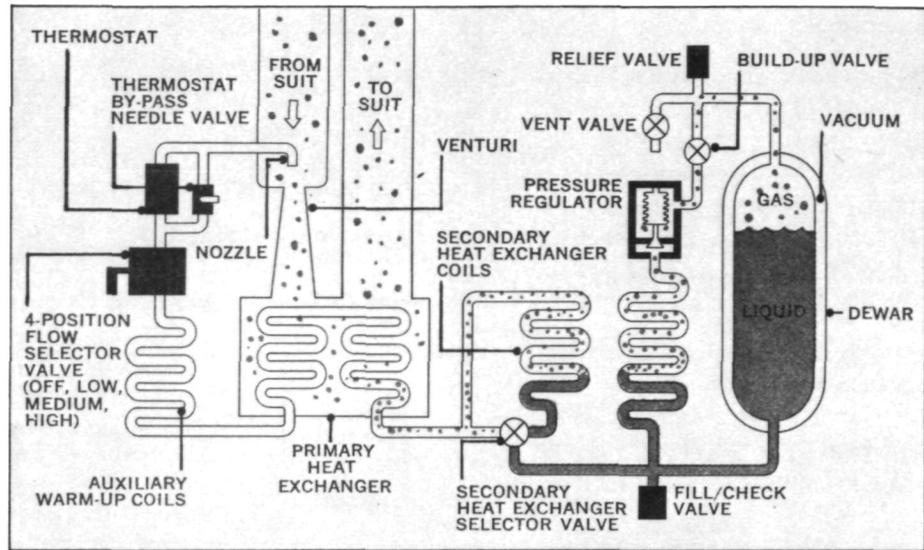
181

Basic Ventilation System

The basic environmental control unit (ECU) illustrated, provides a two to four hour supply of breathing and cooling air. Flow rate is wearer adjustable to control temperature, and match cooling capacity with metabolic demand. A thermostatic valve prevents freeze-up should the wearer set flow rate too high. The manifold in the suit-mounted portion of the disconnect divides the flow to the helmet and the extremities. Air to the helmet flows through a large duct to a disconnect which is an integral part of the neck ring. From this point, flow continues through a tube into the helmet distribution chamber between the helmet shell and its liner. A row of outlets provides an antifogging wash down across the visor.

The chest mounted exhaust valve dumps suit air at a rate equal to the rate of evaporation of liquid air from the supply system.

Under emergency conditions the wearer may also use a compressed air supply. An attachment point is provided on the left chest.

Arrowhead Products has developed special test facilities for suit infiltration testing and for materials permeability tests. All suit materials have complete traceability. Tests have checked permeability at a sensitivity level of 1 part per billion of contaminants in air.

Tests use many procedures developed by Arrowhead Products, including a colorimetric procedure that provides accuracies an order of magnitude greater than procedures described in MIL-P-26359A for detecting N_2O_4. Suits also have been tested with, and are fully compatible with all common decontamination agents related to the toxic and contaminated environments with which the suits may be used.

Arrowhead Products has had extensive experience in protective ensembles for personnel working in hazardous environments. The SCAPE-Self Contained Atmosphere Protective Ensemble—used extensively by missile and rocket propellant handling crews is a development of Arrowhead Products.

DELTA

NITROGEN TETROXIDE

FUELING OPERATIONS

R. B. Grigsby, T. M. Cross, T. D. Rucci
National Aeronautics and Space Administration
March 30, 1978

INTRODUCTION

The Delta Program began as an interim measure in 1959 to
utilize existing launch vehicles for unmanned space projects. The initial
configuration combined the Thor IRBM and the Vanguard second and third
stages. The first launch attempt in May 1960 failed, but this was followed
three months later with the orbit of the Echo balloon, the first orbiting
spacecraft visible to the naked eye. The following vehicles, including that
which launched TELSTAR, the first active communications satellite, were suc-
cessful and NASA elevated the Delta Program to a permanent status. Since
that time, the launch vehicle configuration has been periodically upgraded
from a 100-pound synchronous orbit payload in 1960 to the present 2000-pound
synchronous orbit capability. The Delta evolution is shown in Figure 1.

At the present time Delta 140 (the one hundred fortieth Delta)
is being prepared to launch a Japanese experimental communications satellite
(BSE). Delta vehicles are also launched at Vandenberg Air Force Base in
California for polar launches such as required by the Nimbus and ITOS weather
satellites.

Today the majority of the Delta missions are reimbursable
launches for commerical companies such as RCA, Intelsat, and Western Union;
for foreign governments like the Japanese BSE; or for other U.S. government
agencies, e.g., NOAA, the weather bureau. Thus, the program has progressed
from the research and development phase to one of applications, where the

spacecraft are used in everyday life for communications, weather, earth resources, etc.
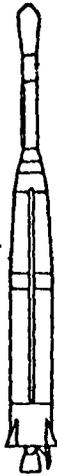
The Delta second stage nitrogen tetroxide fueling system, like the parent Delta vehicle, has undergone an evolutionary process to reach the present configuration, which will be discussed here. For instance, the origin of the propellant trailers even precedes the Delta Program to the Thor-Able Program of the 1959 timeframe. At that time and during the early portion of the Delta Program, the propellants used were red fuming nitric acid and Unsymmetrical Dimethyl Hydrazine (UDMH).

The original Delta second stage engine was a modified Aerojet Vanguard second stage engine system. It was replaced with the Aerojet Transtage engine which required that the propellant loading system be modified for N_2O_4 and A50. The present second stage engine, a derivation of the TRW Apollo LEM descent engine, also utilizes the same propellants.

Other modifications to the loading system have been made to simplify it to meet more stringent safety criteria, and to assure that the surrounding environment is protected. Particular emphasis has been placed on assurance that the spacecraft environment is protected from the toxic N_2O_4 fumes.

The following will describe the N_2O_4 fueling system and the equipment used to insure the protection of the environment.

DELTA HISTORY

DELTA	DELTA A	DELTA B	DELTA C	DELTA D	DELTA E
1960	1962	1962	1963	1964	1965
45 kg	68 kg	68 kg	82 kg	104 kg	150 kg
(100 lb)	(150 lb)	(150 lb)	(180 lb)	(230 lb)	(330 lb)
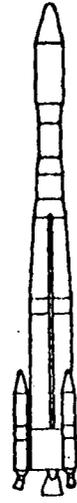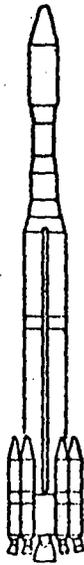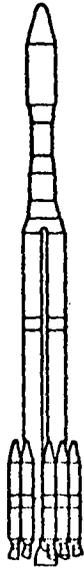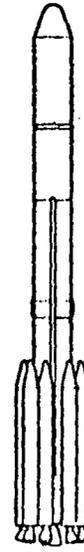
DELTA J	DELTA M	DELTA M-6	DELTA 904	DELTA 2914	DELTA 3914
1968	1968	1969	1971	1972	1975
263 kg	356 kg	454 kg	635 kg	703 kg	907 kg
(580 lb)	(786 lb)	(1,000 lb)	(1,400 lb)	(1,550 lb)	(2,000 lb)

N_2O_4 TRANSFER SYSTEM DESCRIPTION

The Delta second stage propellant loading system consists of fuel (A50) and oxidizer (N_2O_4) transfer systems. These two systems are essentially the same in design and function. In keeping with the symposium topic, only the N_2O_4 transfer system will be considered in this paper.

Both are pressure fed, closed systems which utilize gaseous helium, a storage tank pressurant, for liquid transfer. A closed system, for the purpose of this paper, is defined here as a system in which all toxic liquid and vapors are contained within the system and all venting is accomplished through scrubbers containing a neutralizing solution. The transfer systems are both manually and remotely controlled during loading operations. Manual control is accomplished at the propellant transfer units (PTU's) and upper mobile service tower (MST) levels. Remote operation of PTU and MST valves is controlled from the propellant loading console (PLC) located in the blockhouse.

The N_2O_4 transfer system consists of the following major components:

a. Mobile Trailers (PTU's)

b. Ullage Tank
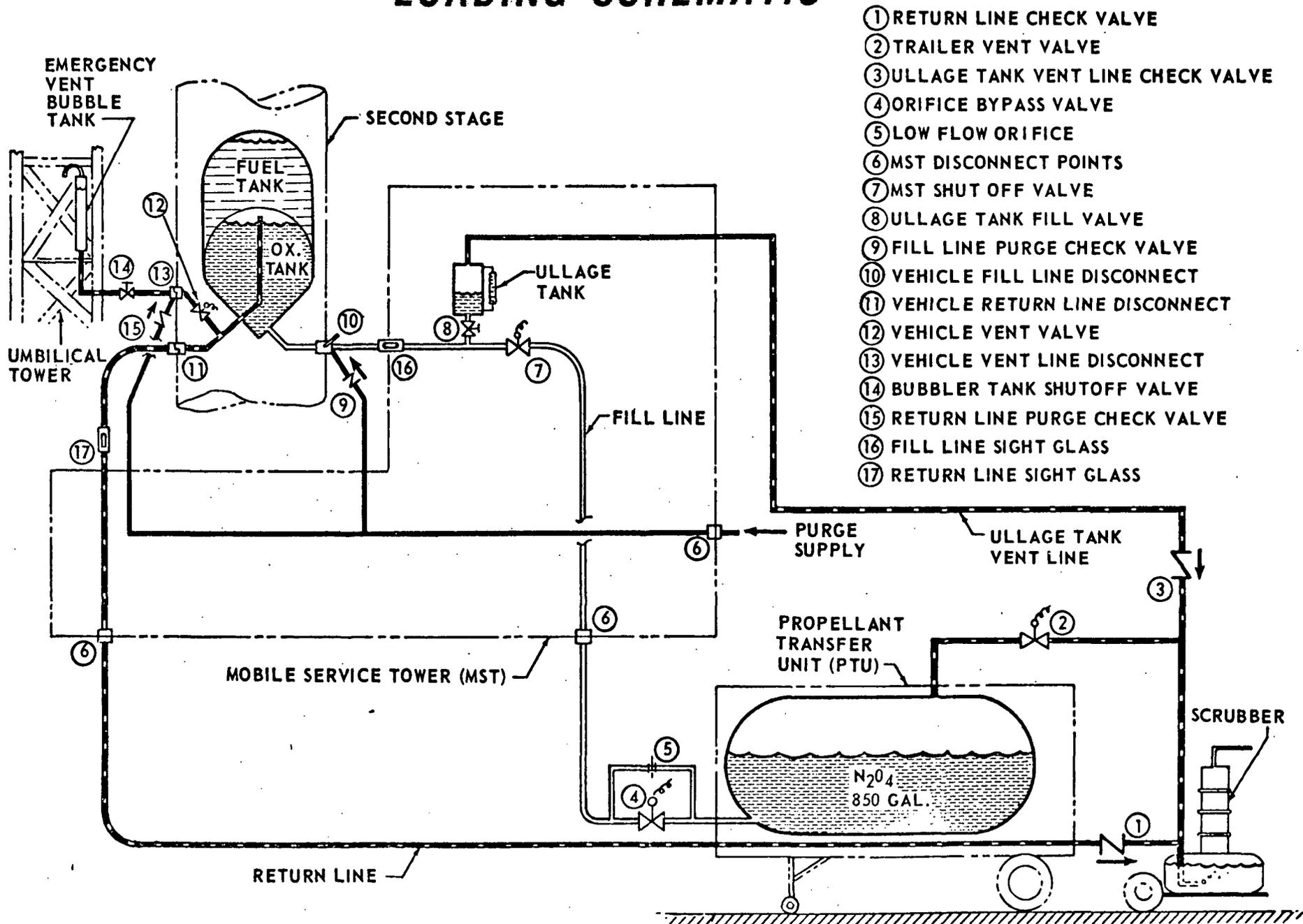
c. Scrubber

d. Bubbler Tank

SYSTEM OPERATION

The second stage N_2O_4 loading system uses helium as a storage tank pressurant for propellant transfer. During a loading operation the storage tank is pressurized to 150 psig and an initial flow rate of 4 to 5 gpm established. This flow rate is maintained through the low flow orifice until all ground and vehicle lines have been wetted and verified not leaking. At this point the orifice bypass valve (4)* is opened and the flow rate increases to approximately 20 gpm. When the vehicle tank is 95% full, a slow fill of 5 gpm is then initiated by closing the orifice bypass (4)* and filling until liquid is seen in the return line sightglass. The MST shutoff valve (7)* is closed to stop propellant flow into the vehicle.

To obtain the correct vehicle tank gas ullage volume, a calculated amount of liquid N_2O_4 is drained back into the ullage tank. This allows for thermal expansion of the vehicle propellant between loading and liftoff.

In order to drain this ullage tank the PTU supply tank is vented by opening valve (2)* through the oxidizer scrubber which neutralizes the contaminated gas. The vehicle is then isolated from the fill line by closing valve (10)* and the ullage tank liquid is drained back down the tower into the PTU supply tank by opening valves (7)* and (4)*. Both the fill and return lines are then purged out and disconnected at vehicle points (10)* and (11)*.

*See Schematic

DELTA ROCKET SECOND STAGE PROPELLANT LOADING SCHEMATIC

1. RETURN LINE CHECK VALVE
2. TRAILER VENT VALVE
3. ULLAGE TANK VENT LINE CHECK VALVE
4. ORIFICE BYPASS VALVE
5. LOW FLOW ORIFICE
6. MST DISCONNECT POINTS
7. MST SHUT OFF VALVE
8. ULLAGE TANK FILL VALVE
9. FILL LINE PURGE CHECK VALVE
10. VEHICLE FILL LINE DISCONNECT
11. VEHICLE RETURN LINE DISCONNECT
12. VEHICLE VENT VALVE
13. VEHICLE VENT LINE DISCONNECT
14. BUBBLER TANK SHUTOFF VALVE
15. RETURN LINE PURGE CHECK VALVE
16. FILL LINE SIGHT GLASS
17. RETURN LINE SIGHT GLASS

EMERGENCY VENT BUBBLE TANK

SECOND STAGE

FUEL TANK

OX. TANK

ULLAGE TANK

UMBILICAL TOWER

FILL LINE

PURGE SUPPLY

ULLAGE TANK VENT LINE

MOBILE SERVICE TOWER (MST)

PROPELLANT TRANSFER UNIT (PTU)

SCRUBBER

N₂O₄ 850 GAL.

RETURN LINE

189

SAFETY PRECAUTIONS

A typical propellant loading begins with Pad Safety clearing a 600-foot radius around the launch pad on which the loading is to be carried out. Only fire, medical, and SCAPE support personnel are allowed within this area during propellant flow and usually take up a position approximately 500 feet west of the mobile service tower (MST). Manual N_2O_4 loading operations at both the PTU and upper MST levels are carried out by personnel dressed in SCAPE. The "buddy system" is used at all times and the SCAPE crews are continuously monitored by a network of remotely controlled TV cameras. In addition, constant voice communication is maintained between blockhouse and SCAPE personnel. Fuel and oxidizer loading is controlled by a blockhouse test conductor and usually takes four to five hours.

Prior to N_2O_4 loading, the vehicle and transfer lines are leak checked with helium to insure that they will not leak liquid which could drip onto flight hardware. Drip shields are installed beneath the second stage and vehicle propellant lines to protect the first stage from drip damage in the event a leak would develop during loading. Neutralizer solution is also provided in the second stage area for washing off tools and treating drip areas. High capacity water hoses for major spill control are located at the PTU and upper MST levels. Fortunately, Delta has never had a major spill.

Throughout N_2O_4 loading, SCAPE personnel are constantly watching for visible evidence of leakage as well as monitoring an in-place toxic vapor detector for leakage past the rocket engine flow control valve. Loose hardware and tools are dipped in a bucket of neutralizer before use on the fuel system. At the completion of N_2O_4 loading, SCAPE personnel dip their gloves in neutralizer and shower in their suits before proceeding into fuel loading. In addition, Pad Safety "sniffs" the area around the N_2O_4 PTU and second stage for possible toxic fumes before giving permission to proceed with fuel loading or opening the launch pad for normal work.

TOXIC VAPOR TREATMENT

Toxic vapor treatment on the Delta Program has evolved from direct atmospheric discharge in the early part of the program to complete containment and chemical treatment of all toxic vapors. The thrust toward full containment was initiated by several factors, the most important of which, in their chronological order, are payload protection, personnel safety, and ecology. A water scrubber was initially used to reduce the greatest concentration of vapors which occurs when the PTU supply tank is vented. This scrubber satisfied most toxicity requirements for a number of years. However, increased payload and safety restrictions necessitated the replacement of the water scrubber with the chemical one now in use. The following paragraphs describe toxic vapor treatment at the major system component level.

N_2O_4 PTU. The oxidizer PTU is filled with N_2O_4 at the fuel storage area on the Cape. The PTU is filled to within one percent (8.5 gallons) of overflow. A blanket pressure of 5 to 10 psig helium is then placed on the PTU supply tank until it is raised to 150 psig for transfer to the vehicle. After propellant transfer the supply tank is vented down to a blanket pressure of again 5 to 10 psig, then disconnected from the MST and scrubber. It is then transported back to the fuel storage area to be refilled for the next launch. The PTU dates back to the 1958 era and has undergone many

improvements since then. Most notable is the addition of the scrubber and chiller units. Improved sealing and the reduction in leakage paths have also resulted in its improved reliability. The PTU supply tank is mounted inside of a catch tub which is designed to hold the entire tank contents should it rupture.

Transfer Lines. All propellant transfer lines are purged with helium for several minutes after use and before being disconnected from the second stage and MST. The purging insures that all liquid N_2O_4 is blown back into the PTU supply tank and toxic vapors routed to the scrubber for treatment. Quick disconnect fittings installed in the transfer lines at the second stage interface insure against loss of toxic vapor or liquid to the atmosphere. Hand valves installed in the transfer lines near the MST/PTU connect point provide the same insurance at ground level. A caution sign is placed on the transfer lines after they have disconnected as precaution against inadvertent opening or disconnection of quick disconnects and hand valves. A slight helium blanket pressure is left on the lines between launches.

N_2O_4 Scrubber. The Delta N_2O_4 loading system is designed and operated in a manner so as to minimize the venting of toxic vapors to the atmosphere. To accomplish this all vapors are routed to a chemical scrubber before escaping to the surroundings. The requirement for minimizing the venting of reactive vapors had its origin more out of the protection of sensitive payloads than environmental or safety aspects. With increased emphasis on environmental protection, the system can meet essentially any discharge requirement by reducing the flow rate through the scrubber.

The N_2O_4 scrubber was manufactured by the Peabody Engineering Corporation of Stamford, Connecticut, for the McDonnell Douglas Astronautics Company. Design specifications were that the scrubber "should be capable of reducing 115,030 ppm NO_2 down to 500 ppm from 400 scfm for 15 minutes." This value represents the maximum NO_2 concentration and supply tank vent flow rate; however, actual concentration and vent down rates are considerably less. The scrubber is a two stage design utilizing five percent sodium bicarbonate solution as a vapor neutralizer.

It is a mobile unit which allows for easy transfer from one launch pad to the other as well as permitting it to be towed to a contaminated waste disposal area for draining. The unit stands approximately twelve feet high and eight feet long. It consists of a 250 gallon neutralizer holding tank at the base and a vertical spray column made up of four cylindrical spray nozzle tray sections which are mounted one on top of the other. An electric pump forces neutralizer from the holding tank to five nozzles located in the spray column at 15 gpm and 20 psig.

N_2O_4 fumes from the PTU supply tank, vehicle oxidizer tank, and the ullage tank, as well as from other sources, enter the scrubber through a header located at the top of the holding tank. As the vapors migrate toward the spray column they are partially neutralized by the sodium bicarbonate liquid solution in the first stage of scrubbing. Next, vapors pass through the cylindrical nozzle tray sections where the toxic concentration is reduced in stages until an acceptable level is reached for release to the atmosphere.

Bubbler Tank.   After completion of fuel and oxidizer loading the N_2O_4

scrubber is disconnected from the MST and PTU and removed from the launch

pad area in order to protect it from rocket motor exhaust at liftoff.   In

its place a bubbler tank on the umbilical tower provides for toxic vapor

treatment until launch.   The bubbler tank is essentially a six-inch diameter

piece of stainless steel pipe six feet long.   It is filled with a 5% solution

of sodium bicarbonate.   Vapors from the second stage N_2O_4 tank enter the

bottom through a diffuser and migrate upward toward a vent located on the

end cap at the top.   Vent flow rates and volumes are low and experience with

this unit indicates no detectable toxic vapor in the area of the bubbler tank

vent.   This method of venting is only used for N_2O_4 tank pressure level adjust-

ment or in case of an emergency vent.   A typical pressure adjustment operation

due to N_2O_4 expansion in the tank would result in venting approximately

150 sci of N_2O_4 vapor through the bubbler tank, an amount easily neutralized

by this technique.   The bubbler tank solution is checked for sodium bicarbonate

concentration after every launch.

CONCLUSION

Environmentally speaking, the payload requirements for emission control are more stringent than those allowed by various safety and environmental organizations. The present sodium bicarbonate scrubber meets these requirements at Complex 17. The elaborate safety precautions surrounding a Delta propellant loading operation are for personnel safety because of the potentially high explosive yield of N_2O_4 and Aerozine 50 when they are brought in close proximity to one another.

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