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HANDBOOK
ON
HYPERGOLIC PROPELLANT DISCHARGES AND DISPOSAL

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PREFACE

This Handbook was prepared by personnel of the Mechanical Engineering Department and Medical Research Institute of Florida Institute of Technology, under Contract NAS 10-3399, administered by the National Aeronautics and Space Administration, John F. Kennedy Space Center, Florida. The NASA Technical Representative for the contract is Mr. Harold Franks, DD-MDD-41. Study Manager is Dr. Thomas E. Bowman, Professor of Mechanical Entineering at Florida Institute of Technology.

The present version of the Handbook was prepared under Phase Six of the overall study, and is based on work performed during Phases One, Two, Three and Five. The organization of the Handbook is such that additional material based on other work performed during Phase Six can be readily added at a later date, and section headings for this material are included in the Handbook. More comprehensive treatments of the work on which the Handbook is based can be found in the Final Reports for the earlier phases of the study.

ACKNOWLEDGEMENTS

We wish to especially acknowledge the contributions of Dr. Thomas L. De Fazio, Associate Professor of Mechanical Engineering, who prepared Appendix F and portions of Appendices A, B, and D, and of Mr. Edward R. Folger, Research Associate,who performed many of the laboratory investigations described herein. We also wish to acknowledge the tremendous efforts and endless patience of Mrs. Jani Mc Cray, who typed the manuscript, and Mr. James Baker, who prepared the graphs and sketches.

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CHAPTER 1

INTRODUCTION

The disposal of chemical and industrial wastes of all types has become one of the major areas of technological endeavor during the 1960's and 70's, and will no doubt continue to demand the best efforts of many thousands of engineers and scientists for the foreseeable future. So much has been said and written on this subject in recent years that there is surely no point repeating here the many reasons why the disposal of all substances, from the most pernicious to the seemingly innocuous, must be a matter for study and concern.

A number of disposal situations occur in connection with aerospace launch operations, including possible atmospheric releases of vapor as well as liquid waste disposal. Increased attention to finding the best means of treating these releases has been indicated both because of the national and worldwide concern with all forms of chemical releases, and the increased frequency of launch activities anticipated with the avdent of the Space Shuttle. While such activities have never been a very significant source of air or water pollution, the fact that they represent our society's finest example of technological accomplishment implies that they should also be setting an equally high example with regard to the effective treatment of the potentially hazardous wastes.

Since August, 1973, Florida Institute of Technology has studied many aspects of these waste disposal situations resulting from launch operations, under contract to NASA's John F. Kennedy Space Center (Contract NAS 10-8399). The results have been covered in a series of Final Reports treating the various phases of the study. The purpose of this Handbook is to bring together in one place those results felt to be of general interest outside the immediate KSC community, and pertaining specifically to the disposal of hypergolic propellents: the hydrazine-type fuels and nitrogen tetroxide, red fuming nitric acid, and hydrogen peroxide oxidizers.

Releases of these propellants can occur in a number of situations. Vapor releases can result from purges both prior to propellant tank loading and following the end of a mission, venting of displaced ullage gas during propellant tank loading, and venting of storage tanks and loaded vehicle tanks to maintain pressure within limits. Liquid waste can result from draining and cleaning operations, emptying of liquid vapor separators, or contamination of supplies. Aqueous solutions containing hypergolic propellants can be generated at vapor scrubbers or during various cleaning operations. Other situations can also exist, including unplanned events such as spills. Our studies were concerned with minimizing the environmental impact of all of these operations, planned or unplanned. We were concerned with all methods of treatment currently in use or used in the past, with treatment methods in use in other segments of industry that might be applicable to aerospace launch operations, with advances in the state of the art (new treatment methods), with evaluating the impact of untreated releases, and with evaluating the economics of various treatment methods and of untreated release. Our approaches included surveys of the literature, written and verbal communications with appropriate individuals in all segments of the aerospace industry and appropriate segments of the chemical and pollution control industries, theoretical analyses, laboratory investigations, and full-scale prototype testing.

This Handbook presents all of our results regarding the effectiveness of the various treatment methods. It is not our primary purpose here to compare different treatment methods, as comparisons depend to a large degree on the specific application. Rather, we attempt to present our results and evaluations in sufficient detail that others can compare the treatment methods in terms of their own needs. (Our own comparisons in terms of KSC applications have been presented in earlier reports.) Our evaluations on the basis of economics - both first cost and operating cost - are generally not included, because of the variation of these factors with time, location, specific application, etc. Other considerations that were primarily concerned with KSC applications, such as flow rate calculations, sizing calculations, specific design criteria, etc., have also been omitted as not having sufficient general interest. Details of how we arrived at some of our information regarding current and past disposal practices - who we contacted, what questions we asked, etc. - have also been omitted for the same reason.

The propellants of interest are treated separately in the chapters that follow except for the hydrazine-type fuels, which are all treated in Chapter 2. To some extent, later chapters refer back to earlier chapters where possible to avoid repetition, and hence are not entirely self-contained. Maximum emphasis is on the Space Shuttle propellants, MMH and N_2O_4, since these were investigated most thoroughly by us.

It is interesting to observe that all of these propellants are nitrogen-based except for hydrogen peroxide, and hence can potentially be reduced to valuable plant nutrients. None of them contain any elements other than carbon, nitrogen, hydrogen, and oxygen except for inhibited fuming nitric acid, which contains a small amount of fluorine, and hence with this exception they can all in theory be reduced to these four harmless elemental substances.

Our overall evaluation of the current state of the art - disposal alternatives that exist at the time this Handbook is being written, including recent developments and methods still in the prototype stage - is that virtually any hypergolic propellant disposal problem can be solved in a manner that is economically viable and environmentally satisfactory. In most cases, the environmental aspects of launch-related ground support activities can easily be made to set a high example for other segments of the economy to work toward. The notorious red nitrogen dioxide plumes of years past, for example, can readily be scrubbed to levels that compare very favorably with the latest single-automobile emissions standards. A few problems do still exist, and are identified in the chapters that follow, as are potential further improvements that may be on the horizon. We fully expect that in the years to come, hypergolic propellant handling and disposal activities at Kennedy Space Center and other testing and launch facilities will be among the least harmful, environmentally, of all man's activities.

CHAPTER 2

ANHYDROUS HYDRAZINE
MONOMETHYL HYDRAZINE
UNSYMMETRICAL DIMETHYLHYDRAZINE
AEROZINE 50

2.1 MATERIAL DESCRIPTIONS[1]

In this chapter we are concerned with the three hydrazines that are used as aerospace propellants - anhydrous hydrazine (N_2H_4), monomethyl hydrazine (MMH)(CH_3NHNH_2), and unsymmetrical dimethylhydrazine (UDMH)($(CH_3)_2NNH_2$) - and with Aerozine 50, a 50/50 UDMH/N_2H_4 blend.

All of these hydrazines are clear, colorless liquids with characteristic organic amine (ammonia, "fishy") odors. All are hygroscopic, mildly alkaline, and are very strong reducing agents. They all have positive heats of formation at 77°F, and hence are subject to decomposition with attendant energy release.

N_2H_4 and MMH mix with water in all proportions, and with low molecular weight alcohols. N_2H_4 is insoluble in hydrocarbons, while MMH is soluble. UDMH is completely miscible with water, hydrazine, diethylene-triamine, ethanol, and most petroleum fuels. It is unique in that it is completely miscible with both polar and nonpolar solvents.

The chief reason for mixing UDMH and N_2H_4 to form Aerozine 50 is to overcome the instability and high freezing point of N_2H_4. The resultant fuel will not ignite spontaneously in air below the critical point (482°F). The vapors are, however, highly flammable in air over a wide range of concentrations, and are readily ignited by low energy sparks. The mixture is highly toxic, as are the individual constituents (see below).

The following excerpts from manufacturers' data bulletins provide additional information on the behavior of the three primary fuels.

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[1] Source material for this section was taken from the following publications:

"Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation." Prepared by the Liquid Propellant Handling and Storage Committee, assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD 870259, May 1972.

"Liquid Propellants Safety Handbook." Prepared by the Safety Office, John F. Kennedy Space Center, NASA. Report No. GP 359, August 1, 1968.

"Anhydrous Hydrazine Handling and Storage." Olin Chemicals, 745 Fifth Ave., New York, N.Y. 10022.

"Monomethyl Hydrazine Handling and Storage." Olin Corp., Chemicals Division, 120 Long Ridge Road, Stanford, Conn. 06904.

"Dimazine: Unsymmetrical Dimethylhydrazine." FMC Corp., Inorganic Chemicals Division., 633 Third Avenue, New York, N.Y. 10017.

Anhydrous hydrazine

Decomposition of hydrazine is caused by elevated temperatures and the presence of catalytic surfaces or ion impurities.

At increased temperatures, hydrazine will slowly decompose to yield nitrogen and ammonia. Studies at temperatures up to 500°F have shown that most of the decomposition takes place in the vapor phase, and that the rate of decomposition is a direct function of temperature. No rapid decomposition has been observed, even at 500°F, in the absence of catalytic agents.

Certain metallic ions and metallic oxide surfaces exhibit a marked catalytic effect upon the decomposition of hydrazine. Laboratory studies have shown that chromic, ferric, and cupric ions catalyze decomposition of hydrazine at reflux conditions under a nitrogen blanket. At ambient conditions, there is no noticeable effect from dissolved ions.

A surface area catalytic effect occurs when molybdenum, iron, Raney nickel, rust, copper oxide or cobalt in finely divided form come into contact with hydrazine. A film of hydrazine on iron rust will burst into flame if ventilation is inadequate to keep it cool.

Anhydrous hydrazine is completely insensitive to shock, friction, or electrical discharge. A No. 10 Army detonator with a booster charge of 20 grams of tetryl fails to affect hydrazine, even at 221°F.[2] In cases where hydrazine vapor has been exploded over the liquid, the liquid has remained unaffected. There is no danger, other than splashing, from dropping heavy equipment upon spilled hydrazine.

Mixtures of hydrazine vapor in air are flammable between the limits of 4.7% and 100% hydrazine by volume at normal temperatures. Combustion of cold liquid hydrazine is difficult to initiate, however. Ignition occurs only when the temperature has been raised above roughly 126°F, the fire and flash points for hydrazine. When burning freely in air, hydrazine behaves much like gasoline. However, at elevated temperatures it burns fiercely.

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[2] Scott, F. E., Burns, J. J., and Lewis, B.: "Explosive Properties of Hydrazine," Report of Investigations 4460, U.S. Department of the Interior, Bureau of Mines, Pittsburgh, Pa. (May 1949).

Water solutions of hydrazine at any concentration below 40% cannot be ignited.[3] A 50% solution will burn only near its boiling point; with increasing concentration the burning temperature decreases to about 126°F for the anhydrous product.

Hydrazine vapors are irritating to the eyes, nose, and throat. Inhalation causes dizziness, nausea, and hoarseness. These effects are not immediately noticeable, but appear gradually over a period of several hours' exposure.[4] Exposure of the eyes to hydrazine vapors causes itching, swelling, and blistering of the eyelids accompanied by acute pain. Severe exposure of the eyes to the vapor will produce burns similar to those which can be caused by a welding arc. The result may cause temporary blindness, lasting about a day, but will not result in permanent damage.

Contact of hydrazine with any body tissue will produce a caustic-like burn if not washed off immediately. Ingestion or absorption through the skin will cause nausea, dizziness, headache, and may prove fatal.

Monomethyl Hydrazine

MMH is stable up to its atmospheric boiling point (189°F), only when kept out of contact with oxygen. When MMH was refluxed for seven to ten hours under one atmosphere of nitrogen, there was no appreciable decomposition.[5] MMH is more stable than hydrazine under conditions of mild heating. Even at bulk temperatures of 300°F there is no evidence of explosive decomposition.[6]

Spontaneous ignition of MMH can occur in either of two ways - by direct oxidation or catalytic decomposition.

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3. "A Study of Extinguishment and Control of Fires Involving Hydrazine-Type Fuels with Air and Nitrogen Tetroxide." Atlantic Research Corp., First Quarterly Progress Report, 1960.

4. Liberto, R.R.: "Research and Development on the Basic Design of Storable High-Energy Propellant Systems and Components." Bell Aerosystems Co., Buffalo, N.Y., Final Report AFFTC TR-60-61, Contract AF 33 (616)-6689 (May 1961).

5. "Semi-anual Technical Program Report AF04 (647)-171, Volume III." Rocketdyne Report R-833-3P (20 July 1959).

6. Ibid.

Exposure of MMH to air and especially on large surface areas (such as rags, cotton waste, sawdust, and excelsior) may result in spontaneous ignition due to the heat evolved by oxidation with atmospheric oxygen.

Catalytic decomposition can be caused by contact with rust, molybdenum, copper and its alloys, and spontaneous fire will result. When a film of MMH comes in contact with certain metallic oxides, particularly those of iron, copper, lead, and manganese, it may cause the MMH to decompose due to a chemical heat of decomposition. This heat may be sufficient to raise the temperature high enough to cause spontaneous ignition.

Mixtures of MMH vapors in air at normal temperatures are flammable bwtween 2.5% and 98%. Mixtures within the flammable limits can be exploded by an electric spark or open flame.

Liquid MMH is insensitive to impact or friction. Shock sensitivity of the liquid phase has been investigated by blasting cap techniques. In an inert atmosphere, an explosion temperature of 300°C has been observed for MMH vapor. In thermal stability tests, the explosion temperature for MMH was found to be between 545° - 700°F.[7]

Ocular and skin tests have indicated that MMH is only temporarily irritating. MMH in contact with the skin or eyes can cause local damage resembling burns. Continuous exposure of the eye to vapors will cause eye irratation and conjunctivitis.

Inhalation of the vapor can cause local irritation of the respiratory tract, with respiratory distress, and systemic effects resulting. Data from acute exposures indicate that a single exposure to MMH does not cause liver damage; however, repeated, prolonged exposures can cause damage to the liver and kidneys.

Unsymmetrical Dimethylhydrazine

UDMH is resistant to air oxidation, but the vapor reacts slowly at ambient temperatures to form traces of several products. Carbon dioxide reacts

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7. Jacobson, K.H., et al: "The Inhalation Toxicity of Methylated Hydrazine Derivatives." Chemical Corps. Medical Laboratories, Army Chemical Center, Maryland, ML Research Report No. 292 (June 1954).

with UDMH to form a salt and extended exposure of UDMH to air or other carbon dioxide-containing gases could lead to eventual precipitation of the material.

The spontaneous decomposition temperature of UDMH, in an atmosphere of nitrogen or helium, is 740°F to 750°F (393 to 399°C) at one atmosphere pressure. The decomposition does not become explosive up to at least 1112°F (600°C). Some carbonization takes place at 700 to 800°F.

UDMH is not shock sensitive. In work done by the Bureau of Mines it was demonstrated that it could not be detonated in the conventional card-gap tests even after deliberate contamination with materials which are potential sensitizers such as rust, copper and magnesium turnings and aluminum powder. Negative results were also obtained in a series of tests designed to place it under even more severe conditions.

UDMH is a flammable material was a flash point of 34°F (Tag closed cup) and flammability limits in air from 2.5 to 95 volume %. The autoignition temperature in air is 482°F. Although more stable than the other hydrazines, the flash point is the lowest of the three: 5°F open cup, 34°F closed cup (comparable to gasoline, and a consequence of UDMH's greater volatility.)

UDMH is mildly irritating to the skin and eyes, and can penetrate the skin causing systemic toxicity. The vapor is irritating to the eyes and respiratory tract and can also cause systemic effects. UDMH is significantly different from hydrazine as a toxicant in that no cases of permanent liver damage have been documented in human exposures. Animal studies indicate that the most serious after effect is convulsions. Depending on the degree of exposure, these range from mild tremors to acute convulsions. Chronic low level exposures may cause anemia.

Additional information on the toxicology and exposure limits of all three hydrazine fuels is given in Appendix G.

Physical Properties

A number of physical properties, taken from the sources listed at the start of this section, are presented in Table 2.1.1 for the three primary hydrazine fuels.

TABLE 2.1.1

PHYSICAL PROPERTIES OF HYDRAZINE FUELS

Property		N_2H_4	MMH	UDMH
Molecular Weight		32.04	46.08	60.08
Boiling Point (at one atm)	°F	236.3	189.5	146
	°C	113.5	87.5	63
Freezing Point	°F	35.6	-62.27	-71
	°C	2.0	-52.37	-57.2
Liquid Density at 77°F (25°C)	lb/gal	8.379	7.297	6.54
	g/cc	1.0040	.8743	0.784
Critical Pressure	atm	145	81.3	53.5
	psia	2135	1194	786
	pascal	1.47×10^7	8.24×10^6	5.42×10^6
Critical Temperature	°F	716	593.6	482
	°C	380	312	250
Heat of Vaporization (@ 77°F, 25°C)	Btu/lb	607	376.9	251
	kcal/mole	10.7	9.648	8.37
Heat of Formation (liquid @ 77°F, 25°C)	Btu/lb	+675	+512.2	+381.5
	kcal/mole	+11.999	+13.109	+12.734
Heat of Combustion (Liquid @ 77°F, 25°C)	Btu/lb	8359	12,177.5	14,200
	kcal/mole	148.6	311.7	473
Heat Capacity	Btu/lb-°F	0.737@77°F	0.698@68°F	0.653@77°F
	cal/mole-°C	23.62@25°C	32.17@20°C	39.2@25°C
Flash Point (Tag Open Cup)	°F	125.6	63	5
	°C	52.0	17.2	-15
Autoignition Temperature	°F	518	382	482
	°C	270	194.3	250
Flammability Range (Vol.%) in Air		4.7-100	2.5-98	2-95

2.2 RECOMMENDATIONS FROM OTHER SOURCES

At the time of the beginning of our study, a number of recommendations already existed regarding the disposal of these propellants. The manufacturers of the three primary hydrazine fuels all present recommended disposal procedures in their technical bulletins, and in addition anhydrous hydrazine had been included in a very extensive study of the disposal of hazardous industrial and municipal wastes performed by TRW Systems Group for the Environmental Protection Agency.[1] These various recommendations are quoted below, where the report by Ottinger et al is referred to as "The TRW Report".

The "Hazards of Chemical Rockets and Propellants Handbook" recommends that N_2H_4, MMH, UDMH, Aerozine 50 and MAF (Mixed Amine Fuels) "be disposed of by burning... Small quantities and dilute solutions can be collected in a basin and reacted with compounds such as 10 percent hydrogen peroxide or calcium hypochlorite. Neutralizing agents should be applied in excess."[2]

Anhydrous Hydrazine

Olin Chemicals: "Waste hydrazine from spills or process effluent presents a problem of neutralization prior to sewering. Commercial calcium hypochlorite, containing 70% available chlorine (HTH), provides an ideal solution to this problem. The reaction between the hydrazine and calcium hypochlorite yields nitrogen and calcium chloride. Other decontaminants may also be used (see Table 2.2.1).

"Drains from areas of hydrazine handling should lead to a sump or holding pond where neutralization can be effected in a very dilute solution. One mole of calcium hypochlorite is required per mole of hydrazine. On a weight basis this is equivalent to 6.4 pounds of HTH per pound of hydrazine. Recommended usage is seven to ten pounds of HTH per pound of hydrazine to provide an excess

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[1] Ottinger, R.S.; Blumenthal, J.L.; Dal Porto, D.F.; Gruber, G.I.; Santy, M.J.; and Shih, C.C.: "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste." Report No. EPA-670/2-73-053-1 (August 1973). NTIS PB-244 591.

[2] "Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation." Prepared by the Liquid Propellant Handling and Storage Committee, assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD 870259, May 1972.

of HTH. This is roughly equivalent to 0.6 to 1.0 per pound of HTH per gallon of 1% solution of hydrazine.

"Neutralization of hydrazine with HTH is complete and rapid at pH 5.0 to 8.0. At lower pH, the reaction is complete, but may require a longer period of time. At higher pH, the reaction may not proceed to completion.

"A dilute solution of hydrogen peroxide may also be used to neutralize dilute hydrazine wastes. One mole of hydrogen peroxide is required per mole of hydrazine. A slight excess of peroxide is recommended to ensure complete destruction of the hydrazine. The addition of a trace amount of copper sulfate will catalyze the reaction, causing it to proceed more rapidly.

Table 2.2.1. Decontaminants for Hydrazine[3]

Decontaminant	Possible Reaction Products	Approximate Heat Liberated Kcal/Mole N_2H_4
H_2O	$N_2H_4 \cdot xH_2O$	3.9
$NaHCO_3$	$(N_2H_5)_2CO_3$, Na_2CO_3	10
H_3BO_3	A salt	5
$KMnO_4$	N_2	177
H_2O_2	NH_3, N_3H	91-121
Cl_2 gas/HTH	N_2	160/177

"For larger quantities, disposal is usually carried out by burning in increments in a small, concrete-lined pit. Hydrazine and aqueous solutions of hydrazine are placed in the pit by means of a pipe or surface channel. The hydrazine can be ignited by an igniter (squib-fired), an oxidizer such as nitrogen tetroxide, or a torch. Concentrations as low as 40 percent by weight hydrazine in water can be burned. Concentrations lower than 40 percent can be burned by enriching the dilute mixture with a soluble flammable liquid, such as alcohol."[4]

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3. Scott, F.E.; Burns, J.J.; and Lewis, B.: "Explosive Properties of Hydrazine." Report on Investigations 4460, U.S. Department of the Interior, Bureau of Mines, Pittsburgh, Pa., May 1949.

4. "Anhydrous Hydrazine Handling and Storage." Olin Chemicals, 745 Fifth Avenue, New York, N.Y. 10022.

Fisons Ltd.[5] recommended the following reactions for disposal of concentrated hydrazine solutions:

(1) With alkaline H_2O_2 in the presence of iron or copper (II) salts:

$$N_2H_4 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

(2) With excess sodium hypochlorite:

$$N_2H_4 + 2NaOCl \longrightarrow 2NaCl + 2H_2O + N_2$$

(3) With atmospheric oxygen in the presence of copper (II) salts:

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

The TRW Report:"Hydrazine as a waste will generally be encountered as excess material, as contaminated material from spills, or in aqueous streams from chemical process industries. Because of the hazards involved (unpredictable decomposition), hydrazine is usually not recovered in a concentrated form from contaminated or dilute systems. In ponds or holding tanks dilute hydrazine is decomposed by the air and bacteria into nitrogen, hydrogen, water and ammonia. In concentrated form, hydrazine is destroyed by burning.

"The safe disposal of hydrazine is defined in terms of the recommended provisional limits in the atmosphere, water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Hydrazine	0.01 ppm	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Hydrazine	0.1 ppm	Quantity will rapidly oxidize to near-zero concentration

"Hydrazine is generally destroyed by oxidation to water and nitrogen. In dilute solution, dissolved oxygen, catalysis, or bacterial action convert hydrazine to nitrogen, hydrogen, ammonia and water. Therefore, there are no problems in dealing with the products from waste treatment. Current disposal practices for hydrazine are briefly described in the following paragraphs together with recommendations as to adequacy.

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[5] Written communication from Mr. M.W. Whitmore, Chemical Development Department, Fisons Ltd., Harston, Cambridge, England.

Option No. 1 - Open Pit Burning

"Hydrazine poured into an open pit is burned to nitrogen and water. The transfer of the hydrazine and the ignition must be accomplished by a remote means. For drum quantities of hydrazine this method is generally acceptable although since excessive NO_x might be generated another option would be preferred.

Option No. 2 - Incineration

"The Air Force has a minimum of ten trailer-mounted incinerators capable of incinerating up to 6 GPM of hydrazine in a variety of mixtures with water (from 100 percent hydrazine to 100 percent water). The effluent from the units is limited to 0.03 lbs/min NO_x when incinerating hydrazine. These units are acceptable for disposing of large quantities of hydrazine.

Option No. 3 - Catalytic Decomposition

"One of the applications for hydrazine is its use as a monopropellant. When hydrazine is passed over a support (usually aluminum oxide) coated with certain metals or metal oxides, it is decomposed into nitrogen, hydrogen and ammonia. The details of catalyst composition are usually found in the classified literature. In most cases the catalyst is expensive, but TRW Systems has preliminary data on a low cost catalyst that should be further investigated.

Option No. 4 - Diluting with Water and Holding

"If hydrazine is diluted with water, e.g., after spills, and placed in open lined ponds or holding tanks, the hydrazine is decomposed to water, nitrogen and ammonia by air oxidation and bacterial action. For small quantities of hydrazine in aqueous solution this method is acceptable if adequate space is available.

Option No. 5 - Chemical Treatment

"Small quantities and dilute solutions are collected in open containers and treated with oxidizing compounds such as 10 percent hydrogen peroxide or calcium hypochlorite. The oxidizing agents should be applied slowly until in excess. This method is not recommended except for small quantities because considerable heat is liberated during decomposition."[6]

Recommended treatment: "Controlled incineration with facilities for effluent scrubbing to abate any ammonia formed in the combustion process."[7]

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[6] Volume XII, pages 329-331.

[7] Volume I, page 215.

Monomethyl Hydrazine

Olin Chemicals: "To reduce fire hazards, spilled MMH may be diluted with large amounts of water and neutralized by dilute hydrochloric acid or sulfuric acid. This procedure ensures the trapping of MMH vapors and forms a MMH-type salt.

"Diluted MMH, while no longer a fire hazard, may still be dangerous if not disposed of properly. MMH must not be permitted to drain into a potable water system. Provisions must be made to permit liquid drainage into a disposal area where it may be burned in small increments or decomposed by a chemical decontaminant such as calcium hypochlorite (HTH^{tm}) or hydrogen peroxide.

"Empty drums and containers should be rinsed with water and steamed for 15 minutes to remove toxic and flammable vapor."[8]

Unsymmetrical Dimethylhydrazine

FMC Corporation: "Equipment can generally be decontaminated rather simply by thorough flushing with large volumes of water or with dilute acid. It may be conveniently steamed thereafter. It should, of course, be thoroughly dried prior to return to Dimazine* service, making sure that no water has been trapped at low points in the system.

"Our suggestion for deliberate destruction of comparatively large quantities of Dimazine is to burn it under proper supervision and safeguard This technique has been successfully used in the field. Small quantities such as minor spills, etc., usually can be disposed of most conveniently through sewering with water.

"Copious water flushing is recommended for personnel decontamination."[9]

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* FMC's trademark for UDMH.

[8] "Monomethyl Hydrazine Handling and Storage." Olin Chemicals, 120 Long Ridge Road, Stamford, Conn. 06904.

[9] "Dimazine Properties, Applications, Reactions, Storage and Handling." FMC Corporation, Organic Chemicals Division, 633 Third Avenue, New York, N.Y. 10017.

2.3 WASTE DISPOSAL PONDS: WATER DILUTION, AIR OXIDATION, BACTERIAL ACTION

2.3.1 Introduction

Water dilution of liquid hydrazine wastes followed by discharge to untreated holding ponds is one of the most common means of disposal of this fuel. In the holding pond, air oxidation and bacterial action slowly convert the fuels to nitrogen, carbon dioxide, and water acording to the following stoichiometric equations:

1a. $2N_2H_4 + \frac{1}{2}O_2 \longrightarrow N_2 + 2NH_3 + H_2O$

2a. $N_2H_4 + O_2 \longrightarrow 2H_2O + N_2$

1b. $(CH_3)\, N_2H_2 + O_2 \longrightarrow 2NH_3 + CO_2$

2b. $(CH_3)\, N_2H_3 + 2.5O_2 \longrightarrow CO_2 + 3H_2O + N_2$

1c. $(CH_3)_2\, N_2H_2 + 2.5O_2 \longrightarrow 2NH_3 + 2CO_2 + H_2O$

2c. $(CH_3)_2\, N_2H_2 + 4O_2 \longrightarrow 2CO_2 + 4H_2O + N_2$

Even in cases where a holding pond is chemically treated, these air oxidation reactions are often significant factors in the destruction of the hydrazines, and can result in considerable savings in the quantities of chemicals used.

Decomposition can be speeded by use of a catalyst, such as copper sulfate or iron oxide, and by aeration - either bubbling air through the pond, or spraying water from the pond into the air in a fountain. In any case, the oxidation reaction is very slow at atmospheric temperature, and the heat release in a pond will not significantly raise the temperature such as to increase the rate of reaction.

In normal sewage treatment practice, an oxidation pond utilizes bacteria to aerobically stabilize the organic material present in the waste water, resulting in the conversion of C to CO_2, H_2 to H_2O, and N_2 to NH_3. The oxygen for the bacteria is supplied by both air surface transfer and the metabolism of algae in the pond. The cycle is completed when the algae use the waste stabilization products CO_2 and NH_3 to synthesize new cells in the presence of sunlight, and thereby liberate oxygen as an end product to be used by the bacteria for oxidizing the organic wastes and synthesizing bacterial protoplasm. In addition to biological stabilization, other processes taking place in oxidation ponds may include balancing of the acids, coagulation and sedimentation of solids, and neutralization of any alkalinity.

If a pond has sufficient surface area relative to the rate of inflow, and climatological factors are not too adverse, normal evaporation will be sufficient to control the liquid level in the pond and no liquid waste need ever be withdrawn from the pond. The effect of the pond on the environment will then be limited to an atmospheric discharge only, plus whatever impact - adverse or otherwise - the pond itself will have on the surroundings.

If periodic liquid discharges are required, the ammonia content of the water could be a problem, especially if the very restrictive ammonium hydroxide "Provisional Limit" recommended by the TRW Study[1] (0.01 ppm in water and soil) should be adopted. In addition, because of the slowness of the air oxidation reaction, two ponds (probably in series) might have to be used so that the pond to be emptied could be protected from addition of new fuel for a period of time prior to discharge. Selection of a ground waste disposal site should be such that the discharged waste infiltrates and percolates into the ground surface where no possibility of impairment exists. Disposal of wastes should not be near fresh water aquifers, wells, or other usable water sources.

Near the beginning of our study, we visited existing oxidation ponds at Vandenberg Air Force Base, Johnson Space Center, and White Sands Proving Ground to observe the ponds and their operation first hand, and to discuss their design, maintenance, and operation. Of particular concern was the question of their atmospheric discharges.

The only operational aeration pond was at Johnson Space Center, where a very large flow of air is introduced through two H-shaped manifolds at the bottom of a fairly deep concrete holding pond. The bubbles generated are quite large, and result in a general roiling motion of the central part of the pond and visible circulation throughout most of the pond. At Vandenberg AFB, a spray pond has been constructed for experimental purposes, and one batch of hydrazine had been oxidized in the pond for data collection purposes at the time of our visit. Oxidation ponds at White Sands Proving Ground are essentially untreated

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[1] Ottinger et al, op. cit., Volume XII, page 105.

holding ponds, with air oxidation taking place naturally at the surface but no aeration.

Measurements at both Vandenberg and Johnson Space Center show that during aeration a period of time passes in which dissolved oxygen levels in the water increase, but there is no significant reduction in hydrazine level. This period is followed by a reduction in hydrazine content once the dissolved oxygen reaches saturation.

Operating experience at the one operational holding pond has apparently been quite satisfactory. It should be noted, however, that very little hydrazine disposal had taken place at JSC between the time the aerator had been installed and our visit. The primary reason for installation of the aerator was to provide a means of quickly oxidizing the hydrazine in case of emergencies - the need for pumping water from the pond to prevent overflow during very rainy weather, for example. Starting with a 300 ppm N_2H_4 concnetration in 0.5 million gallons of water, the hydrazine concentration can be reduced to 5 ppm in about twenty hours, with most of the reduction occurring in the last two to three hours. The addition of copper sulfate or iron oxide as a catalyst contributes to the speed of oxidation.

In the experiment at Vandenberg, a concrete neutralization pond from the Titan II program was reconfigured to allow recirculation of a water/fuel solution through a pair of vertically mounted spray nozzles, the solution being sprayed upward and allowed to fall back into the pond. The following paragraphs are quoted from an informal report that we were given describing the experiment.

"Seventy thousand gallons of approximately 75 parts per million mixed hydrazine fuels in water was contacted with atmospheric oxygen in the presence of 0.2 mg/l copper ion. An attempt to maintain saturated solution of dissolved oxygen was made by spraying the fuel/water solution through a spray head back into the pond at a flow rate of 60 liters per minute. Oxidation was complete in 20 days with a superficial rate constant of 1.3 $(\text{days})^{-1}$. There was no significant emission to the environment and (energy consumed was) 450 kW - hours.

"It is interesting to note that dissolved oxygen concentrations for the first eight days were considerably below saturation, indicating oxygen was rate limiting during this period. After the 11th day it was not necessary to operate the spray heads to maintain saturation. During the first six days of the test a marked evaporation of water occurred, on the order of 10,000 -

14,000 gallons, which was followed by a rainy period in which the water level rose to above initial levels. These fluctuations in water level had some effect on concentrations measured, however the exact variations were not recorded. From the data it can be inferred that three separate rate limiting steps or mechanisms are involved in fuel detoxification, occurring at different times. Initially there is a rapid decrease lasting approximately one day. At these high concentrations it may be thought that atmospheric emissions are occurring. UDMH was only detected once at the surface of the pond and that was 30 minutes after transfer; the level was 6 ppm by volume as measured by a MSA Billionaire instrument on the 0-10 scale. Atmospheric levels measured at two hours after transfer indicated only trace UDMH levels at 6 inch over the pond surface - no further UDMH levels were detected for the remainder of the test.

"Auto-oxidation methods can be utilized safely to oxidize waste hydrazine fuels to nontoxic waste less expensively than the current procedures. Published data indicates higher reaction rates when performed with the optimum catalyst concentrations; rates leading to complete detoxification with one week contact time could be expected."

We would add the comment that the very high loss of water during the non-rainy period might not all be explained by evaporation: wind-blown spray seemed to be very substantial the day we saw the spray heads in operation.

Our visits and discussions did not reveal any obvious problems in terms of atmospheric releases, even though there undoubtedly is a certain amount of ammonia release with any oxidation pond. Ammonia is the only undesirable end product expected if no chemicals (other than small quantities of catalyst) are added to the pond. It will be largely dissolved in the water (ammonium hydroxide) but a certain amount will be released to the air. The threshold Limit Value for ammonia in air established by the American Conference of Governmental Industrial Hygienists is 18 mg/m^3 (25 ppm by volume), and the provisional Maximum Exposure Limit recommended by the TRW Study[2] is .02 mg/m^3. Actual levels above oxidation ponds are difficult to calculate because of undetermined effects of numerous variables such as insolation (intensity, hours per day, etc.), bacterial action, surface area versus depth, temperature, relative humidity,

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[2] ___ Op. cit., Volume XII, page 104.

wind velocities, etc. In view of the slow rates involved with oxidation pond processes, and the absence of reports of ammonia odors, we see no reason to expect atmospheric ammonia releases to be a problem except perhaps in the case of spray ponds.

This destruction method therefore looked very attractive to us from almost all points of view except the time factor - an important consideration when dealing with highly toxic or carcinogenic substances, as there is considerable virtue in destroying such materials as quickly as possible rather than keeping them for days or weeks in open ponds. Two series of experiments were performed for the purpose of learning more about the rates of reaction, means of speeding the reactions, and obtaining general design criteria and guidelines for these air oxidation ponds. These experiments are described in the following sections; they were concerned primarily with aeration, since natural pond surface oxidation alone is even less favorable in terms of destruction rates.

In addition, a review of the mechanisms of bubble formation, growth, and detachment was carried out, and is included in this Handbook as Appendix C.

2.3.2 Description of Aeration Experiments

The experimental configuration used for performing the series of N_2H_4 and MMH aeration experiments is shown in Figure 2.3.1. Two 10 gallon aquariums each contain five gallons of diluted solution having N_2H_4 or MMH concentrations from 15 to 1100 ppm. Either $CuSO_4$ or Fe_2O_3 or both were introduced as catalyst. Diluted N_2O_4 was added to several runs. Three medium porosity spargers located near the bottom of each large tank provided air flows from zero to approximately two liters per minute; maximum air flow through the 500 ml bubbler was approximately one liter per minute.

A Gast pump provided air for the system. This air was filtered through a large cotton wad in an erhlenmeyer flask. An agitator was provided for stirring, but was infrequently used since sufficient agitation was provided by the rising air bubbles to maintain homogeneity. Pinch clamps on the hose lines adjusted air flow to the spargers, and the flow rate was measured by an in-line flow-meter. Usually a much larger amount of air was injected than was

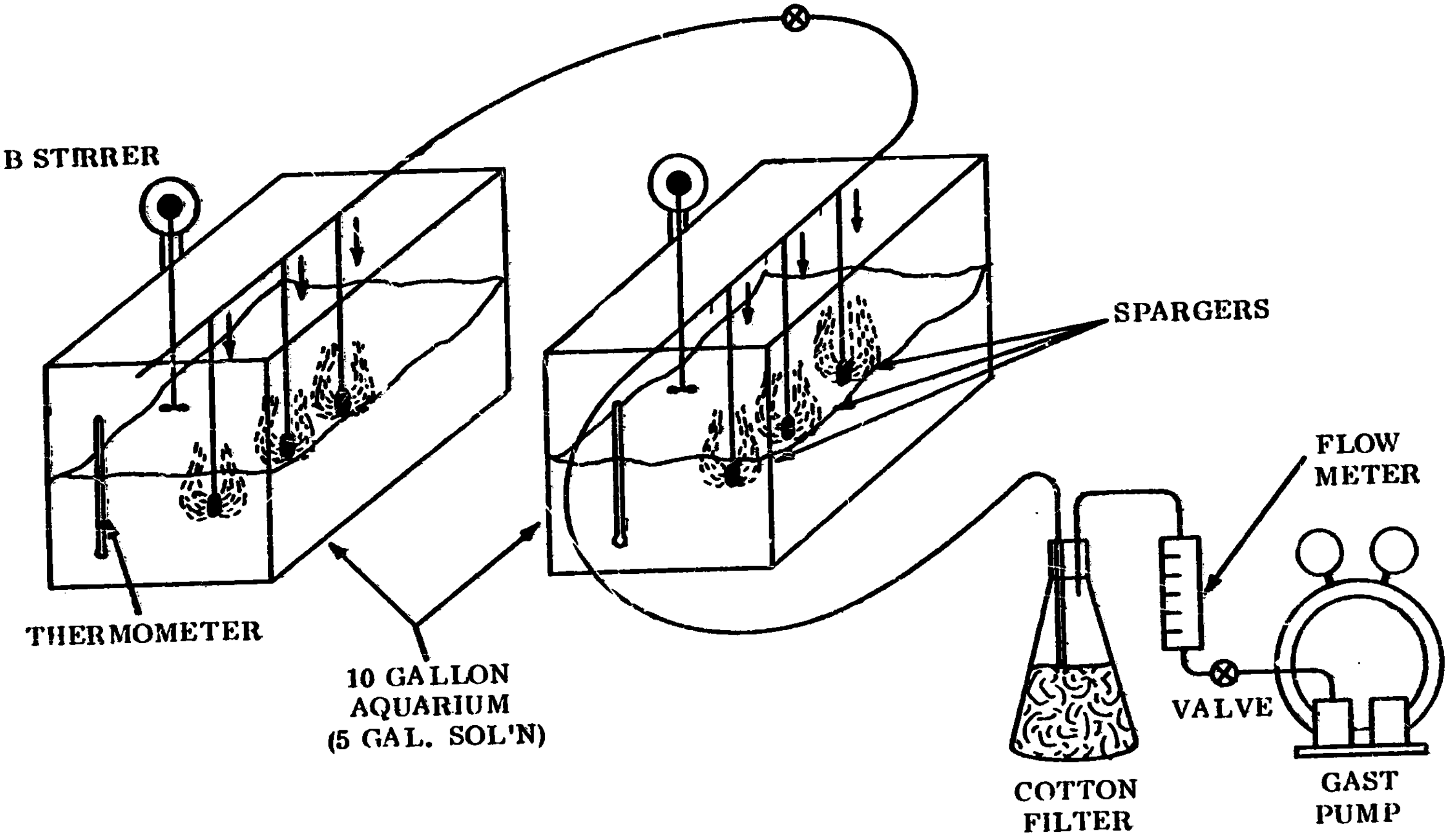


Figure 2.3.1 Schematic of lab set-up for air sparging runs.

necessary to maintain saturated oxygen (D.O.) levels in the solution. The tanks were loosely covered with aluminum foil to minimize evaporation losses.

The duration of runs was from two hours to nine days. Samples of liquid were removed periodically and analyzed for (1) residual N_2H_4 or MMH concentration, (2) pH, (3) dissolved oxygen. Chlorine demand was measured in a few cases. The temperature of the bath was measured at intervals. Analysis of the hydrazines was performed using p-dimethylamino benzaldehyde.

2.3.3 Results

Figure 2.3.2 shows that the rate of decomposition of N_2H_4 was considerably higher when using .02 mg/l Cu^{++} catalyst than without the catalyst. Without the catalyst the oxidation of N_2H_4 proceeded slowly in spite of ample air bubbling and good agitation in the tank. Figure 2.3.3 shows that the Fe_2O_3 catalyst was not as effective in increasing the rate of N_2H_4 decomposition as the Cu^{++} catalyst (Run 3-3). The primary difficulty with the Fe_2O_3 catalyst was its insolubility, resulting in most of it settling to the bottom of the tank so that contact opportunity was considerably lessened. Runs 3-4 and 3-6 both show a rapid decomposition rate, the N_2H_4 concentration being reduced from over 300 ppm to 1 ppm in one day. The curve for Run 3-5 also shows rapid decomposition of N_2H_4 in the first day. This run was discontinued when the air hose disconnected during the run.

Figure 2.3.4 shows that the decomposition of N_2H_4 was rapid when using either Cu or Cu/Fe catalyst. The tests were not conclusive in deciding on the more efficient catalyst. Almost complete disappearance of N_2H_4 occurred after two days of air treatment with either catalyst, starting with high concentrations. Figure 2.3.5 also shows high rates of decomposition of the hydrazines. The MMH decomposed more slowly than N_2H_4.

In Figure 2.3.6, the MMH concentration decreased faster (Runs 5-1A, 5-1C) during the first 10-20 hours of aeration than thereafter. In all three runs the reaction rate was relatively high until the concentration dropped to the 20-40 ppm level. Such a dropoff in reaction rate with depletion of one of the reactants is normal in many chemical reactions, as the contact opportunity of the reacting molecules is greatly reduced when nearing the depletion level. The oxidant

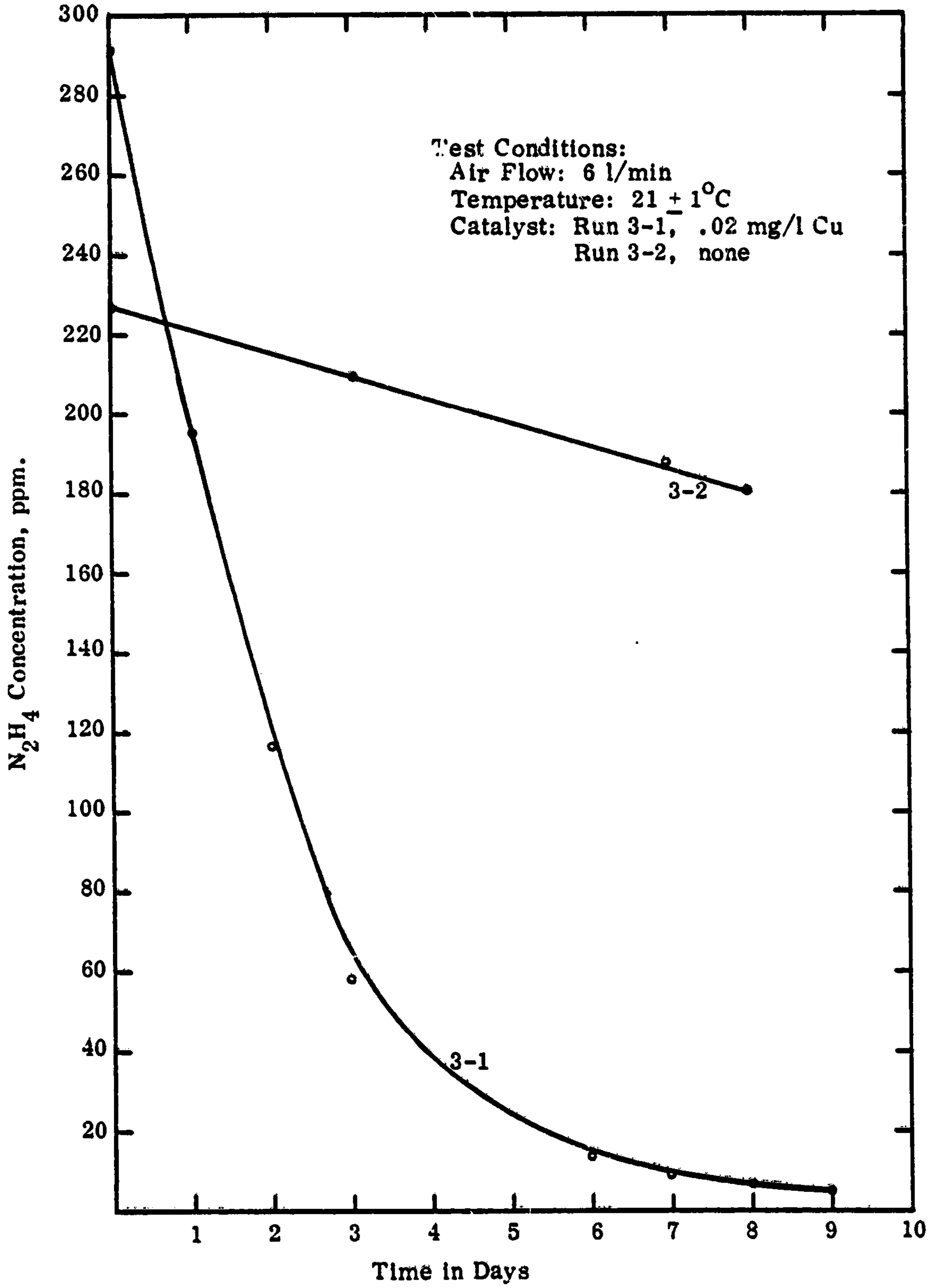


Figure 2.3.2 Air oxidation of N_2H_4.

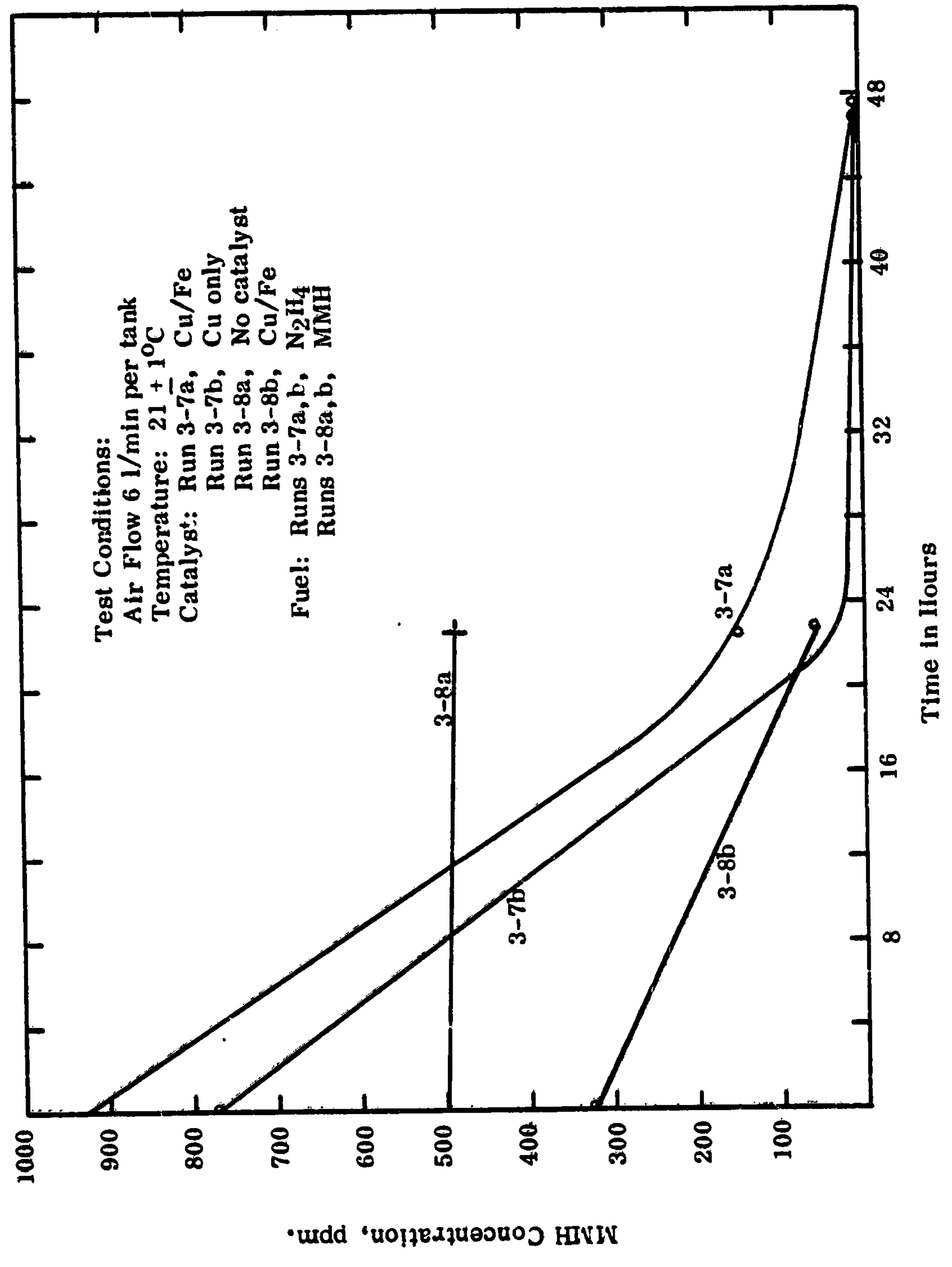


Figure 2.3.4 Air oxidation of N_2H_4 and MMH.

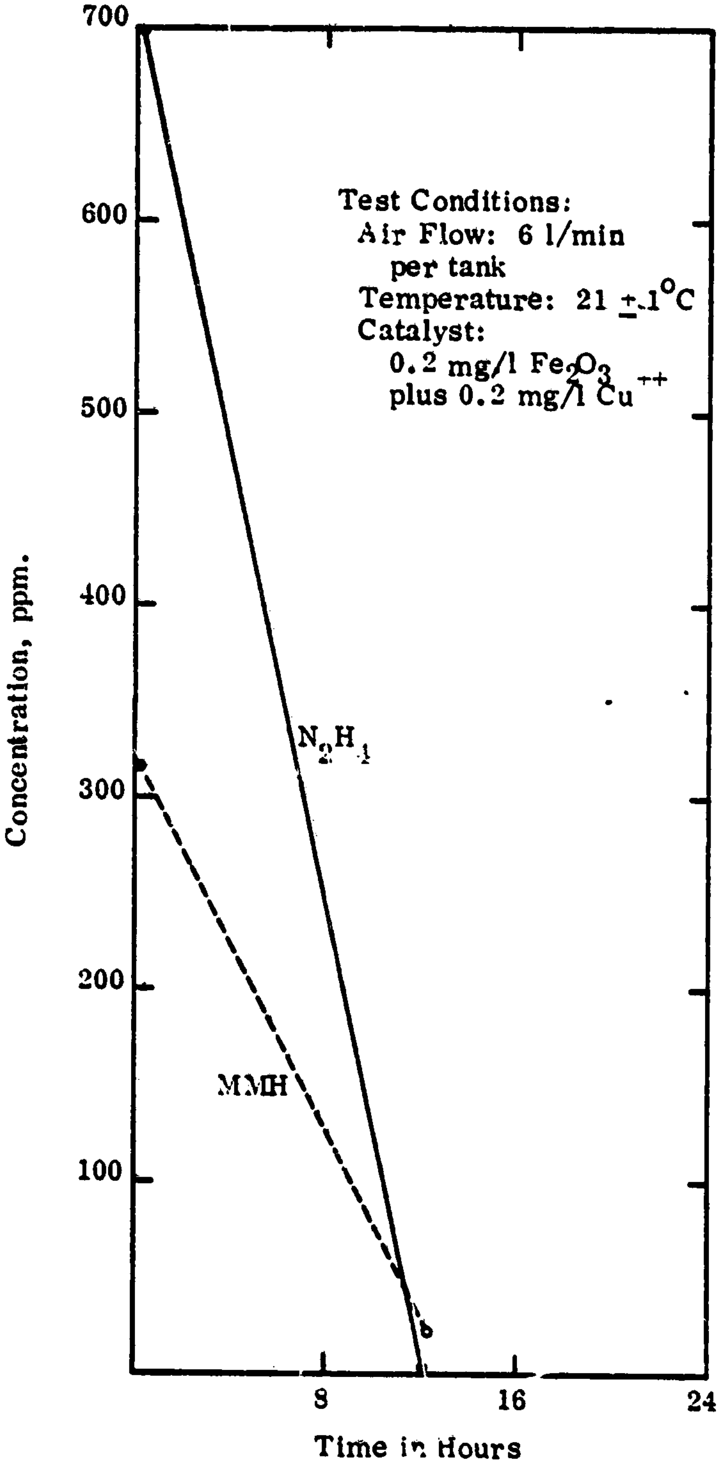
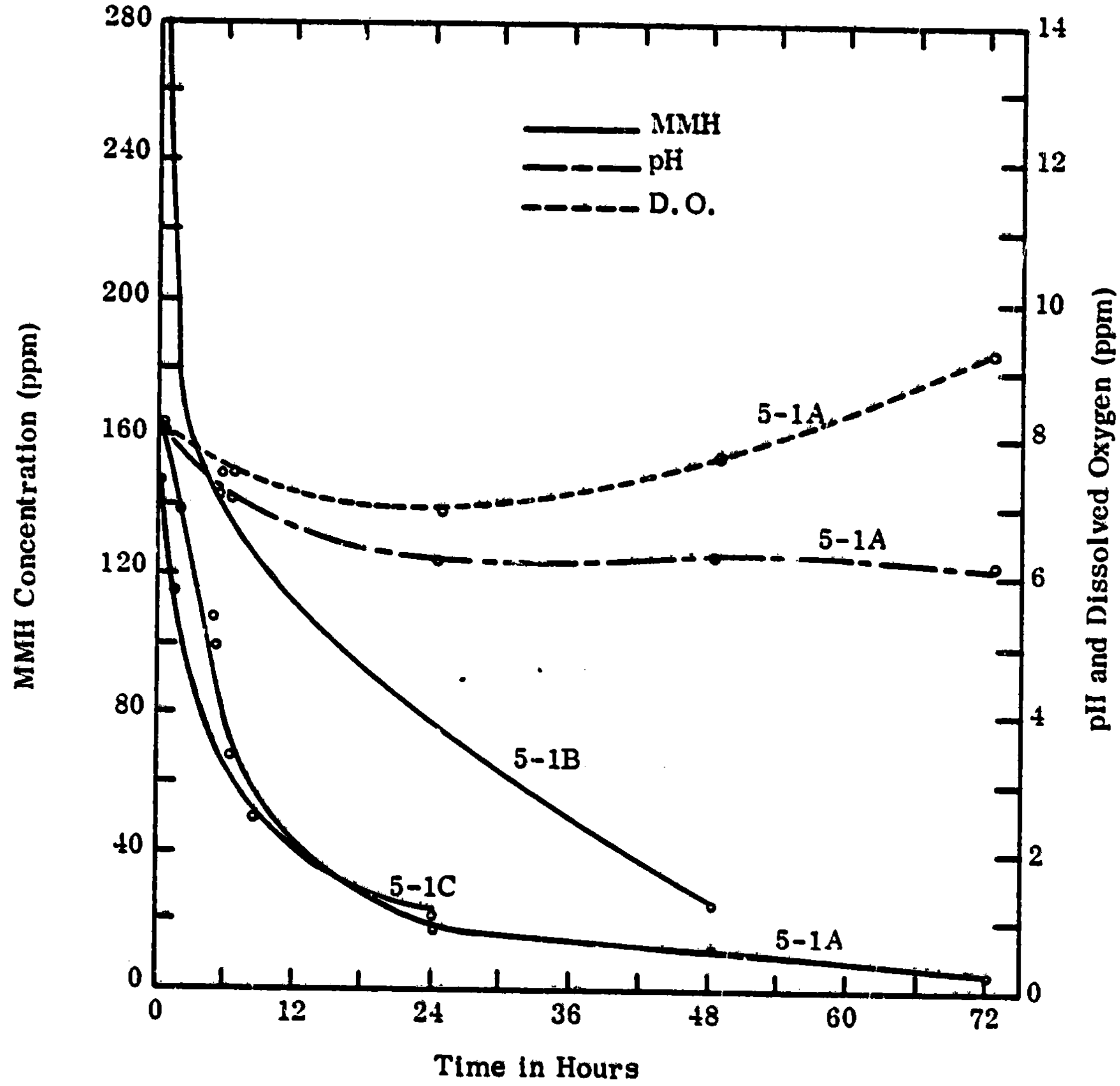


Figure 2.3.5 Air oxidation of N_2H_4 and MMH, Runs 3-9a, 3-9b.



Run #	5-1A	5-1B	5-1C
Volume of Solution	19.0 liters	19.0 liters	19.0 liters
Catalyst	0.2 mg Cu^{++}/liter	0.2 mg Cu^{++}/liter	0.2 mg Cu^{++}/liter
Oxidant	Air	Air	Air
Oxidant Flow Rate	6 liters/min	0.5 liter/min	0.5 liters/min
Initial MMH Concentration	160 ppm	285 ppm	140 ppm
R_T	1.93×10^5 min	1.72×10^4 min	2.10×10^4 min
Time Required for 50% Decomposition	270 min	300 min	288 min

Figure 2.3.6 Air oxidation of MMH.

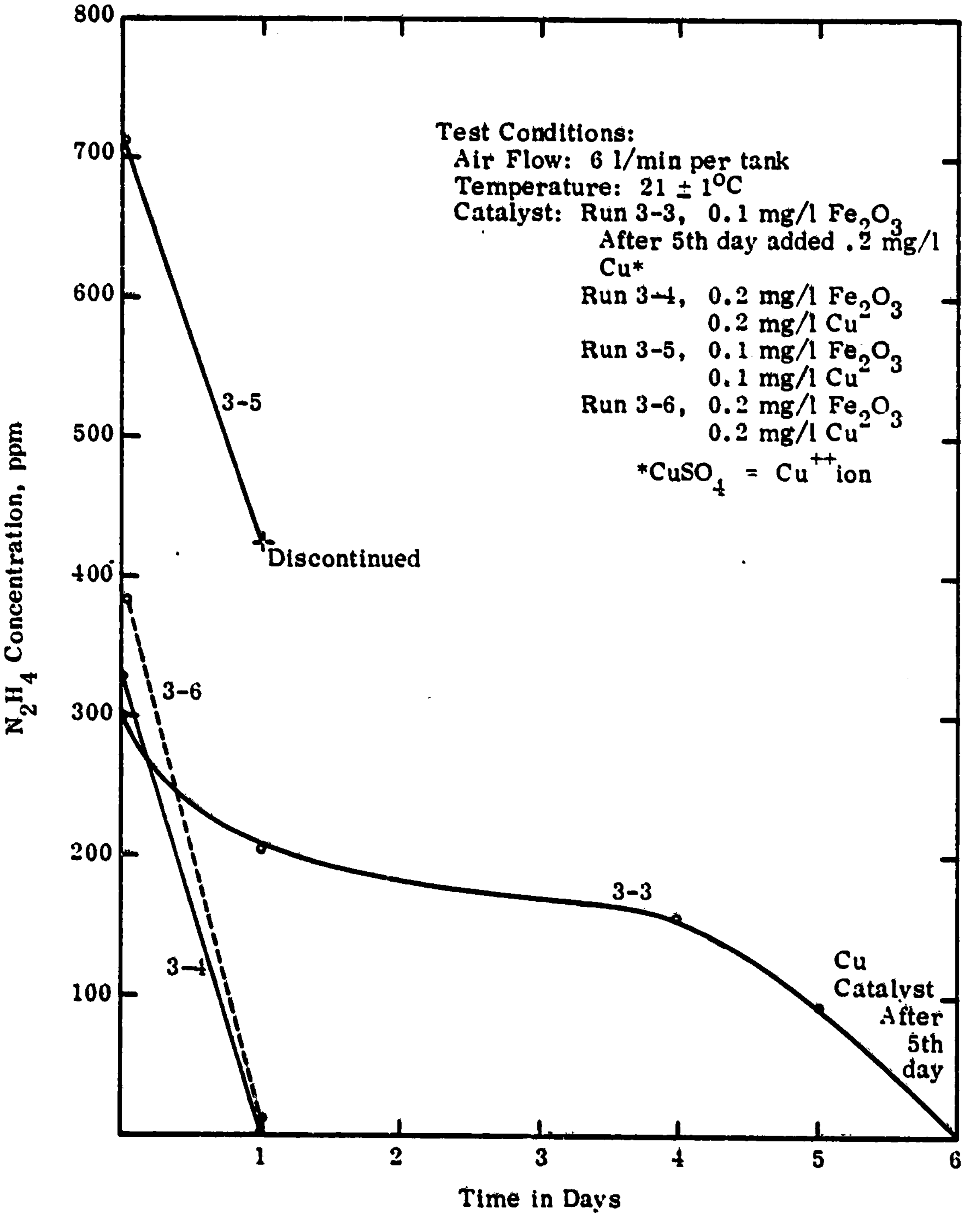


Figure 2.3.3 Air oxidation of N_2H_4.

flow rates in all three runs, but particularly in Run 5-1A, were probably excessive. This high flow rate, rather than a slow reaction rate, is the cause of the high value of R_I in Run 5-1A.

R_I, the Reaction Index, in an arbitrarily established index to permit a relative comparison of rates of reaction of various Oxidants. By definition the reaction index is

$$R_I = \frac{Qt_{\frac{1}{2}}}{M}$$

where $t_{\frac{1}{2}}$ = the time in minutes required for 50% destruction of fuel, as measured by the p-DAB analytical method.

Q = quantity of oxidant pumped into the solution during this time interval, in mg per liter of liquid.

M = initial fuel concentration in mg/liter.

We can further write

$$Q = \frac{mt_{\frac{1}{2}}}{V}$$

where

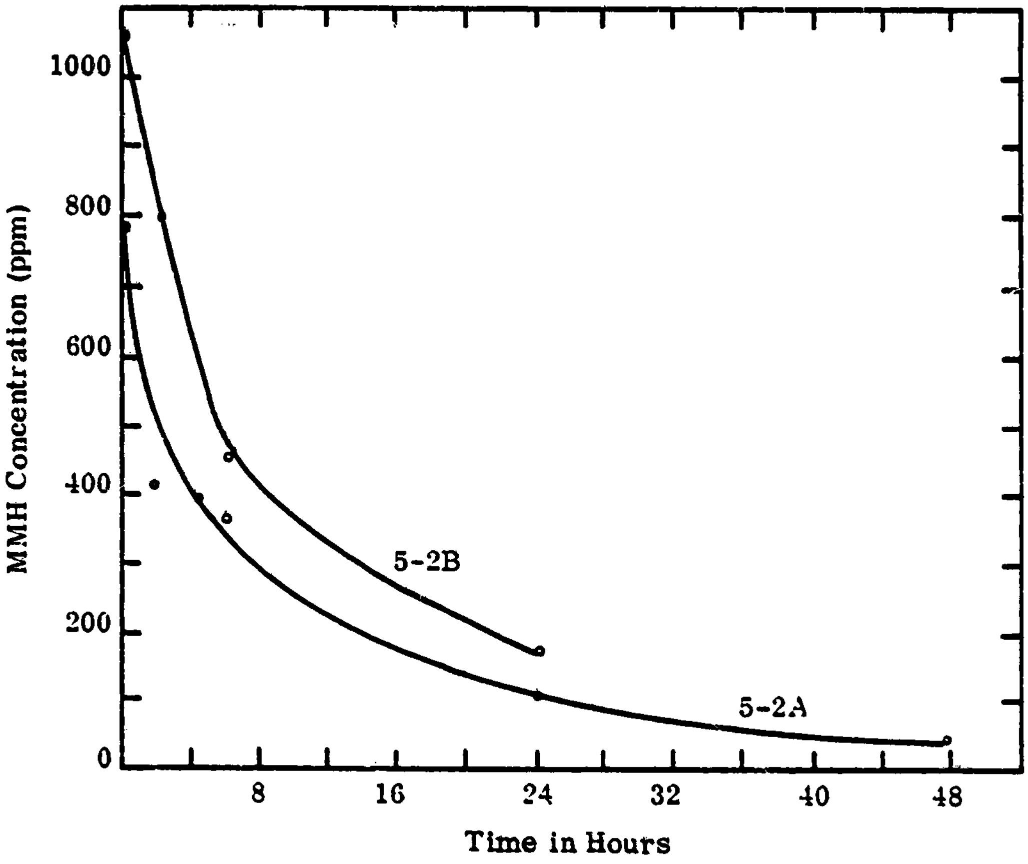
m = the oxidant mass feed rate to the treatment tank, in mg/min.

V = the liquid volume in the treatment tank, in liters.

It will be noted that the Reaction Index has dimensions of time. R_I was found to be useful for correlating parameters such as reaction rate, reactant concentrations, volume and mass feed rate.

The D.O. in Run 5-1A increased slowly with time and reached approximately 9 ppm after 72 hours aeration. An increase in D.O. as the MMH is destroyed is to be expected since MMH is an oxygen scavenger. Neither the D.O. nor the pH are shown for 5-1B and 5-1C, to prevent clutter. The curves shown are typical. The pH dropped from approximately 8 to 6 during aeration, showing an increase in acidity from the oxidation products formed. The time required to decompose 50% of the MMH was on the order of 4 to 5 hours.

Figure 2.3.7 shows that the R_I was only slightly higher in Runs 5-2A and 5-2B than in 5-1B and 5-1C, although the MMH concentration was increased from about 200 to about 1000 ppm. The time to decompose 50% of the MMH was on the order of 4 to 5 hours.



Run #	5-2A	5-2B
Volume of Solution	19.0 liters	19.0 liters
Catalyst	0.2 mg Cu^{++}/liter	0.2 mg Cu^{++}/liter
Oxidant	Air	Air
Oxidant Flow Rate	6 liters/min	6 liters/min
Initial MMH Concentration	780 ppm	1060 ppm
R_I	3.13×10^4 min	3.32×10^4 min
Time Required for 50% Decomposition	240 min	288 min

2.3.7 Air oxidation of MMH.

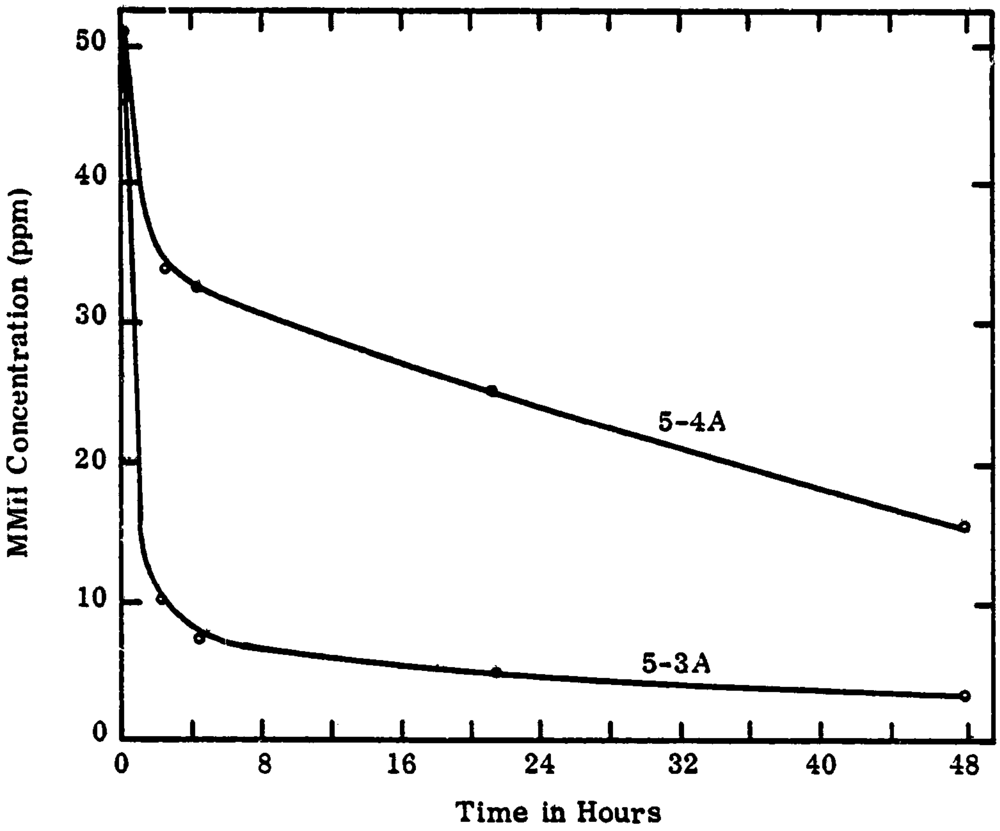
The curves for Runs 5-3A and 5-4A (Figure 2.3.8) show the pronounced effect the Cu^{++} catalyst had on R_I. Without catalyst R_I was about 500 times higher than with catalyst. The time required to decompose 50% of the MMH without catalyst was about 20 times longer than to decompose it with catalyst: 22 hours versus 1 hour.

Figure 2.3.9 shows the effects of no catalyst and of not bubbling air through the MMH solution. The R_I in Run 5-5 was 1.46×10^5, which is one of the poorest results with Cu^{++} catalyst. However, in the absence of a catalyst the R_I increased to 5.7×10^6 in Run 5-5A. The absorption of O_2 occurred at a lower rate than when bubbling air through the solution. In Run 5-11, the 50% decomposition time was 33 hours even though a catalyst was present. In Run 5-5A, without catalyst, the 50% decomposition time was 30 hours. Thus in the latter two runs MMH decomposition was six to seven times slower than in Run 5-5, containing catalyst.

The D.O. and pH are shown for Runs 5-5A and 5-11. The pH varied little in either run. The D.O. naturally was lower in Run 5-11, without air agitation, and fluctuated as absorption occurred.

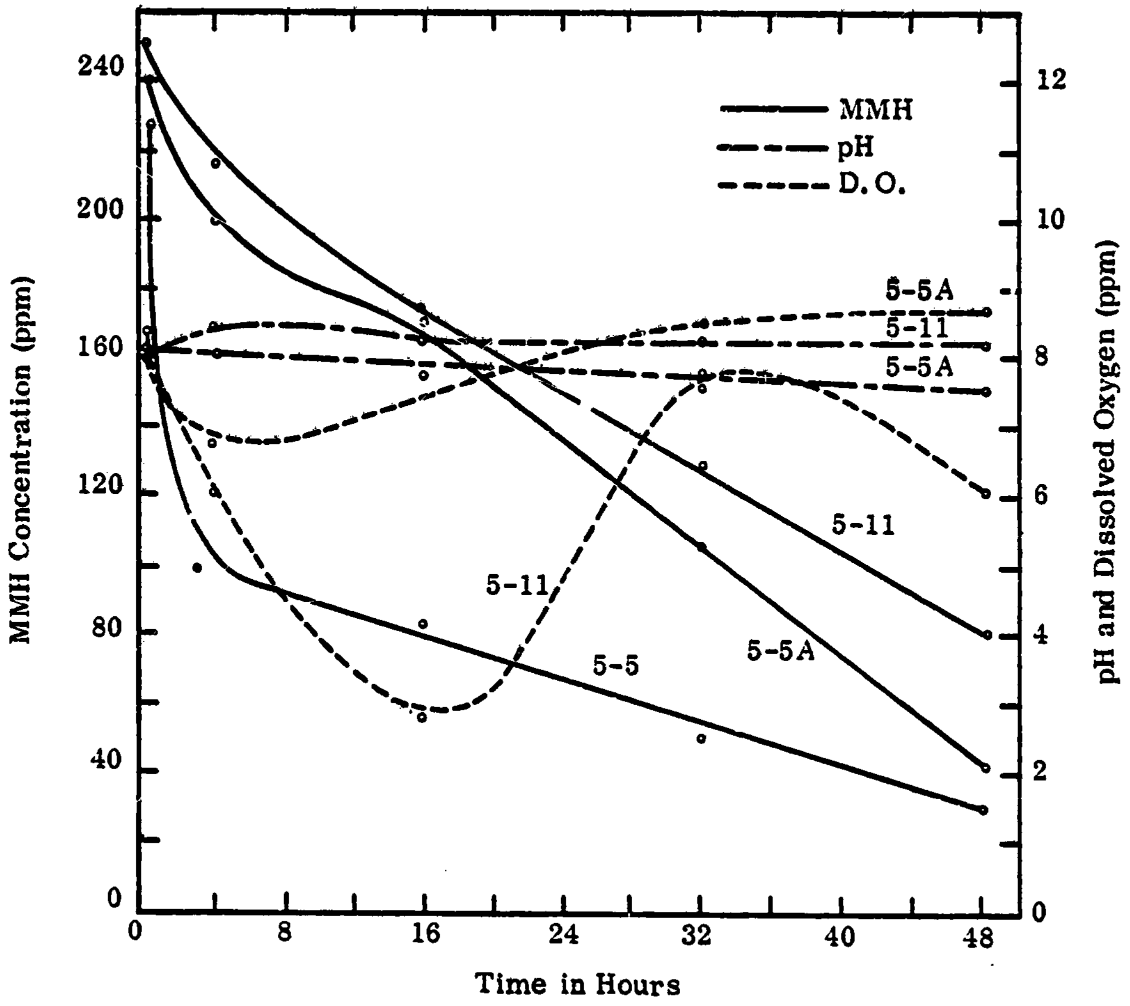
Run 5-13 (Figure 2.3.10) exhibited a more rapid reaction rate than those obtained in previous similar runs. The reason for this could not be found, and might be due to an experiment error in the MMH analysis step. The reaction rates in Run 5-13B, without catalyst and containing N_2O_4, and in Run 5-13C, no air bubbling and containing N_2O_4, were very slow compared to the previous runs.

The results are also presented in Tables 2.3.1 and 2.3.2. The values obtained for R_I are seen to cover a range of approximately three orders of magnitude, depending on the various operating conditions. Optimum operating conditions obviously could not be established by the runs performed in the laboratory. It is evident from these data, however, that the presence of catalyst plays a major role in controlling the rate of reaction. At low pH, as derived



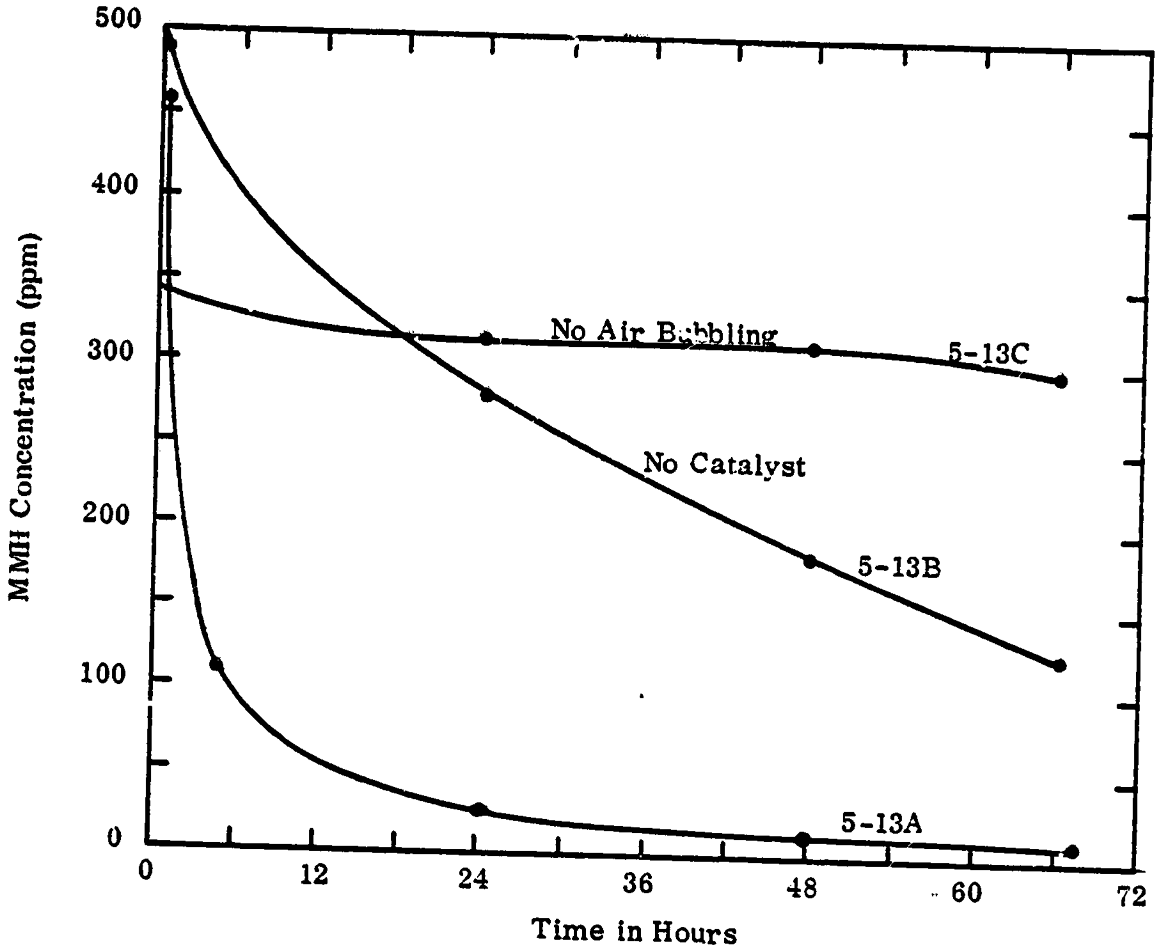
Run #	5-3A	5-4A
Volume of Solution	19.0 liters	19.0 liters
Catalyst	0.2 mg Cu^{++}/liter	No catalyst
Oxidant	Air	Air
Oxidant Flow Rate	6 liters/min	6 liters/min
Initial MMH Concentration	51 ppm	51 ppm
R_T	3.00 x 10^4 min	1.45 x 10^7
Time Required for 50% Decomposition	60 min	1320 min

2.3.8 Air oxidation of MMH.



Run #	5-5	5-5A	5-11
Volume of Solution	19 liters	19 liters	19 liters
Catalyst	0.2 mg Cu^{++}/liter	None	0.2 mg Cu^{++}/liter
Oxidant	Air	Air	Air
Oxidant Flow Rate	6 liters/min	6 liters/min	None
Initial MMH Concentration	228 ppm	240 ppm	250 ppm
R_I	1.46×10^5 min	5.73×10^6 min	-------
Time Required for 50% Decomposition	280 min	1800 min	1980 min

2.3.9 Air oxidation of MMH



Run #	5-13A	5-13B	5-13C
Volume of Solution	19.0 liters	19.0 liters	19.0 liters
Catalyst	0.2 mg Cu^{++}/liter	No catalyst	0.2 mg Cu^{++}/liter
Oxidant	Air	Air	Air
Oxidant Flow Rate	6 liters/min	6 liters/min	None
Initial MMH Concentration	460 ppm	480 ppm	340 ppm
N_2O_4 Concentration	None	200 ppm	200 ppm
R_T	7.47×10^3 min	3.33×10^6	--------
Time Required for 50% Decomposition	90 min	1940 min	After 3 days only 9% decomposed

2.3.10 Air oxidation of MMH

TABLE 2.3.1

SUMMARY OF MMH AERATION RUNS (Second Series)

Run No.	Catalyst	MMH Concentration ppm	R_I Minutes	Remarks
5-1A	Yes	160	1.93×10^5	Excessive amount of air used
5-1B	Yes	295	1.12×10^4	
5-1C	Yes	140	2.10×10^4	
5-2A	Yes	780	3.13×10^4	
5-2B	Yes	1060	3.32×10^4	
5-3A	Yes	51	[illegible].00 $\times 10^4$	
5-4A	No	51	1.45×10^7	
5-5A	No	240	5.73×10^6	
5-5	Yes	228	1.46×10^5	
5-11	Yes	250	--- - ---	No air bubbling
5-12A	No	125	--- - ---	Contains 150 ppm N_2O_4
5-12B	Yes	125	--- - ---	Contains 150 ppm N_2O_4
5-13A	Yes	460	7.47×10^3	
5-13B	No	480	3.33×10^3	Contains 200 ppm N_2O_4
5-13C	Yes	340	--- - ---	Contains 200 ppm N_2O_4 No air bubbling
5-14	No	18	--- - ---	No air bubbling (natural evaporation)

TABLE 2.3.2

% REDUCTION OF MMH VERSUS AIR BUBBLING TIME

Run No.	MMH ppm	Air Flow Rate	Catalyst	% Reduction			
				Time in Days			
				1/2	1	2	3
5-1A	160	6 l/min	Yes	73	88	92	97
5-1B	285	0.5 l/min	Yes	64	79	92	--
5-2A	780	6 l/min	Yes	72	87	94	--
5-2B	1060	6 l/min	Yes	71	84	--	--
5-3A	51	6 l/min	Yes	88	92	94	--
5-4A	51	6 l/min	No	44	54	71	--
5-5	228	6 l/min	Yes	55	62	77	86
5-5A	240	6 l/min	No	20	29	56	81
5-11	250	0	Yes	19	30	48	68
5-12A	125	6 l/min	No	16	24	28	30

TABLE 2.3.2 (continued)

% REDUCTION OF MMH VERSUS AIR BUBBLING TIME

Run No.	MMH ppm	Air Flow Rate	Catalyst	% Reduction Time in Days			
				1/2	1	2	3
5-12B	125	6 1/min	Yes	23	37	52	61
5-13A	460	6 1/min	Yes	78	94	97	98
5-13B	480	6 1/min	No	16	41	61	75
5-13C	340	0	Yes	3	4.5	7	9
5-14	18	0	No	0	0	0	0

from introducing N_2O_4, the reaction rate was adversely affected. The R_I values of runs without catalyst are 100 to 1000 times longer than the R_I values of runs with catalyst. Aerated runs have much lower R_I values (higher reaction rates) than runs under stagnant conditions.

It is believed that even the best R_I figures in the table can be lowered by adjusting the air flow to an optimum value.

The chlorine demand, which corresponds roughly to the amount of fuel in solution, was measured in some runs, with results in good agreement with the other measurements.

2.3.4 Conclusions

The major disadvantage of the aeration method is the amount of time required. For initial concentrations in the range studied (up to 1100 ppm) we have shown that 90% or more of the fuel is oxidized within two to three days in runs with catalyst, adequate air bubbling, and no dissolved N_2O_4. However, the rate decreases as the concentration drops below 40 ppm or so, and really low concentrations will require long periods of time. In many cases, even the two day time period will be unacceptably long, especially in the case of the methylated hydrazines with their possible carcinogenic risks.

Oxygenation (use of pure O_2 instead of air), which is covered in the following section, is of interest because of the possibility of increasing the reaction rate and at the same time reducing the size of equipment, time and space requirements.

One of the characteristic aspects of aeration is the relatively high energy requirement for O_2 dissolution from the atmosphere into the aqueous solution of fuel. This cost is a consequence of the basic mass transfer process which is almost entirely liquid phase controlled, a feature which is a characteristic of all processes involving the dissolution of sparingly soluble gases in liquids. The presence of the large amount of N_2 in air further impedes the O_2 transfer by reducing the available O_2 partial pressure driving potential for the interphase transfer process. As a result, substantial amounts of energy are expended in creating a large gas-liquid surface area and a high degree of interfacial turbulence to enhance the interphase mass transfer rate. The high energy costs of the aeration method are at least partially offset, however, by relatively low expected maintenance and equipment costs, low labor requirement, and the small amounts of chemicals required.

The major advantage of this method is its simplicity, the fact that potentially harmful chemicals are not required, and the fact that any need for secondary disposal of a liquid effluent can be precluded by proper design. The pond water can be reused indefinitely, and evaporative losses made up by water addition if rainfall is inadequate. The copper ions contained in the pond will serve as an effective algaecide.

The question of atmospheric release is still largely unresolved. The primary oxidation products are water, nitrogen, carbon dioxide, and ammonia. An odor of NH_3 or amine was noticed in the vicinity of the laboratory tanks for one or two hours after adding hydrazine or MMH. No air sample was taken to ascertain the concentration of NH_3 above the liquid surface, or the possible presence and concentration of N_2H_4 or MMH above the surface. Because of the likelihood that these gases are evolved during the early stages of the process, we believe application of the aeration process in an open pond should be approached with considerable caution except as a final step following some other primary treatment stage. In a closed system, the process is a very attractive one provided the time involved is not a problem, and that the following conditions are met:

1. Continuous air bubbling.
2. Use of copper catalyst, or equivalent.
3. pH maintained above nine.

2.4 OXYGENATION

2.4.1 Introduction

An alternative approach to the oxidation of hydrazine fuels in dilute aqueous solutions, mentioned briefly at the end of the preceding section, is to bubble pure oxygen through the solution rather than air. This variation is currently seeing increased application in sewage treatment and potable water treatment processes; McKinney and Pfeffer[1] reviewed the state-of-the-art several years ago and listed several advantages relative to aeration:

1. The possibility of avoiding excessively high gas flow rates, thereby decreasing power requirements.
2. Increased rate of stabilization of organic material.
3. The ability to operate at increased organic loadings.
4. Reduction in plant size and equipment.
5. Increase in D.O. content of pregnant solution being treated.

One disadvantage of oxidation using pure O_2 or O_3 is the need for a closed system. The space occupied by such a system can be small compared to a pond, however. Furthermore, the possible need for a closed system even in the case of aeration, because of the release, of NH_3 and fuel vapors, was mentioned in the preceding section.

The basic oxidation equations for O_2 treatment are the same as those written at the beginning of the preceding section. The experiments described below are also quite similar to the aeration experiments described in the preceding section.

2.4.2 Experimental Results

The laboratory apparatus used for the O_2 runs is shown in Figure 2.4.1. The experimental procedure was the same as in the aeration runs. The solution contained MMH in all of these runs, at concentrations up to 4500 ppm. N_2O_4 was also present in two of the runs, at concentrations up to 4000 ppm.

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[1] McKinney, R.E. and Pfeffer, J.T.: "Oxygen-Enriched Air for Biological Waste Treatments." Water and Sewage Works, October 1965.

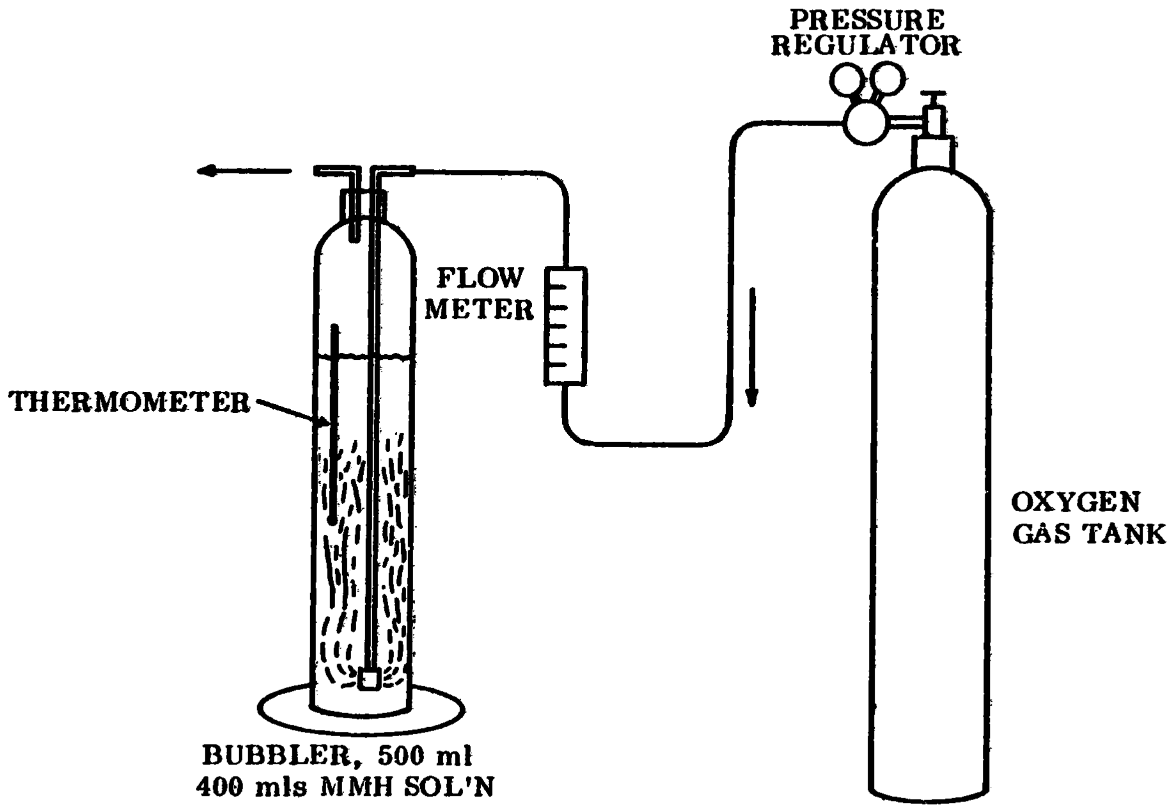


Figure 2.4.1 Schematic of lab set-up for oxygen sparging runs.

Table 2.4.1 shows that the five runs with catalyst, and without N_2O_4, had R_I values in the 1300 to 4800 minute range, which is about one order of magnitude lower than those obtained by aeration. It also shows that the three runs without catalyst had essentially little or no reduction of MMH within the time period. In the two runs containing dissolved N_2O_4, the reduction was only about 20% after two hours of oxygenation. In general, these results are similar to those obtained in the aeration runs except for the higher reaction rate. The pH generally did not change much with pure O_2, in contrast to O_3 or air. With air, pH changed by 1 ± 1 pH unit. In O_2 runs, pH decreased by 5 ± .5 units in runs containing only MMH.

Figure 2.4.2 shows the slope of curve 21 to be very steep, while the slope of curve 21A is about zero. The D.O. curves increase to the 11 or 12 ppm level, then drop off somewhat after 90 minutes to about 8 - 10 ppm. The initial pH of Run 21A was 8.8 and changed very little during oxygenation. The pH of Run 21 dropped about 1 pH unit indicating formation of some acidic reaction products, as was expected.

Figure 2.4.3 shows the steep slopes of curves 22 and 37, with a catalyst, compared to zero slope in curve 22A without a catalyst. The D.O. for Run 37 could not be measured after 15 minutes of sparging, probably as a result of miscalibration of the D.O. instrument. The D.O. of treated solutions in Runs 22 and 22A was approximately 9 ppm.

Figure 2.4.4 again shows the deleterious effect of dissolved N_2O_4 on rate of reaction in Runs 24 and 25, compared with Run 23 without N_2O_4. The D.O. curves are similar to previous runs. The pH in Runs 24 and 25 was approximately 2.

Figure 2.4.5 shows the steep slopes of curves 23 and 26 with a catalyst and the slight slope of curve 23A not containing a catalyst. The pH was between 8 and 10 in the three runs and did not change appreciably during the oxygenation period.

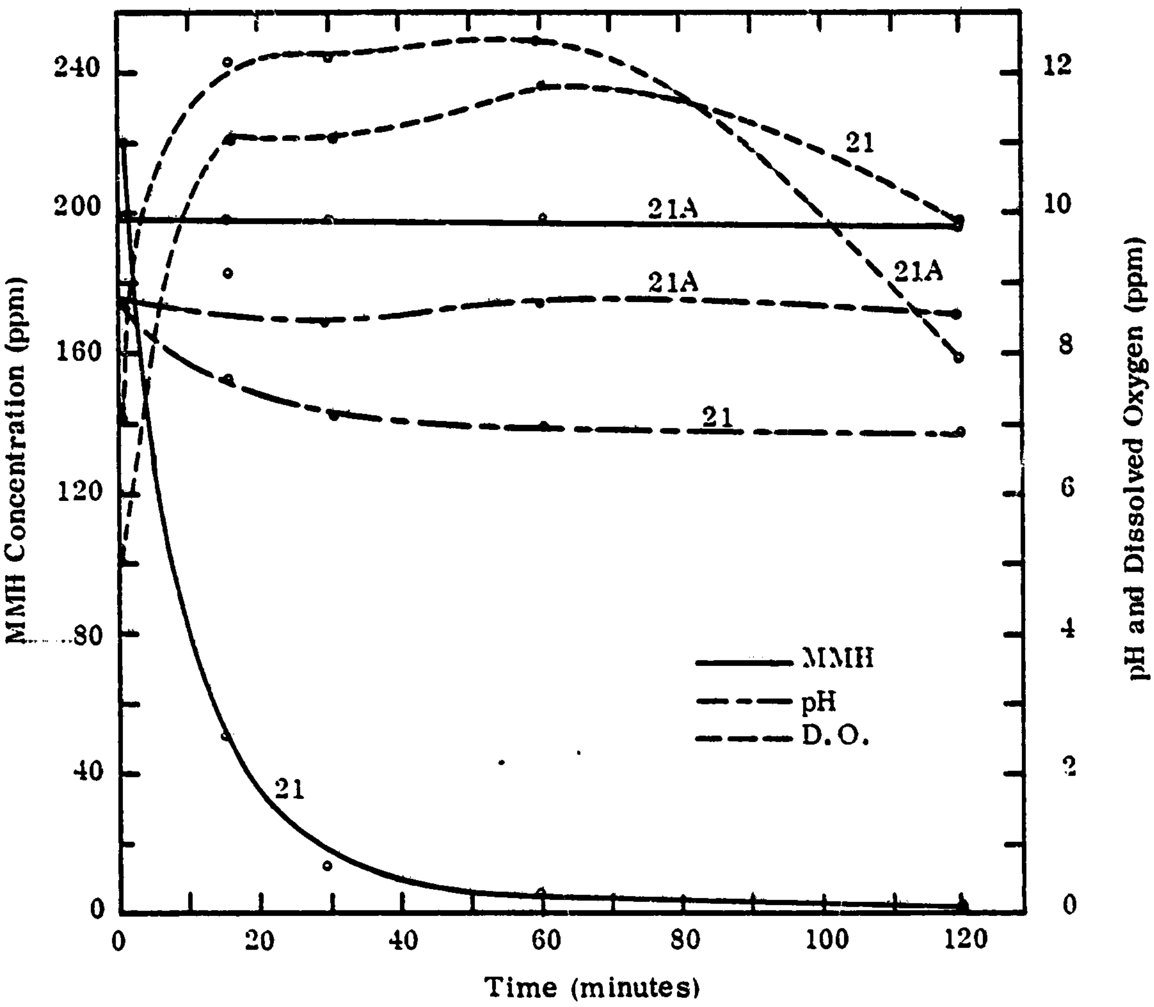
In general, the time required to decompose 50% MMH in oxygenated runs with catalyst was on the order of 35 minutes, except in Run 21, which was a special (low concentration) case.

TABLE 2.4.1

SUMMARY OF OXYGENATION EXPERIMENTS

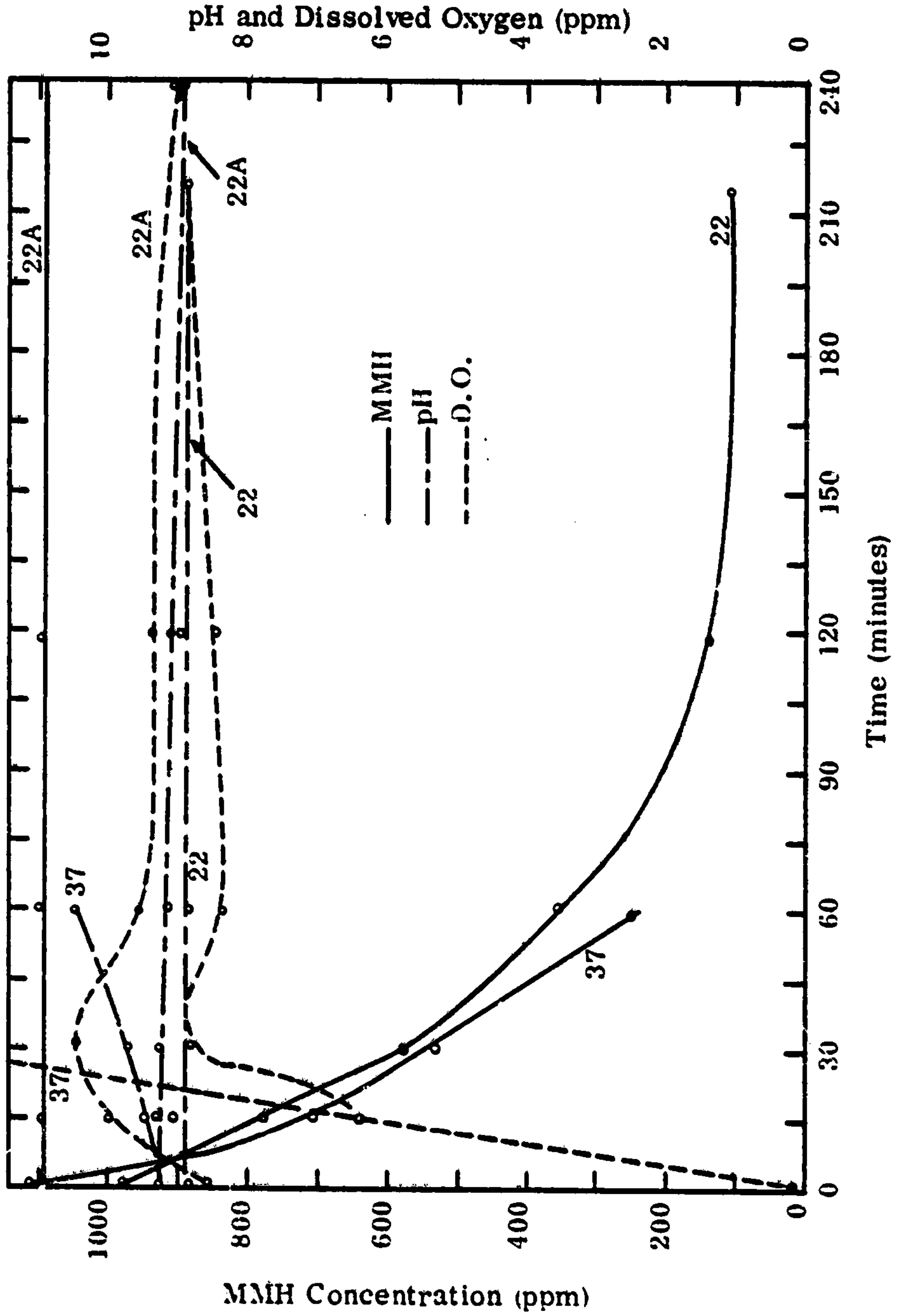
Volume 400 ml in bubbler

Run No.	$\frac{MMH}{N_2O_4}$ (ppm)	Catalyst	R_I, Min.	% Reduction Time in Hours 1/4	1/2	1	2	pH Initial	pH Final
21	$\frac{170}{0}$	Yes	2.19×10^3	82	92	96	97	8.6	7.0
21A	$\frac{200}{0}$	No	--- - ---	0	0	0	1	8.8	8.8
22	$\frac{1000}{0}$	Yes	5.37×10^3	15	43	82	90	8.8	8.8
22A	$\frac{1150}{0}$	No	--- - ---	1	2	4	5	---	---
23	$\frac{2600}{0}$	Yes	1.75×10^3	27	48	79	91	8.9	9.1
23A	$\frac{2100}{0}$	No	--- - ---	0	0	0	0	7.1	7.8
24	$\frac{1050}{2000}$	Yes	--- - ---	14	17	20	23	2.2	2.0
25	$\frac{2100}{4000}$	Yes	--- - ---	16	17	18	19	1.9	1.9
26	$\frac{4500}{0}$	Yes	1.46×10^3	23	39	68	86	9.9	9.8
37	$\frac{1125}{0}$	Yes	3.38×10^3	22	45	63	--	10.2	---



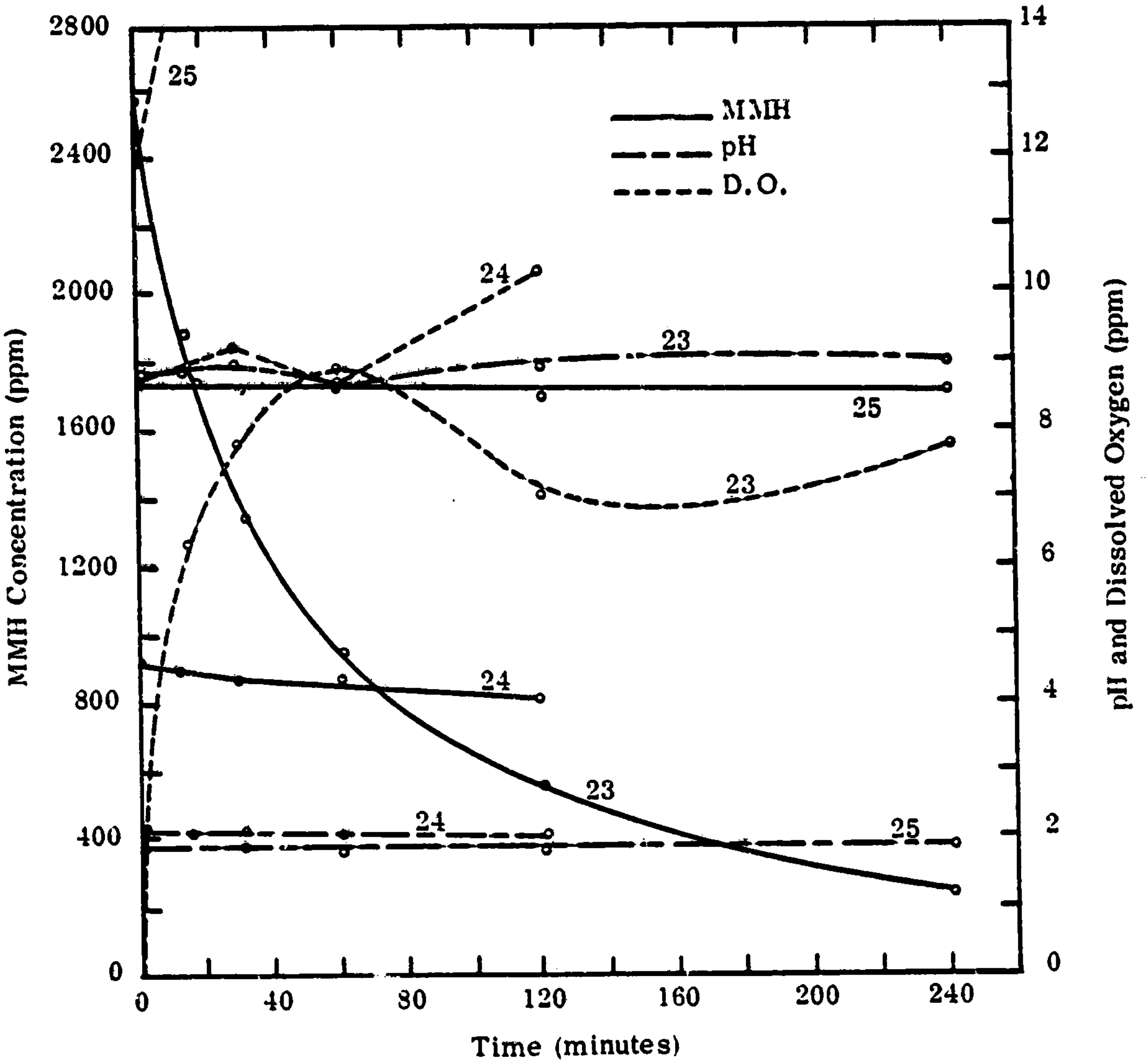
Run #	21	21A
Volume of Solution	400 ml	400 ml
Catalyst	0.2 mg Cu^{++}/liter	No Catalyst
Oxidant	Oxygen	Oxygen
Oxidant Flow Rate	1 liter/min	1 liter/min
Initial MMH Concentration	170 ppm	200 ppm
R_I	2190 min	-------
Time Required for 50% Reduction	10 min	-------

Figure 2.4.2 Oxygenation of MMH



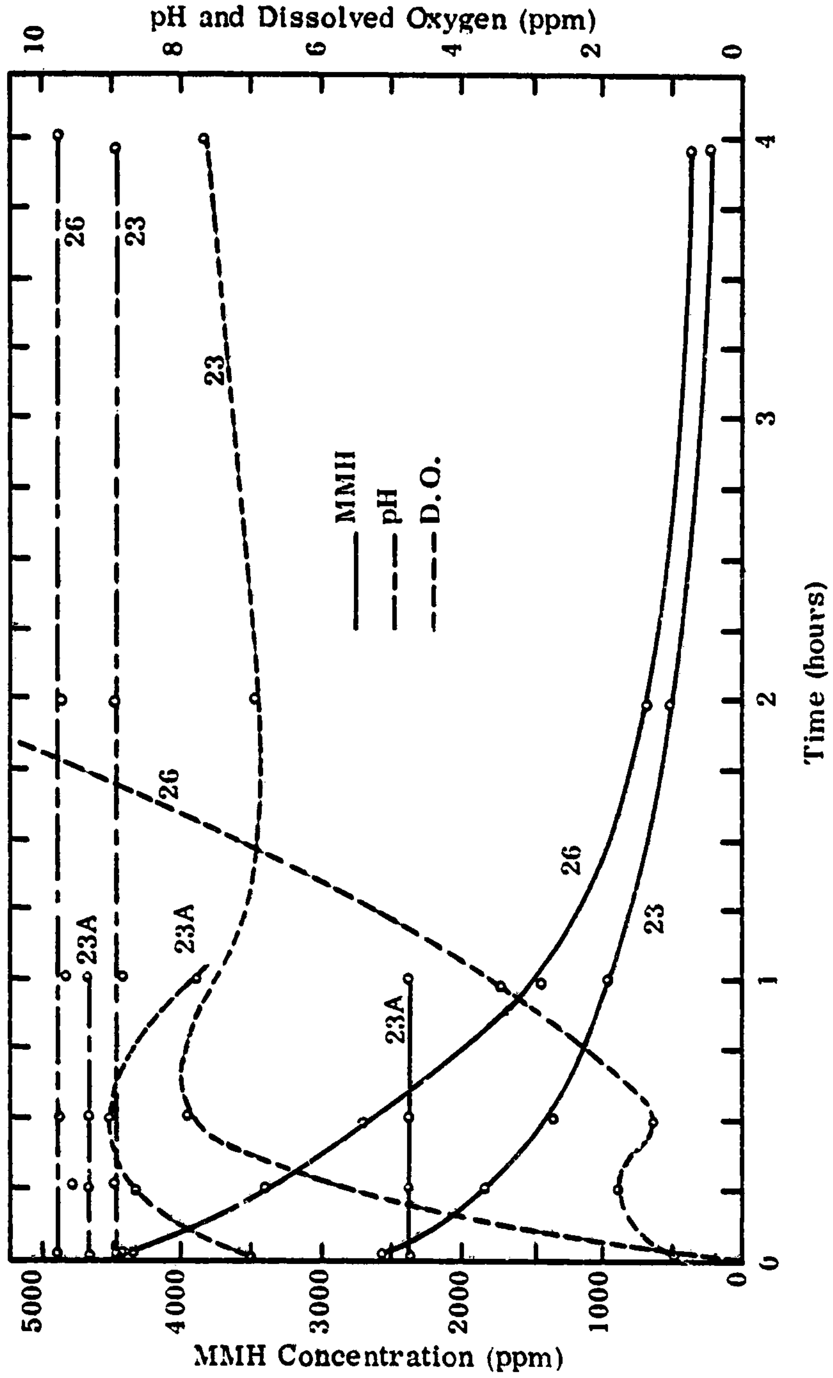
Run #	22	22A	37
Volume of Solution	400 ml	400 ml	400 ml
Catalyst	0.2 mg Cu^{++}/liter	No catalyst	0.2 mg Cu^{++}/liter
Oxidant	Oxygen	Oxygen	Oxygen
Oxidant Flow Rate	1 liter/min	1 liter/min	1 liter/min
Initial MMH Concentration	1000 ppm	1500 ppm	1125 ppm
R_I	5370 min	-------	3380 min
Time Required for 50% Decomposition	38 min	-------	32 min

Figure 2.4.3 Oxygenation of MMH



Run #	23	24	25
Volume of Solution	400 ml	400 ml	400 ml
Catalyst	0.2 mg Cu^{++}/liter	0.2 mg Cu^{++}/liter	0.2 mg Cu^{++}/liter
Oxidant	Oxygen	Oxygen	Oxygen
Oxidant Flow Rate	1 liter/min	1 liter/min	1 liter/min
Initial MMH Concentration	2600 ppm	1050 ppm	2100 ppm
Initial $N2O_4$ Concentration	------	2000 ppm	4000 ppm
MMH Concentration after adding N_2O_4	2600 ppm	900 ppm	1750 ppm
R_I	1750 min	------	-------
Time Required for 50% Reduction	35 min	------	-------

Figure 2.4.4 Oxygenation of MMH



Run *	23	23A	26
Volume of Solution	400 mls	400 mls	400 mls
Catalyst	0.2 mg Cu^{++}/liter	No catalyst	0.2 mg Cu^{++}/liter
Oxidant	Oxygen	Oxygen	Oxygen
Oxidant Flow Rate	1 liter/min	1 liter/min	1 liter/min
Initial MMH Concentration	2600 ppm	2100 ppm	4500 ppm
R_I	1750 min	-------	1460 min
Time Required for 50% Reduction	35 min	-------	42 min

Figure 2.4.5 Oxygenation of MMH

2.4.3 Conclusions

These experiments showed that destruction of MMH by oxygenation requires a moderate period of time under the various conditions provided in the experimental runs. Use of a catalyst increases the reaction rate of MMH with O_2 by a factor of ten to one hundred. The presence of dissolved N_2O_4 hinders the reaction of MMH with O_2.

2.5 OZONATION

2.5.1 Introduction

A variation on the oxygenation process described in the preceding section involves the addition of an ozonator between the O_2 supply and the treatment tank. The ozonator converts some of the flowing O_2 to O_3, a much more powerful oxidizing agent, for the purpose of destroying hydrazine fuels in the aqueous solution more rapidly and completely. Disadvantages of this process, in addition to the increased cost and complexity, are the toxicity of the ozone itself and the increased corrosiveness of the O_3. However, unlike chlorine and chlorine-containing compounds (discussed in the following sections) this process need not introduce a new type of atom to the solution with the attendant risk of forming still more harmful products. The initial capital cost of an ozone facility is higher than that of a chlorine facility, but operating costs are lower. Residual O_3 at the end of the process is easily decomposed either by thermal means or by a chemical reducing agent. Problems of temperature and pressure are minimal and readily solvable.

Ozone is a colorless gas at room temperature and is an allotropic form of oxygen. Like O_2, O_3 is a supporter of combustion and is one of the most powerful oxidizing agents known. It has an electronegative oxidation potential exceeded only by flourine. O_3 attacks almost all organic compounds. The reaction mechanism is believed to involve the free radical formed by dissociation of the O_3 molecule,

$$O_3 \longrightarrow O_2 + \underset{\text{(Free Radical)}}{O^{\cdot}},$$

although this has been disputed by certain authours.[1] Among the many organic functional groupings which are oxidized by O_3 are amines, mercaptans, aldehydes, and hydrocarbons.

The major reaction products of ozonation of organic compounds may include CO_2, N_2, or NO_3^-. Minor reaction products may include intermediates

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[1] Trambarulo, R., et.al.: "The Molecular Structure, Dipole Moment & Factors of Ozone from its Microwave Spectrum". The Journal of Chemical Physics, Volume 21, page 851 (1953).

which were not investigated or quantified in the laboratory experiments that we performed. The treatment by-products are usually harmless or only slightly toxic, and may be beneficial (O_2). There is normally an increase in dissolved oxygen (D.O.) as water undergoes this treatment process. The small amount of NO_3^- formed should not interfere with regulations for dumping into streams.

In the ozone oxidation, only one atom of oxygen from the O_3 molecule is highly reactive. On this basis, for example, one pound of MMH should consume 4.5 lbs. O_3 and yield 9 lbs. of molecular O_2 as by-product:

$$CH_3N_2H_3 + 2O_3 \rightarrow CH_3OH + N_2 + H_2O + 2O_2$$

some of the O_2 would also react with the MMH.

At normal temperatures O_3 residuals disappear rapidly from water, according to the equation:

$$P = 100 \exp(-0.275t)$$

where P = percent of residual O_3 at time t.

O_3 is more soluble in water than O_2, but because its available partial pressure is very low, concentrations of O_3 above a few mg/l are difficult to obtain under normal conditions of temperature and pressure. Figure 2.5.1 shows the theoretical solubility of O_3 in water. The presence of reactive species in solution will greatly alter the solubility of bubbling O_3 by shifting the equilibrium.

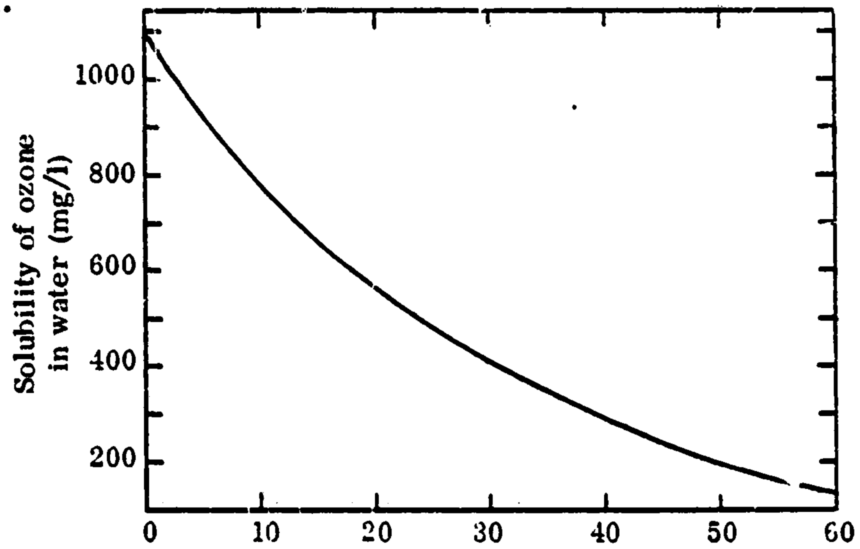

Figure 2.5.1 Solubility of ozone in water, in the absence of other reactive species.

Decomposition of O_3 is accelerated[2] by the presence of silver, maganese dioxide, sodium hydroxide, Cl_2 and other materials. It also decomposes photochemically in moist air in the presence of certain pollutants. However, decomposition is slow enough to permit the use of O_3-air or O_3-O_2 mixture streams for effecting destruction of many organic compounds. O_3 retains its strong oxidizing ability in aqueous solution. Temperature, pH, concentration of reaction products, and other factors may be important for achieving satisfactory results.

Ozone is toxic and can be dangerous to humans, plants, and aquatic forms of life. In water the half-life of O_3 is approximately 15-20 minutes, but in air O_3 exists for much longer periods (hours or days). It is therefore quite important to monitor atmospheric O_3 levels around the generating site.

The effects of O_3 on humans are described by Evans as follows: "The clinical effects immediately recognized from inhaling O_3 range from dislike of odor, headaches, drying of the mucous membranes of the mouth, nose, and throat, and changes in visual acuity. Continued exposure results in more serious changes such as functional derangements of the lung, pulmonary congestion, and edema."[3] A threshold range was assigned by Stern for each of these manifestations:[4]

Odor Detection	.02 to .05 ppm
Irritation of nose, throat	.05
Dryness of the upper respiratory mucosa	.1
Dryness of throat begins at	.1
Headaches, 30 minutes or longer	1.0
Changes in visual parameters	.2 to .5
Changes in pulmonary functions	0.1 to 1.0

The established TLV for ozone is 0.1 ppm by volume in air, or 0.2 mg/m^3.

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[2] Hann, V.A. and Manley, T.C.: "Ozone". Encyclopedia of Chemical Technology, Volume 9, page 735 (1952).

[3] Evans, F.L., editor: Ozone in water and Waste Water Treatment. Ann Arbor Science Publishing, Inc., Ann Arbor, Michigan (1972).

[4] Stern, A.C.: Air Pollution, Volume 1, Second edition. Academic Press, New York, N.Y. (1968).

Ozone is also believed to injure the parenchyma in the leaves of plants causing cellular collapse and pigmentation of the cell walls.[5] Small pale buff to reddish-brown lesions may appear at the injury threshold level of .03 ppm after 4 hours exposure. By comparison with chlorine the epidermis and mesophyll cells are affected. A bleaching occurs between the veins, tip and margin. Burn and leaf abscission also occur.

Because of the potential effectiveness of ozone as a means of destroying hydrazine fuels in dilute aqueous solutions, and the complete absence of any previous work done on this method either in the laboratory or in field applications, an experimental investigation was performed as a part of our study, as described in the following subsections. Economic considerations are also treated briefly at the end of this section.

2.5.2 Description of Ozonation Experiments

Figure 2.5.2 shows schematically the experimental apparatus that was used. The system was arranged so that either air or pure oxygen could be used as input to the ozonator. The O_3/O_2 or O_3/air mixture was bubbled into the water/fuel solution as in the aeration and oxygenation experiments discribed in the preceding sections, and the gaseous chlorine experiments described in the following section. A contactor system for adsorbing the O_3 would have provided more economical operation; the bubbler was used instead to provide maximum conformity with the other experiments.

O_3 for the experimental study was provided by a small commercial electrical discharge unit. Both dry O_2 from a commercial tank, and air from a Gast pump, were tried as an O_3 source. Measured amounts of the gas mixture were bubbles through a medium porosity difuser, located near the bottom of the gas absorption bottle, for periods of time necessary to effect complete or nearly complete destruction of the fuel. Contemporaneous gas and liquid analyses were performed to obtain rates, end products, temperature, D.O., pH and residual N_2H_4 or MMH concentrations.

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[5] Stern, A.C., et al: Fundamentals of Air Pollution. Academic Press, New York, N.Y. (1968).

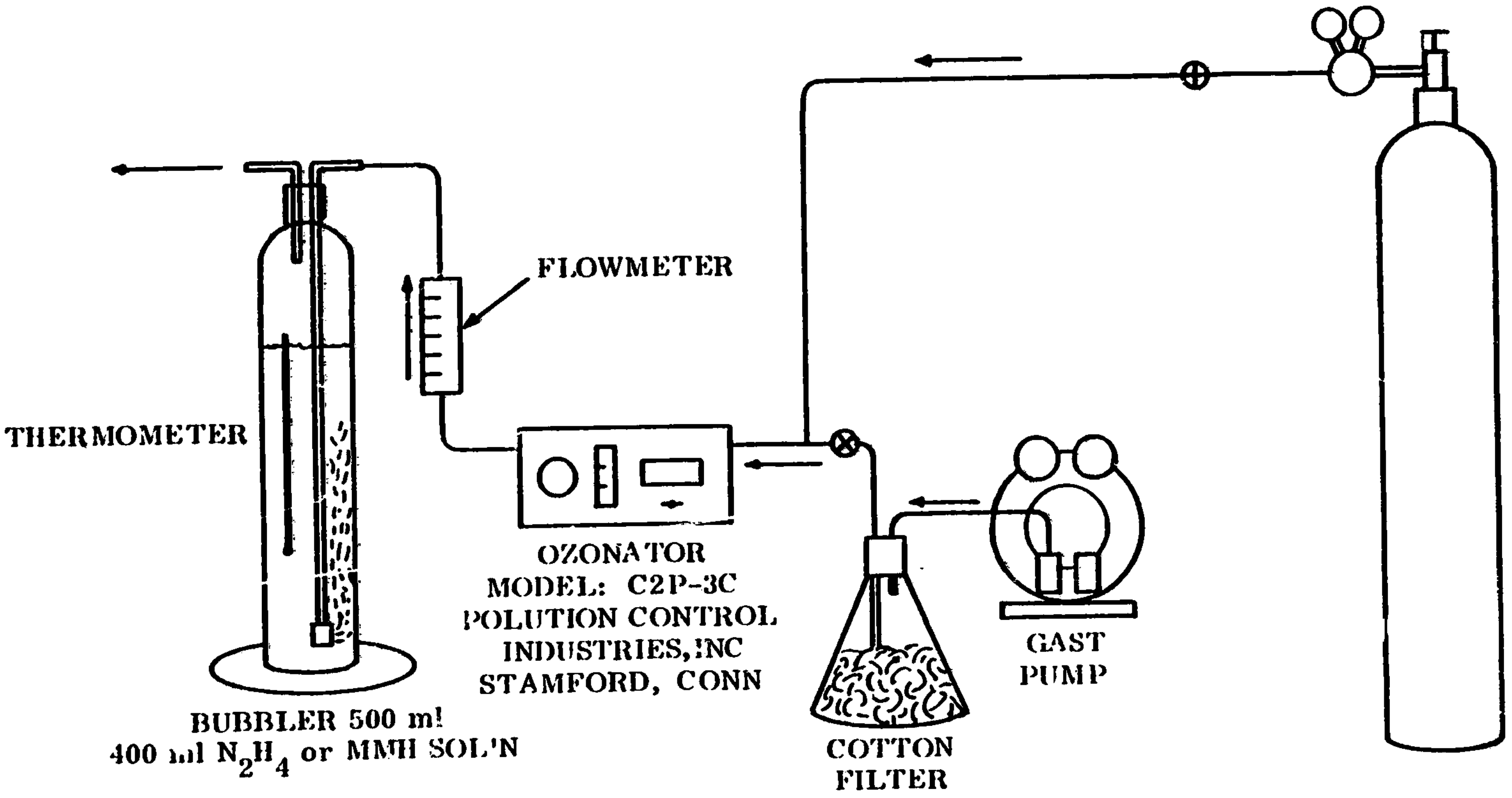

Figure 2.5.2 Schematic of lab set-up for ozone runs using air or O_2 feed source

Two series of experiments were run: a series of nine experiments with N_2H_4 solutions, followed by a series of ten experiments with MMH solutions. The amounts of O_3 generated varied somewhat depending on the oxygen source and the setting of the instrument; the approximate rates were 17 and 33 mg/min, using air and O_2 respectively, in the MMH runs, and 20 mg/min (using O_2 only as the feed for the ozonator) in the N_2H_4 runs. These generation rates have been estimated from the manufacturer's data sheet supplied with the ozonator; they were not measured. In all cases they represent small quantities relative to the O_2 flow rate, which was between 3150 and 9500 mg/min when pure O_2 was the feed stream, and 1325 mg/min when air was used.

Small samples (5-10 ml) were removed periodically during each run and analyzed for residual N_2H_4 or MMH, using the p-DAB reagent method. Ozone was analyzed using the orthotolidine reagent method[6] after establishing a concentration curve. The temperature was measured at 5 - 10 minute intervals.

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[6] "Standard Methods for the Examination of Water and Waste Water." American Public Health Association, New York, (1966).

2.5.3 Results

The N_2H_4 concentration and temperature vs. bubbling time are plotted for the N_2H_4 tests in Figures 2.5.3 through 2.5.7. The feed to the ozonator was O_2 in all of these runs, at a flow rate of 7.1 l/min. The O_2 generation rate was 20 mg/min, or approximately one part O_3 to 475 parts O_2, by mass.

Figure 2.5.3 shows (Tests 2, 3, and 4) that a 5000 ppm N_2H_4 solution was oxidized by O_3 in a controlled manner within a two hour period to about the 5 ppm concentration - a 99.9% reduction. As a comparison, in Test 5, a similar N_2H_4 solution was reduced by air bubbling only to the 3825 ppm level - a 24% reduction. Evaporation losses were not determined, but they may be assumed to be nearly identical for both set ups or slightly higher in Test 5 due to initial preheating.

In Test 6 (Figure 2.5.4), the ozonation of a preheated solution was only very slightly less effective than in tests 1 through 4 - a 97.9% reduction in 110 minutes. This is opposite to the anticipated quicker reaction at elevated temperature. This result was probably due to the more rapid disintegration (or lower solubility) of ozone in warm water. The shape of curve 6 corresponds closely with the shape of curve 7, resulting from a solution approximately 10 times stronger.

In Figure 2.5.5 are plotted the results of Tests 7, 8, and 9, with solutions containing higher initial N_2H_4 concentrations. The curves do not follow any particular pattern. There may be yet undetermined variables affecting the ozonation. Alternately, the ozonator itself was misbehaving during these runs, which may partly account for the variations.

In Figures 2.5.6 and 2.5.7 are plotted curves showing temperature as a function of bubbling time. The temperature increased as the reactions proceeded, then leveled off and finally dropped when the N_2H_4 was reduced to a low level.

Table 2.5.1 shows O_3 concentration in distilled water after bubbling for the stated times. These figures indicate (very roughly) the O_3 concentration to be expected in the N_2H_4 solution.

The results are summarized in Table 2.5.2, where R_I values are calculated on the basis of the total oxygen flow rate. It is clearly seen that the

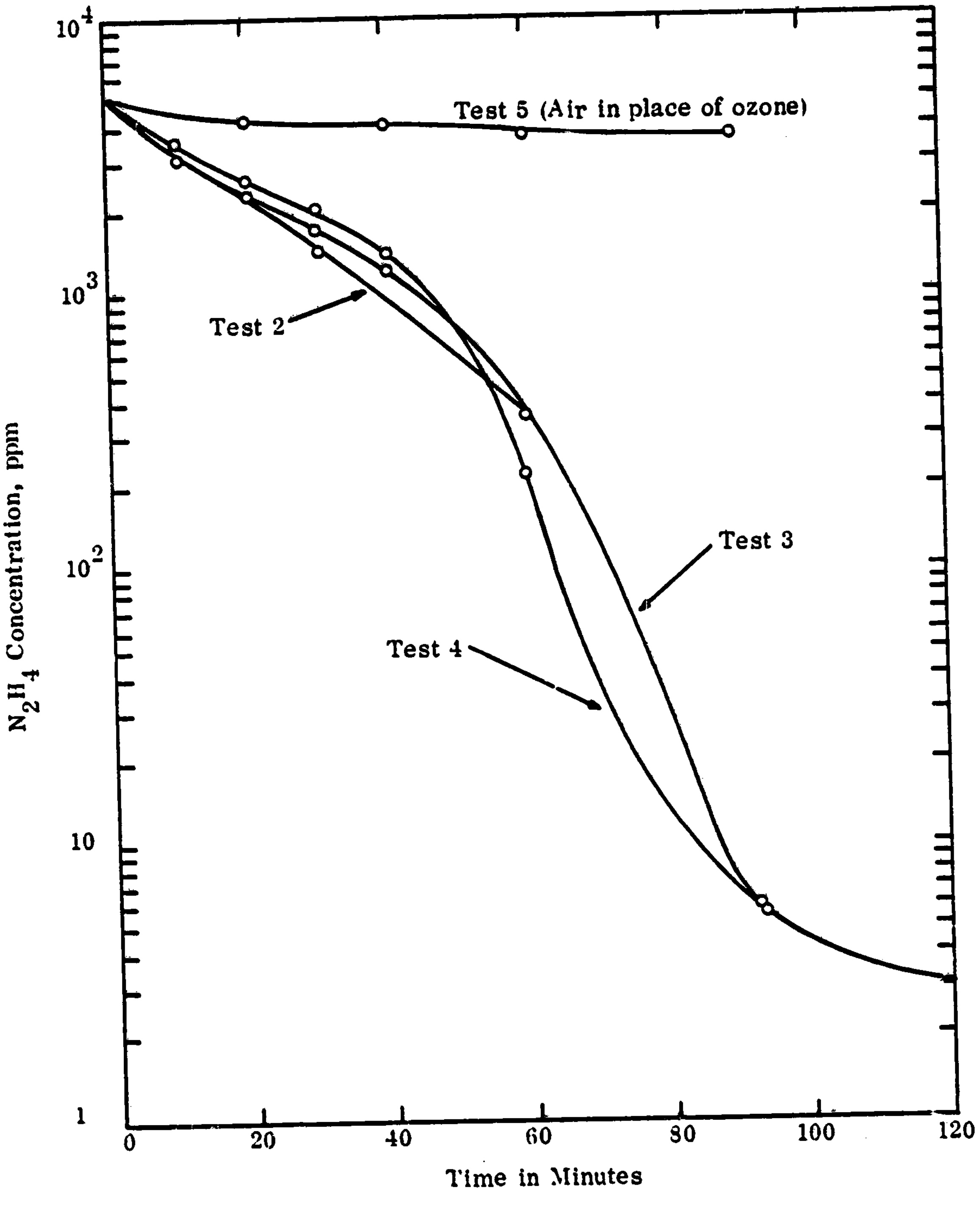


Figure 2.5.3 Ozonation and air oxidation of N_2H_4: fuel concentration as a function of time

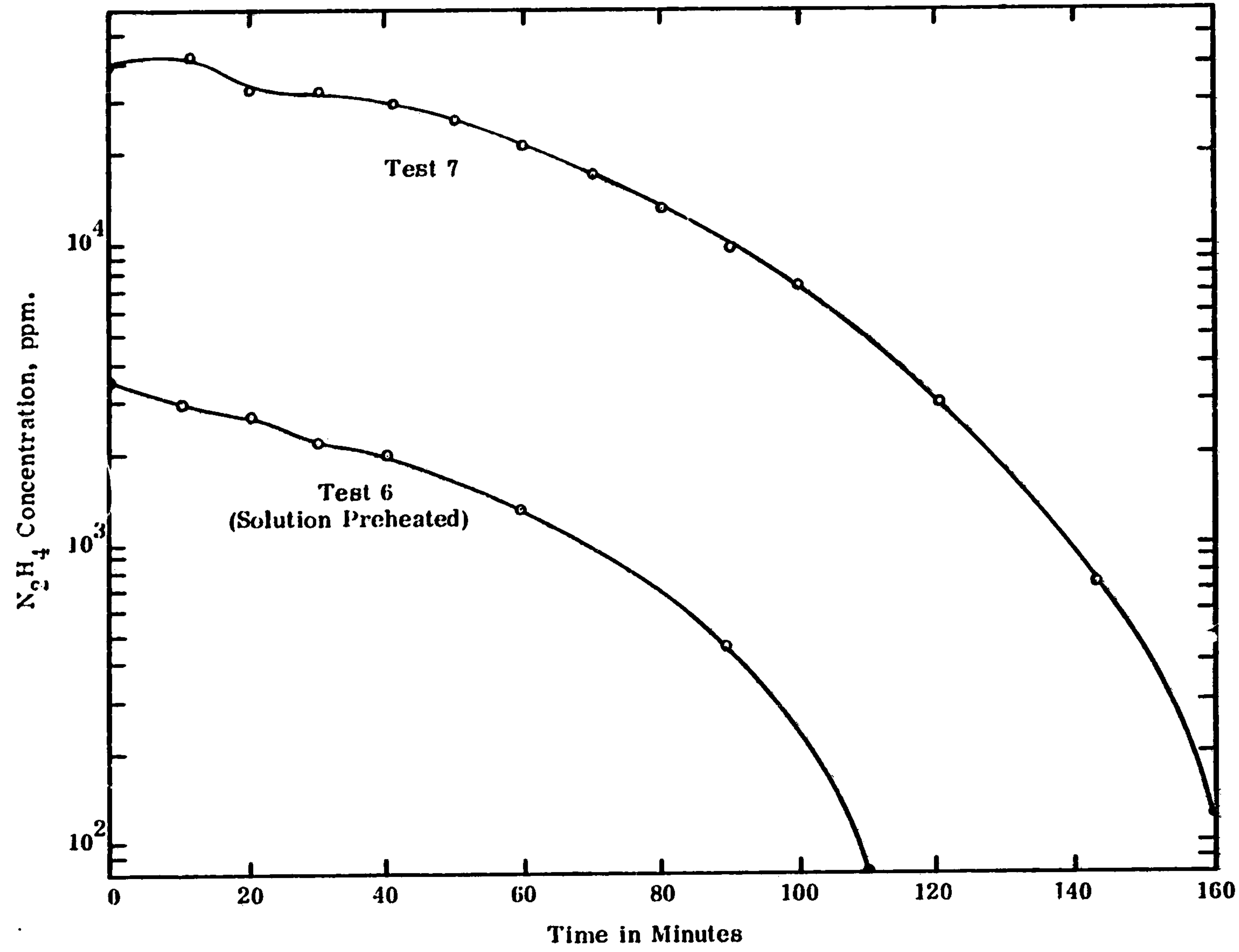


Figure 2.5.4 Ozonation of N_2H_4: fuel concentration as a function of time.

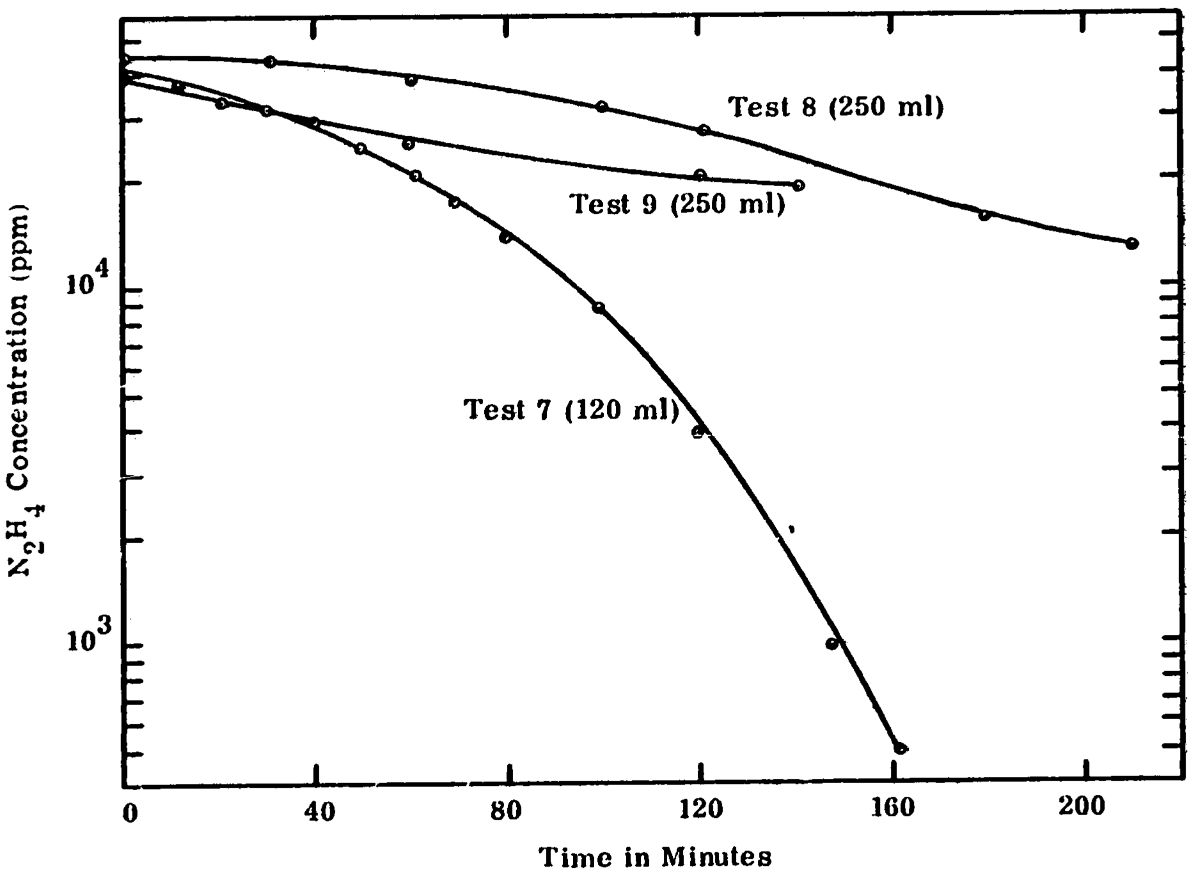


Figure 2.5.5 Ozonation of relatively concentrated solutions of N_2H_4: fuel concentration as a function of time.

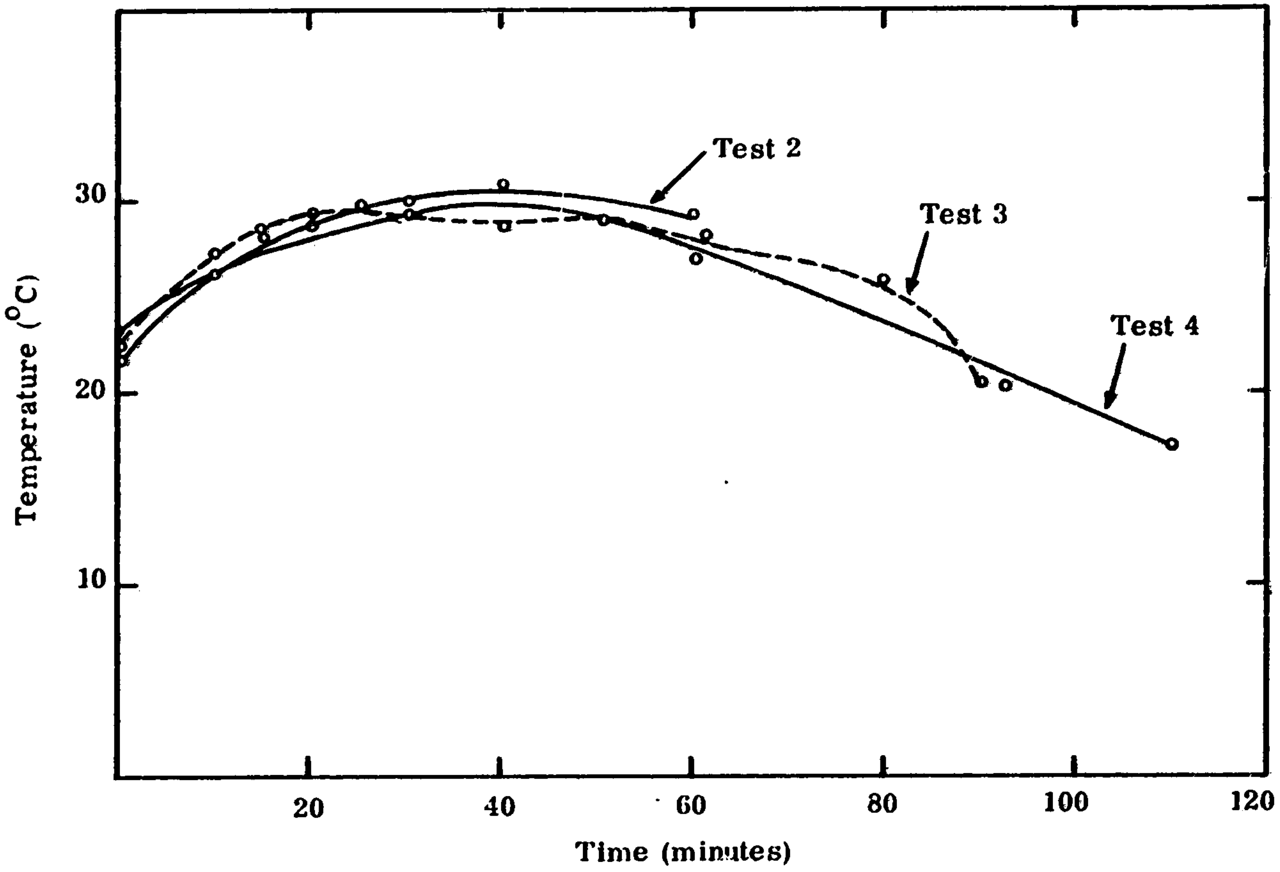


Figure 2.5.6 Ozonation of N_2H_4: temperature histories.

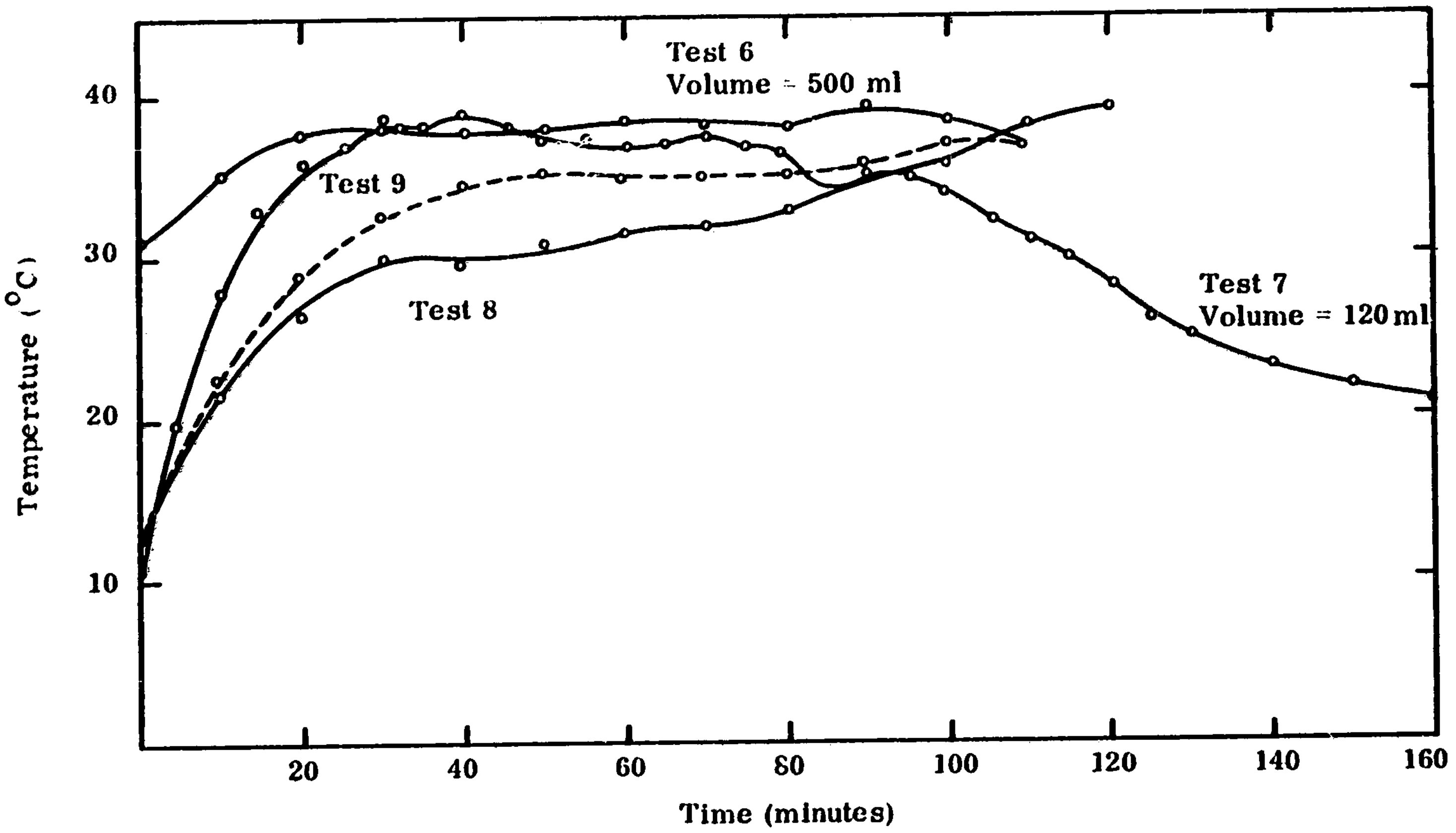


Figure 2.5.7 Ozonation of N_2H_4: temperature histories.

TABLE 2.5.1

CONCENTRATION OF O_3 IN DISTILLED WATER

(Vol. = 250 ml)
(lab. ambient temp)

TIME OF BUBBLING O_3 (min.)	O_3 CONCENTRATION (Average of 2 Determinations) (ppm)
5	.69
10	.80
20	.71
30	.60
40	1.12

Note: Lange's "Handbook of Chemistry" gives the following solubility data for O_3 in H_2O: 0.88 cc @ 0°C, 0cc @ 60°C.

TABLE 2.5.2

SUMMARY OF N_2H_4 OZONATION EXPERIMENTS

Oxygen flow rate = 7.1 liters per minute

Ozone generation rate = 20 mg per minute

Test Number	Volume Treated (ml)	Initial N_2H_4 (ppm)	$t_{\frac{1}{2}}$ (min)	R_I (min)
2	250	5150	17	2370
3	250	5100	17	2390
4	250	5100	20	3310
6*	500	3550	47	13,100
7	120	38,250	62	8800
8	250	42,750	142	19,900
9	250	37,250	128	18,600

* Solution was heated before introducing oxidant

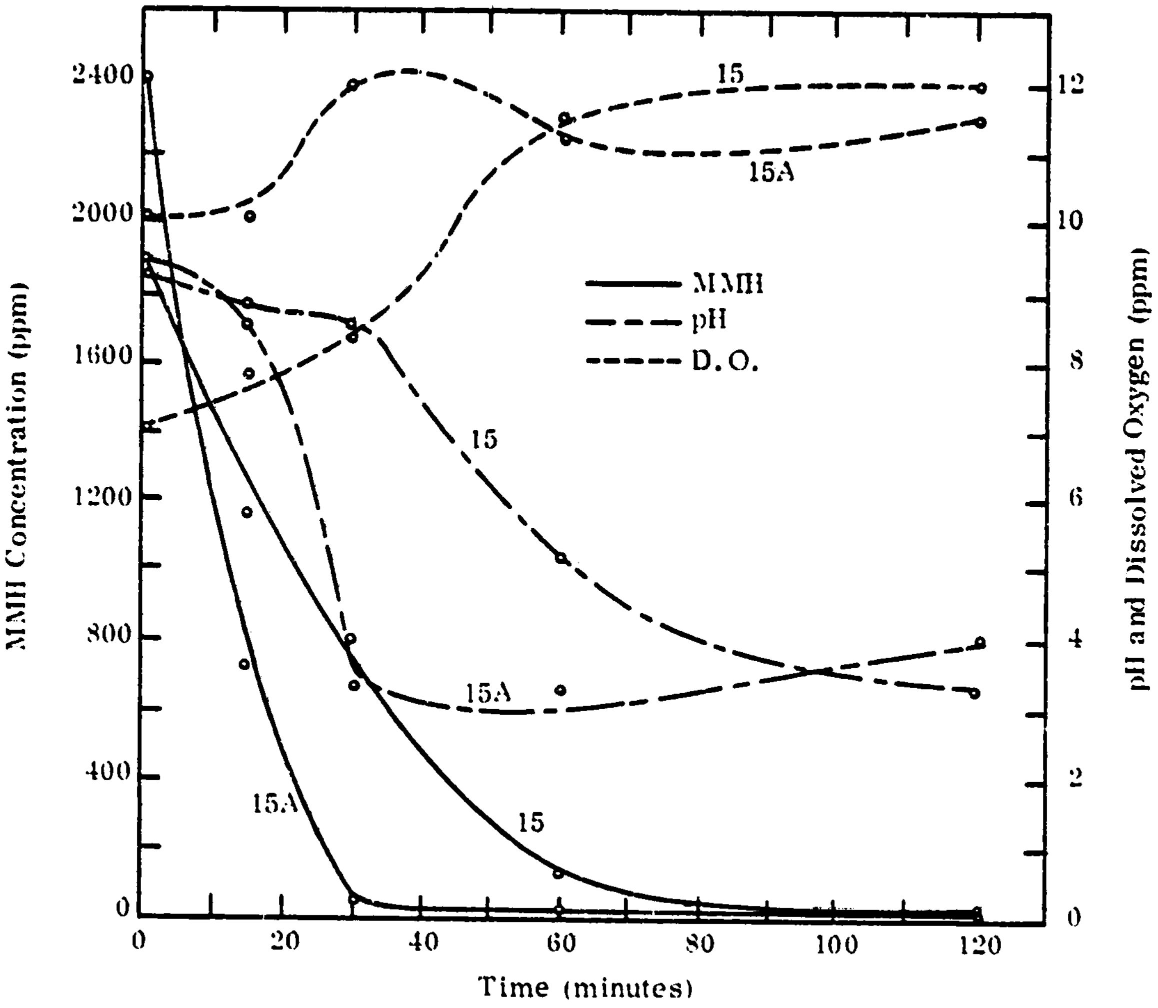
best R_I values were about 50% higher than the best values obtained in the case of oxygenation of MMH. The probable cause is the failure to use a catalyst in the ozonation runs; it will be recalled that oxygenation runs without catalyst yielded extremely slow destruction rates. Compared to those runs, the beneficial effect of generating small quantities of ozone can clearly be seen.

To further investigate this question of what effect, if any, O_3 generation will have on fuel decomposition, a second series of experiments was run on MMH solutions with catalyst addition in the last three runs. Initial fuel concentrations were limited to more realistic levels so that a larger number of meaningful data points would be obtained. The results are shown in Figures 2.5.8 through 2.5.13.

Generally, a first order kinetic reaction rate could be assumed between O_3 and MMH. The plots show typical reduction curves in which MMH concentration is plotted vs. reaction time. The evident characteristic is that the initial reaction at higher concentration is quite rapid, but the rate slows down as the MMH concentration decreases to near exhaustion. Strictly speaking, the curve is not truly representative of the reaction rate, since the O_3 addition was restricted by the generating capacity of the ozonator. Although an O_3 concentration of only about 1 ppm existed in the water solution, the MMH concentration (up to 5600 ppm) was reduced to zero within reasonable time periods.

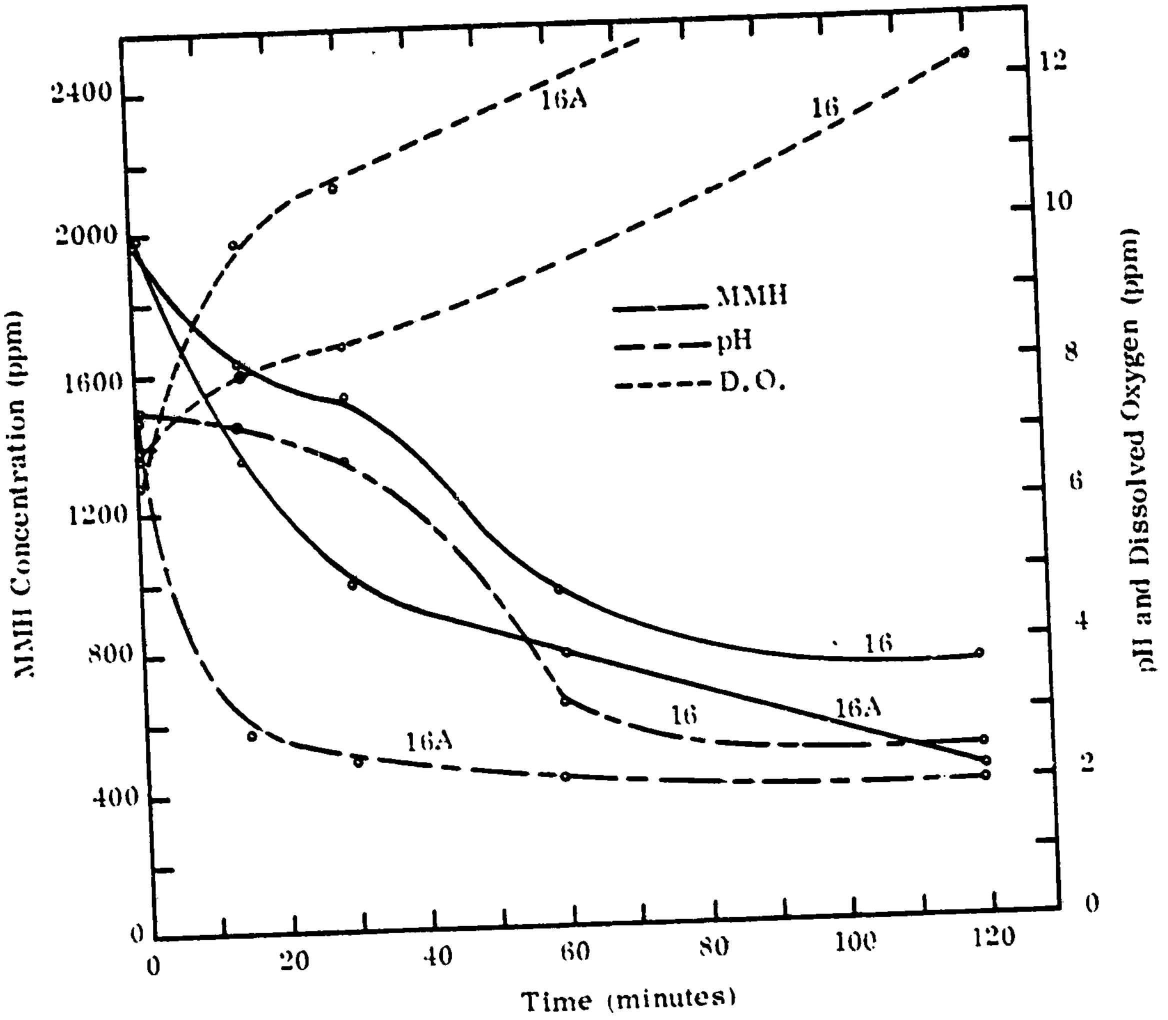
The results are also presented in Table 2.5.3. The O_2/O_3 runs without catalyst gave generally better results than the previous series of tests, and in fact are slightly better than the best oxygenation (no ozone) runs with catalyst. When catalyst was added, the results improved very significantly, yielding R_I values one to two orders of magnitude better than straight oxygenation, and far better than aeration.

Table 2.5.4 presents percent reduction as a function of time. The three runs with catalyst are not included in this table because of their much greater rates of destruction; MMH reduction was already essentially complete at fifteen minutes in these runs.



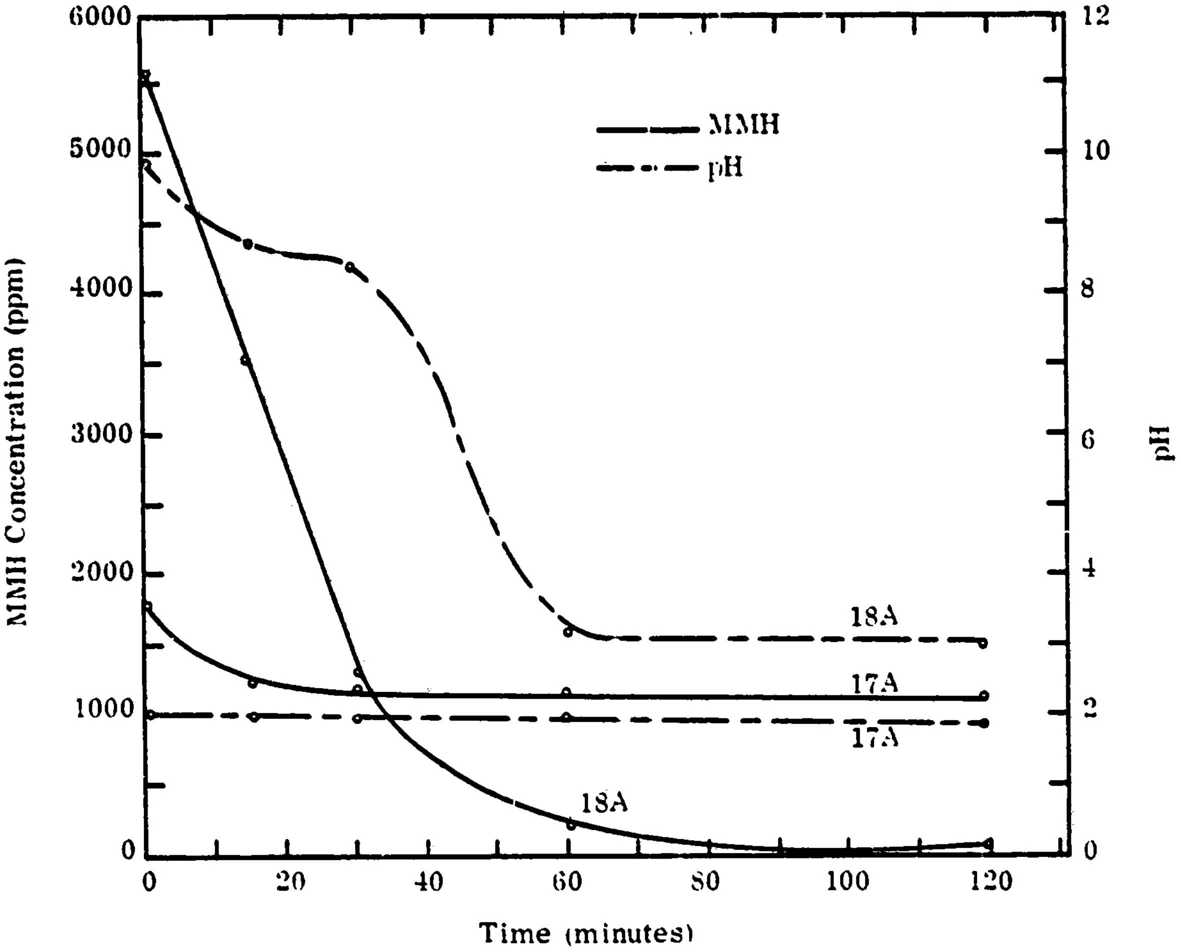
Run #	15	15A
Volume of Solution	400 ml	400 ml
Catalyst	No catalyst	No catalyst
Oxidant	Ozone/air	Ozone/O_2
Oxidant Flow Rate	4.7 l/min	4.7 l/min
Ozone Generation Rate	17 mg/min	33 mg/min
Initial MMH Concentration	1900 ppm	2400 ppm
R_T	4020 min	880 min
Time Required for 50% Reduction	22 min	11 min

Figure 2.5.8 Ozonation of MMH



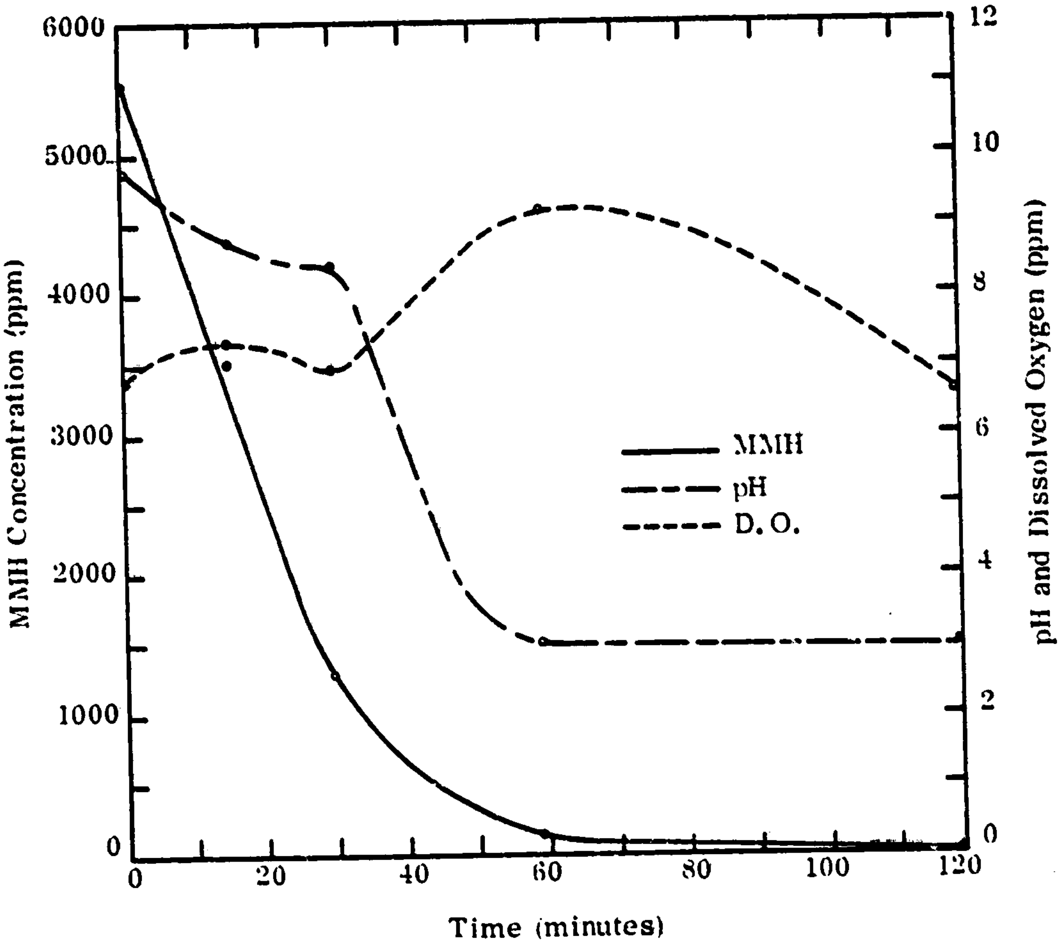
Run #	16	16A
Volume of Solution	400 ml	400 ml
Catalyst	No catalyst	No catalyst
Oxidant	Ozone/air	Ozone/O_2
Oxidant Flow Rate	4.7 l/min	4.7 l/min
Ozone Generation Rate	17 mg/min	33 mg/min
Initial MMH Concentration	2280 ppm	2250 ppm
Initial N_2O_4 Concentration	2000 ppm	2000 ppm
MMH Concentration after adding N_2O_4	2000 ppm	2000 ppm
R_I	18,700 min	6990 min
Time Required for 50% Decomposition	52 min	30 min

Figure 2.5.9 Ozonation of MMH



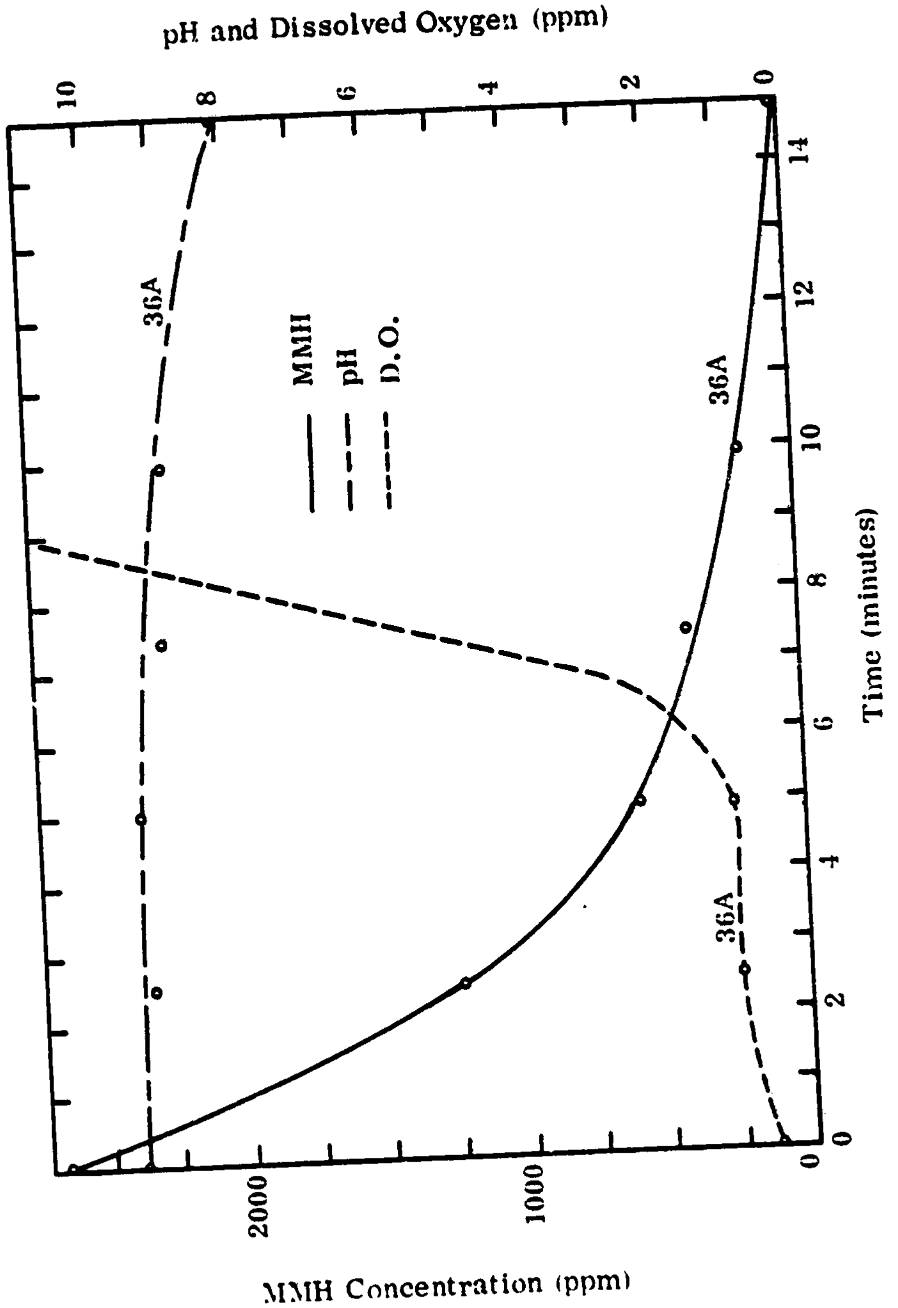
Run *	17A	18A
Volume of Solution	400 ml	400 ml
Catalyst	No catalyst	No catalyst
Oxidant	Ozone/air	Ozone/O_2
Oxidant Flow Rate	2.3 l/min	4.7 l/min
Ozone Generation Rate	33 mg/min	33 mg/min
Initial MMH Concentration	2250 ppm	5600 ppm
Initial N_2O_4 Concentration	4000 ppm	-------
MMH Concentration after adding N_2O_4	1820 ppm	-------
R_I	-------	1250 min
Time Required for 50% Decomposition	-------	20 min

Figure 2.5.10 Ozonation of MMH



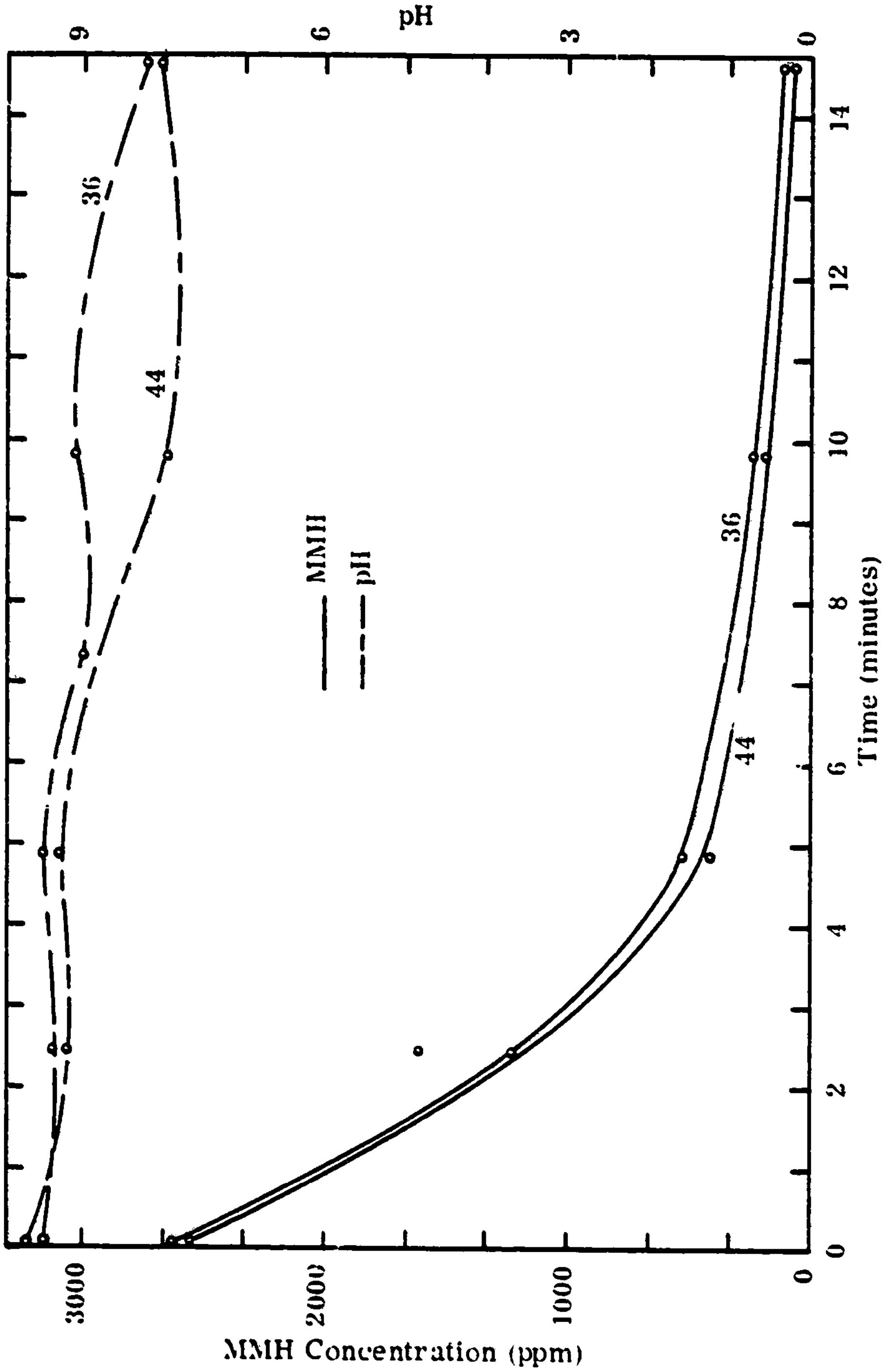
Run #	18
Volume of Solution	400 ml
Catalyst	No catalyst
Oxidant	Ozone/O_2
Oxidant Flow Rate	4.7 l/min
Ozone Generation Rate	33 mg/min
Initial MMH Concentration	5625 ppm
R_I	1120 min
Time Required for 50% Decomposition	19 min

Figure 2.5.11 Ozonation of MMH



Run #	36A
Volume of Solution	400 mls
Catalyst	0.20 mg Cu^{++}/liter
Oxidant	Ozone/O_2
Ozone Generation Rate	33 mg/min
Initial MMH Concentration	2700 ppm
R_T	31.3 min
Time Required for 50% Decomposition	2.2 min

Figure 2.5.12 Ozonation of MMH



Run *	36	44
Volume of Solution	400 mls	400 mls
Catalyst	0.2 mg Cu^{++}/liter	0.2 mg Cu^{++}/liter
Oxidant	Ozone/O_2	Ozone/O_2
Ozone Generation Rate	33 mg/min	33 mg/min
Initial MMH Concentration	2650 ppm	2650 ppm
R_T	34.9 min	29.1 min
Time Required for 50% Decomposition	2.3 min	2.1 min
Comments	adjust pH≥9.0	adjust pH≥9.0 UV irradiated

Figure 2.5.13 Ozonation of MMH

TABLE 2.5.3

SUMMARY OF MMH OZONATION EXPERIMENTS

Run #	Oxygen feed source to ozonator	Catalyst	MMH ppm (initial)	50% decomposition time (minutes)	% MMH decomposed	Remarks
15	Air	none	1900	23	99.4% in 2 hours	
15A	O_2	none	2400	11	99.9% in 1 hour	
16	Air	none	2280	52	66% in 1 hour 50 min.	Contains dilute N_2O_4 ~ 2000 ppm
16A	O_2	none	2250	30	78% in 2 hours	Contains dilute N_2O_4 ~ 2000 ppm
17A	O_2	none	2250	--	40% in 2 hours	Contains dilute N_2O_4 ~ 4500 ppm
18	O_2	none	5625	19	99.9% in 2 hours	
18A	O_2	none	5600	20	99.9% in 2 hours	

TABLE 2.5.3 (continued)

SUMMARY OF MMH OZONATION EXPERIMENTS

Run #	Oxygen feed source to ozonator	Catalyst	MMH ppm (initial)	50% decomposition time (minutes)	%MMH decomposed	Remarks
36	O_2	Cu^{++}	2650	2.3	97.7% in 15 minutes	Maintained pH above 9
36A	O_2	Cu^{++}	2700	2.2	97.8% in 15 minutes	Maintained pH above 9
44	O_2	Cu^{++}	2650	2.1	98% in 15 minutes	pH $\geqslant$ 9.0 UV irradiated

TABLE 2.5.4

REDUCTION OF MMH AS A FUNCTION OF O_3 BUBBLING TIME

Run #	ppm MMH / ppm N_2O_4	O_2 feed source to ozonator	% Reduction			
			1/4 hour	1/2 hour	1 hour	2 hours
15	$\frac{1900}{0}$	Air	32	88	95	99.4
15A	$\frac{2400}{0}$	O_2	78	98.8	99.9	100
16	$\frac{2280}{2000}$	Air	28	32	58	66.5
16A	$\frac{2250}{2000}$	O_2	31	50	60	78
17A	$\frac{2250}{4000}$	O_2	28	30	35	42
18A	$\frac{5600}{0}$	O_2	35	76	97	99.9

The following additional observations can be made based on these graphs and tables:

1. The rate of MMH reduction by O_3 was greater in Run 15A, where the ozonator is supplied with pure O_2 rather than undried air, than in Run 15. This result is attributed to a higher conversion efficiency in the ozonator, and to the higher partial pressure of the O_3/O_2 gas mixture resulting in a greater reaction rate.
2. In Runs 15, 15A, and 18A, two hours time was required to essentially complete the MMH reduction.
3. In Runs 16, 16A, and 17A destruction of MMH was only 66, 78, and 42% complete after two hours. It is obvious the reaction rate was decreased considerably by the presence of dissolved N_2O_4. This N_2O_4 created a highly acidic condition by virtue of the NO_3 and NO_2 ions formed in solution. In Run 17A, containing the highest amount of N_2O_4, the percent reduction was the lowest of the ten runs.
4. UV light did not materially affect the reaction rate (Run 44).

2.5.4 Economic Considerations

Our experimental study was too limited, both in scale and scope, to allow predictions of reliable operating costs for the ozonation system, or cost comparisons with other treatment processes. A rather thorough study of costs in a quite comparable situation, the treatment of cyanide wastes, was found in the literature, however, and those results are presented here as a rough gide to both order of magnitude costs involved and cost comparisons. It should be noted that the Chemical Oxygen Demand (COD) figures for MMH treatment and cyanide treatment are similar.

Figure 2.5.14 presents the cost curves from the cyanide study for three oxidants that are of interest for the treatment of hydrazine fuels (see the following sections.) Although the scales of the quantity and cost coordinates would be somewhat different for hydrazine fuels, the general trends are expected to be similar. It is seen that ozone treatment is economically most attractive in cases where very large amounts must be treated per day, whereas sodium

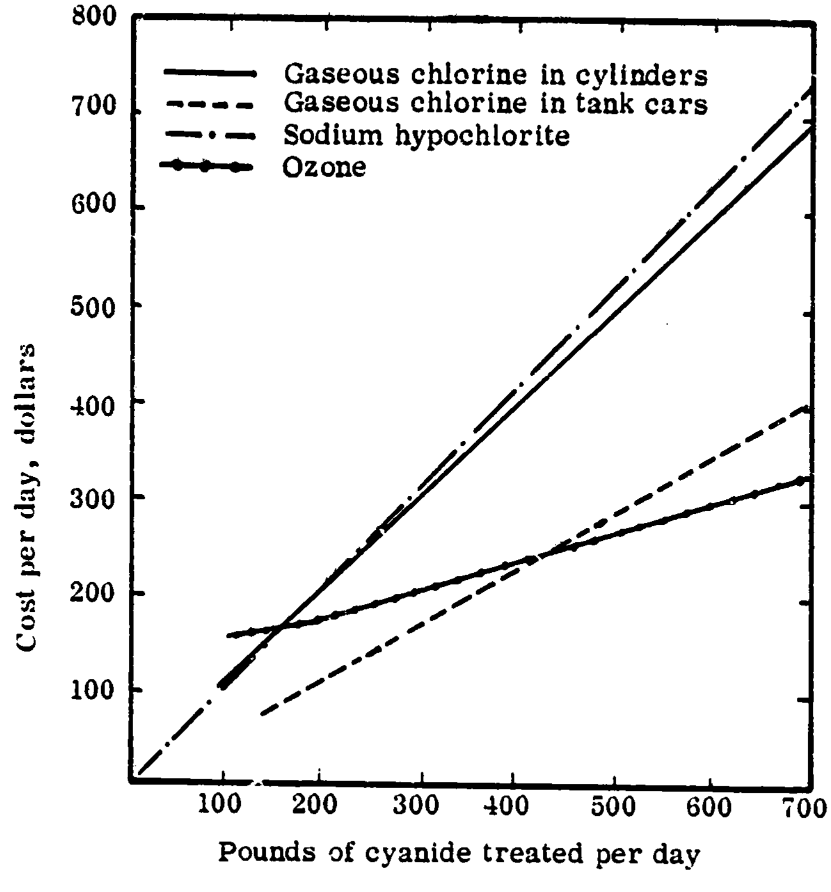


Figure 2.5.14 Costs of cyanide treatment using ozone, gaseous chlorine, or sodium hypochlorite. From Besselievre, E.B., The Treatment of Industrial Wastes, McGraw-Hill Book Company, New York, N.Y. (1969).

hypochlorite is most attractive for small quantities, up to the point where the use of gaseous chlorine in tank car quantities becomes practical. Gaseous chlorine is most economically favorable in the intermediate region, where tank car quantities are indicated but below the ozone crossover point.

Operating costs of an ozone plant should include not only the power being consumed in the corona ozonator but also the power being consumed by the auxiliary equipment such as pumps, compressors, dryer, and refrigeration systems. A rough estimate is that 2/3 of the power is consumed by the O_3 generator and 1/3 is consumed by the auxiliary equipment. Cost figures based on reports from Philadelphia, Pennsylvania, where O_3 has been used in the treatment of water for many years, indicate that the electrical power requirements to produce one pound of O_3 from air are 11.6 kw-hr, which includes the current for lighting, heating, and the recording equipment.[7]

2.5.5 Discussion

The use of an oxygen feed system with an ozonator is technically quite attractive if a catalyst is added to the aqueous fuel solution. Destruction rates are equivalent to those obtained by chlorination (presented in the following two sections) and far greater than what is possible by aeration or oxygenation without an ozonator. Economically, the ozone treatment is not expected to be competitive with chlorination unless extremely large quantities are routinely treated, and of course is never competitive with aeration. Ozone treatment has a major disadvantage relative to aeration in terms of toxicity and corrosiveness. This problem is probably no worse than in the case of chlorination, however, and in terms of environmental hazards the ozonation process has some advantages relative to chlorination. Both ozonation and chlorination are routinely used for large scale water treatment in various parts of the world.

One lesson indicated very strongly by our experiments with ozone, as with all of our experiments, is the need to keep fuel and oxidizer wastes separate until after initial treatment. Even though diluted fuel and oxidizer may be safely added to the same holding pond (see also Appendix B), to do so seriously impedes the fuel destruction rates obtained by any of the oxidation processes that were studied.

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[7] Evans, F.L., loc. cit.

2.6 CHLORINATION

2.6.1 Introduction

The gaseous chlorine method for destroying hydrazine fuels in dilute aqueous solutions has been used to a limited extent at Johnson Space Center, and possibly at other sites. It is quite similar in operation to the oxygenation method described in Section 2.4. Chlorination is in widespread use for the sterilization of water supplies and the treatment of sewage.

The chief advantage of chlorine relative to oxygen or air in all these applications is the fact that, like ozone, it is a much more powerful oxidizer, so that destruction of contaminants is much faster and more complete. The chief disadvantages of chlorine are its toxicity and highly corrosive nature, requiring safe handling procedures and special materials of construction. Problems such as temperature or pressure rise are minimal, and solvable by well known, everyday procedures.

Cl_2 concentrations of 30 ppm or more induce coughing, and exposure for 30 minutes to 50 ± 10 ppm Cl_2 is dangerous. At 1000 ppm Cl_2 is rapidly fatal. Cl_2 attacks the membrane of the throat, lungs, and nose and causes serious injury even at high dilutions. It combines with moisture to liberate nascent O_2 and form HCl. Both these substances, if present in quantity, cause inflammation of the tissues. Because of its intensely irritating properties, severe industrial exposure seldom occurs, as the workman is forced to leave the area before he can be seriously affected. The established Threshold Limit Value (TLV) for airborne concentrations of chlorine is 1 ppm by volume, or 3 mg/m^3.

The solubility of Cl_2 in water is about 7,300 mg/l at 68^oF and 1 atmosphere. Below 49^oF, Cl_2 combines with water to form chlorine hydrate ($Cl_3 \cdot 8H_2O$), usually called chlorine ice. This hydrate will obstruct lines in the feeding equipment. For this reason, feed or sealing water in contact with Cl_2 should be kept above that temperature.

Dechlorination of excess Cl_2 is performed by adding a reducing chemical, passage through beds of activated carbon, or aeration. The reducing chemicals include sodium bisulfite ($NaHSO_3$), sodium sulfite (Na_2SO_3), sulfur dioxide

(SO_2), and sodium thiosulfate ("HYPO", $Na_2S_2O_3$), e.g.:

$$NaHSO_3 + Cl_2 + H_2O \longrightarrow NaHSO_4 + 2\ HCl.$$

Activated carbon sorbs Cl_2 and is oxidized to CO_2. In aeration the Cl_2 is released to the atmosphere in highly diluted concentration.

2.6.2 Description of Experiments

All of the experiments in this series used aqueous solutions of MMH; it is assumed that the results would be similar for N_2H_4 or UDMH. The apparatus configurations used are shown in Figures 2.6.1 and 2.6.2, and are quite similar to those used in the experiments described in preceding sections.

In Figure 2.6.1, the chlorine gas is introduced as a predetermined rate through a flowmeter into a medium porosity sparger in the 500 ml bubbler. The small chlorine bubbles dissolve in the water and react with the MMH to form N_2, CO_2, chlorides, and minor amounts of other end products. Liquid samples are periodically withdrawn and immediately treated with sodium thiosulfate solutions to stop the chlorine reaction, and analyzed for residual MMH. Temperature, pH, and D.O. measurements are obtained as required.

In Figure 2.6.2, similar apparatus is used except that the amount of solution treated in each tank is nearly fifty times as great - five gallons in each ten gallon aquarium. Additional agitation beyond that provided by the three spargers resulted from laboratory stirrers used to help distribute Cl_2 throughout each vessel. Liquid samples were periodically analyzed, and temperature, pH, and D.O. measured, as with the smaller experiments.

The residual Cl_2 was not checked during the course of this work. The Cl_2 build up at the end of the run was probably at the several thousand ppm level. Reference should be made to "Standard Methods for Examination of Water and Waste Water", a publication of the American Public Health Association, for methods of analysis for free and/or combined chlorine.

Twelve test runs were made. That number was sufficient to provide a familiarity with the important operating parameters and to assure ourselves of the feasibility of a system based on chlorination. Further optimization of the parameters in the small pilot size facility would be of value prior to design of a full scale facility, and would minimize the uncertainties that might arise.

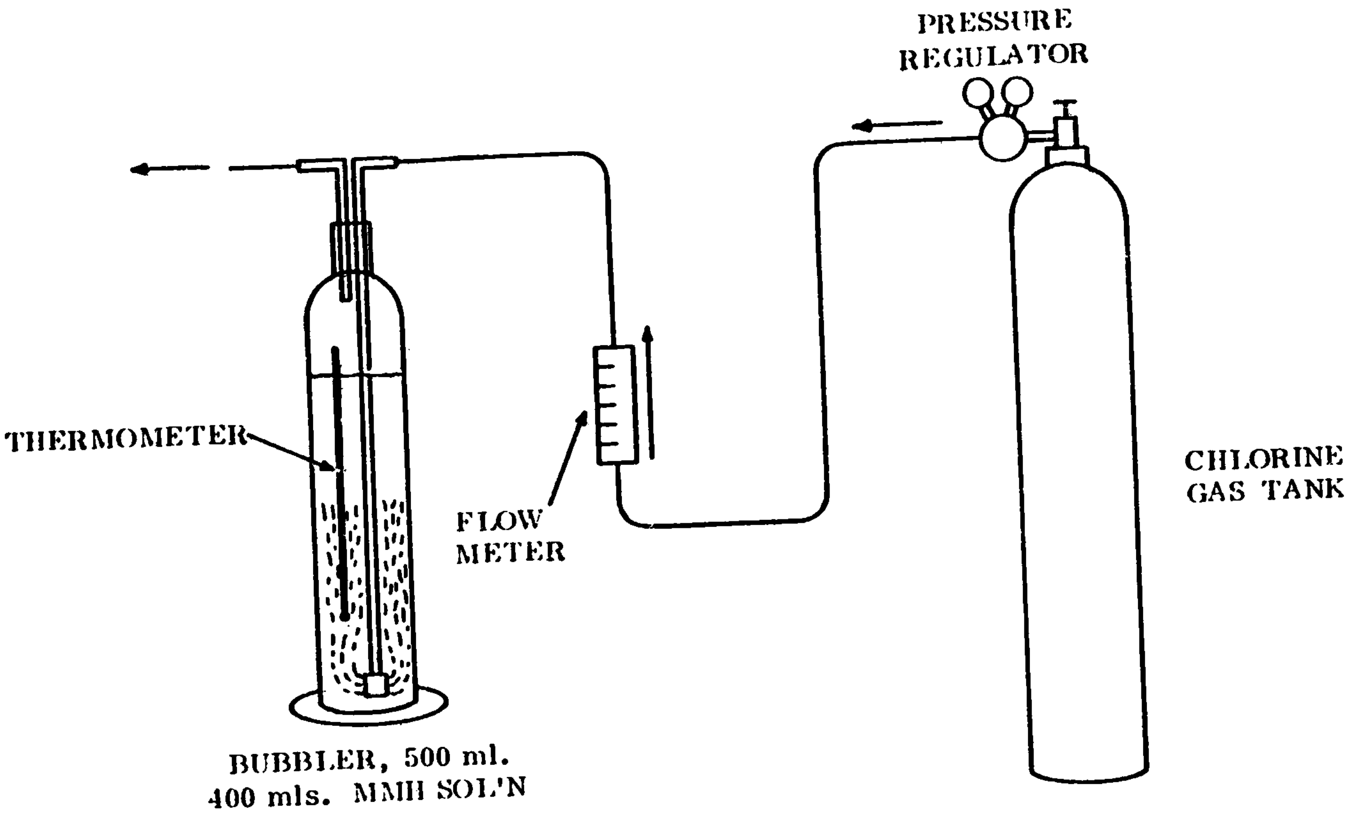


Figure 2.6.1 Schematic of lab set-up for chlorine sparging runs (400 ml batches)

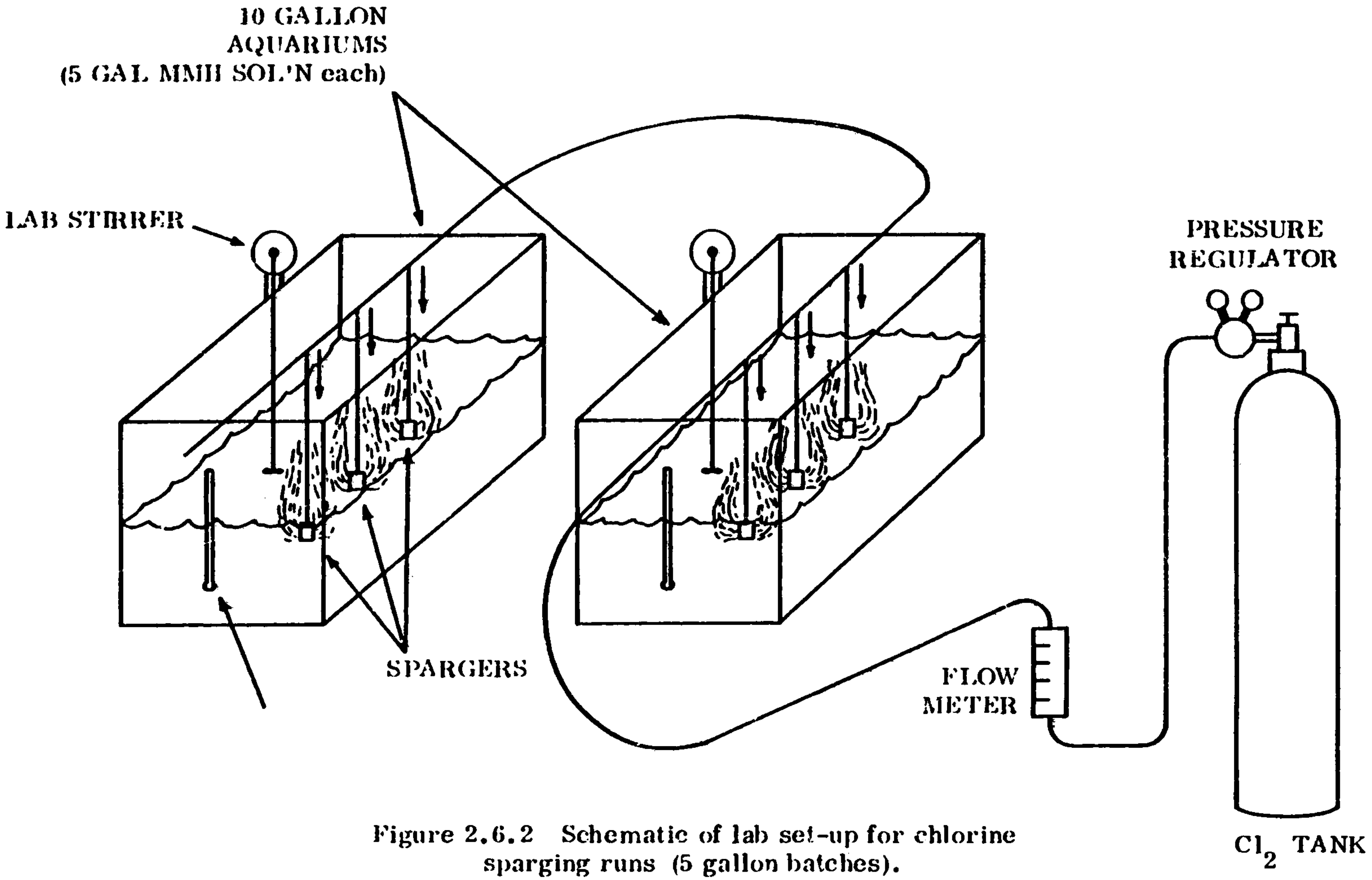


Figure 2.6.2 Schematic of lab set-up for chlorine sparging runs (5 gallon batches).

2.6.3 Results

Results of the twelve chlorination tests are presented in Table 2.6.1. The reactions proceeded quite rapidly in all cases, due in part to the good solubility of Cl_2 in water. There was little or no Cl_2 starvation during the bubbling period. Complete destruction of MMH occurred within 5 - 15 minutes or less on all runs containing from 185 to 4500 ppm MMH. Reaction of MMH with Cl_2 probably occurs as fast as the Cl_2 is introduced into the vessel.

Solutions containing less than 1000 ppm MMH in the presence of a Cu^{++} catalyst were completely decomposed in less than five minutes in Runs 30, 31, and 32, even though Run 32 contained 2000 ppm N_2O_4. Solutions containing 3800 ppm MMH plus Cu^{++} catalyst (Runs 33 and 34) and 4500 ppm MMH but without catalyst (Run 35) were completely destroyed in less than fifteen minutes (see Figure 2.6.3).

In Runs 39 and 40 (Figures 2.6.3 and 2.6.4) the initial pH was adjusted to about 10. The pH dropped to 3 or lower on Cl_2 addition. A pH adjustment was deemed unnecessary in Cl_2 runs since the reaction rate is rapid without it. Furthermore, the alkaline material will cause an unnecessary consumption of Cl_2, thereby adding to the operating cost. Run 43 (Figure 2.6.5), containing the highest MMH concentration, 7500 ppm, showed a very rapid reaction rate, possibly exhibiting the effect of concentration on reaction rate.

Comparing the reaction rates in the two large volume runs (46 and 47, Figure 2.6.6) shows that the presence of a Cu^{++} catalyst increased the reaction rate. However, due to the decreased Cl_2 feed rate per unit volume (about 1/6 of the earlier runs), R_I and $t_{\frac{1}{2}}$ values were an order of magnitude higher than in the 400 ml runs. Complete decomposition also required 5-10 times as much time.

Note the steeper slopes in Runs [illegible] and 34, containing a catalyst, than in Run 25 without a catalyst. The R_I values further corroborate the reaction rates. In Figure 2.6.5, curve 43 is steeper with a higher MMH concentration than curve 42. The temperature rise (for an unexplained reason) is higher in Run 42 than in 43, although the MMH concentration is higher in the latter at the same Cl feed rates.

TABLE 2.6.1

SUMMARY OF Cl_2 RUNS

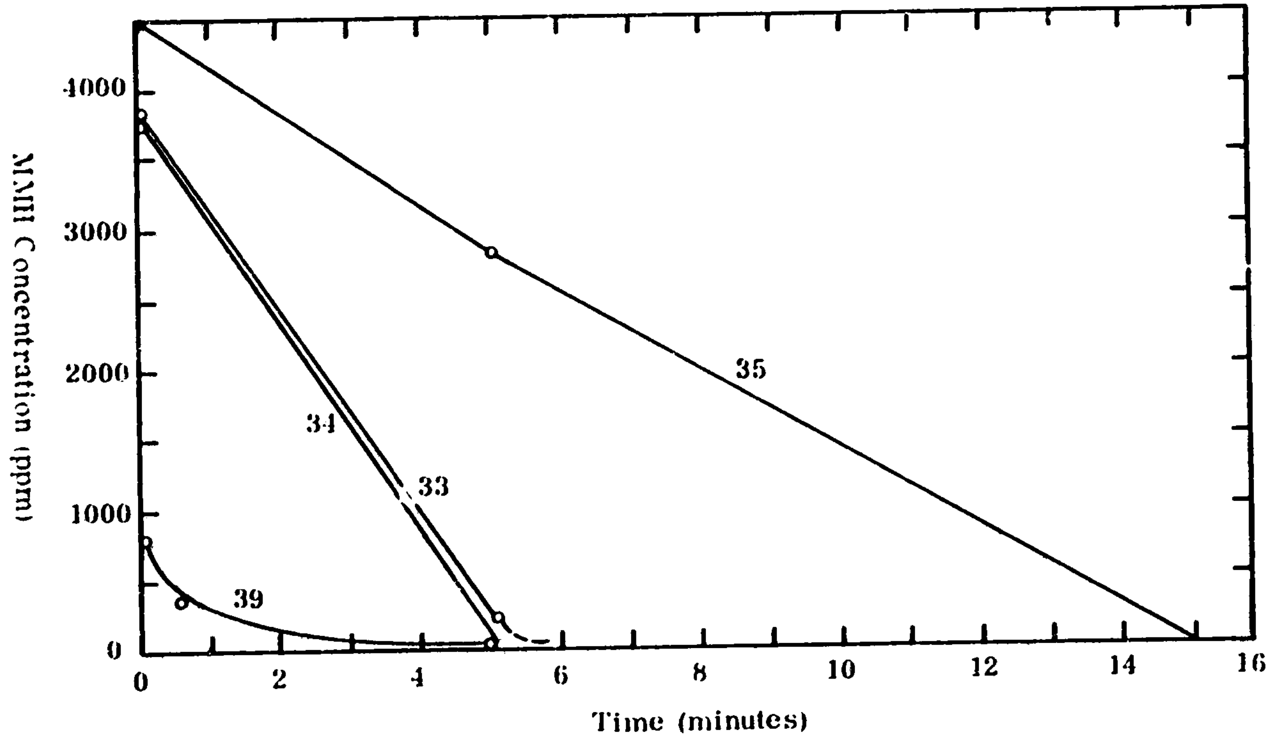
Chlorine feed rate - 3210 mg/min/liter unless specified
Volume = 400 ml (above line) 5 gallon (below line)

Run #	MMH concentration (ppm)	Catalyst	R_I (min)	$t_{\frac{1}{2}}$ (min)	% Decomposed / time	Remarks
30	185	yes	---	----	100% in less than 5 min.	
31	1000	yes	---	---	100% in less than 5 min.	
32	1000	yes	---	---	100% in less than 5 min	contained 2000 ppm N_2O_4
33	3800	yes	5.9	2.6	100% in less than 15 min.	
34	3800	yes	5.6	2.5	100% in less than 15 min.	
35	4500	no	36.4	7.0	100% in less than 15 min.	
39	750	yes	10.0	1.5	100% in less than 5 min.	pH adjusted between 10-12

TABLE 2.6.1 (continued)

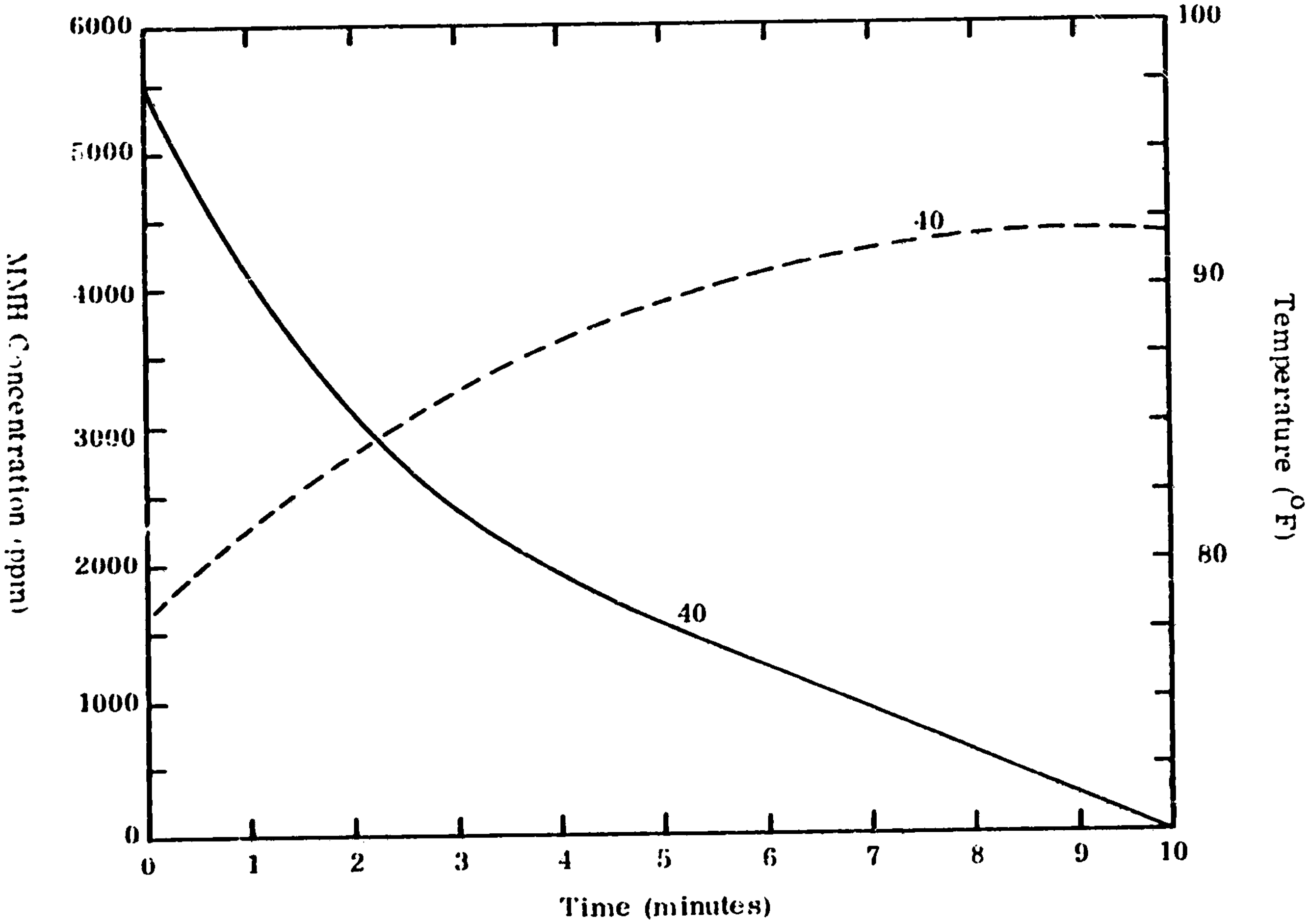
SUMMARY OF Cl_2 RUNS

Run #	MMH concnetration	Catalyst	R_I (min)	$t_{\frac{1}{2}}$ (min)	% Decomposed / time	Remarks
40	5600	no	7.7	3.6	100% within 15 min.	pH adjusted ≥ 9.0 contained 2500 ppm N_2O_4
42	4200	yes	9.2	3.4	100% in less than 15 min.	
43	7500	yes	1.8	2.0	100% in less than 5 min.	
46	10,000	no	169	59	100% in about 2 1/2 hours	Cl_2 feed rate: 462 mg/min/l
47	5000	yes	61.0	24	100% in about 1 hour	Cl_2 feed rate: 505 mg/min/l



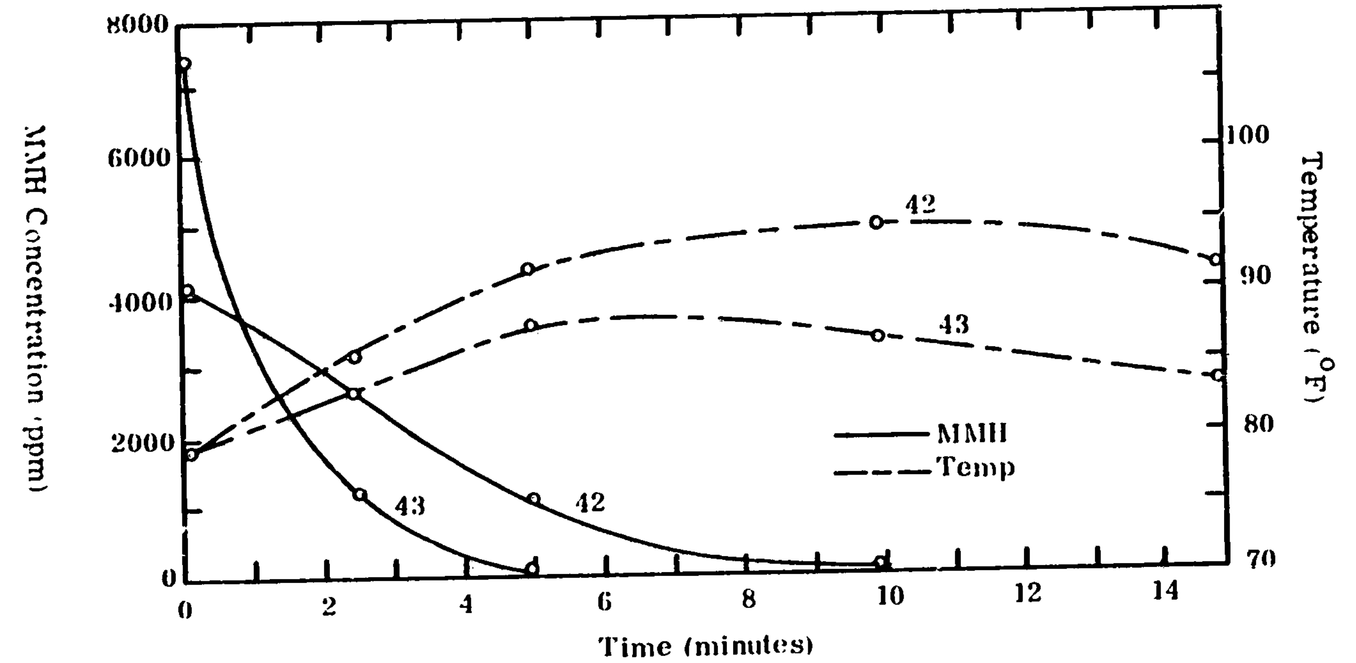
Run #	33	34	35	39
Volume of Solution	400 ml	400 ml	400 ml	400 ml
Catalyst	0.2 mg Cu^{++}/liter	0.2 mg Cu^{++}/liter	No catalyst	0.2 mg Cu^{++}/liter
Oxidant	Chlorine	Chlorine	Chlorine	Chlorine
Oxidant Flow Rate	0.4 liters/min	0.4 liters/min	0.4 liters/min	0.4 liters/min
Initial MMH Concentration	3800 ppm	3750 ppm	4500 ppm	750 ppm
R_I	5.9 min	5.6 min	36.4	10.0
Time Required for 50% Decomposition	2.6 min	2.5 min	7 min	1.5 min
Comments				Adjusted pH $\geq$ 9.0

Figure 2.6.3 Chlorination of MMH



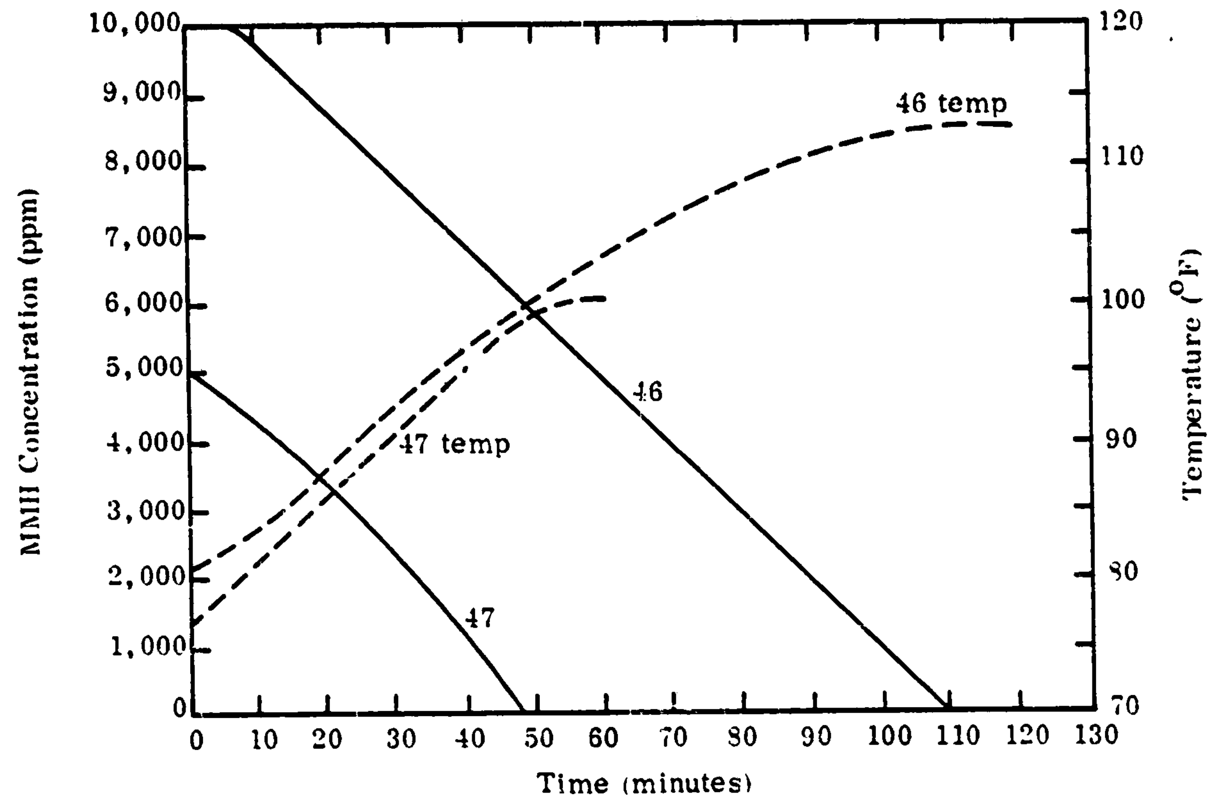
Run #	40		
Volume of Solution	400 ml	Initial MMH Concentration	5600
Catalyst	None	R_I	7.7 min
Oxidant	Chlorine	Time Required for 50% Decomposition	3.6 min
Oxidant Flow Rate	0.4 l/min	Comments	pH adjusted
initial N_2O_4 Concentration	2500 ppm		

Figure 2.6.4 Chlorination of MMH



Run #	42	43
Volume of Solution	400 ml	400 ml
Catalyst	0.20 mg Cu^{++}/liter	0.20 mg Cu^{++}/liter
Oxidant	Chlorine	Chlorine
Oxidant Flow Rate	0.4 liters/min	0.4 liters/min
Initial MMH Concentration	4200 ppm	7500 ppm
R_1	9.2 min	1.8 min
Time Required for 50% Reduction	3.4 min	2.0 min

Figure 2.6.5 Chlorination of MMH



Run #	46	47
Volume of Solution	5 gal	5 gal
Catalyst	None	0.2 mg Cu^{++}/liter
Oxidant	Chlorine	Chlorine
Oxidant Flow Rate	2.75 l/min	3 l/min
Initial MMH Concentration	10,000	5,000
R_I	169 min	61.0 min
Time Required for 50% Decomposition	59 min	24 min
Comments	Extra Mechanical Agitation	

Figure 2.6.6 Chlorination of MMH

2.6.4 Comparison of Reaction Rates

Figure 2.6.7 allows comparison of the R_I values obtained using all of the various treatment methods that have been discussed in this and the preceding sections. For the purpose of this comparison, tests in which there were obvious problems, such as the presence of N_2O_4, were excluded. The aeration and ozonation runs in which N_2H_4 solutions were treated were also excluded - only MMH tests were used for the sake of this comparison.

The results show that O_2/O_3 with a catalyst, and chlorine with or without catalyst, are generally much faster than the air or oxygen methods, or ozonation without a catalyst. Of the three fastest methods, chlorine with a catalyst seems to be clearly superior to the others, although more extensive testing would be required before rankings could be established with any degree of certainty.

2.6.5 Economic Considerations

The stoichiometric reaction of chlorine with MMH is:

$$CH_3NHNH_2 + 2Cl_2 + H_2O \longrightarrow CH_3OH + 4HCl + N_2$$

Since the molecular weights of MMH and Cl_2 are 46 and 71, respectively, the amount of chlorine required to react with one pound of MMH is

$$\frac{(2)(71)}{46} = 3.1 \text{ pounds}$$

Similar calculations were made for three chemicals that can be used as chlorine sources, that would not require gaseous storage and handling. The results are shown in the following table;

CHLORINE COMPOUND	AVAILABLE CHLORINE	QUANTITY REQ'D, LBS PER LB MMH
Sodium Hypochlorite	10%	32.20
Chlorinated Lime	25%	18.70
Calcium Hypochlorite (hth)	65%	6.67
Gaseous Chlorine	100%	3.1

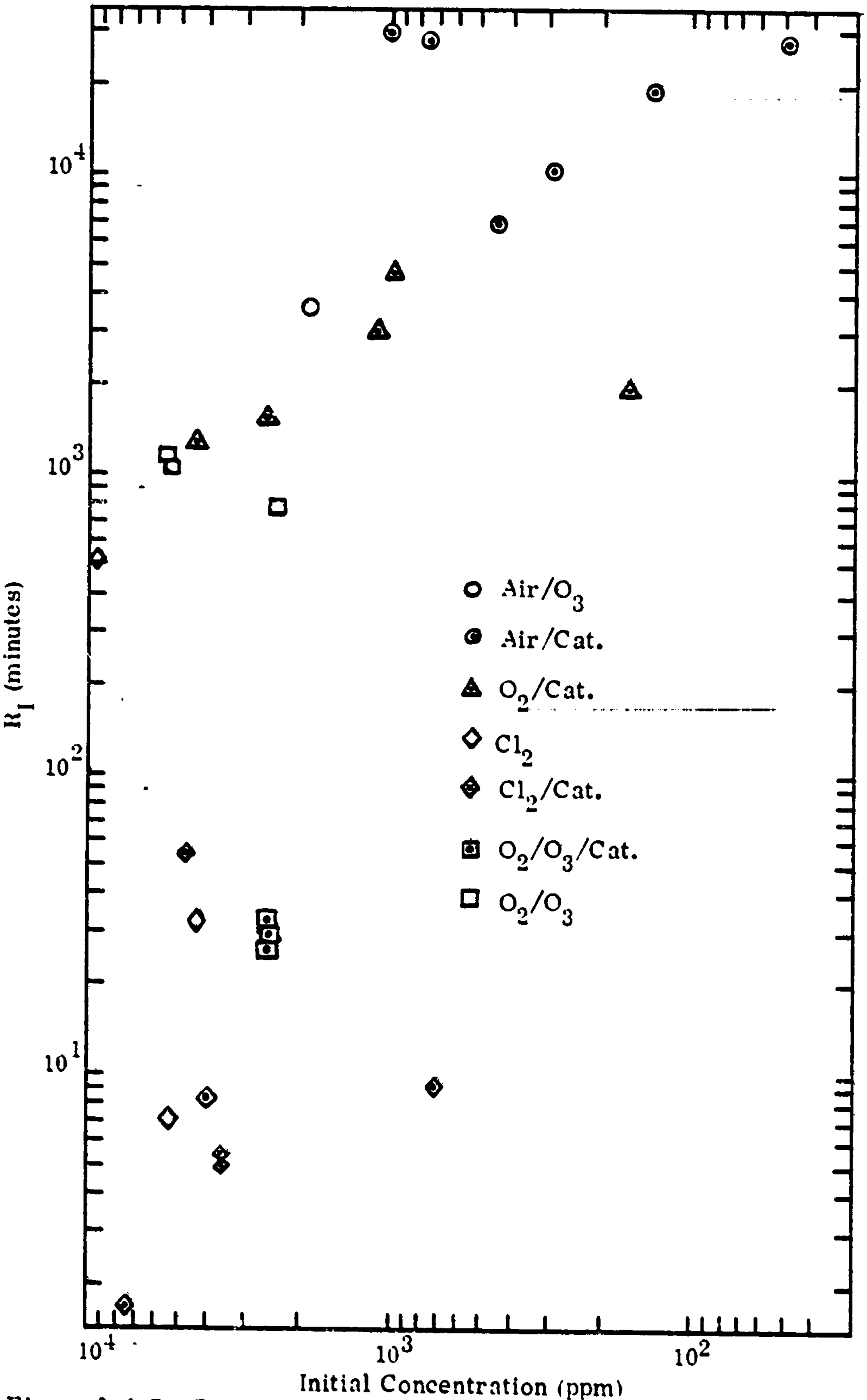


Figure 2.6.7 Comparison of R_I values for MMH treatment by aeration, oxygenation, ozonation, and chlorination, with and without catalyst.

Economic comparisons can only be made on the basis of comparative costs of the four chemicals, comparative capital costs, and amounts involved. Further comparisons of the use of gaseous chlorine versus sodium hypochlorite and ozonation were presented in Section 2.5.5, where it was shown that sodium hypochlorite is probably economically advantageous when the amounts to be treated are small, and ozonation becomes advantageous at the other end of the spectrum.

2.6.6 Conclusions

(1) The reaction of Cl_2 with MMH is rapid and complete. Complete destruction of MMH occurred within fifteen minutes in tests containing up to 7500 ppm MMH with Cl_2 feed rates of about 3200 mg/minute/liter.

(2) The rate of reaction of Cl_2 with MMH is roughly proportional to the flow rate, per unit volume of reaction vessel, of the Cl_2.

(3) The temperature rise during reaction was barely perceptable at MMH concentrations below 1000 ppm; at higher MMH concentrations, the temperature rise exceded 15°C. Provision for temperature sensing in an operating facility is an excellent means for controlling the Cl_2 feed rate into the reactor tank.

(4) The reaction rate in runs containing a Cu^{++} catalyst was higher than in runs without a catalyst.

(5) Low pH has a hindering effect on the reaction rate of Cl_2 with MMH, although this effect is not nearly as pronounced as with air or O_2.

2.6.7 Description of an Operational Chlorination System

It is envisioned that a working system for treating 250 pounds of waste MMH would be similar to that shown in Figure 2.6.8. This system would comprise (1) a lined 5-10,000 gallon reactor tank, (2) a Cl_2 metering device, (3) an automatic Cl_2 sensing device with a shut off solenoid valve, (4) a temperature operated Cl_2 shut off device, (5) sequential timers, (6) a small gas scrubber and pressure vent, and (7) the required liquid pumps, pressure control valves, piping and appurtenances to conform to established design guidelines and specifications. The closed tank feature would allow location and operation in proximity to other buildings rather than at a remote site.

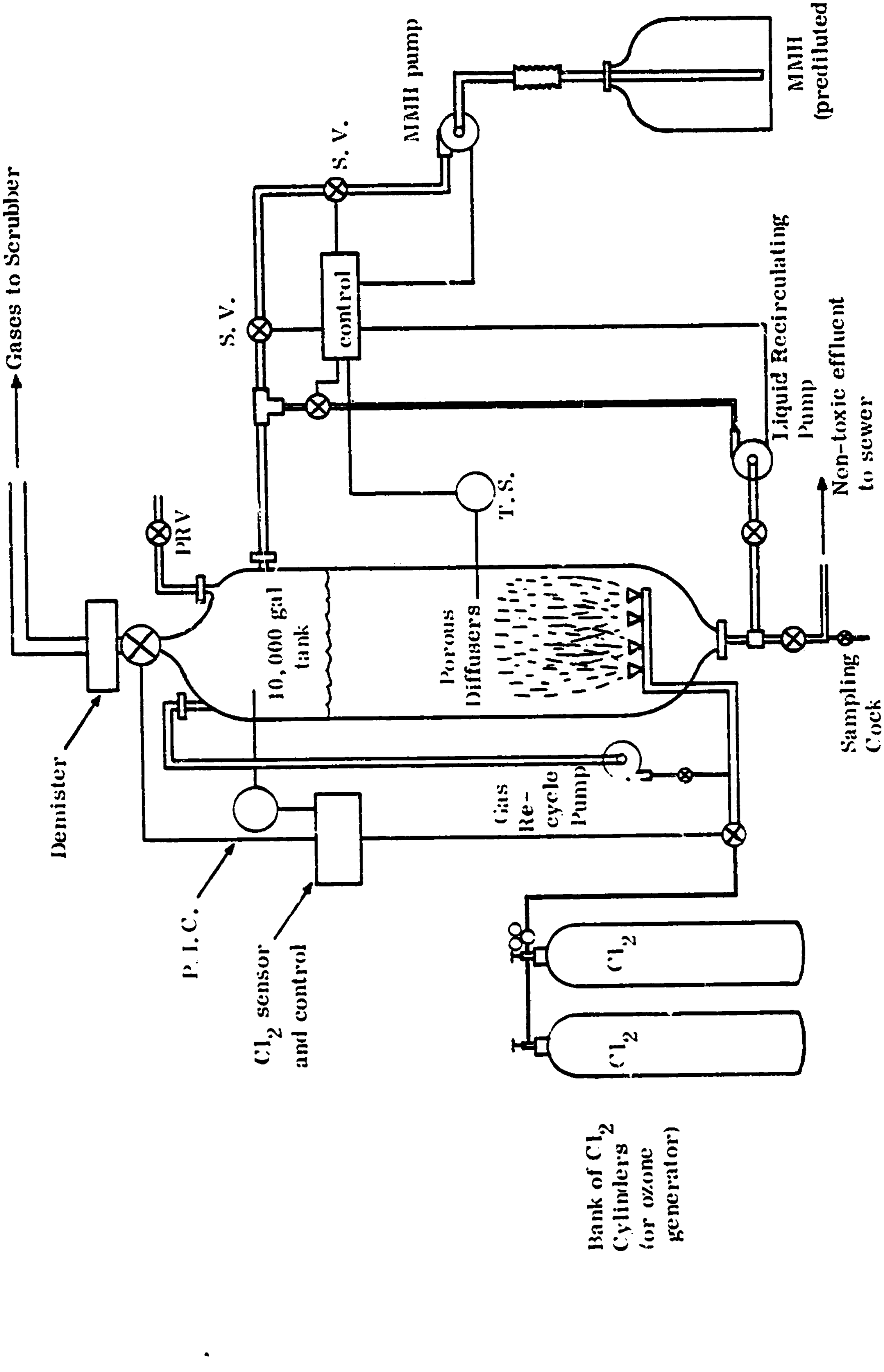


Figure 2.6.7 Schematic of Reactor for MMH Destruction.

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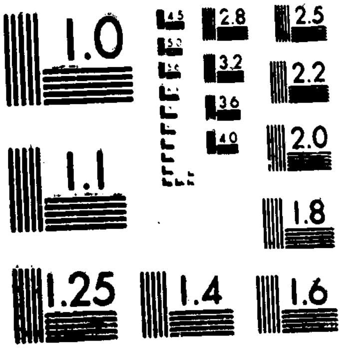

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

Diluted MMH solutions are pumped into the reaction tank. Cl_2 gas is introduced through the diffusers at a predetermined rate until a slight excess is sensed by the Cl_2 sensing instrument. A liquid recirculating pump provides agitation when required. A demister removes entrainment. Exit or vent gases are conducted to a scrubber. Treated solutions, after completion of reaction, are analyzed and discharged to a sewer. A sequential controller can be added to automate the operation if desired.

Use of a large excess of Cl_2 would not increase the rate of reaction, which is very rapid with or without a copper catalyst. A convenient rate of Cl_2 addition can be used to control the speed of the chlorination operation.

Identification analyses with a gas chromatograph indicate that treatment of MMH with Cl_2 produces small amounts of chlorinated end products, such as CH_3Cl, CH_2Cl_2, etc., which are undesirable species. An ideal process to treat MMH wastes is one which will either not produce the undesirable species or change them to a harmless form by a second simple step. Furthermore, Cl_2 itself is a highly toxic material and must be converted to a less toxic substance which can be disposed of easily. Small addition of sodium triosulfate will instantly convert residual Cl_2 to non-toxic substances (salt and sulfur).

If necessary, bioassays could be conducted to evaluate the toxicity of the treated MMH effluent to determine or identify effects of the chemical variables. Bioassays are used to judge compliance with water quality standards established by water pollution control authorities.

C-2

2.7 OTHER CHEMICAL TREATMENTS

2.7.1 Introduction

In addition to the gaseous treatments described in the preceding sections, a number of other chemicals could also be used to treat the hydrazine fuels. These chemicals include calcium hypochlorite (sold under the trade name "hth" for swimming pool use), sodium hypochlorite (household bleach), hydrogen peroxide, hydrochloric acid, sulfuric acid, hydroxyacetic acid, and others. These chemicals could be added to holding ponds containing dilute fuel mixtures, used in special treatment tanks, or used directly in the scrubbing liquor of vapor scrubbers. In addition, nitrogen tetroxide has been used in concentrated form for direct reaction with concentrated hydrazine fuels for the purpose of waste disposal.

The catalyzed (normally with copper sulfate catalyst) hydrogen peroxide reaction is currently being used for hydrazine disposal by several of the aerospace organizations contacted during Phase I of our study. Two of them precede the hydrogen peroxide reaction with a caustic (sodium hydroxide) treatment, and one organization uses caustic alone for hydrazines.

Nitrogen tetroxide is also commonly used, especially in the sense of dilute solutions of both fuel and oxidizer being added to the same holding ponds. We studied this case fairly extensively and found that, while it is quite safe, it is also rather ineffectual, the rate of reaction being very slow in dilute solution. A chemically identical treatment method would involve the use of nitric acid directly. These methods have the added disadvantage of nitric oxide formation during dilution of the N_2O_4 or HNO_3.

Although calcium hypochlorite has been recommended by the hydrazine fuel manufacturers for disposal, the formation of insoluble calcium deposits is a problem, as is the fact that the material is a solid and hence handling is complicated. In general, operational and maintenance problems would seem to be higher with this material than with many others that have been studied.

The Ducon Company of Mineola, New York, has suggested that MMH in particular could be reduced to ammonia and water using sulfuric acid, rather than oxidized as in most treatment processes, and further that equipment of their manufacture could be used for this purpose.

Another interesting item of proprietary equipment that would be applicable to the treatment of hydrazine fuels is Engelhard's "Chloropac", an electrolytic sodium hypochlorite generator. The sodium hypochlorite solution is produced directly from ocean water or brine solution, hence reducing the hazards and inconvenience of handling and storing quantities of chemical, and the possibility of over-chlorination with attendant releases of chlorine gas. This device is marketed as a modular system in a wide range of capacities, and similar units are currently available for residential swimming pools. It might be necessary to keep the fuel solutions away from the electrolysis cell itself, however, to avoid formation of other harmful products, as we experienced difficulties along these lines in the laboratory tests described later in this section.

2.7.2 Chemical Description

The following equations show reactions in dilute solution, for N_2H_4 treatment by several of the most common chemicals:

1. $N_2H_4 + 2H_2O_2 \xrightarrow{\substack{Cu^{++} \\ \text{Catalyst}}} N_2 + 4H_2O$

   In basic solution N_2H_4 acts as a reducing agent:

   Possible 1/2 reactions: $\longrightarrow NH_3,\ H_2,\ H_2O$

   $\longrightarrow NH_3,\ N_3^-,\ H_2O$

2. $N_2H_4 + Ca(ClO)_2 \longrightarrow N_2 + H_2O + 2HCl + CaO$

   In solution CaO reacts: $CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

   $CaO + H_2O \longrightarrow Ca(OH)_2$

3. $N_2H_4 + 2NaOCl \longrightarrow N_2 + 2H_2O + 2NaCl$

4. $N_2H_4 + HCl \longrightarrow N_2H_5^+ + Cl^-$

   $\longrightarrow N_2,\ H^+$

   $\longrightarrow N_2,\ NH_4^+,\ H^+$

   $\longrightarrow NH_3,\ NH_4^+,\ H^+$

5. $N_2H_4 + N_2O_4 \longrightarrow N_2 + 2NO + 2H_2O$

6. NaOH is used primarily to adjust the pH of the solution, and does not react with the hydrazine to any significant extent.

The comparable reactions for MMH are:

1. $CH_3N_2H_3 + 5H_2O_2 \xrightarrow{\overset{Cu^{++}}{\text{Catalyst}}} N_2 + 8H_2O + CO_2$
2. $2CH_3N_2H_3 + 5Ca(ClO)_2 \longrightarrow 2N_2 + 6H_2O + 2CO_2 + 5CaCl_2$
3. $CH_3N_2H_3 + 5NaOCl \longrightarrow N_2 + 3H_2O + 5NaCl + CO_2$
4. $CH_3N_2H_3 + 2N_2O_4 \longrightarrow \frac{3}{2}N_2 + 3NO + CO_2 + 3H_2O$

The same reagents react with UDMH as follows:

1. $(CH_3)_2N_2H_2 + 8H_2O_2 \xrightarrow{\text{Cat.}} N_2 + 12H_2O + 2CO_2$
2. $(CH_3)_2N_2H_2 + 4Ca(ClO)_2 \longrightarrow N_2 + 4H_2O + 2CO_2 + 4CaCl_2$
3. $(CH_3)_2N_2H_2 + 8NaOCl \longrightarrow N_2 + 4H_2O + 2CO_2 + 8NaCl$
4. $(CH_3)_2N_2H_2 + 3N_2O_4 \longrightarrow 2N_2 + 4NO + 4H_2O + 2CO_2$

These equations are idealized for complete reaction. As in most chemical reactions, trace amounts of possible products formed are not shown.

The normal procedure for treatment is as follows. Small quantities of fuel collected in a sump, tank or pond are highly diluted with H_2O (at least 1:100). The pH is adjusted and catalyst added, if required. The reagent is then applied slowly, to allow heat dissipation from the reaction, and in slight excess. The treated solution is checked for pH and presence of amines prior to ultimate disposal, or simply allowed to evaporate.

Heat is generated in each of the reactions so that controlled addition of reagent is necessary. Some means is required for insuring complete decomposition of propellant during treatment, without excessive addition of reagent.

2.7.3 Economic Considerations

The relative costs of the various chemical treatments were compared using prevailing prices for ton lots of the chemicals at the time this portion of the study was performed (early 1974). The prices per pound of N_2H_4 treated (assuming stoichiometric amounts of the reagents) for several of the chemicals of interest were found to be:

HCl:	\$0.24
H_2O_2:	\$1.15
$NaOCl$:	\$1.49
$Ca(ClO)_2$	\$1.58

The prices for treating MMH and UDMH would be correspondingly higher.

Hydroxyacetic was found to be excessively expensive (\$3.75 per kg for 70% concentration.)

2.7.4 Environmental Considerations

The only standards we found regarding allowable hydrazine levels in water or soil are the recommendations of the TRW report referred to in Section 2.1. This study was funded by EPA and probably represents an important part of the basis for future EPA standards. It also recommends provisional limits in air and water for several of the other constituents that might appear in neutralization pond effluents, as listed in Table 2.7.1.

These recommended provisional limits are obviously very low, and in fact the limits for all of the neutralization reagents, as well as reaction products such as slaked lime and quicklime, are actually much lower than the limit for hydrazine itself. We must therefore conclude that if any of these reagents is to be used, quantities must be very carefully controlled and concentrations continuously monitored to avoid excess reagent addition. Since these reagents are all water soluble, excess addition will result in the reagent appearing in any pond effluent that might exist.

Even more severe than the restriction on neutralization reagents in the effluent is the restriction on ammonium hydroxide, or ammonia gas dissolved in water. If this restriction is incorporated in future liquid waste discharge standards, it would be a strong factor against the selection of those reagents that result in the formation of ammonia gas and ammonium radicals.

The liquid effluents from these systems could contain ions of Ca^{++}, Na^{+}, Cl^{-}, NO_2^{-}, or NO_3^{-}. Selection of a ground waste disposal site should be based so that the discharged liquid waste infiltrates and percolates into the ground surface where no possibility of impairment exists. Disposal of wastes should not be near fresh water aquifers, wells, or any other usable water sources.

TABLE 2.7.1

RECOMMENDED PROVISIONAL LIMITS FOR POSSIBLE NEUTRALIZATION POND EFFLUENT CONSTITUENTS[1]

Contaminant in Water and soil	Provisional Limit	Basis for Recommendation
Calcium hydroxide (slaked lime)	0.25 ppm	Stokinger and Woodward Method
Calcium oxide (quicklime)	0.25 ppm	Stokinger and Wookward Method
Ammonium hydroxide (ammonia water)	0.01 ppm	Stokinger and Woodward Method
Hydrochloric acid	0.35 ppm	Stokinger and Woodward Method
Hydrogen peroxide	0.07 ppm	Stokinger and Woodward Method
Mixed acid	0.05 to 0.25 ppm	Stokinger and Woodward Method
Nitric acid	0.25	Stokinger and Woodward Method
Sulfuric acid	0.05 ppm	Stokinger and Woodward Method
Sodium hypochlorite-NaOCl	0.10 ppm	Stokinger and Woodward Method
Calcium hypochlorite-$Ca(ClO)_2$	0.125 ppm	Stokinger and Woodward Method
Hydrazine-N_2H_4	1.0 ppm	Quantity will rapidly oxidize to near-zero concentration

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[1] Ottinger, R.S.; Blumenthal, J.L.; Dal Porto, D.F.; Gruber, G.I.; Santy, M.J.; and Shih, C.C.: "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste." Report No. EPA-670/2-73-053-1 (August 1973). NTIS PB-224 591. Volume XII, pages 62, 105, 133, 329.

Because of the overall controllability of neutralization ponds - the fact that, with adequate capacity, unplanned releases need not occur, and effluent discharge can await "satisfactory" conditions within the pond - it is our conclusion that neutralization ponds using any of these reagents are environmentally acceptable as means of destroying hydrazine fuels. This acceptability is, of course, dependent on the provision of adequate equipment and procedures for monitoring and controlling the composition of the pond. It might also be necessary in some cases to provide a means of secondary dilution, such as a separate discharge pond.

Acceptability does not imply practicality, however, and we believe that the practicality of these neutralization systems is very dependent on the severity of future restrictions on ground water discharges. As long as reasonable amounts of dissolved hypochlorites, and slaked lime and quicklime, are allowed, the "swimming pool treatments," NaOCL and $(CaClO)_2$, are practical, although somewhat expensive. If dissolved ammonia is also allowed in small quantities, the H_2O_2 system would also be quite practical, and if very dilute HCl can also be discharged, the low chemical cost of this reagent could make it quite attractive.

2.7.5 Products of Reaction - Chemical Analyses

In our study, we were particularly concerned with MMH, since it is to be the fuel for the Space Shuttle Orbiter.

In spite of the fact that MMH has been used as a rocket fuel for many years, we could find no reports treating quantitatively the products of reaction of MMH with oxidizing or reducing agents used for disposal of MMH liquid wastes, or in MMH vapor scrubbers. This information is particulary important in view of the fact that oxidation of MMH could result in the formation of hydrogen cyanide or other toxic products.

Because of the importance of learning precisely what the products are for various agents, a major effort was devoted to gas-liquid chromatograph (GLC) studies of the products of reaction of MMH with NaOCl (sodium hypochlorite), $Ca(OCl)_2$, H_2O_2 with copper (Cu^{++}) catalyst, and other oxidizing agents. The results of these studies are presented in Table 2.7.2. The

TABLE 2.7.2

THE DECOMPOSITION PRODUCTS OF MONOMETHYL HYDRAZINE (MMH) USING VARIOUS AGENTS

AGENT	MOLE RATIO MMH/AGENT	CONCENTRATION MMH ppm	TEMP RISE °C	TIME HOURS	PRODUCTS
1. $Ca(OCl)_2$ "hth"	1.67	10,000	0	0.5	MMH**
2. $Ca(OCl)_2$	1.33	10,000	8	1.0	CH_2Cl_2, CH_3OH
3. $Ca(OCl)_2$	0.83	10,000	5	0.5	No MMH**
4. $Ca(OCl)_2$	0.80	1,000	0	0.5	CH_3OH (4 times)
5. $Ca(OCl)_2$	0.80	10,000	25	0.5	$CHCl_3$, CH_3OH and 4 other unidentified products.
6. $Ca(OCl)_2$	0.68	10,000	0	0.5	CH_3OH
7. $Ca(OCl)_2$	0.67	10,000	16	2.0	$CHCl_3$, CH_3OH
8. $Ca(OCl)_2$	0.10	10,000	75	0.5	No MMH**
9. $Ca(OCl)_2$	0.10	5,000	75	0.5	No MMH**

TABLE 2.7.2 (continued

	AGENT	MOLE RATIO MMH/AGENT	CONCENTRATION MMH ppm	TEMP RISE ^{o}C	TIME HOURS	PRODUCTS
10.	$Ca(OCl)_2$ "hth"	0.10	5,000	75	0.5	No MMH**
11.	$Ca(OCl)_2$ "hth"	0.10	2,500	75	0.5	No MMH**
12.	$Ca(OCl)_2$ "hth"	0.10	1,000	75	0.5	No MMH**
13.	$Ca(OCl)_2$ "hth"	0.10	500	75	0.5	No MMH**
14.	$Ca(OCl)_2$ "hth"	0.10	250	75	0.5	No MMH**
15.	NaOCl 3%	0.33	10,000	0	2.0	None Found
16.	NaOCl 5%	0.35	10,000	0	0.5	CH_3OH and no other peaks
17.	Electrolysis of NaCl solution	concentration unknown	10,000	0	0.5	HCN***
18.	Urea/N_2O_4		1,000			9 peaks found
19.	Air Final Sample	(Run No. 1)	1,000			None found

TABLE 2.7.2 (continued)

	AGENT	MOLE RATIO MMH/AGENT	CONCENTRATION MMH ppm	TEMP RISE °C	TIME HOURS	PRODUCTS
20.	Air Initial Sample	(Run No. 2)	1,000			4 peaks found
21.	Air Final Sample	(Run No. 2)	1,000			3 peaks found
22.	O_3, Cu^{++}		1,000			2 peaks found
23.	H_2O_2	0.33	10,000	0	96.0	MMH, CH_3OH
24.	H_2O_2, Cu^{++}	0.72	10,000	0	0.25	CH_3OH. No other products found
25.	H_2O_2, Cu^{++}	0.15	10,000	0	0.25	CH_3OH and 3 unknowns found plus a toxic gas

** Only MMH assay obtained

*** Evolved gas caused nausea and dizziness for laboratory personnel.

investigations were limited because of the extremely time-consuming nature of these tests.

Our conclusions from these tests are as follows:

1. Use of $Ca(OCl)_2$ as an oxidizing agent for MMH has serious disadvantages:
    a. Upon reaction with MMH a serious exotherm may occur.
    b. This exotherm apparently causes the formation of chlorinated hydrocarbons all of which are considered somewhat toxic.
    c. A heavy precipitate forms.
    d. Any excess calcium hypochlorite is also toxic to biota in the receiving waters.
    e. Practical disadvantages are also associated with the large quantities of this agent that are required -- approximately 6.7 pounds per pound of MMH treated. Handling and storage are both problems, as well as the high chemical cost, that would be significant in any but the smallest of treatment systems.
2. Use of sodium hypochlorite has almost none of these disadvantages and at the same time produces only the relatively innocuous CH_3OH.
3. Hydrogen peroxide without a catalyst is essentially ineffective as an oxidizing agent for MMH, but does produce CH_3OH over a long period of time.
4. Electrolytic chlorination of MMH apparently produces a toxic gas.
5. Hydrogen peroxide with a Cu^{++} catalyst produces CH_3OH, but when a large excess of H_2O_2 is present a toxic product is formed.

2.7.6 Neutralization of Dilute Fuel Using Vapor Phase Nitrogen Tetroxide

One of the possibilities that we investigated involved the venting of N_2O_4 vapors directly to a nearby disposal pond containing diluted fuel. We were interested in the safety and effectiveness of this method for those cases where it might be practical to locate a fuel disposal pond near a vent for oxidizer vapors.

A one liter solution of hydrazine, NH_2NH_2 (5%), was prepared. The temperature was 27°C and the pH was 11.1. Fifty ml. of N_2O_4 was distilled into this solution through a sparger over a three hour period. The temperature rose to 32° and a final pH of 7.7 was obtained, as expected since the hydrazine is in excess (mole ratio hydrazine to N_2O_4 is 1.7 to 1). No red NO_2 vapor was seen over the receiving solution.

A similar experiment using MMH was conducted. A 5% MMH solution was prepared (pH 10.5, temp. 28°C). 50 mls. of N_2O_4 were added over a two hour period and the temperature rose to 39°C while the pH declined to 7.2. The mole ratio of MMH to N_2O_4 in this case is 1.1 to 1. Again, no red cloud was observed.

It is concluded that disposal of vaporous N_2O_4 into dilute hydrazine solutions seems to be a safe and potentially effective method of disposing of both these hypergols. The experiments were not extensive enough to allow a thorough evaluation of the effectiveness of destruction of the two constituents.

2.8 GAMMA IRRADIATION

2.8.1 Introduction

In the irradiation of water solutions, destructive oxidation of organic/inorganic molecules takes place by direct energy absorption which ruptures the bonds in the molecules, followed by O_2 combining with the free radicals formed. Much of the oxidation occurs due to the indirect attack by the hydroxyl radical (OH^-) resulting from radiolysis of water as well as from the hydrated electron (e^-_{aq}). The hydrated electron is a highly reactive negative ion that appears to be a more powerful reducing agent than the hydrogen atom. The e^-_{aq} particle is considered to be the dominant species in irradiated water and is utilized to explain many of the radiolytic processes.[1]

The nature of the reaction of the hydrated electron is given by:

$$e^-_{aq} + X \longrightarrow Y$$

For example, in the case of N_2H_4,

$$e^-_{aq} + N_2H_4 \longrightarrow NH_2 + NH_2^-$$

There are several empirical values used to assess the efficiency of a radiation-initiated reaction, including the G value and the absorbed radiation dose (Rads) required to achieve the destruction of a species or combination of organic/inorganic species. The G value is defined as the number of molecules of chemical compounds which are formed, changed, or disappear, or the number of oxidation reactions which occur, as a result of the absorption of 100 electron volts of energy. A Rad is an energy density of 100 ergs per gram - approximately the absorbed dose delivered to material exposed to one roentgen of medium-voltage x-radiation.

Although work has been done for several years, at Florida Institute of Technology and elsewhere, on the use of gamma irradiation for the treatment of sewage and industrial wastes, we are not aware of any applications of gamma irradiation for the destruction of hypergolic propellants prior to our laboratory experiments.

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[1] Hart, E.J.: Record Chem. Prog., Vol. 28, p. 25 (1967).

2.8.2 Description of Experiments

Diluted samples of MMH and N_2H_4 were poured into 4 oz. glass bottles, capped and exposed to a Co^{60} gamma source for the periods required for dosages of 10^4, 10^5, or 10^6 rads. These experiments were carried out in Florida Institute of Technology's Cobalt - 60 facility, operated by the University Center for Pollution Research. The gamma rays from the 27,000 Curie source are of the electromagnetic type which are more suitable for treatment of liquids because of the lack of residual radioactivity in the irradiated material.

The exposed samples and controls were analyzed for residual concentrations of undecomposed hydrazine fuels using the p-DAB procedure, as in the experiments described in preceding sections. A Bausch and Lomb Spectronic-20 spectrophotometer was also utilized in determining the hydrazine concentrations.

As shown in Table 2.8.1, irradiation of aqueous solutions of MMH and N_2H_4 results in partial destruction of the fuel. In Test 1, N_2H_4 concentration was reduced by more than 8% in approximately 1 1/4 hours from the 75,000 ppm level (7.5%). In Tests 3 and 6 the MMH concentration was reduced approximately 17% in 7 1/2 minutes and approximately 26% in 1 1/4 hours. The results of Test 6 are plotted in Figure 2.8.1, in terms of residual MMH concentration as a function of total dosage.

It was noticed that under the test conditions (screw-capped bottle) there was a build up of pressure in the bottle due to gas generation. In addition to the expected N_2 gas an odor of NO and the brown fumes of NO_2 were noticed on uncapping the bottle. These NO_x present a secondary disposal problem.

A possible synergistic effect by bubbling O_2 or O_3 during irradiation was not explored due to time limitation. It is believed that destruction of MMH would be enhanced due to strong oxidizing conditions.

TABLE 2.8.1

GAMMA IRRADIATION EXPERIMENTAL RESULTS

Test	Dose in KR	Time Irradiated	N_2H_4 ppm	MMH ppm	% Reduction from control
1	0(Control)	0	74,500		8.72
	1,000	74.5 min.	68,000		
3	0			12.1	
	10^4	45 sec.		10.7	11.5
	10^5	7.5 min.		9.9	18.2
6	0	0		52,500	
	10^4	45 sec.		50,000	4.75
	10^5	7.5 min.		43,400	17.3
	10^6	74.5 min.		38,800	26.1

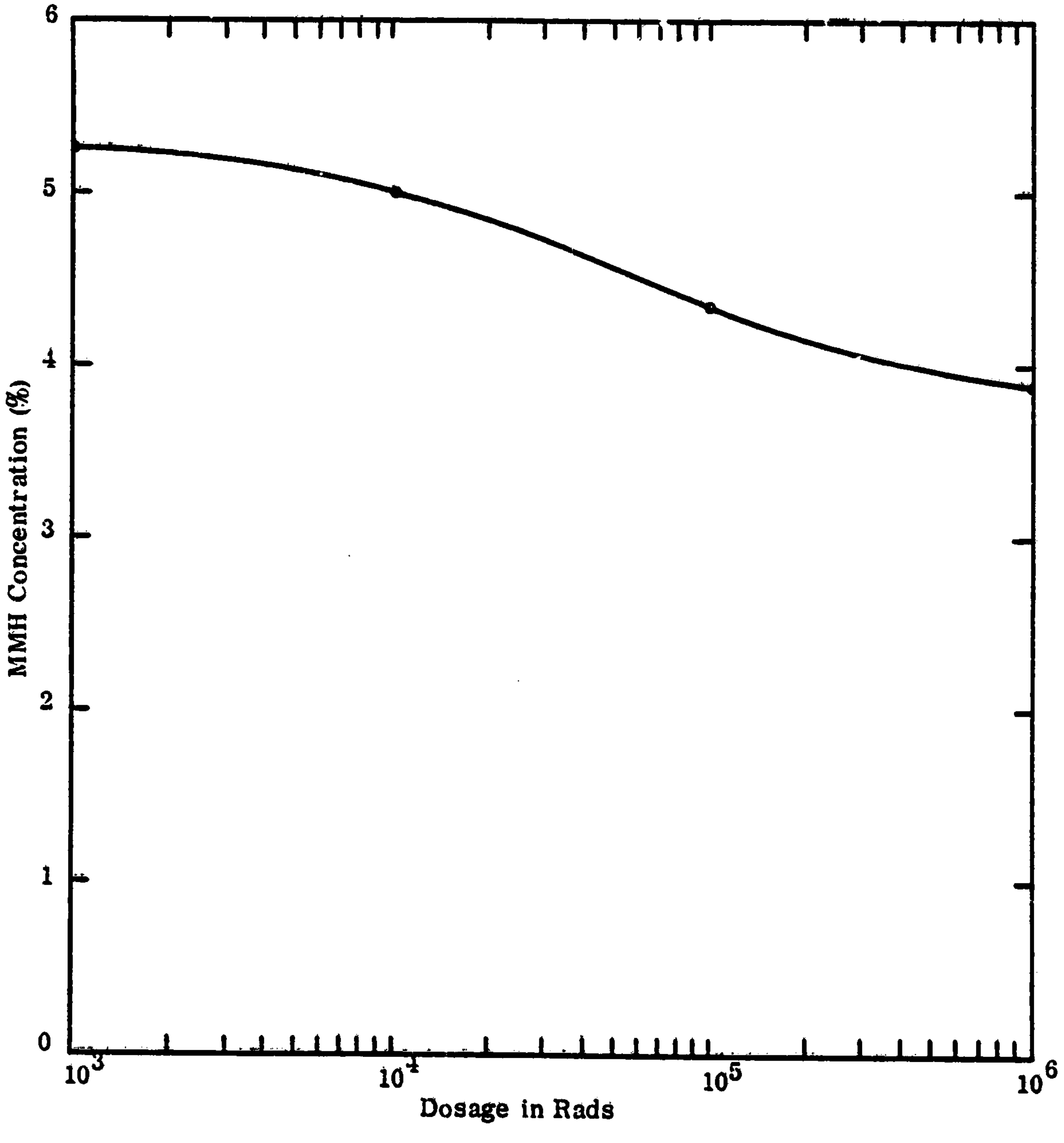

Figure 2.8.1 MMH decomposition by cobalt-60 irradiation.

2.8.3 Economic Considerations

Past experience at Palmdale* indicated direct operating costs of under \$1.00 per 1,000 gallons of waste water treated, including a filtration system. The initial construction cost of a radiation facility is approximately twice the cost of a conventional water treatment facility. Operating costs for a hypergol treatment facility may be anticipated to be higher due to the larger dosages required for chemical compound destruction, with concomitant increased exposure time and pump recirculation costs. Our preliminary estimate is that operating costs would be less than five times the above cost - \$5.00 per 1,000 gallons treated - considerably less than the chemical costs for a sodium hypochlorite, calcium hypochlorite, or hydrogen peroxide treatment system.

2.8.4 Conclusions

Results of this work indicate that the destruction of N_2H_4 or MMH by gamma radiation from Co^{60} is possible. More decomposition occurred than was anticipated for hydrazine type compounds at the relatively small dosages used.

Effectiveness of this method was not conclusively demonstrated by this limited series of experiments, however. Additional laboratory and prototype testing would have to be performed if an operating system were to be designed. The problem of NO_x formation could be a formidable one.

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* This was a 16,000 curie Co^{60} facility treating approximately 10,000 gallons daily, for disinfection purposes, located at Palmdale, Florida.

2.9 INCINERATION

2.9.1 Introduction

Incineration is a controlled combustion process to convert waste propellant to a less toxic, less bulky, less noxious or more easily disposable material. The principal undesirable incineration products from an environmental viewpoint are usually NO_x and CO. Occasionally, NH_3 or hydrocarbons or soot are released when operating under non-optimum conditions. Undesirable compounds formed during incineration may require a secondary treatment, such as scrubbing, to lower their concentration to acceptable levels prior to atmospheric release. Alternatively, they can generally be avoided, or at least minimized, by careful incinerator design. The ideal products of combustion - CO_2, H_2O, and N_2 - are harmless and can be released directly to the atmosphere.

Two of the organizations we contacted at the beginning of this study are currently operating incinerators for the disposal of aqueous solutions of hydrazines (and, in one particular instance, a solution of MMH in isopropyl alcohol). One incinerator uses natural gas as primary fuel and maintains a flame temperature of 1900 F; the other uses diesel fuel and maintains 2700 F or higher (3200 F was also mentioned).

In addition, the Marquardt Company of Van Nuys, California, has developed and is marketing a more specialized incinerator capable of disposing of raw liquid hydrazine. A research program carried out under Air Force sponsorship demonstrated the effectiveness of this incinerator in disposing of the hydrazine cleanly and efficiently, with acceptably low formation of oxides of nitrogen and other undesirable products.

The TRW study[1] recommended controlled incineration for the disposal of hydrazine, with effluent scrubbing to remove ammonia that might be among the products of combustion. The manufacturers recommend open pit burning

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1. Ottinger, R. S.; Blumenthal, J. L.; Dal Porto, D. F.; Gruber, G. I.; Santy, M. J.; and Shih, C. C.: "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste". Report No. EPA-670/2-73-053-1 (August 1973). NTIS PB-224 591. Volume 1, page 215.

for disposal of large quantities of hydrazine. The TRW study labeled this latter method "generally acceptable", but warned of excessive NO_x generation.[2] Aqueous solutions containing less than 40% N_2H_4 cannot be ignited in an open pit.

Open pit burning is still practiced by some users of hydrazines, but not to such an extent as several years ago.

Important criteria for an adequate incineration system include the following:

1. The effluent should be inconspicuous and safe
2. The system should not be prohibitively expensive to operate and maintain.
3. It must meet air pollution standards.

Gas sampling techniques and analysis must be adequate to provide meaningful data. Two key problems include the need for representative samples, and for preserving the integrity of samples until the analysis can be performed.

The variables which have the greatest effect on completion of the oxidation of the propellant waste are:

1. combustibility,
2. reaction temperature,
3. residence time in the incinerator, and
4. gas turbulence in the reaction zone.

Hydrazine, UDMH, and MMH have very broad flammability limits. With proper feed rates and the use of auxiliary fuels combustibility is readily controllable. Temperature can be controlled over a wide range by varying the air-fuel ratio, secondary air addition, two-stage combustion or water injection. Rates of oxidation reactions are increased rapidly by higher temperatures. A design range of 2400°F to 3000°F or higher may be specified depending upon the waste propellant being disposed.

Sufficient resistance time must be provided to allow the waste fuel to be completely oxidized. From 0.1 to 1 second or more may be required. The evaluation of this time factor can only be made by tests of individual incinerators or from manufacturers' data.

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[2] Ibid., Volume XII, page 330.

The degree of turbulence in the reaction zone significantly affects the incinerator performance. Intimate mixing of the air and waste propellant gases is required for completeness of combustion.

NO is a pollutant common to incineration processes which utilize air. NO formation results from O_2 and N_2 reacting at elevated temperature. Figure 2.9.1 presents graphically the thermodynamic equilibrium concentration of NO as a function of percent excess air at various reaction temperatures, for the combustion of hydrocarbons. The incineration of hydrazine fuels might yield higher values than shown since they are high-percentage nitrogen-containing compounds.

2.9.2 Commercially Available Incinerators

Of the many incinerators now on the market, at least a few seem suitable for hydrazine fuel disposal. Two have seen considerable use for this purpose already. One, designed by Thermal Research and Engineering Corp., of Conshohocken, Pa., has been in use at Cape Canaveral for over a decade and still seems to be giving very satisfactory performance; it has been used for aqueous solutions of hydrazines and N_2O_4, and for hydrocarbon fuels. Thermal has not designed any other incinerators for this purpose since then, but is still active in burner design and emissions control. Another incinerator, build by Hirt Combustion Engineers of Montebello, California, in 1968, is still in active use for disposing of aqueous solutions containing hydrazines and has also been used for hydrocarbon fuels and exhaust gas. In addition to these, the Marquardt Company of Van Nuys, California, markets commercial fume incinerators and liquid incinerators which are an outgrowth of their work in aerospace propulsion, and have run tests on disposal of N_2H_4, UDMH and N_2O_4 in their Sudden Expansion (SUE) incinerator.

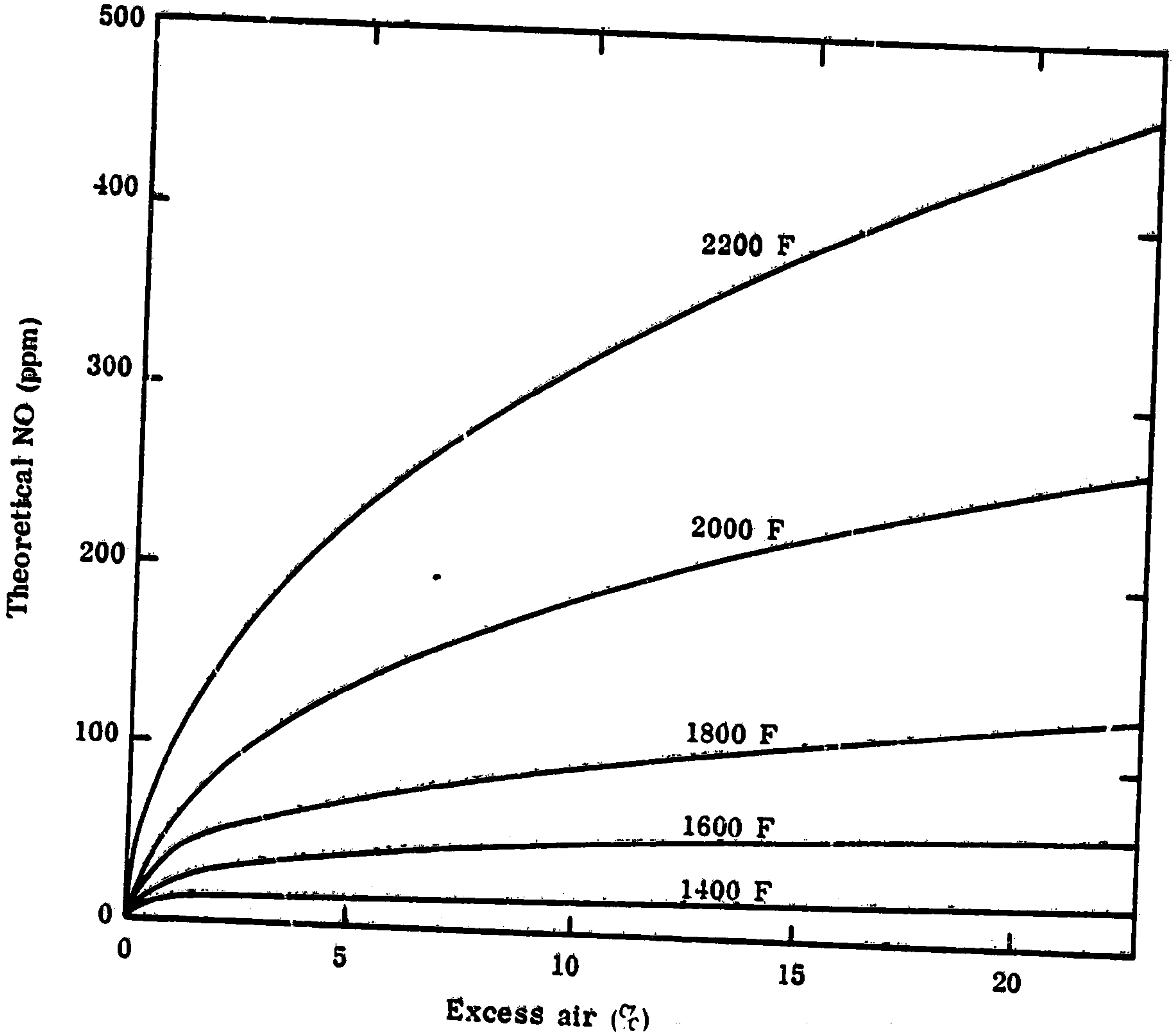


Figure 2.91. Equilibrium NO Concentrations in Combustion Effluents (R.D. Ross: Industrial Waste Disposal. Van Nostrand - Reinhold Corp., New York, N.Y., 1968, p. 340; quoted by R.S. Ottinger et al, Report No. EPA-670/2-73-053-1, August 1973.)

2.9.3 Thermochemical Description

The stoichiometric combustion equations for hydrazine, MMH, and UDMH in air are, respectively,

$$N_2H_4 + (O_2 + 3.76\ N_2) \longrightarrow 2H_2O + 4.76\ N_2$$

$$(CH_3)\ N_2H_3 + 2.5(O_2 + 3.76\ N_2) \longrightarrow CO_2 + 3H_2O + 10.3\ N_2$$

$$(CH_3)_2\ N_2H_2 + 4(O_2 + 3.76\ N_2) \longrightarrow 2CO_2 + 4H_2O + 16.04\ N_2$$

In addition, the stoichiometric combustion equations for the auxiliary fuels methane (natural gas), propane, and butane, are respectively,

$$CH_4 + 2(O_2 + 3.76N_2) \longrightarrow CO_2 + 2H_2O + 7.52\ N_2$$

$$C_3H_8 + 5(O_2 + 3.76\ N_2) \longrightarrow 3CO_2 + 4H_2O + 18.8\ N_2$$

$$C_4H_{10} + 6.5(O_2 + 3.76\ N_2) \longrightarrow 4CO_2 + 5H_2O + 24.4\ N_2$$

In a typical incineration process, one of the hydrazine fuels (or a mixture of two of them, such as Aerozine 50) is burned in air, in conjunction with natural gas (which is primarily methane) or liquified petroleum gas (propane or butane) as an auxiliary fuel used for preheating, start-up, and usually to maintain combustion in case of a somewhat irregular supply of the waste fuel.

A starting point for the chemical description of the incineration of hydrazine fuels would therefore consist in simply adding the appropriate stoichiometric equations above. In actual practice, however, the complete description of the reactions is consideralby complicated by the following factors:

a. Non-stoichiometric mixtures and incomplete combustion result in the formation of partial products, such as carbon monoxide and ammonia, and might allow discharge of some raw fuel.

b. High combustion temperatures result in the dissociation of water and CO_2, and in the formation of oxides of nitrogen.

c. In some incinerators, the hydrazine fuels must be supplied as aqueous solutions, hence introducing additional H_2O in the equations and altering the equilibrium composition of the products.

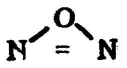
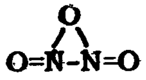
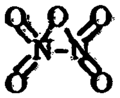
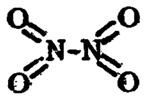
Hence a complete combustion description must include the possibility of formation of a number of trace products, including H_2, O_2, H, O, OH, CO, NO, NO_2, N_2O, hydrocarbons (HC), NH_3, amines (RNH_2) and unburned fuel.

Emission of unburned fuels can be minimized by combustion chamber design (good mixing, high turbulence, long dwell times), by lean mixtures or secondary air injection, and by high combustion temperatures. Unfortunately, high combustion temperatures result in the formation of oxides of nitrogen, as shown in Figure 2.9.1. Carbon monoxide formation can be reduced by use of excess air (lean mixtures) but this can result in still greater formation of oxides of nitrogen. Long combustion chamber residence times also aggravate the oxides of nitrogen problem.

The incinerator emissions problem is therefore quite similar to the automotive emissions problem: most of the steps that result in "cleaner", more complete combustion create additional problems in terms of the formation of oxides of nitrogen. Of these, N_2O is relatively harmless and NO_2 and N_2O_4 are not stable at elevated temperatures; NO, however, is poisonous, and will oxidize in the atmosphere to form NO_2, the poisonous reddish-brown gas that is such a major air pollution factor. Table 2.9.1 presents additional information on the various oxides of nitrogen.

The problem is not an impossible one, however, and considerable progress has been made in vastly reducing both automotive and gas turbine emissions through improved combustion chamber design. Thorough mixing and turbulence seem to be beneficial from all points of view. Temperature problems can be alleviated by ensuring uniformity of temperature; that is, by eliminating hot spots which serve no functional purpose, but which can be responsible for a large fraction of the NO formation. Some control of residence time seems possible in gas turbine combustors (and, presumably, incinerators). NO formation is a function of time as well as temperature; if the time that a typical gas particle spends at elevated temperature can be controlled to the minimum value consistent with complete combustion, then NO emissions can be minimized. Thorough mixing has the added advantage of shortening the residence time needed to ensure complete combustion, by increasing the probability of early contact between air molecule and fuel molecule. In an incinerator there is no need for a high exit temperature, so that a water

TABLE 2.9.1 OXIDES OF NITROGEN

Name	Formula	Structure	Solubility in H_2O Cold	Solubility in H_2O Hot	Remarks
Nitric Oxide	NO	N = O	$\frac{7.3\text{cc}}{100\text{ ml}}$ H_2O @ 0°C	$\frac{2.4\text{cc}}{100\text{ ml}}$ H_2O @ 60°C	Common air pollutant
Nitrous Oxide	N_2O		$\frac{130\text{cc}}{100\text{ ml}}$ H_2O @ 0°C	$\frac{51\text{cc}}{100\text{ ml}}$ H_2O @ 25°C	Relatively inactive in air or with O_3. Not a pollutant.
Dinitrogen Tetroxide (Nitrous Anhydride)	N_2O_3		Soluble	Dissociates	Unstable
Dinitrogen Pentoxide (Nitric Anhydride)	N_2O_5		Soluble	Dissociates to HNO_3	Unstable
Nitrogen Dioxide	NO_2	O=N=O	Soluble in alkaline solution		Common air pollutant
Dinitrogen Tetroxide (Nitrogen Tetroxide)	N_2O_4		Soluble	Soluble	A dimer of NO_2. An equilibrium mixture of N_2O_4 and NO_2 (16% NO_2 by mass, 27% by vol. at 1 atm, 20°C.)

quench is a possible means of controlling dwell time. Alternatively, secondary air (air added downstream of the primary combustion zone) might be used to bring the temperature to a level too low for NO formation, but high enough for some of the combustion reactions to go to completion.

The most extensive study that has been performed on incineration of waste hydrazines is the Marquardt study performed for AFRPL.[3] This was a combined theoretical and experimental study, based on the Marquardt "SUE" (Sudden Expansion) incinerator. The theoretical portion of the study consisted of calculating the theoretical equilibrium compositions of the products of combustion of various combinations of N_2H_4, UDMH, natural gas, and air. These computations were based on NASA Report SP-273, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations," by Sanford Gordon and Bonnie J. McBride (1971). The results, which of course are not restricted to any particular incinerator design, are presented in Figures 2.9.2 through 2.9.5.

The experimental portion of the Marquardt program was based on these equilibrium curves, the primary objective being to experimentally verify the more desirable operating points identified by the theoretical results. Results of the experimental program were generally satisfactory, giving fair agreement with the theoretical predictions and good operating characteristics. The final report stated that:

> "Using either UDMH or N_2H_4 as the primary fuel and natural gas as an ignition and sustaining fuel, the SUE incinerator ignited easily, burned smoothly, destroyed the primary fuel to less than 2 ppm by weight and produced NO_x at well below the 165 ppm target limit."

The burner used in this test program was an air cooled, 6 inch by 12 inch burner, as shown in Figures 2.9.6 and 2.9.7. Fuel was injected at the sudden expansion plane and directed toward the centerline of the burner. Combustion began at the sudden expansion and continued downstream for a distance of about two chamber diameters. Waste fuel and natural gas nozzles were typically closed-end tubes with slots near the tips, mounted on circular

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3. Hutson, Joel E.: "Toxic Waste Burner Evaluation." Final Report, AFRPL Contract No. F 04611-73-0007, November 1973. Marquardt Co. Report No. S-1271.

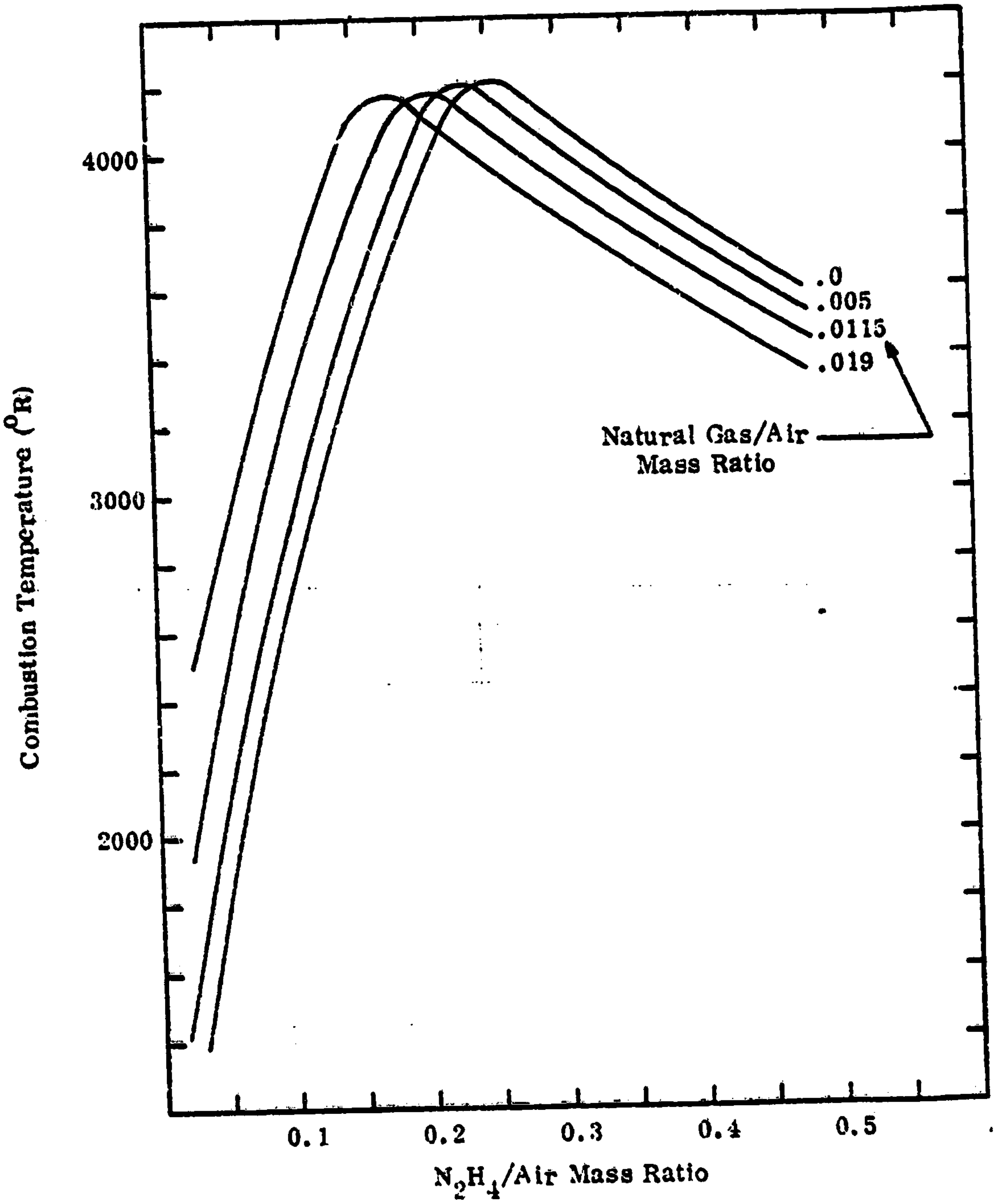

Figure 2.9.2 Adiabatic Flame Temperatures for N_2H_4/Natural Gas/Air Combustion (from Marquardt Co. Report S-1271)

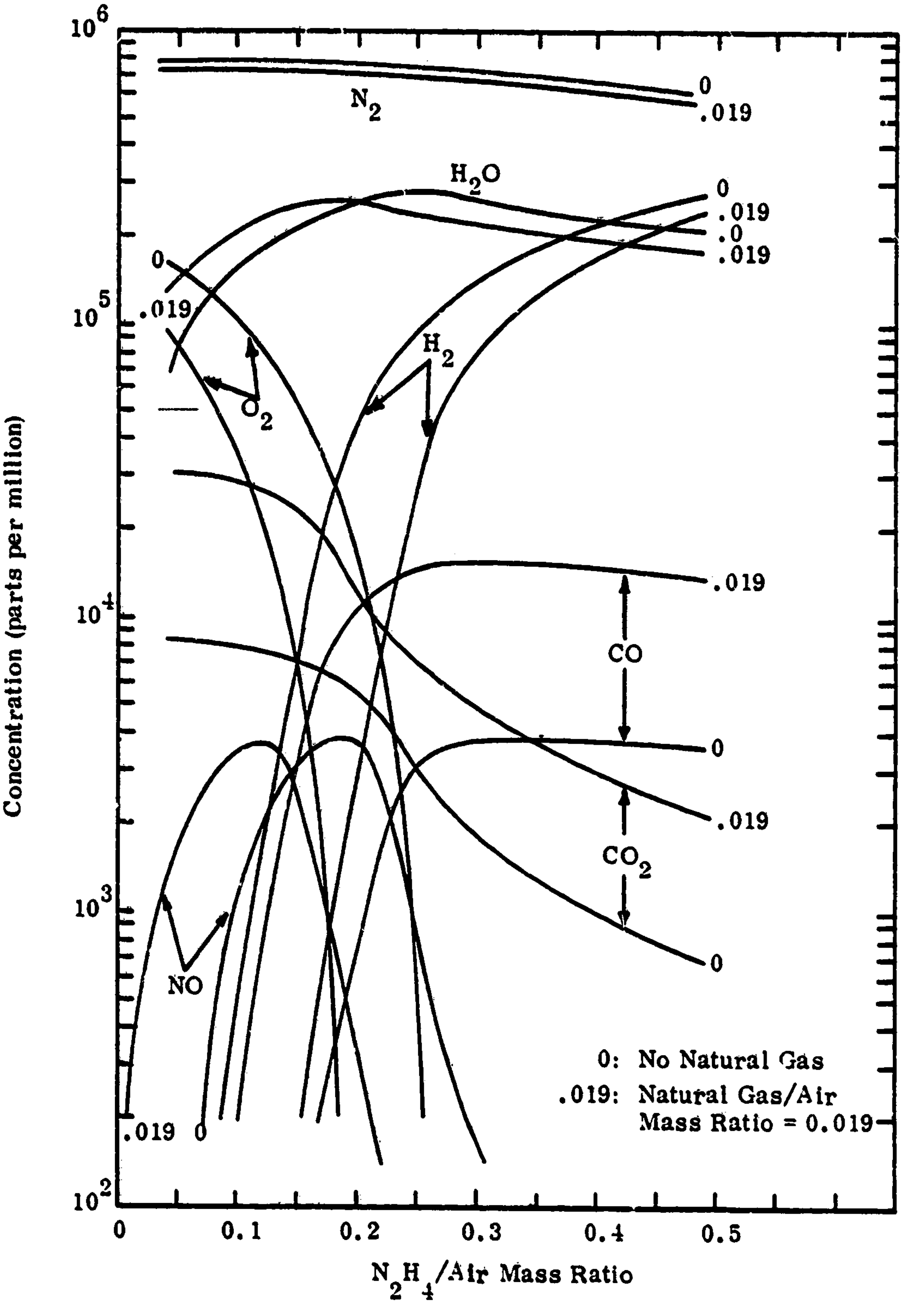

Figure 2.9.3 Theoretical Equilibrium Products for N_2H_4/Natural Gas/Air Combustion (from Marquardt Co. Report S-1271)

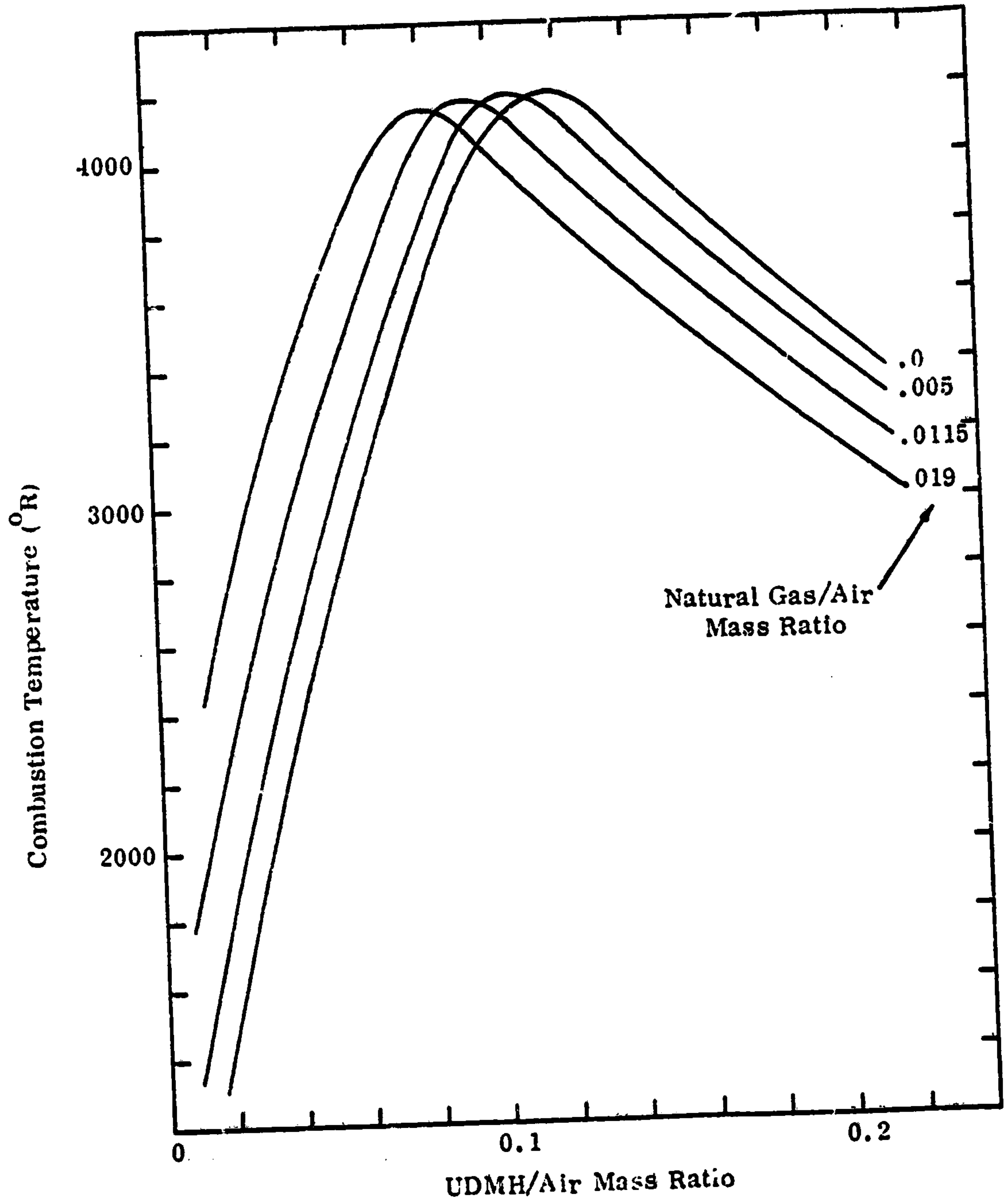

Figure 2.9.3 Adiabatic Flame Temperatures for UDMG/Natural Gas/Air Combustion (from Marquardt Co. Report S-1271)

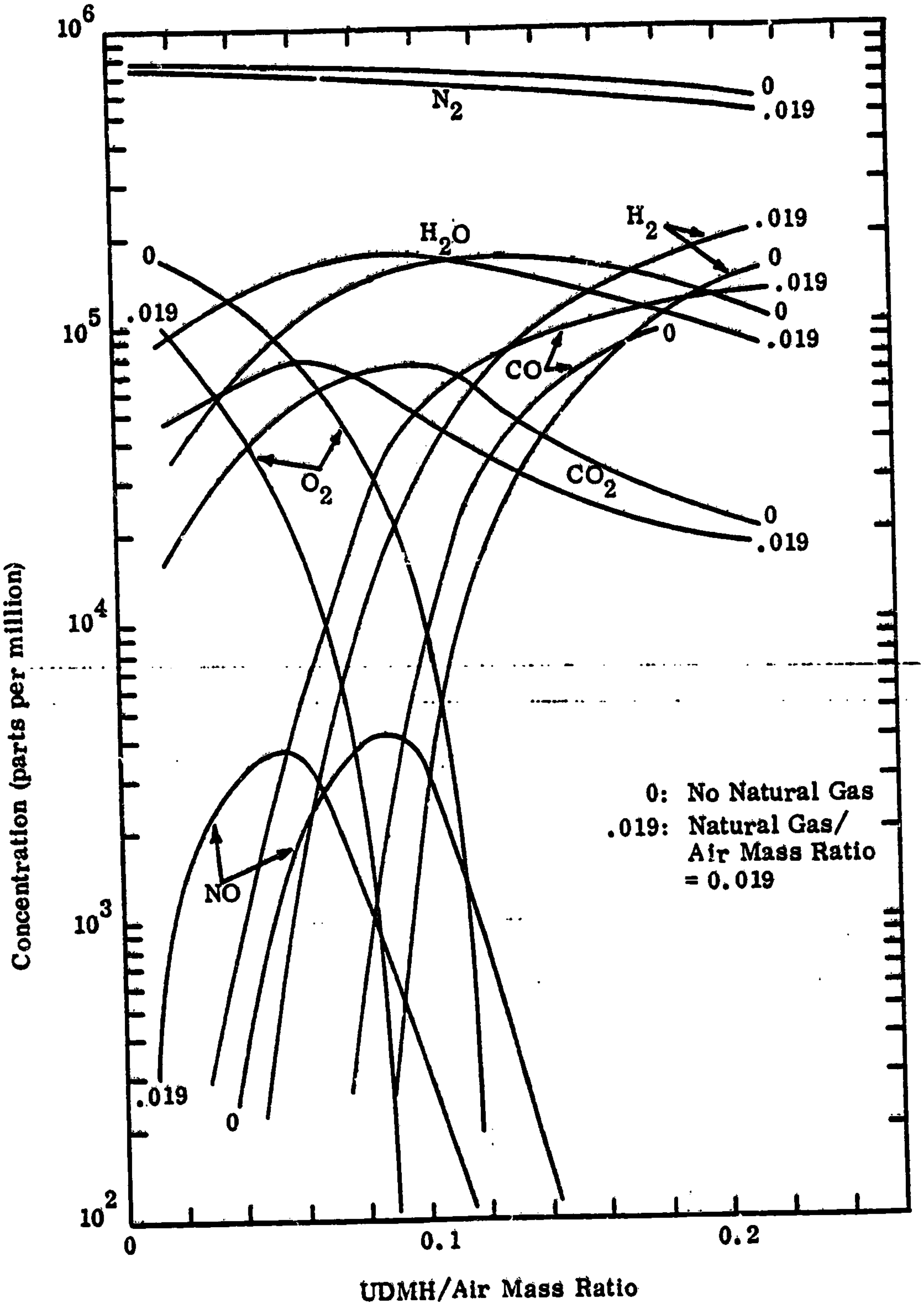

Figure 2.9.5 Theoretical Equilibrium Products for UDMH/Natural Gas/Air Combustion (from Marquardt Co. Report S-1271)

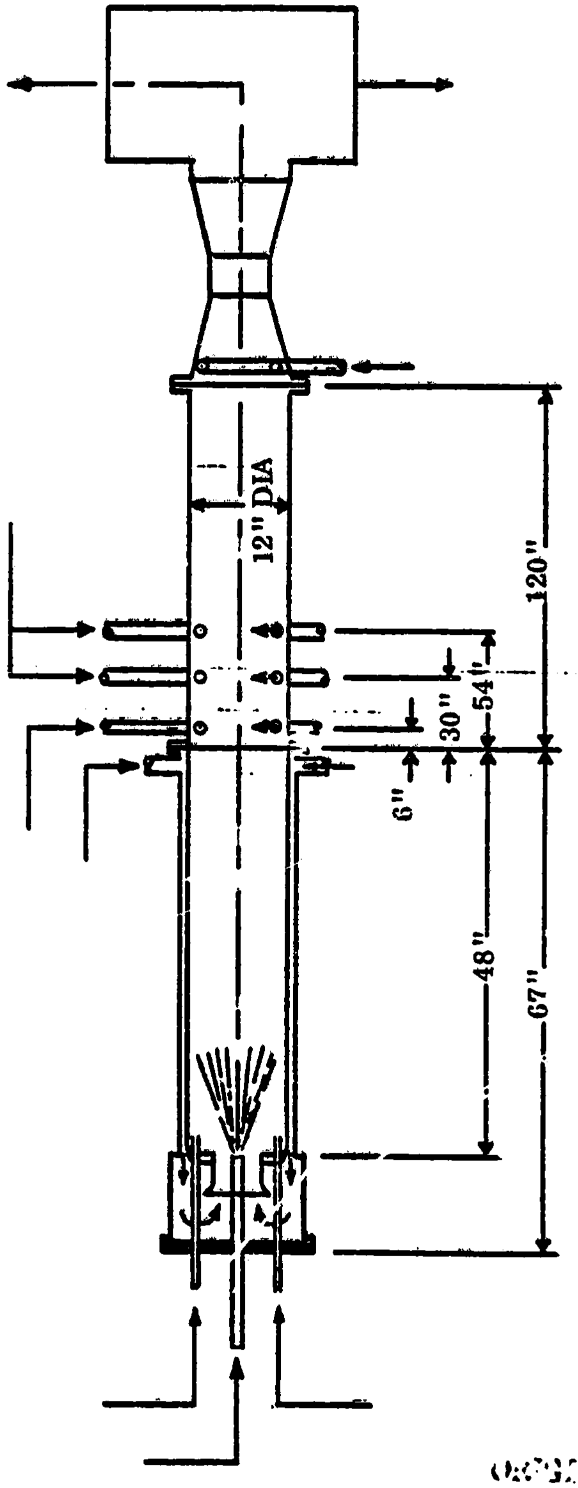

Figure 2.9.6 N_2H_4/UDMH "SUE" Incinerator, Basic Test Arrangement (from Marquardt Co. Report S-1271)

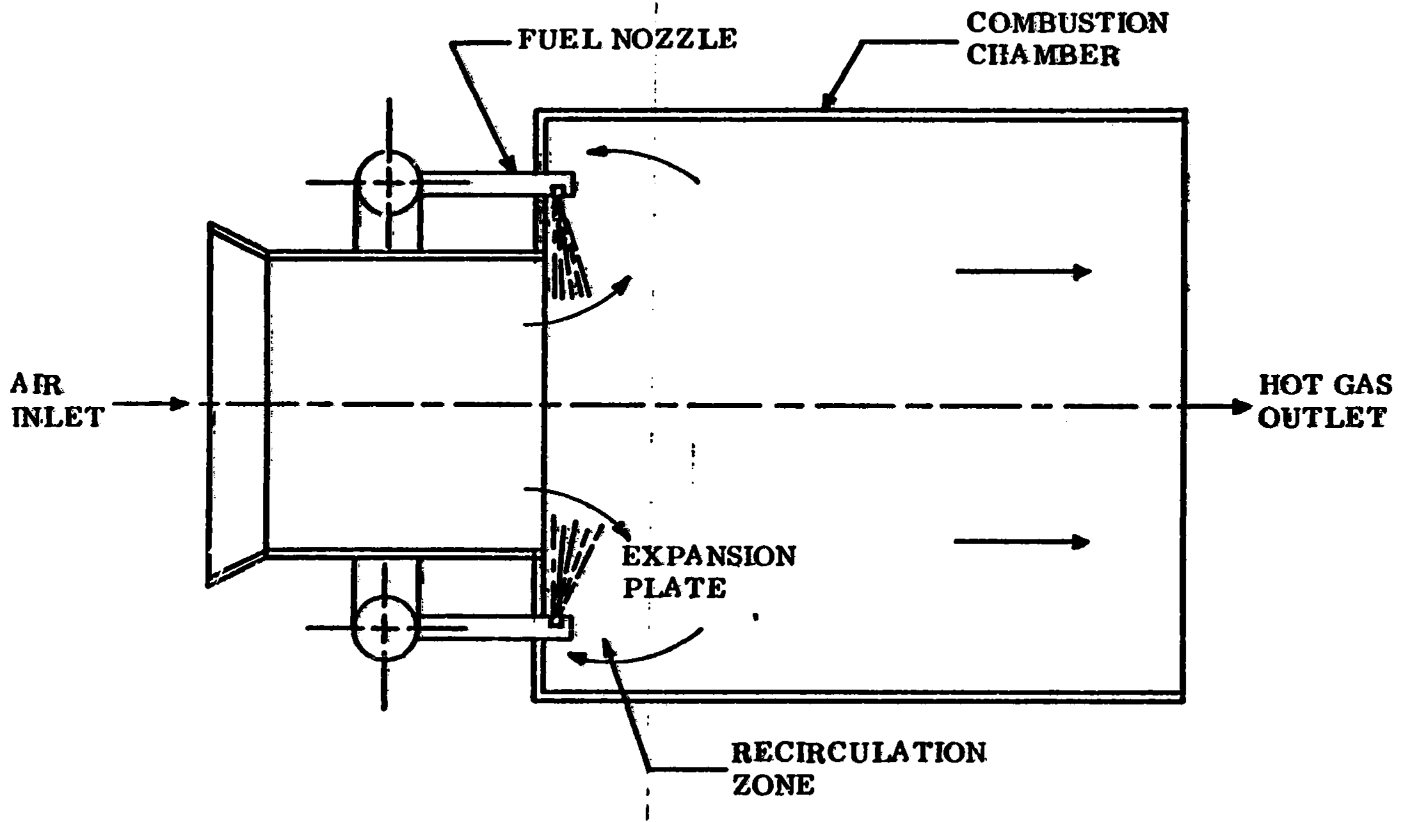

Figure 2.9.7 Typical "SUE" Burner Cross-Section
(U.S. Patent No. 3,074,469)

manifolds at the sudden expansion, although a central poppet nozzle for waste fuel injection was also used in some runs, as shown in Figure 2.9.6. Secondary air injection, to obtain complete combustion in the case of fuel-rich primary combustion, and water injection to quench the hot products of combustion and hence minimize NO formation, were also used in some of the tests. Samples were normally taken at the end of the reaction tail pipe, upstream of the scrubber.

Maximum destruction rates were given as 138 gallons per hour for N_2H_4, 100 gallons per hour for UDMH. These rates were obtained with over-stoichiometric operation, using secondary air injection and water injection to reduce the levels of CO and H_2 in the exhaust. Satisfactory propellant destruction was also obtained at very lean ratios, with acceptable NO_x levels, but in this case destruction rates were very low. Because of the use of natural gas as an auxiliary fuel, there need be no minimum flow rate of the waste propellant. Warm-up time for the SUE unit (required to stabilize the flame, etc.) is five to ten minutes. The test results, in terms of NO_x measurements, are given in Figures 2.9.8 and 2.9.9. It is seen that NO_x concentrations are generally considerably higher than the theoretical predictions, especially in the case of over-stoichiometric operation.

As a practical matter, it would be desirable if the same incinerator could be used for disposal of both liquid hydrazines and hydrazine vapors. Such a modification would probably require a development and test program to establish its effectiveness. Other development work might also be beneficial, and Marquardt's final contract report mentions that a desirable modification might be a longer reaction tailpipe, with a turbulator section, to more effectively reduce CO and CH_x emissions when operating over-stoichiometric with secondary injection.

Other incinerators might also be developed that would be at least equally effective, making use of recent advances in the state-of-the-art of combustor design, particularly with regard to reducing the emission of trace species.

Large incinerators of the type used at Cape Canaveral Air Force Station are also environmentally acceptable in terms of point-of-use emissions, on the basis of data obtained from Pan American World Airways and other unpublished data. The overall environmental impact of these larger units might be judged unfavorable on the basis of their very high consumption of hydrocarbon fuels, however. In addition, their more complex operational requirements, special

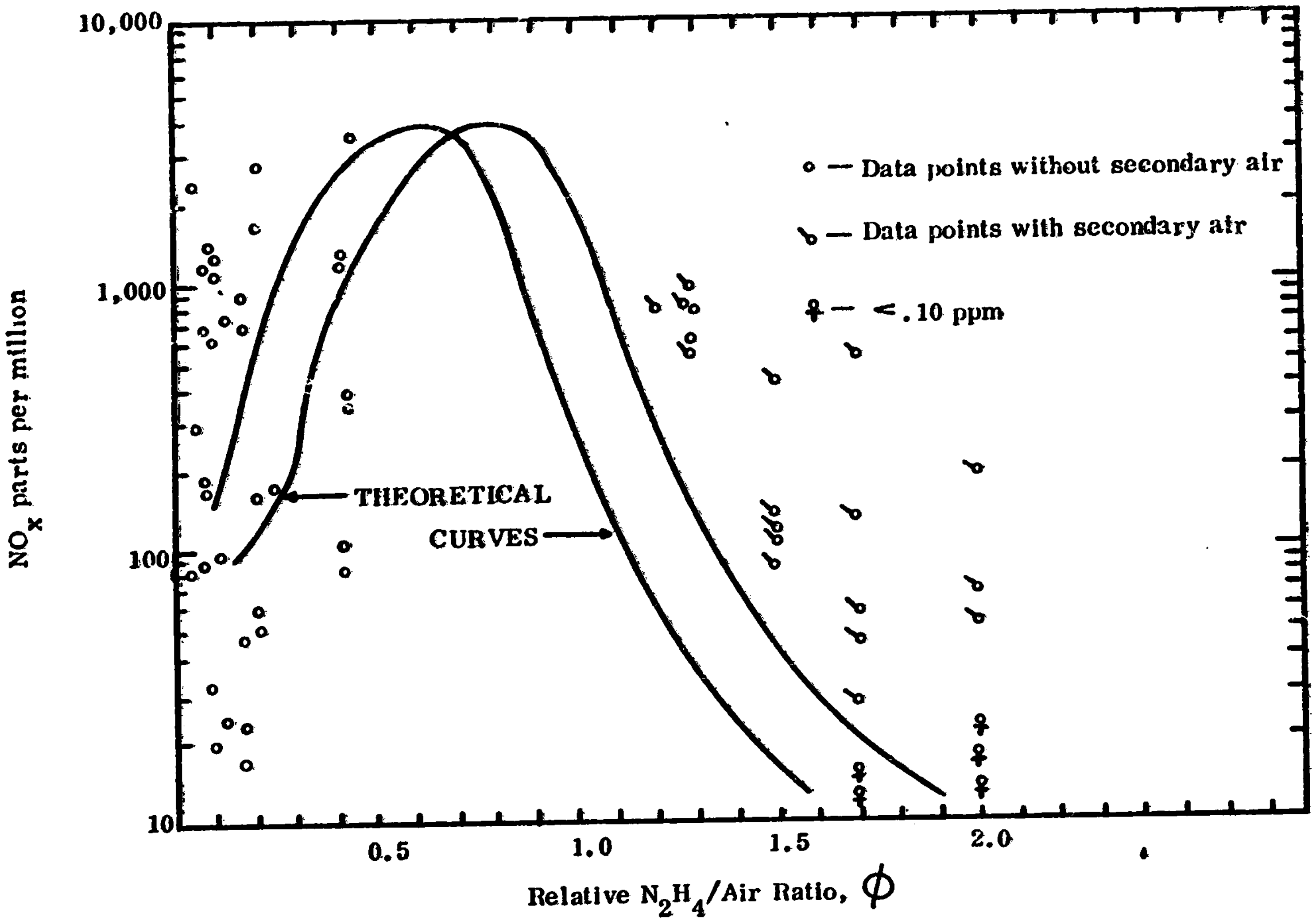

Figure 2.9.8 Toxic Waste Program Test Results: NO_x Emission from N_2H_4/Air/Natural Gas Combustion (from Marquardt Co. Report S-1271)

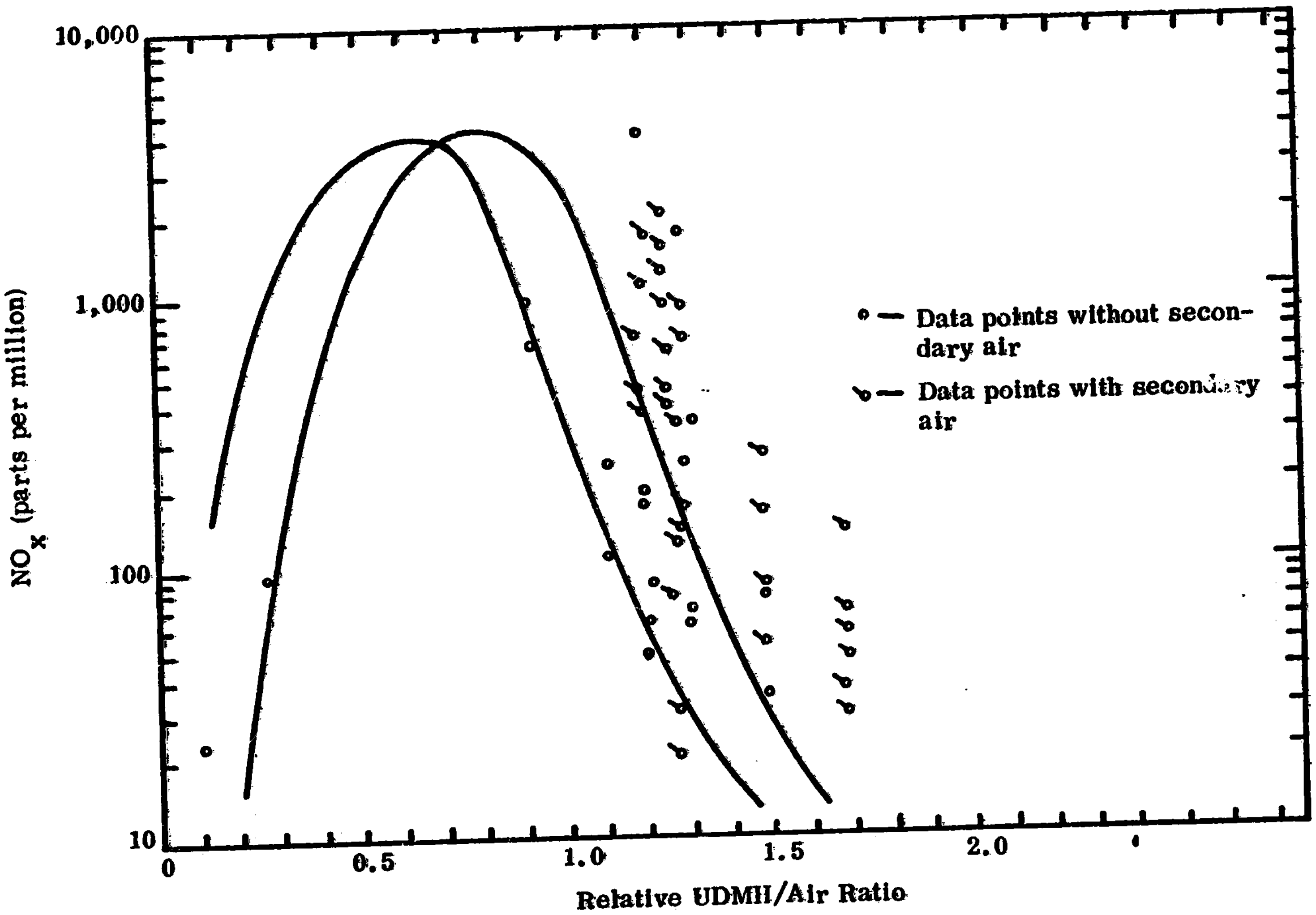

Figure 2.9.9 Toxic Waste Program Test Results: NO$_x$ Emission from UDMH/Air/Natural Gas Combustion (from Marquardt Co. Report S-1271)

siting requirements, and long warm-up cycles all place them at a disadvantage. Their chief advantage over smaller units is the ability to destroy aqueous solutions - a requirement that can also be met very effectively by aeration, ozonation, chlorination, or other chemical treatments as described in the preceding sections.

2.9.4 Open Pit Incineration

An open pit incinerator consists of a rigid shell or lined pit of suitable width and height with an open top. An array of closely spaced nozzles can be used to provide high velocity air over the burning zone.

High burning rates, long residence time, and high flame temperature are achieved. Smoke can be controlled but some particulate matter (soot) and a visible plume of toxic gas (NO_2) are produced. Exit gases are released directly to the atmosphere.

Mixture ratios and temperatures are not well controlled in this process, and can vary substantially with both position and time. Formation of partial products and oxides of nitrogen is to be expected. The usual means of minimizing these emissions do not seem applicable to open pit burning.

Although open pit incineration is an effective means of destroying hydrazines, the probability of excessive generation of oxides of nitrogen, and CO in the case of the methyl-substituted hydrazines, render it environmentally undesirable, in our view. Because of the number of other options available and their overall acceptability, we do not believe open pit incinerators should be considered in cases where new facilities are to be constructed.

2.9.5 Incineration of Hydrazine Vapors

We know of only one organization that has the capability of destroying hydrazine vapors by incineration, and this organization's systems are used primarily for products of combustion (or dissociation) rather than directly for hydrazine.

These systems are used in conjunction with testing of small hydrazine gas generators and APU's. Exhaust from the test cells is carried to small rooftop incinerators - essentially 55 gallon drums with equipment panels at one end and exhaust deflectors at the other. Natural gas is fed through the equipment panel, which also includes a squirrel cage blower and a spark plug. The air and gas are mixed, and ignition is initiated by the spark plug. The flame enters the drum through a central hole in the firebrick lining on the end; the waste (exhaust) gas from the test cells is fed into the flame in the central part of the drum by means of a downstream facing duct. The unit is fired prior to the beginning of a test in the cell below it. These units were installed after hydrazine testing began, in order too eliminate a problem with ammonia odors in the test buildings, and they have been quite successful.

In addition to the rooftop units used at this installation, there also is a large incinerator, originally manufactured by Hirt Combustion Engineers, that services the test facility. Deluge water from the cells is drained to a sump adjacent to this incinerator; when enough accumulates, the incinerator is fired and the contents of the sump injected into it. In addition, six-inch lines come directly to the incinerator from two of the test cells carrying exhaust gas from engines running in those two cells. Both liquid and vapor can be fed to this incinerator simultaneously. Natural gas and waste vapors are injected into the main air stream through an array of nozzles, and the liquid is sprayed into the flame region through a central nozzle. The sump pump, which supplies liquid to this central nozzle, can draw either from the sump, from a liquid-vapor separator on the waste vapor lines, or from a small external tank that can be used to dispose of contaminated liquid propellants directly. In case of flame-out, the sump pump is shut off, and a burst disc directs the waste gas flow to the bottom of the sump, where it bubbles through the sump water to atmosphere.

Since the hydrazines are normally liquid at standard atmospheric conditions, their vapors are encountered only in mixtures containing noncondensible gases. The vapor pressures of N_2H_4, MMH and UDMH at 25°C are given in Table 2.9.3. The mole fraction of any constituent in a mixture of perfect gases is equal to the ratio of its partial pressure to the mixture pressure, and in equilibrium the partial pressure cannot exceed the vapor pressure corresponding to the temperature of the mixture. The maximum, or saturation, mole fractions for hydrazine vapors mixed with other gases at standard atmospheric conditions are also given in Table 2.9.3, as well as saturation mass

TABLE 2.9.3

LIQUID-VAPOR SATURATION PROPERTIES OF HYDRAZINE FUELS

	N_2H_4	MMH	UDMH
Boiling Point @ 1 Atm (14.7 psia)	113.5°C (236.3°F)	87.5°C (189.5°F)	63°C (146°F)
Vapor Pressure @ 25°C (77°F)	14.38 mm Hg (0.28 psia) (1917 Pa)	49.63 mm Hg (0.96 psia) (6617 Pa)	157 mm Hg (3.04 psia) (20,932 Pa)
Saturation Mole Fraction at 25°C, 1 Atm	.0189	.0654	.206
Saturation Mass Fraction with N_2 at 25°C, 1 Atm	.0216	.103	.358

fractions in mixtures with nitrogen at one atmosphere. At higher pressures, saturation mole fractions and mass fractions will be smaller; at higher temperatures, they will be larger.

The presence of a noncondensible gas, such as nitrogen, will tend to lower the flame temperature considerably, particularly in the case of N_2H_4. Formation of oxides of nitrogen could actually be reduced by extra nitrogen but there might be considerable difficulty obtaining complete combustion. One solution might be combustion at a very lean hydrazine-air ratio, with large amounts of natural gas or other auxiliary fuel used to provide an adequate flame temperature. In this case, however, destruction rates would be very low and there is still some question whether the percentage of hydrazine actually destroyed would be increased significantly, or whether the hydrazine discharge would simply be considerably diluted by the excess air and other combustion products.

An alternate solution might be the use of hydrogen, with its very high flame temperature and wide combustion limits, as the auxiliary fuel.

2.10 CATALYTIC DECOMPOSITION

In addition to using catalysts to speed reactions in dilute solutions, it is also possible to directly catalyze the decomposition of undiluted hydrazine fuels, and their vapors, because of the positive heats of formation of all these fuels. Appropriate catalysts are expensive compared to the copper sulfate catalyst used in conjunction with the oxidation processes described in earlier sections, but not nearly as expensive as the catalysts used in hydrazine monopropellant thrusters and auxiliary power units. Various nickel catalysts available at approximately $5 per pound could be used, for example.

Reactions occurring entirely within a single phase are referred to as homogeneous, while those occurring at an interface are heterogeneous. Experimentally one finds that the activation energy for the latter is lower; the magnitude of the differential is a complex function of several thermodynamic parameters. Catalysts are simply a relatively stable interface introduced into the system to supply a favorable reaction site.

Catalysts are particularly important for exothermic reactions. Although the equilibrium constant is such that the reaction should proceed at, say, room temperature, the rate may be prohibitively slow. From the empirical Arrhenius equation

$$\text{Rate} = A \exp\left(\frac{-\Delta Ea}{RT}\right)$$

where ΔEa is the activation energy, one would expect a satisfactory rate to be obtained by a sufficient increase in temperature. However, according to Le Chatelier's principle, whenever an equilibrium system is perturbed the system will attempt to readjust in such a way as to oppose the applied change. So when the temperature is increased the equilibrium shifts in the direction which causes an absorption of heat, thereby requiring an additional increment of heat to rise the temperature. Stated mathematically the temperature dependence of the equilibrium constant is

$$\frac{\partial \ln K}{\partial (1/T)} = \frac{-\Delta H}{R}$$

Catalysts are the means by which the reaction can be carried out at temperatures where the equilibrium constant is favorable.

During the course of our study, we contacted a number of manufacturers and others who might be able to give us further information on catalysts for hydrazine decomposition. The following paragraphs present some of our findings.

W.R. Grace and Co., Baltimore, Maryland: "The hydrazines would be relatively easy to decompose using Raney nickel catalyst." Decomposition generally requires 3.5 percent catalyst by mass. In lots of 100 to 1000 pounds the cost of Raney Ni 28 is $4.05 per pound.

The Harshaw Chemical Co., Cleveland, Ohio, supplied information on two nickel catalysts developed by the Jet Propulsion Laboratory for the decomposition of hydrazine. Indications are that their use is limited to the controlled decomposition of monopropellant hydrazine used in space probes. The price quoted for the two nickel catalysts in 100 lb lots was approximately $5 per pound.

Shell Development Company's Chemical Research Laboratory in Houston, Texas, commented: "Although one of our customers in West Germany has indicated that they successfully used Shell 405 Catalyst to remove traces of hydrazine from organic process streams, we do not consider its use for disposal purposes as economical (the catalyst currently sells for $2950.00 per pound and is subject to poisoning by chemical impurities)."

Dr. Robert Ottinger, TRW Systems Group, Redondo Beach, California, advised us that the inexpensive catalyst mentioned in the TRW report (see section 2.2) is molybdenum based.

We were told that one supplier's proprietary catalyst for N_2H_4 is a mixture of iron and iron oxide.

In theory, the cost of a catalyst should be a one-time expense, since a catalyst by definition does not take part in a reaction. In practice, however, all catalysts have limited effective lifetimes, and are subject to poisoning and degradation.

We believe this method does show promise of being an economical means of destroying hydrazine fuels, and is worthy of further study to better identify potential problems and better evaluate its economic aspects.

2.11 PLASMA ARC AND MICROWAVE PLASMA DECOMPOSITION

A plasma arc is a device which creates a high temperature (4,000 to 12,000°F) ionized gas stream by striking an arc between two electrodes and injecting the working gas (e.g. nitrogen, air, helium, argon, etc.) through the region of the electric arc discharge. The gas is ducted through a plenum chamber, then exhausted through a nozzle, either directly into the atmosphere or into an evacuated tank.

"The term microwave plasma denotes an ionized gas produced via microwave induced electron reactions with neutral gas molecules."[1] In this method high ionization levels and molecular dissociation are achieved without excessive heating of the gas, and without the need for internal electrodes within the reaction vessel.

Both of these related methods have been developed in recent years for the destruction of pesticides, defoliants, nerve gas, and other toxic chemical vapors, and could be applied to the case of hydrazine decomposition. As a practical matter, one important difference between the two is the fact that the plasma arc process is a continuous process, while the microwave plasma process is essentially a batch process, involving the containment of the generated plasma within the microwave cavity.

The microwave plasma process has been developed and applied primarily by the Lockheed Palo Alto Research Laboratory, and has been described in articles by Bailin et al[2] and Hindlin.[3] The Bailin et al artical reports on the decomposition of two chemicals, dimethyl methylphosphonate (DMMP) and diisopropyl methylphosphonate (DIMP), carried in helium and air streams at concentrations from 0.005 to 0.31 grams per liter. Flow rates in the 32 test runs reported varied from 0.44 to 4.20 grams of contaminant per hour; the microwave power was from 50 to 510 watts, with no obvious correlation in the reported data between power consumption and contaminant flow rate.

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1. Bailin, L.F.; Sibert, M.E.; Jonas, L.A.; and Bell, A.T.: "Microwave Decomposition of Toxic Vapor Simulants." Environmental Science and Technology, Vol. 9, page 254 (March 1975).

2. Ibid.

3. Hindlin, H.J.: "Microwaves Disintegrate Toxic Gases." Microwaves, July 1975, page 14.

In discussions at Florida Institute of Technology, Dr. Bailin argued that expressing his experimental data in terms of watt-hours per gram would be misleading, and that much lower energy costs are possible.

The lockheed experiments were described rather concisely in the article by Hindlin as follows:

"Typically, 10 cubic centimeters (cc) of gas may be processed at a time with the present system. Almost 100% decomposition is obtained at the relatively low temperature of 100-200°C. Depending on the reactants, the breakdown products may be recovered. Current plans call for detoxification of pesticides and other related materials.

"The microwave disintegrator consists of an inert gas carrier supply used to transport the toxic chemicals to a quartz reaction chamber or plasma cavity and various chemical sampling systems, which allow the reaction to be monitored. In the laboratory model a Varian voltage tunable magnetron is used as a power source. (Tuning is ± 50 MHz). It delivers up to 2.5 kW of power at 2.45 GHz -- depending on the type of cooling used for the cavity. Rf radiation at these levels is a concern, and as a result, an rf leakage detector is used for safety. (Levels of 1-3 mW/cm^2 are not detectable even near the discharge tubes with the present system). The plasma tube is made of quartz and is helium filled.

"To operate the system, the pressure in the cavity and waveguide is first reduced to about 20 microns. Then, the gas to be destroyed is introduced, where it flows into the cavity. After the cavity is cooled using air and water, the VTM is turned on and tuned for minimum cavity reflection. A Telsa coil is used to ignite the discharge and the plasma is thus initiated and sustained in the cavity. Constant monitoring of the chemical reaction products is performed by nuclear magnetic resonance, gas chromatography and mass spectroscopy equipment. To protect the magnetron and insure optimum power transfer to the cavity, either an H-plane double stub turner or a coupling hole adjustment is used on the input line. Both incident and reflected waves are monitored and displayed continuously. (In the case of an extreme mismatch, the magnetron is automatically turned off). A circulator and water load may also be used on the input line to protect the tube. Additional tuning is provided by a sliding short on the back of the cavity. The microwave discharge gap length may also be adjusted from 0.75 to 1.70 inches. This is optimum for gases with an impedance in the range from 10^2 to 10^6 ohms which is the case in these experiments."[4]

A comparable application of a plasma arc facility has been carried out at Martin Marietta Corporation, Denver, Colorado. The following excerpt from an informal MCC report describes their results.

"To evaluate the use of a plasma arc for pesticide detoxification, chlorobenzene was selected since it is representative of many organochlorinated toxic agents. Argon was used as the primary working gas (injected between the electrodes of a segmented arc heater) while the chlorobenzene was injected downstream into the 5500°F argon plasma. The flow was exhausted through a 1-1/8 inch exit diameter supersonic nozzle into a large tank maintained at a pressure of 1/2 atmosphere. An evacuated collection vessel was located downstream to sample the chlorobenzene decomposition products. The arc was run under the following conditions:

Power Level	150 kw
Argon Flow Rate	.04 lb/sec
Chlorobenzene Flow Rate	.01 lb/sec (35 lb/hr)

The power level used was only a small fraction of the rated capacity of 5.25 megawatts. At full power, larger exit nozzles would be used and a toxic agent flow rate of 500-1000 lb/hr can be readily projected with our equipment. Thus, large quantities of material can be detoxified in a reasonable time period.

"The collected gaseous decomposition products from the test run were analyzed by means of a mass spectrometer. The only chlorine-containing species detected was HCl. The remaining species were aliphatic hydrocarbons such as methane, ethane, and acetylene, as well as some hydrogen. In addition, elemental carbon in the form of carbon black was deposited throughout the vacuum tank.

"The plasma arc conditions used in the test were selected without regard for maximizing material disposal or minimizing power requirements

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[4] Hindlin, loc. cit.

or primary gas flow rates. To establish the performance envelope for complete and cost effective hypergol vapor destruction in the plasma arc, a number of operational variables should be investigated in a systematic fashion and optimized. These include:

Power level
Primary gas (Argon, Nitrogen)
Primary gas flow rates
Injection of waste organics
  a. into ionized stream
  b. between electrodes with primary gas
  c. into plenum chamber
Hypergolic propellant flow rate

Decomposition products would be monitored by placing a water-cooled mass spectrometer inlet tube directly into the plasma arc exhaust stream. The plasma arc can be used as a research tool, using small quantities of propellants and short run times to evaluate this type of disposal method and subsequently as a pilot plant setup to quantize details of disposal operation."[5]

It should be noted that the power consumption in this chlorobenzene experiment was 4.3 kw-hr per pound of chemical destroyed, while the figures for the tests reported by Bailin et al on DMMP and DIMP ranged from 7.7 to 252 kw-hr per pound. All except the highest of these figures represent relatively economical operation. For example, we showed in Sections 2.6 and 2.7 that 32.2 pounds of sodium hypochlorite are required to treat one pound of MMH; if we consider electricity at $0.05 per kw-hr and sodium hypochlorite at $0.10 per pound, we obtain figures of $3.22 to chemically treat one pound of MMH versus $0.21 to destroy one pound of chlorobenzene in a plasma arc.

There are, of course, a number of disadvantages to the plasma arc and microwave plasma processes, including high capital cost, sophistication and delicacy of the equipment and the need for highly skilled operators. The difficulties associated with taking this sort of equipment out of the laboratory

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[5] Author unknown: "Plasma Arc Disposal of Hypergolic Propellant Vapors." Informal report from Martin Marietta Corporation, Denver, Colorado (no date).

and into the field are hard to evaluate. Considerable additional development, testing and evaluation are required before these processes can be applied in an operational context. We believe further study is justified, however, by the promise of extremely fast, complete and economical destruction of hypergolic propellants.

2.12 ABSORPTION OF VAPOR

2.12.1 Scrubbing with Water

The most common means of removing hydrazine fuel vapors from vent streams involves the use of packed towers in which a spray of water introduced at the top trickles down through the packing material - raschig rings, saddles, quartz or ceramic spheres, stainless steel shavings, or similar - while the vapor stream flows upward, countercurrent to the water flow. A number of variations on this general theme are possible; some of the specific scrubbers that have been used are described in Appendix D, along with a brief theoretical description of scrubber operation and design considerations.

Water scrubbers are highly effective in terms of removing hydrazine vapors from vent streams because of the very high solubility of the hydrazines in water. Contaminant concentrations can readily be reduced to parts per million levels. Their chief disadvantage lies in the fact that the hydrazine is not destroyed in any way - neither reaction nor decomposition takes place. It is simply changed to a form that is more easily handled and stored. The aqueous solution must still be treated if direct release of the untreated fuel is to be avoided. In the meantime, all the usual precautions regarding handling and storage, advoidance of spills, leaks, personnel contact, etc., must be adhered to. A much better approach, in our opinion, is to use a scrubbing fluid that will react with the fuel vapors as they are absorbed, as described in the following subsections.

2.13 CONDENSATION OF VAPOR

2.13.1 Introduction

Hypergolic propellant vapors mixed with other gases in vent streams are usually at or near saturation, except in the case of purge streams. If the vapors are at saturation, then any decrease in temperature (or increase in pressure at constant temperature) will result in condensation of some of the propellant vapors. The resulting liquid propellant will be essentially pure, and can probably be returned to the propellant supply tank with no requirement for treatment or disposal.

Since it is not expected that vapor condensation could ever lower propellant vapor concentrations to very low levels, some form of scrubber, cryogenic trap, or plasma device would still be required before the gas stream could be discharged to the atmosphere. A condensation unit would be a simple and effective means of removing the greater part of the contaminant from the stream, however, thus greatly reducing the load on whatever system is used to achieve an acceptable discharge concentration.

2.13.2 Analysis

A method of analysis that is applicable to any condensible constituent in a gas stream is presented in Appendix E. The analysis depends on knowledge of the vapor pressure curve for the condensible constituent, the heat of vaporization, h_{fg}, and the specific heats at constant pressure for both the condensible constituent and the noncondensible mixture, c_{pC} and c_{pN}.

In the case of the hydrazine types of interest, the following algabraic relationships for vapor pressure in terms of temperature were established by investigators working in the early days of rocketry under the sponsorship of the Bureau of Mines and Office of Naval Research (p in mm Hg, T in °K):

For N_2H_4 [1],

$$\log_{10} p = 7.80687 - 1680.745/(T - 45.42),$$

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[1] Scott, D.W.; Oliver, G.D.; Gross, M.E.; Hubbard, W.N.; and Huffman, H.M.: "Hydrazine: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions." J. Am. Chem. Soc. Vol. 71, pages 2293-97 (1949).

For MMH [2],

$$\log_{10} p = -7.88 \log_{10} T - 3146.0/T + 31.746,$$

For UDMH [3],

$$\log_{10} p = -2717.132/T - 6.745741 \log_{10} T + 28.000194.$$

All of these relationships were based on laboratory measurements, and are believed to result from establishing the empirical constants in theoretical thermochemical equations by least-squares fitting to the measured data. Plots of these equations are presented in Figure 2.13.1.

The values of h_{fg} for N_2H_4, MMH, and UDMH reported in the same references just quoted are 10,700; 9648; and 8366 cal/mole, respectively, at 298.16°K. In the case of the substituted hydrazines these are measured values, while for N_2H_4 it is a theoretical value based on the vapor pressure measurements, using the Berthelot equation of state and critical point data. In the latter case, the estimated uncertainty is given as ± 75 cal/mole. Because this temperature (equal to 77°F) is an appropriate one for our vent gas application, these values were used as constant approximations to h_{fg} throughout the temperature range of interest.

Values for the specific heats c_{pC} were published for N_2H_4 by Scott et al[4], and for MMH by Aston et al[5]. The values given at 298.16°K were 12.6 and 17.0 cal/deg/mole, respectively, and these values were chosen for the constants in equation (4') of Appendix E. In both cases these were the lowest temperatures for which vapor phase specific heats were given. Data for UDMH have not been found; on the basis of the data above, and the data

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[2] Aston, J.G.; Fink, H.L.; Janz, G.J.; and Russell, K.E.: "The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressures, Entropy, and Thermodynamic Functions of Methylhydrazine." J. Am. Chem. Soc., Vol. 73, pages 1939-43 (1951). Note: the equation as published contains a misplaced decimal point in one term; this error was corrected in the equation written above to yield agreement with the experimental data published in the paper.

[3] Aston, J.G.; Wood, J.L.; and Zolki, T.P.: "The Thermodynamic Properties and Configuration of Unsymmetrical Dimethylhydrazine." J. Am. Chem. Soc., Vol. 75, pages 6202-04 (1953).

[4] Op. cit.

[5] Op. cit.

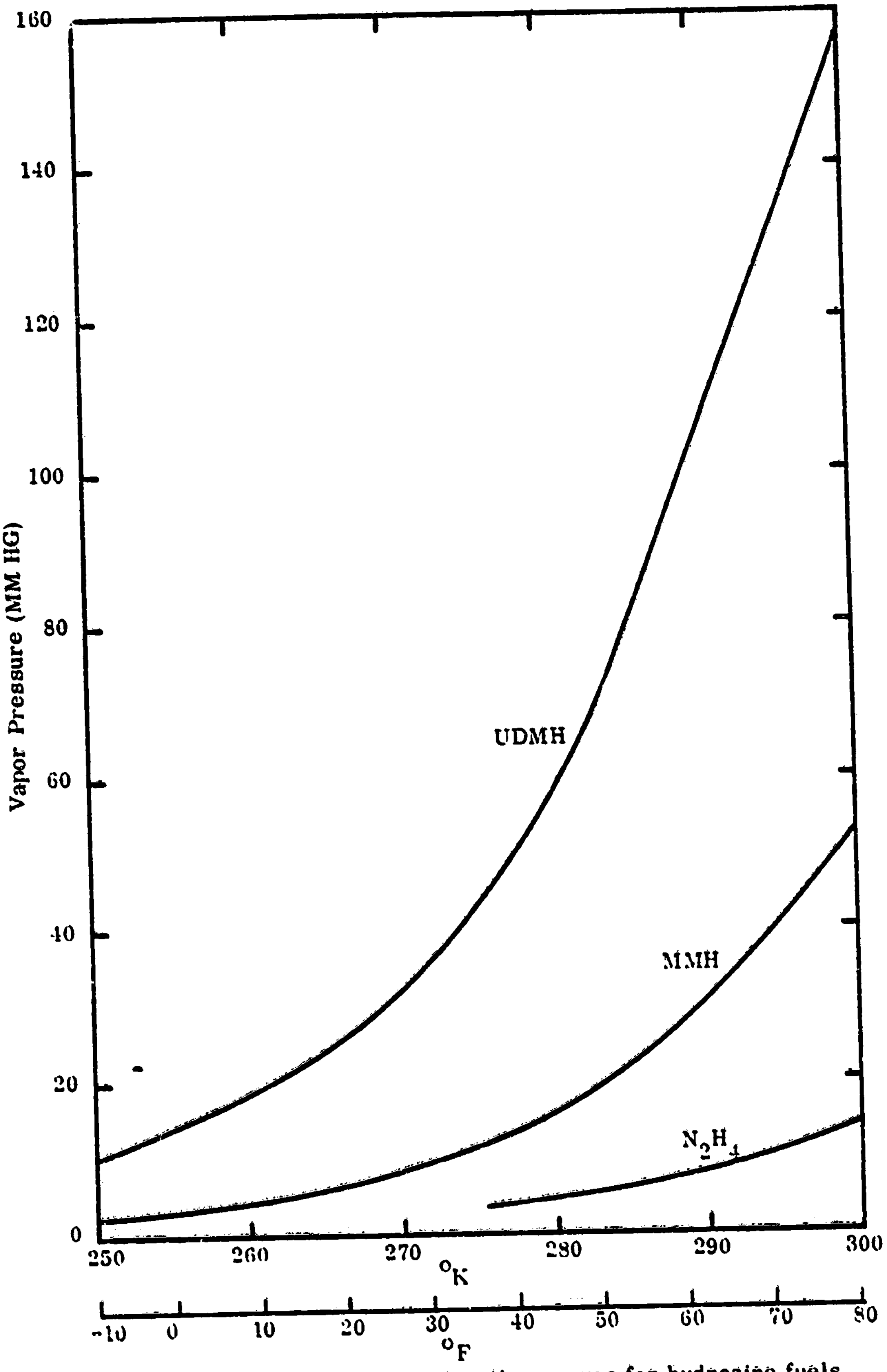


Figure 2.13.1 Liquid-vapor saturation curves for hydrazine fuels

in Table 2.1.1 for the heat capacity of liquid UDMH, MMH and N_2H_4 at 77^oF, a guess of 22 cal/deg/mole for the specific heat of UDMH in the temperature range of interest was made and this value used in equation (4').

The values of c_{pN} used were 6.95 cal/mole-^oC for nitrogen, and 5.00 cal/mole-^oC for helium.

The computer code described in Appendix E was used, with these values, to investigate cases in which saturated mixtures initially at 300^oK (80.33^oF), 2300 mm Hg (44.47 psia) are progressively cooled to 250^oK (-9.67^oF), or to the freezing point, 275^oK (35.6^oF), in the case of N_2H_4.

Figures 2.13.2 through 2.13.6 present the results for nitrogen carrier streams saturated with the respective hydrazine fuel vapors. Figure 2.13.2 shows the actual amount of hydrazine condensed, as a function of temperature. The large differences between UDMH, MMH and N_2H_4 reflect the different amounts of fuel vapors initially present; UDMH, because of its relatively low boiling point (high vapor pressure), is initially present in large quantity, whereas N_2H_4 with the highest boiling point and lowest vapor pressure is present in the vent gas in only very limited quantities. Figure 2.13.3 presents the same information, except that the mass condensed at any point in the process is calculated as a fraction of the initial fuel mass rather than the total initial mixture mass. Here the three curves are much closer together, with N_2H_4 looking most favorable by a small margin. Figure 2.13.4 shows the heat removal required to achieve any given temperature. As in Figure 2.13.2, the UDMH curve is highest because of the relatively large amount of UDMH initially present. This information is combined with the results for mass condensed in Figures 2.13.5 and 2.13.6, which show the "cost", in terms of heat removal per unit mass condensed. Figure 2.13.5 shows total heat removal divided by total mass condensed for each fuel, while Figure 2.13.6 shows the incremental cost - calories per gram for the incremental mass of fuel condensed at any temperature. In these plots it is evident that recovery of UDMH is the most attractive in terms of costs per unit mass of fuel recovered.

To further define the cost, note that

$$1 \frac{\text{cal}}{\text{gram}} = .0005274 \frac{\text{kW-hr}}{\text{lbm}}$$

so that the first UDMH condensed requires 0.0923 kW-hr of energy removal per

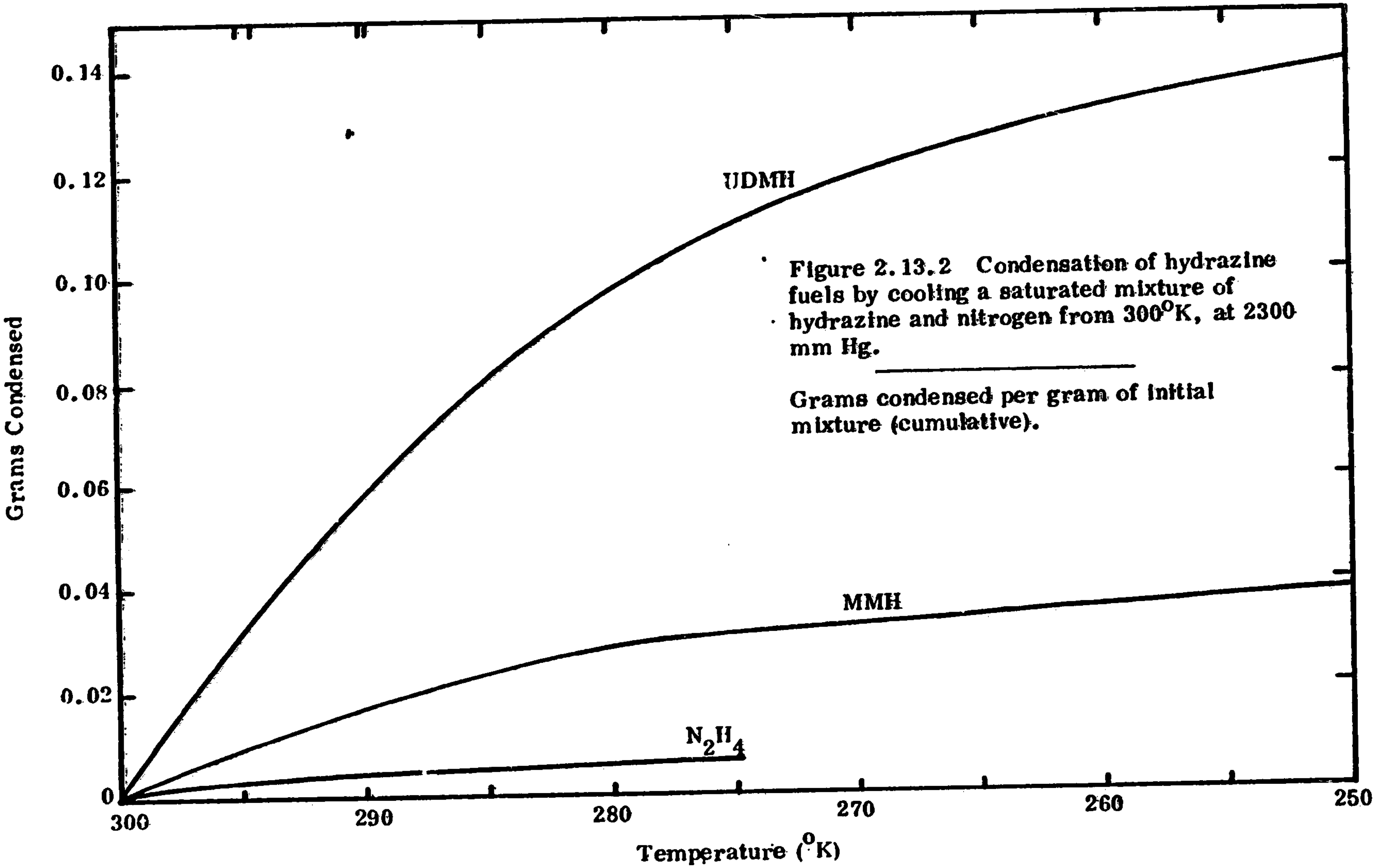


Figure 2.13.2 Condensation of hydrazine fuels by cooling a saturated mixture of hydrazine and nitrogen from 300°K, at 2300 mm Hg.

Grams condensed per gram of initial mixture (cumulative).

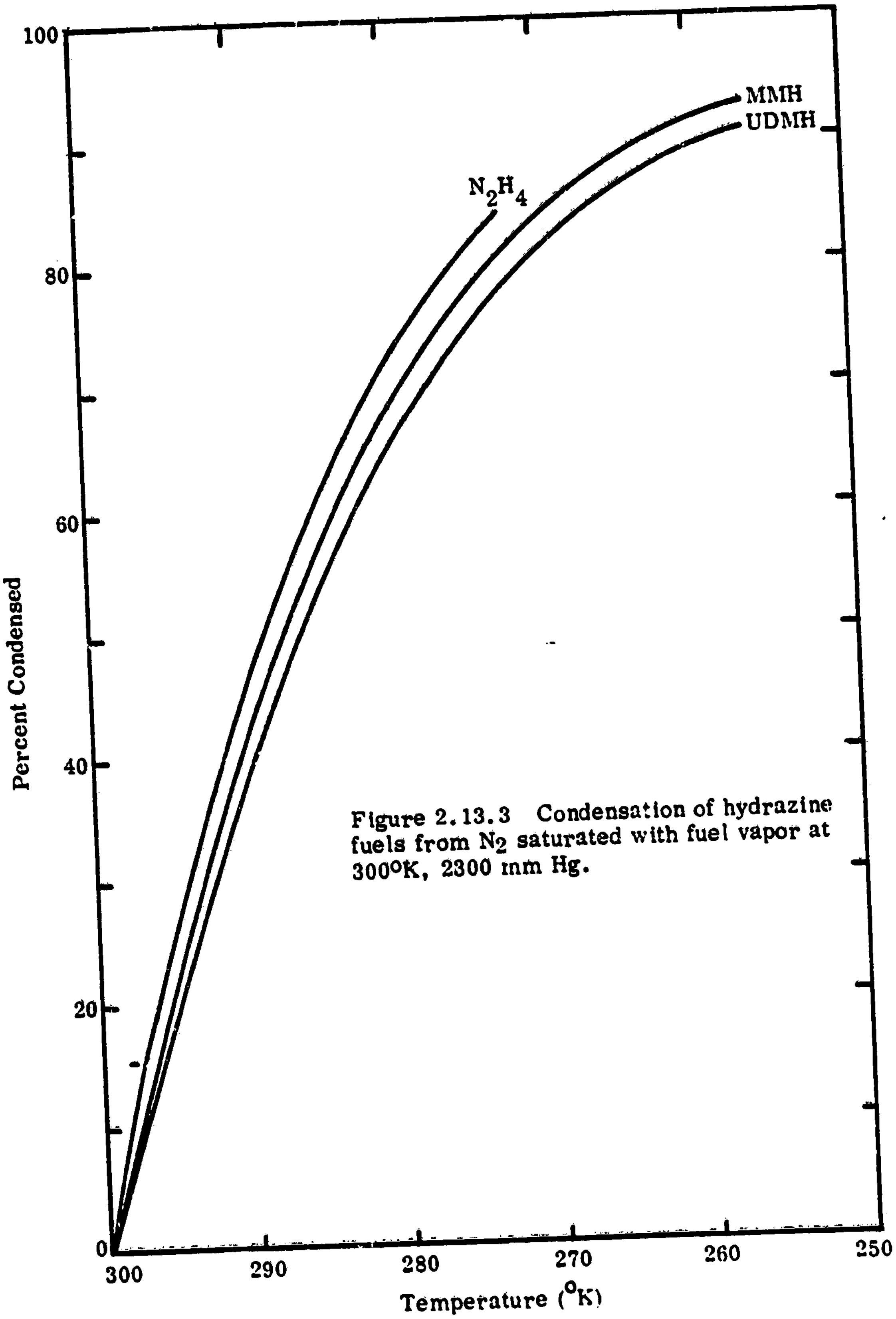


Figure 2.13.3 Condensation of hydrazine fuels from N_2 saturated with fuel vapor at 300°K, 2300 mm Hg.

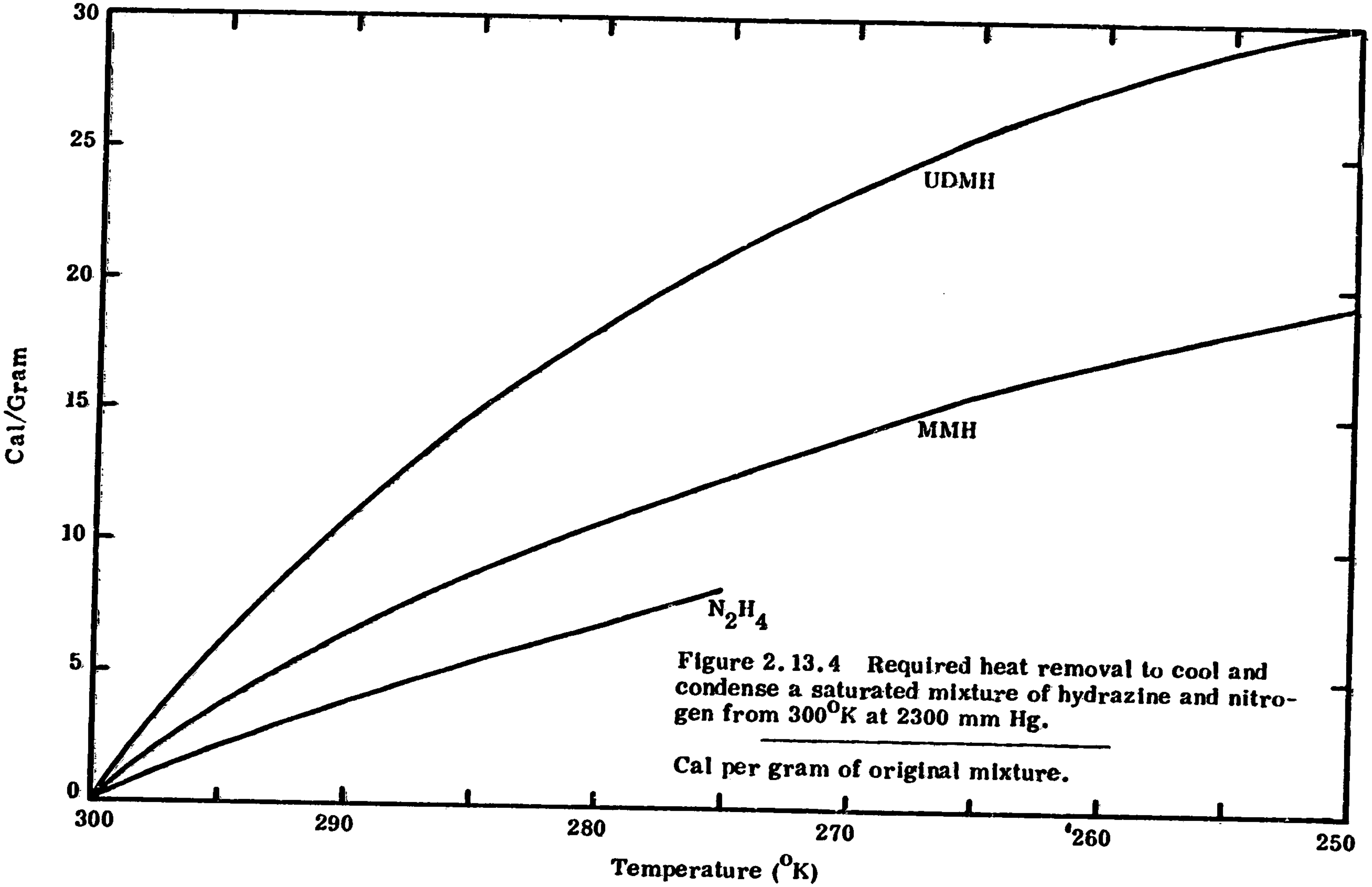


Figure 2.13.4 Required heat removal to cool and condense a saturated mixture of hydrazine and nitrogen from 300°K at 2300 mm Hg.

Cal per gram of original mixture.

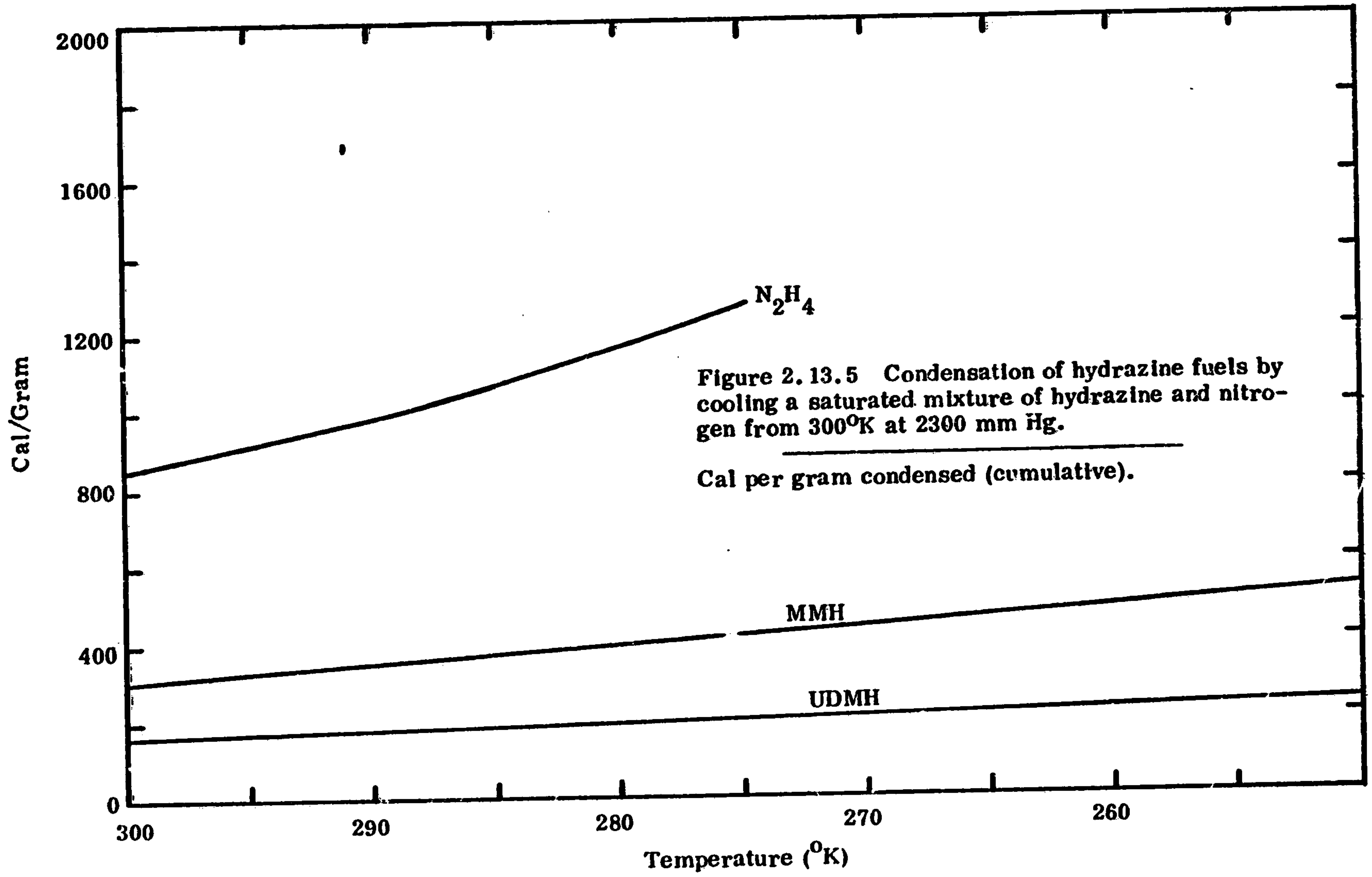
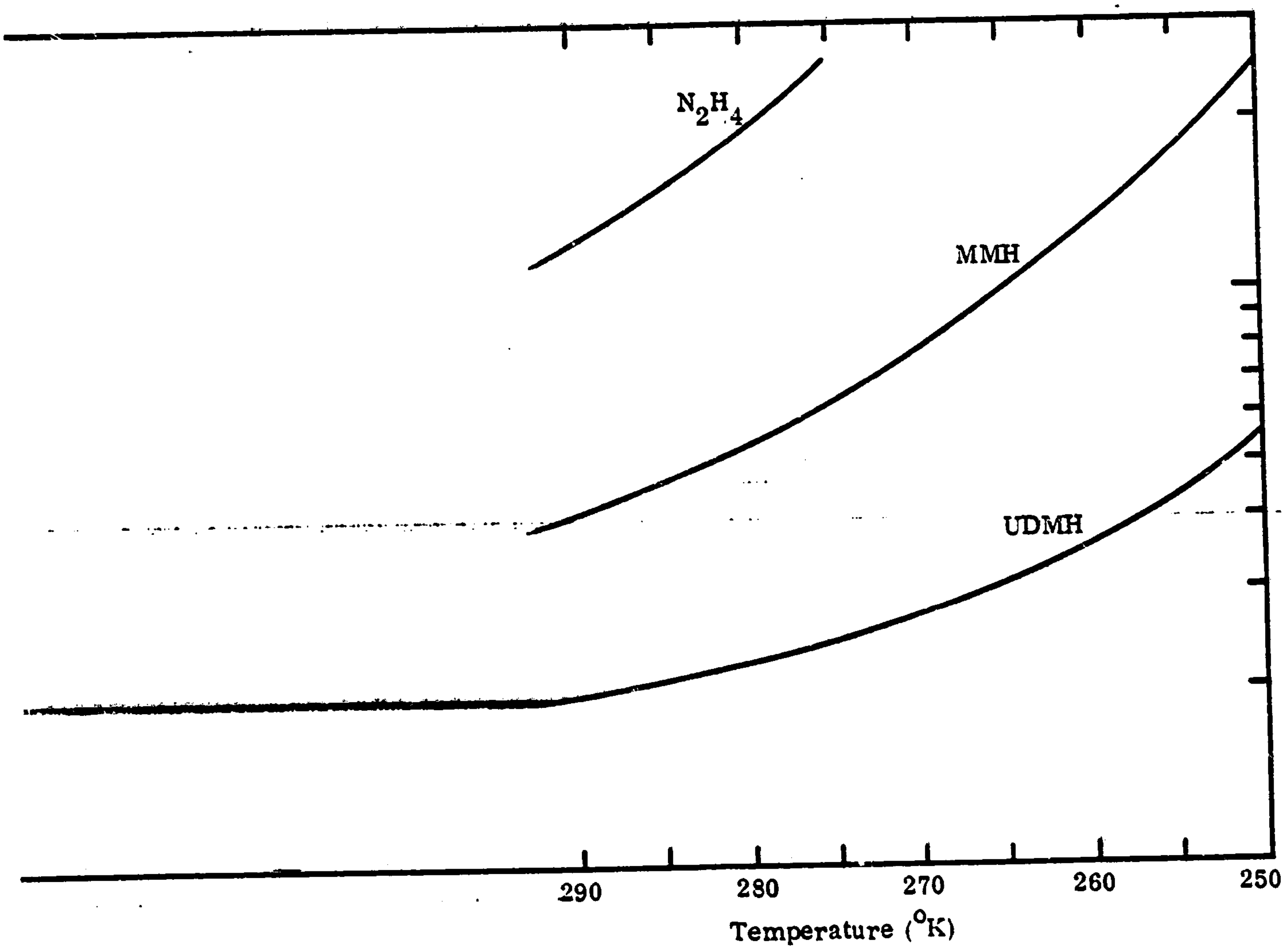


Figure 2. 13. 5 Condensation of hydrazine fuels by cooling a saturated mixture of hydrazine and nitrogen from 300°K at 2300 mm Hg.

Cal per gram condensed (cumulative).



2.13.6 Condensation of hydrazine fuels by
ing a saturated mixture of hydrazine and
nitrogen from 300°K at 2300 mm Hg.

al per gram condensed (incremental).

pound recovered, the first MMH requires 0.1735 kW-hr per pound and the first N_2H_4 requires 0.458 kW-hr per pound. Similar figures at the point when 80% of the original fuel vapors are condensed are 0.1382, 0.349, and 1.292, respectively. If we assume that a refrigeration system with a coefficient of performance of 3 is used, and that electrical costs are 3 cents per kW-hr, then these figures also represent the electrical cost in pennies per pound of propellant recovered - modest figures even in the worst case. Capital equipment costs are of course not included.

Similar cases in which the carrier streams are helium rather than nitrogen are plotted in Figures 2.13.7 through 2.13.11. For these cases the only contaminant vapor considered was MMH. We can see that percent condensed and energy per unit mass condensed are virtually the same as in the nitrogen case: quantities expressed per unit mass of initial mixture are of course much larger because of the very low molecular weight of helium.

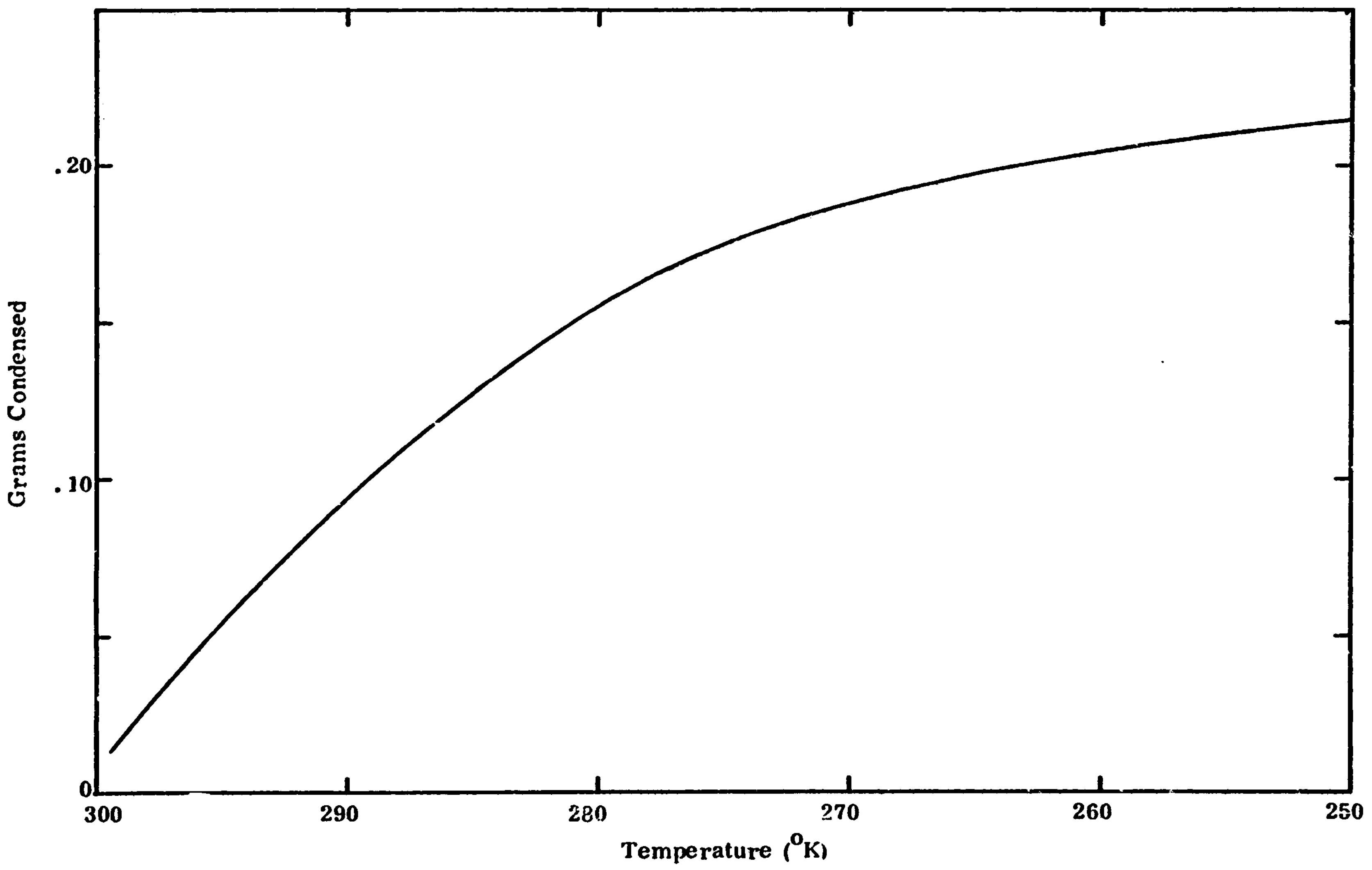


Figure 2.13.7 Condensation of MMH by cooling a saturated mixture of MMH and helium from 300^{o}K, at 2300 mm Hg. Grams condensed per gram of initial mixture (cumulative).

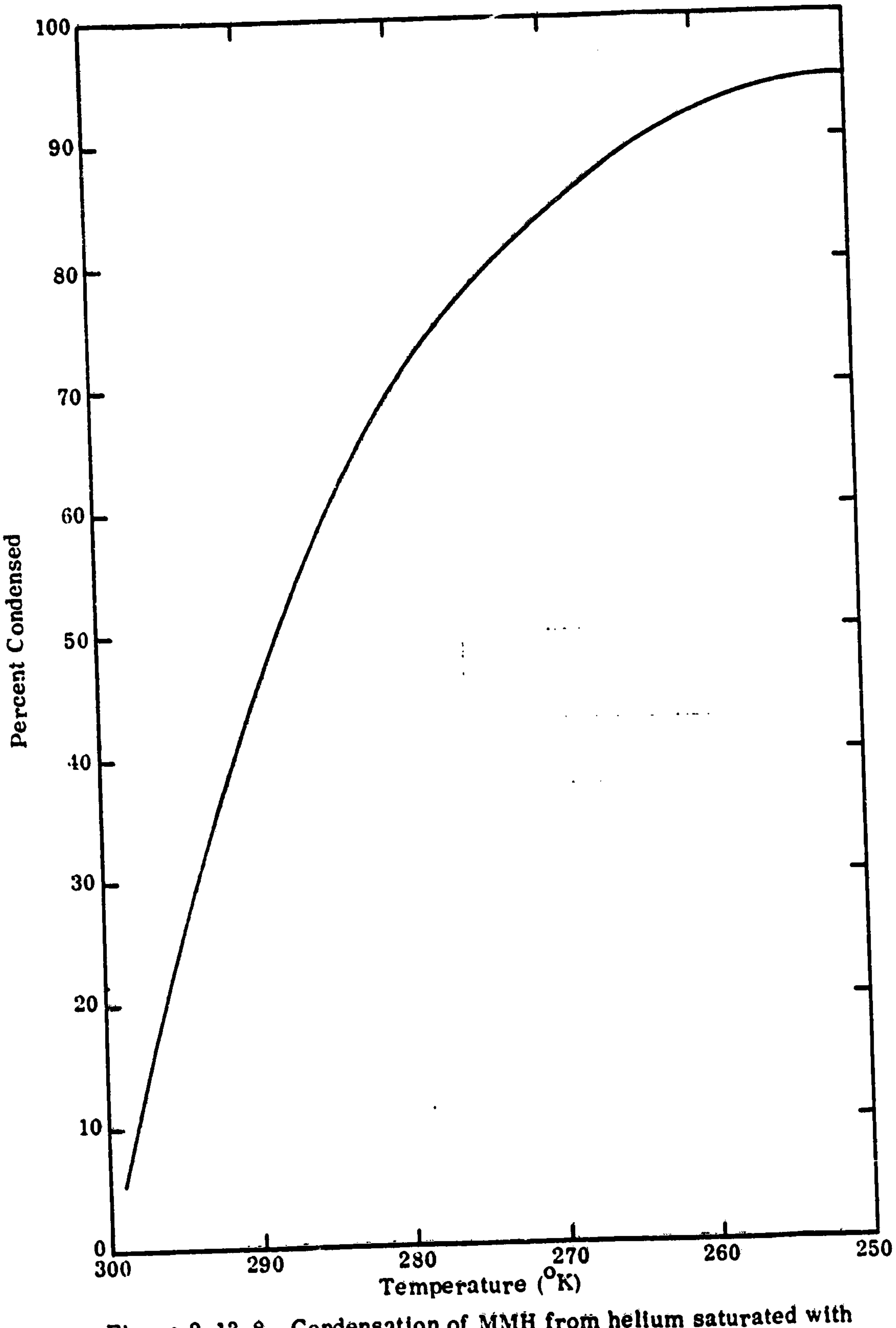


Figure 2.13.8 Condensation of MMH from helium saturated with MMH vapor at 300°K, 2300 Hg.

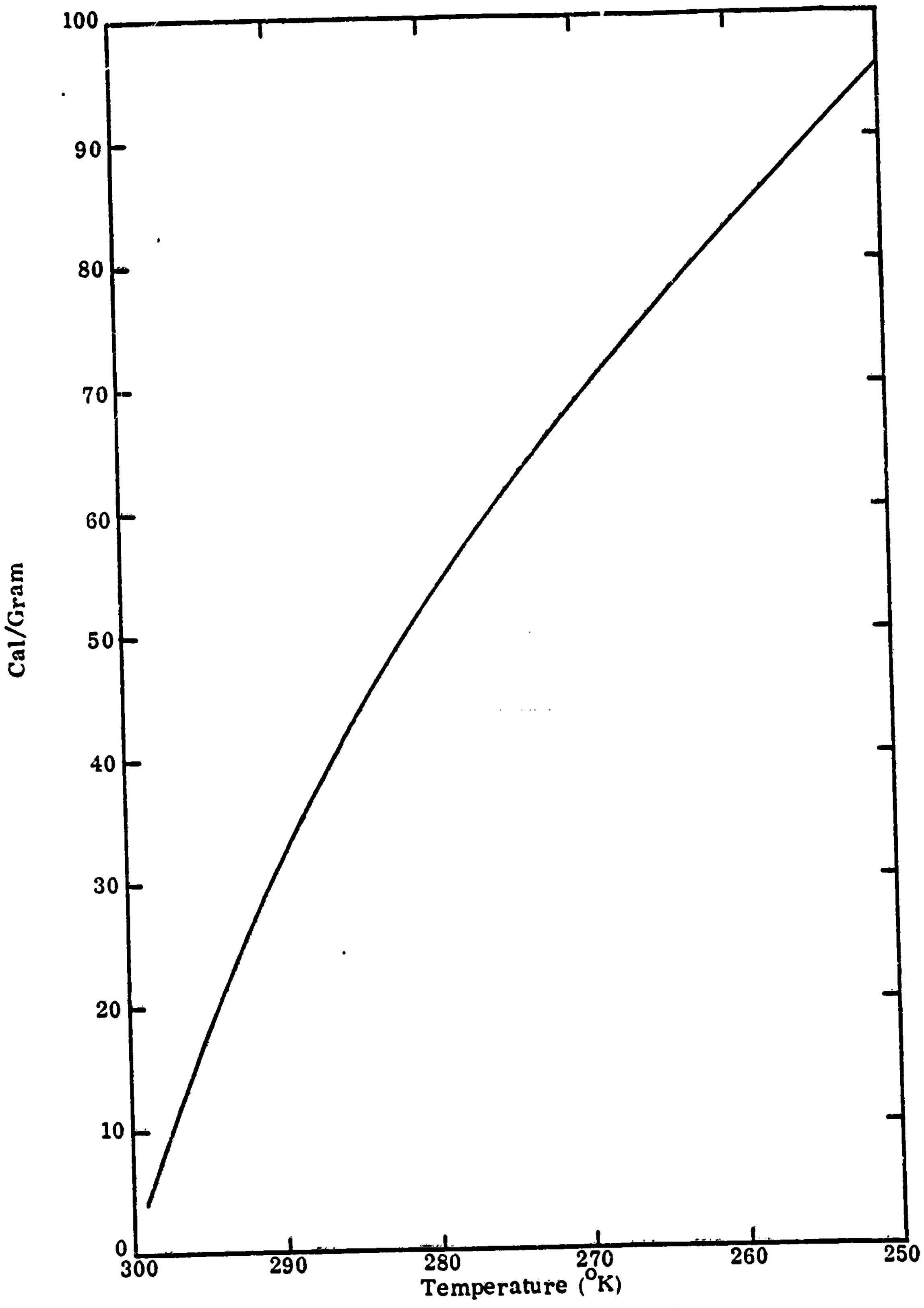


Figure 2.13.9 Required heat removal to cool and condense a saturated mixture of helium from 300°K at 2300 mm Hg. Cal per gram of original mixture.

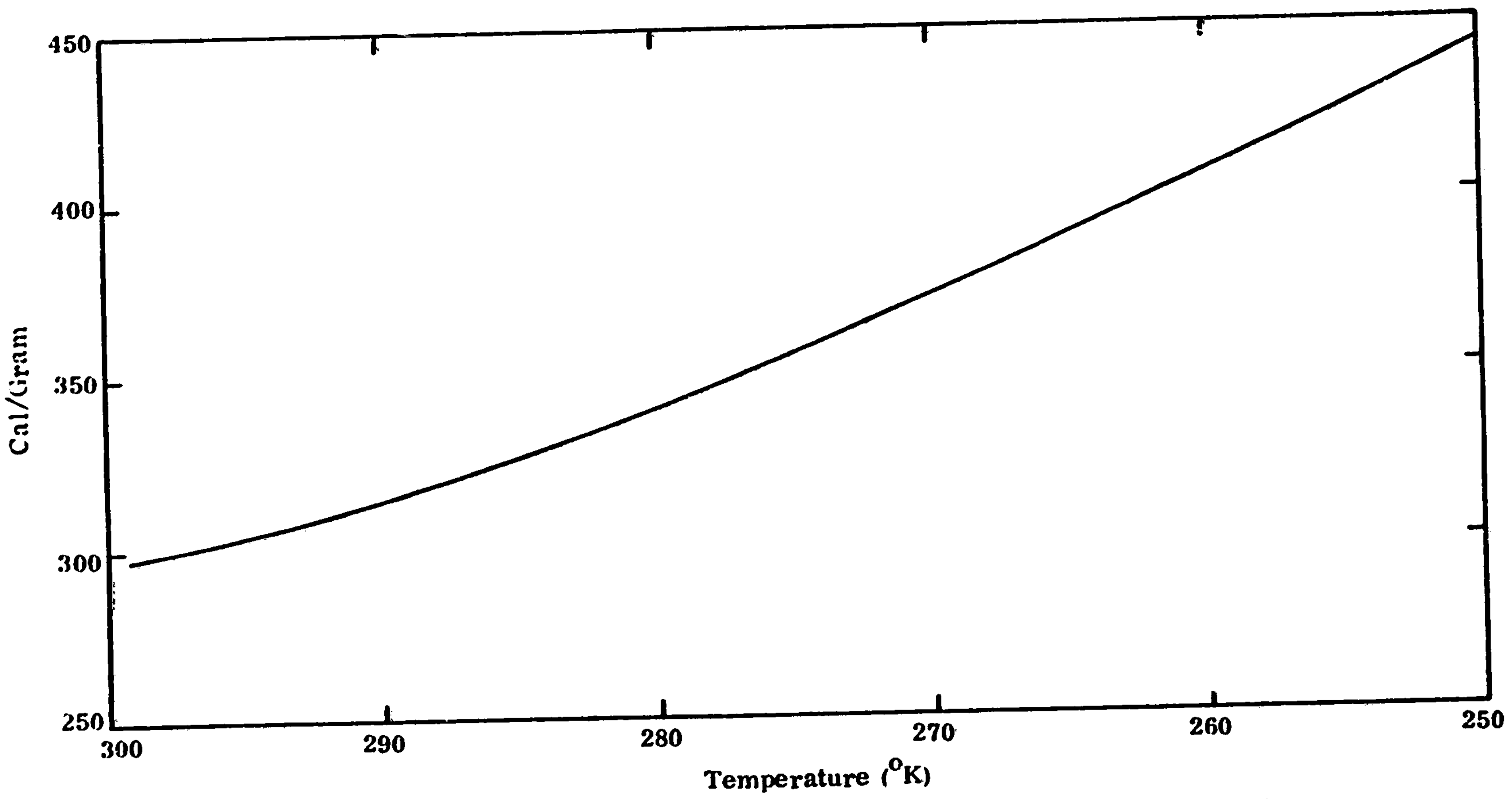


Figure 2.13.10 Condensation of MMH by cooling a saturated mixture of MMH and helium from 300 K at 2300 mm Hg. Cal per gram condensed (cumulative).

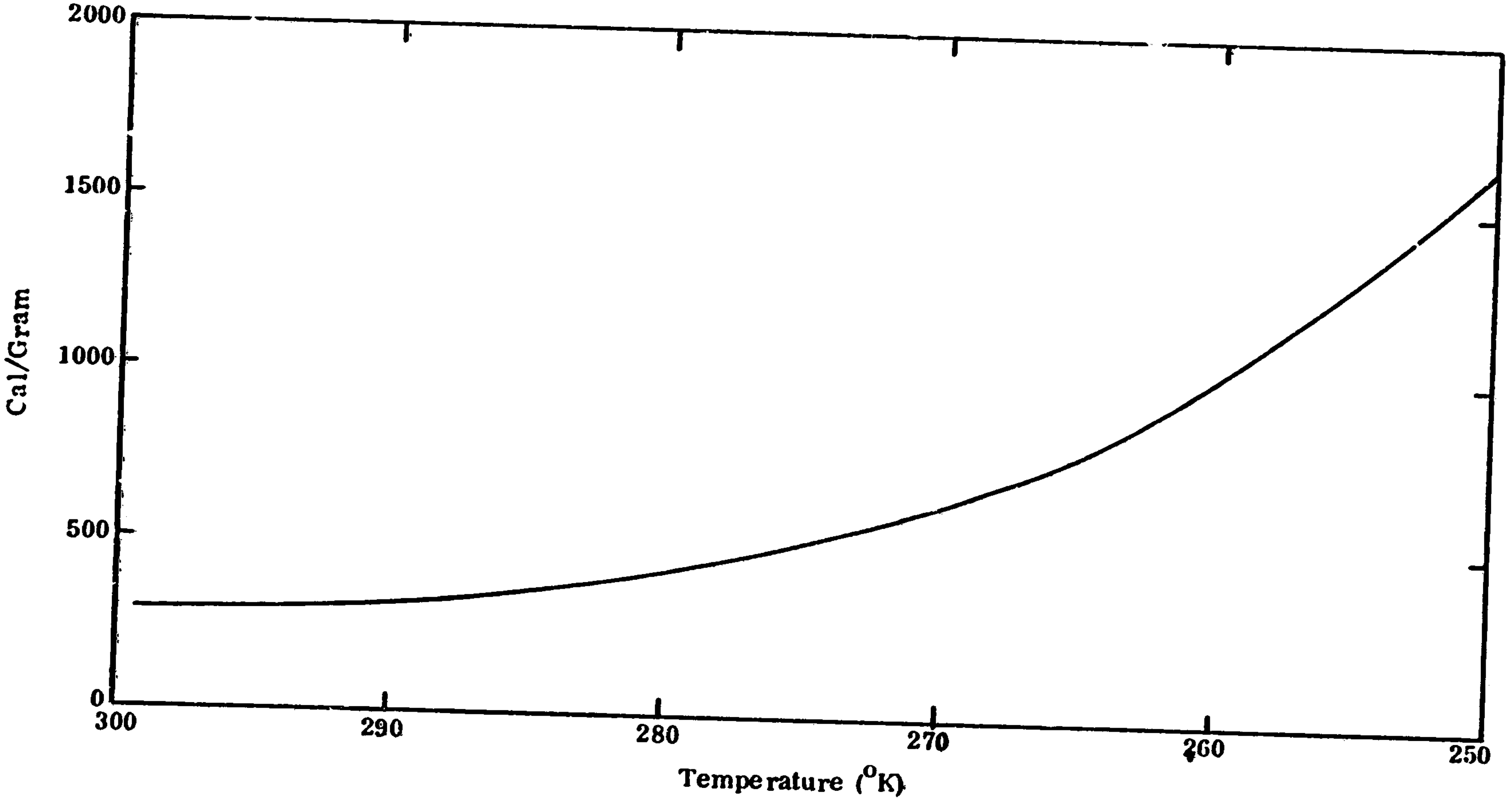


Figure 2.13.11 Condensation of MMH by cooling a saturated mixture of MMH and helium from 300°K at 2300 mm Hg. Cal per gram condensed (incremental).

2.13.3 Experiments

In order to create an experimental model, however imperfect, of the possible recondensation of vented monomethyl hydrazine, the following experiments were conducted.

A simple distillation of MMH was performed using an air-cooled condenser, as shown in Figure 2.13.12. The room temperature at this time was 23°C. Starting with 25 ml. of MMH a total of 22.5 ml. or 90% was recovered in 15 minutes. The ratio of the volume of air in the system to the volume of MMH was 11:1.

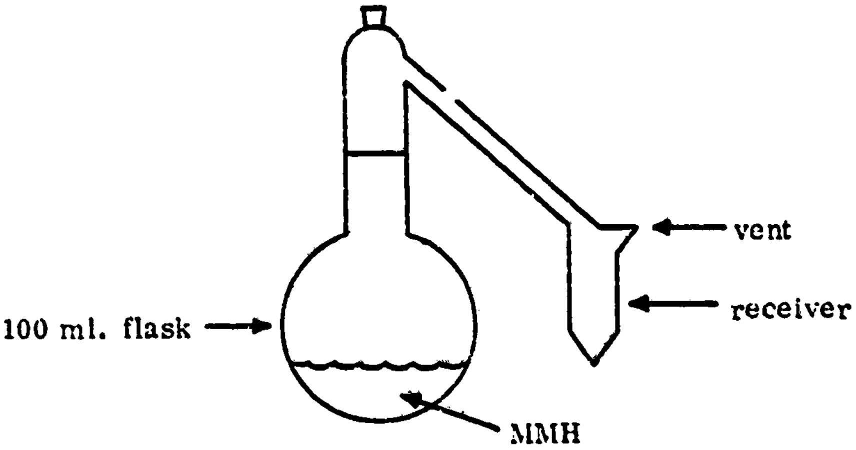
A second series of experiments was run similar to the above except that a water cooled condenser and 5°C cooling water were used, as shown in Figure 2.13.13. The data in Table 2.13.1 denote the initial volumes of MMH, the ratio of the volume of air in the system to the initial starting volume of MMH, the volume of MMH recovered and the percentage recovery.

TABLE 2.13.1

CONDENSATION OF MMH

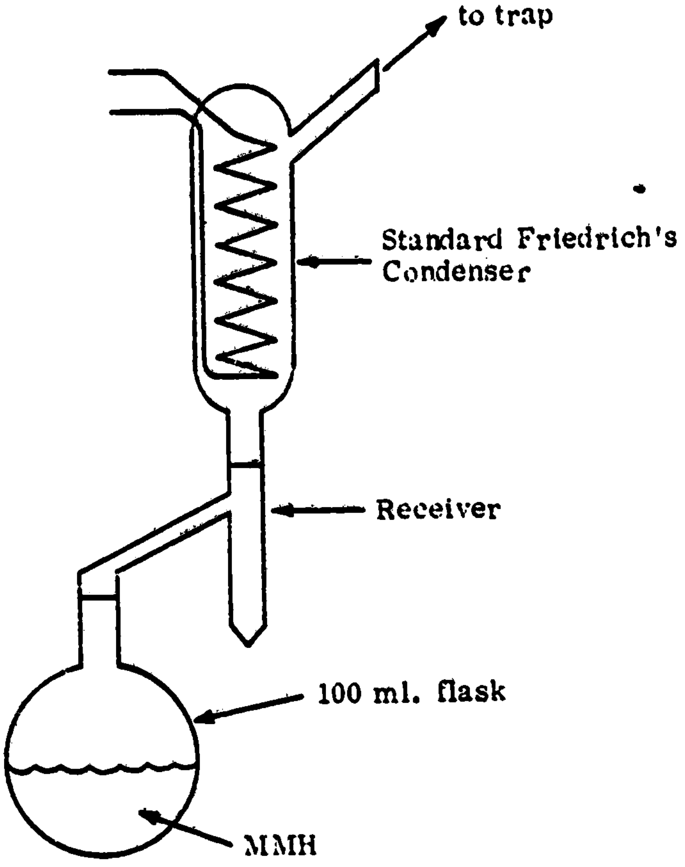
MMH Initial Volume (ml.)	$\frac{\text{Vol. Air}}{\text{MMH Initial Volume}}$	Vol. MMH Recovered (ml.)	Percent Recovered
5	68.4	4.8	96
10	33.7	9.8	98
20	16.4	19.5	98
30	10.6	29.0	97
40	7.7	39.0	98

A third experiment was conducted in which the MMH vapor was mixed with steam, as shown in Figure 2.13.4. 10°C cooling water was used and a starting volume of 25 ml. MMH, with an air to MMH volume ratio of 95.6. Five hundred ml. of water was converted to the steam which was used for scrubbing. 24.0 ml. of MMH (96%) was recovered in the receiver flask, as assayed using the p-DAB method.



Total volume of air outside flask = 203 ml.

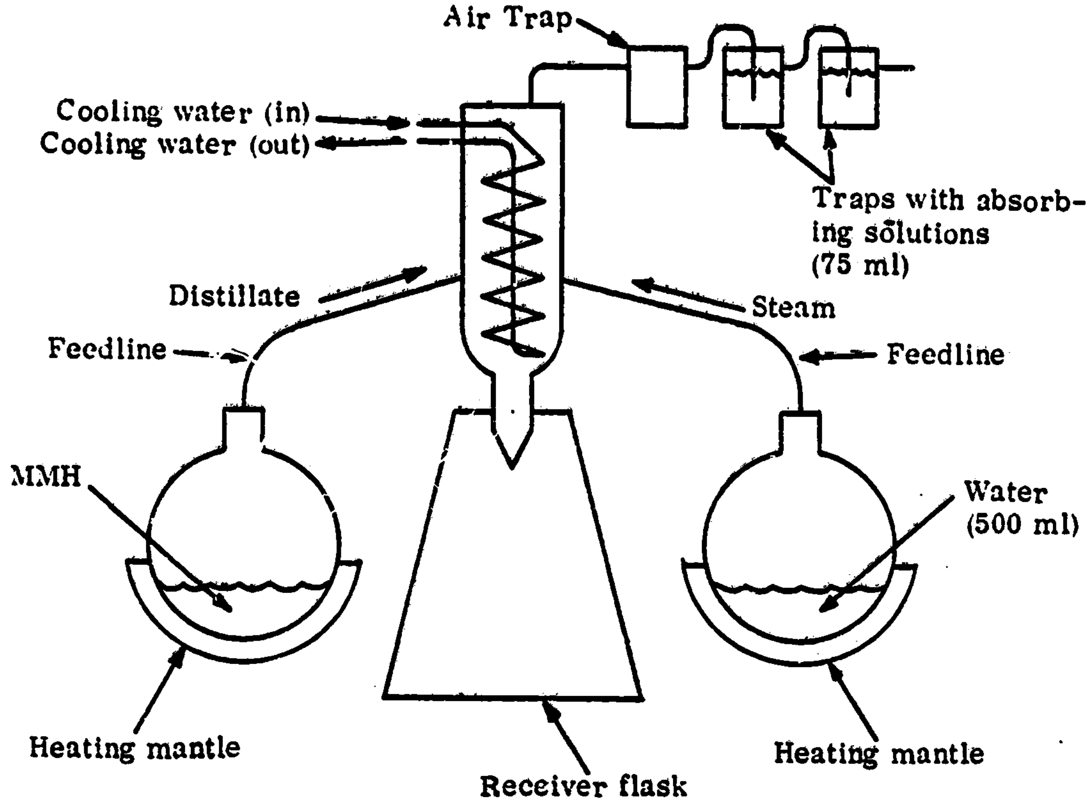
Figure 2.13.12 Experimental apparatus for distillation of MMH and air cooled condensation.



Air volume outside of distillation flask = 247 ml.
Cooling coil volume = 190 ml.

Cooling water flows at a rate of 30 liters/hr. at 5°C.

Figure 2.13.13 Experimental apparatus for distillation of MMH and water cooled condensation.



Dimensions

1.	Receiver (vol.)	1100 ml.	
2.	Steam generator flask (vol.)	1000 ml.	
3.	Distillation flask (vol.)	100 ml.	
4.	Cooling coil (vol.)	38 ml.	
5.	Condenser (vol.)	400 ml.	
6.	Feed line (vol.)	8 ml.	
7.	Feed lines (length)	50 cm.	
8.	Traps (vol.)	150 ml.	(each)
9.	Cooling coil (bore)	0.5 cm.	
	(diam.)	3 cm.	
	(length)	25 cm.	
	(number of turns)	15	

Figure 2.13.14 Model recondensation/steam scrubbing disposal system.

2.14 CRYOGENIC TRAPPING OF VAPOR

Cryogenic trapping refers to the use of liquid nitrogen systems in which gaseous effluent streams containing hydrazine fuel vapors are cooled to below the triple point of the fuel, resulting in accumulation of solid phase hydrazine in a cold trap. This collected fuel can then be treated chemically and disposed of, or perhaps reused.

An intensive experimental program was performed by us to evaluate this means of cleaning gaseous effluents. The concept was not successfully demonstrated, although further development and testing might well establish the viability of this concept. Detailed results of our experiment program were not available in time for inclusion in this Handbook, but are available as a separate report.[1]

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[1] Thomas, John J.: "Disposal of Hypergolic Propellants - Final Report, Task I, Phase VI." Florida Institute of Technology, Melbourne, FL, August 1976.

2.15 ADSORPTION OF VAPOR

Molecular sieves can be used to remove a wide variety of contaminants, including hydrazine fuel vapors, from gaseous effluent streams. In these systems, the contaminant molecules are adsorbed on the surface of the sieve material, which might be, for example, activated carbon, activated alumina, or silica gel, with a very high surface area to volume ratio.

An extensive series of tests were performed by us to evaluate the practiclity of this method for removing hydrazine fuel vapors from nitrogen and helium streams. Adsorbents investigated included calcium hypochlorite, silica gel, acidified alumina and charcoal briquets. Detailed results were not available in time for inclusion in this Handbook, but are available as a separate report.[1]

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1. Sivik, H.; Thomas, J.; Cohenour, B.; Wiederhold, C.: "Hypergolic Propellants - Liquid and Vapor Disposal: Final Report, Phase VI, Task 8, Dry State Scrubbing Systems for N_2O_4 and MMH." Florida Institute of Technology, Melbourne, FL 32901, March 1977.

2.16 UNTREATED DISPOSAL

2.16.1 Open Burning

Open burning is the burning of waste material on open land without the use of combustion equipment. This method is not used frequently for propellant destruction. Emissions of NO_x, CO, NH_3, unburned fuel, and other undesirable products result from uncontrolled combustion temperature, incomplete combustion due to poor gas mixing with air, and insufficient residence time of partial products at elevated temperature.

Open burning is not considered to be an adequate form of waste propellant disposal because of inadequate gaseous effluent control.

2.16.2 Ocean Dumping

Ocean dumping of a wide variety of hazardous wastes, including propellants, has been carried out in many parts of the world as an expedient or an economically attractive disposal technique. Sea water is used as a reactant or neutralizing medium and as a diluent.

It is quite likely that within the forseeable future the United States will totally ban ocean dumping of all toxic industrial and military wastes.

2.16.3 Pouring Directly on the Ground

Informal communications and conversations have indicated that the pouring of waste liquid hydrazines directly on the ground in remote areas is still occasionally practiced, in an informal and unpublicized manner. It would be very difficult to make a strong case regarding the undesirability of disposing of small amounts in this fashion. Hydrazine is not a "persistent" chemical, and will rapidly oxidize and decompose to near-zero concentration. Naturally occurring bacteria and organisms will serve to hasten the decomposition. It is easy to envision circumstances where carefully spreading a small amount of hydrazine on the ground, away from work areas and potable water supplies, would be the fastest and most practical means of destroying it, and probably one of the safest. In general, however, any regular, repeated use of hydrazine fuels implies the need for a properly designed disposal system, which then should be used for disposal of small as well as large quantities.

As a means of disposing of any significant amount of waste fuel, this method certainly cannot be recommended. In addition to the danger involved in actually carrying out the operation there is the likelihood of uncontrolled vapor release, and unpredictable local effects, including possible lingering contamination in the case of significant quantities of hydrazine.

2.16.4 Vent to Atmosphere

Venting of hydrazine vapors into the atmosphere is a common practice; precautions vary from zero to fairly elaborate modeling to determine whether meteorological conditions are such that turbulent mixing will reduce concentrations below certain threshold values within a specified radius. Most common is for wind direction and velocity to be monitored; near-zero wind or certain wind directions can shut down operations.

The provisional maximum exposure limit recommended in the TRW report (Section 2.2 of this Handbook) is 0.01 ppm in the atmosphere. If applied anywhere near the vent stack, this limit would preclude venting directly to the atmosphere at significant flow rates on all but the windiest days. Even more liberal standards could place severe restrictions on vent operations. Very tall vent stacks alleviate the problem of concentrations at ground level under most conditions, but there is no guarantee that air pollution standards will be applied only at ground level.

Direct venting of hydrazine fuel vapors probably does not represent a significant threat to the environment. However, in view of the carcinogenic potential of MMH and UDMH, involving possible long-term, low-level exposure hazards, and considering the ease with which these vapors can be removed from a vent stream, it would seem that direct release to the atmosphere should be avoided.

CHAPTER 3

NITROGEN TETROXIDE
(DINITROGEN TETROXIDE, N_2O_4)
(NITROGEN PEROXIDE, LIQUID NITROGEN DIOXIDE)

3.1 MATERIAL DESCRIPTION

The term "nitrogen tetroxide", as used in aerospace applications, refers to the equilibrium mixture of molecules of the monomer, NO_2, and dimer, N_2O_4. These two substances are present at appreciable mole fractions under all conditions of equilibrium between the liquid and gaseous states.[1] At the normal boiling point, 70.1°F (21.15°C), the equilibrium composition is 16% NO_2, 84% N_2O_4 by mass. As the temperature increases, the equilibrium shifts toward the monomer: at 300°K (80.33°F) and one atmosphere, the equilibrium composition is 20% NO_2, 80% N_2O_4; at 350°K (170.33°F) it is 73% NO_2, 27% N_2O_4. At still higher temperatures, the dissociation of NO_2 into NO and O_2 also becomes significant.

NO_2 is one of the most insidious gases known. Inflammation of lungs may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. The Threshold Limit Value (TLV) is five parts per million by volume, or nine milligrams per cubic meter. The odor threshold is less than 0.5 ppm.

Nitrogen tetroxide is a powerful oxidizing agent, containing about seventy percent available oxygen. It is extremely corrosive in the presence of water. It is toxic in either the liquid or vapor states. It may react with combustible materials, including carbon, phosphorus, and sulfur.

Nitrogen tetroxide is soluble in concentrated sulfuric and nitric acids. It reacts with water to form nitric acid (HNO_3) and nitric oxide (NO), and with alkalies to form nitrates and nitrites.

Several of the physical properties of nitrogen tetroxide are presented in Table 3.1.1.[2]

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[1] Giauque, W.F. and Kemp, J.D.: "The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibrium $N_2O_4 = 2NO_2 = 2NO + O_2$." Journal of Chemical Physics, Vol. 6, pages 40-53 (1938).

[2] "Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation." Prepared by the Liquid Propellant Handling and Storage Committee assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD 870259, May 1972.

TABLE 3.1.1
PHYSICAL PROPERTIES OF NITROGEN TETROXIDE*

Molecular Weights:	N_2O_4: 92.016 NO_2: 46.008 Equilibrium at 300°K (80.33°F), 1 atm: 76.63
Normal Boiling Point:	70.1°F (21.15°C)
Freezing Point:	11.8°F (-11.2°C)
Liquid Density:	12.1 lb/gal (1.45 g/cm^3) at 68°F (20°C)
Critical Pressure:	99.96 atm (1469.0 psia, 1.013 x 10^7 Pa)
Critical Temperature:	316.8°F (158.2°C)
Heat of Vaporization:	9110 cal per 92.016 grams of equilibrium mixture at 21.15°C (178.2 Btu/lb at 70.1°F)

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* Refers to equilibrium mixture of N_2O_4 and NO_2, unless otherwise specified.

The molecular weight of the equilibrium mixture can be found in terms of the degree of dissociation, α , which in turn depends on the equilibrium constant, K. According to the "law of mass action," the equilibrium constant is related to the change in Gibbs free energy, ΔG^o, according to

$$K = \exp(-\Delta G^o/RT),$$

where R is the universal gas constant, T the mixture temperature, and ΔG^o is a function of the mixture temperature. (The superscript "o" refers to the reference pressure, usually taken to be one atmosphere.)

This expression is more easily evaluated if we expand the free-energy change as:

$$\Delta G^o = \Delta G^o - \Delta H_o^o + \Delta H_o^o$$
$$= \Delta(G^o - H_o^o) + \Delta H_o^o$$

where ΔH_o^o is the enthalpy of reaction at standard temperature and pressure. With this expansion, the equilibrium constant becomes

$$R \ln K = -\Delta\left(\frac{G^o - H_o^o}{T}\right) - \frac{\Delta H_o^o}{T}$$

The function $\left(\frac{G^o - H_o^o}{T}\right)$ for each of the constituents, N_2O_4 and NO_2, can be calculated in a fashion quite similar to the entropy, and combined to form the change for the reaction $N_2O_4 = 2NO_2$. These calculations were performed by Giauque and Kemp[3] for a number of temperatures; the results are tabulated in Table 3.1.2.

Giauque and Kemp also devoted a good portion of their paper to ascertaining the best value of the enthalpy of reaction at standard conditions, based on the results of various experimenters over the years and theoretical considerations. The result was

$$(\Delta H_o^o)_{N_2O_4 = 2NO_2} = 12{,}875 \text{ cal per mole}$$

where "per mole" means, as usual, per mole of undissociated N_2O_4. Using

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[3] Op. cit.

this result and the values for the change in $\left(\frac{G^o - H_o^o}{T}\right)$, we calculated the equilibrium constant at each temperature; the results are shown in Table 3.1.2.

If we wish to take account of gas imperfection in using these values of K to find the degree of dissociation, α, at any pressure and temperature, then we must express the equilibrium constant in terms of the fugacities of the constituents:

$$K = \frac{(f_{NO_2})^2}{f_{N_2O_4}} \quad ,$$

where the fugacities f_i are found using approximate equations of state for the constituents. According to Giauque and Kemp, in the vicinity of the normal boiling point both NO_2 and N_2O_4 follow an equation of state of the form

$$pV = RT(1 + \lambda p)$$

where λ has the approximate values -0.01 atm^{-1} for N_2O_4 and -0.005 atm^{-1} for NO_2. Furthermore, this equation can be extended to a wider range of temperatures by using the fact, based on the Berthelot equation of state, that λ is approximately proportional to T^{-3}:

$$\lambda_{N_2O_4} = -0.01\left(\frac{294}{T}\right)^3 \quad ; \quad \lambda_{NO_2} = -0.005\left(\frac{294}{T}\right)^3 \quad atm^{-1}.$$

The fugacities of the components of a mixture are given by

$$\ln f_i = \ln (X_i\, p) + \left[\int_0^p \left(\frac{\overline{V_i}}{RT} - \frac{1}{p}\right) dp\right]_T$$

where X_i is the mole fraction of component i in the mixture, $\overline{V_i}$ is the partial molal volume of component i, and p is the total mixture pressure. In our case, if α is the fraction of the N_2O_4 that dissociates, then considering a hypothetical reaction starting with one mole of undissociated N_2O_4 and proceeding to equilibrium:

$$N_2O_4 \qquad (1-\alpha)N_2O_4 + 2\alpha\, NO_2$$

we see that $X_{N_2O_4} = \frac{1-\alpha}{1+\alpha}$, $X_{NO_2} = \frac{2\alpha}{1+\alpha}$.

TABLE 3.1.2
THERMODYNAMIC FUNCTIONS FOR THE REACTION
$N_2O_4 = 2NO_2$

(From Giauque and Kemp, J. Chem. Phys., Vol. 6, pages 40-52 (1938).)

T, °K	(°F)	$-\Delta\left(\frac{F^o - H_o^o}{T}\right)$, $\frac{cal}{mole}$	$\left(\frac{Btu}{lbm}\right)$	K, atm
275	(35)	39.051	(.7639)	.02002
298.1	(77)	39.298	(.7687)	.14088
300	(80)	39.312	(.7690)	.16283
325	(125)	39.534	(.7734)	.9598
350	(170)	39.711	(.7768)	4.362
375	(215)	39.867	(.7799)	16.222
400	(260)	39.977	(.7820)	50.51
425	(305)	40.093	(.7843)	138.93

Further, using the equations of state given by Giauque and Kemp we obtain

$\frac{\overline{V}_i}{RT} = \frac{1}{p}(1 + \beta p)$ for both N_2O_4 and NO_2, where

$$\beta = \lambda_{N_2O_4} = 2\lambda_{NO_2} = -0.01\left(\frac{294}{T}\right) \text{ atm}^{-1}, \text{ T in } {}^oK.$$

Solving for the fugacities:

$$\ln f_i = \ln (X_i\, p) + \beta p,$$

$$\therefore f_{N_2O_4} = \left(\frac{1-\alpha}{1+\alpha}\right) p\, e^{\beta p}$$

$$f_{NO_2} = \frac{2\alpha}{1+\alpha}\, p\, e^{\beta p/2}$$

Thus the fact that $\lambda_{N_2O_4} = 2\lambda_{NO_2}$ leads to the simple result

$$K = \frac{4\alpha^2}{1-\alpha^2}\, p,$$

the same result that would have been obtained by assuming the component gases to be perfect. It should be noted, however, that the actual dissociation α is not the same as the "apparent" dissociation, α', that would be deducted from experimental measurements if the gases were assumed perfect:

$$\alpha' = \frac{pV}{RT} - 1 \text{ (for this reaction)},$$

and it can be shown that the relationship between α and α' for our case is

$$\alpha = \alpha' + \beta p.$$

Table 3.1.3 presents values for α at various temperatures and presures, calculated from the equation

$$\alpha = \sqrt{K/(4p - K)}$$

and using the values of K in Table 3.1.2.

It should be noted that all of the computations in Table 3.1.3 neglect any dissociation of the NO_2 that might occur. Fan and Mason[4] have considered the

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[4] Fan, S.S.T., and Mason, D.M.: "Properties of the System $N_2O_4 = 2NO_2 = 2NO + O_2$." Journal of Chemical and Engineering Data, Vol. 7, pp. 183-186 (1962).

TABLE 3.1.3

DEGREE OF DISSOCIATION

$N_2O_4 \rightleftharpoons 2NO_2$

NEGLECTING NO_2 DISSOCIATION

T \ p	0.5 atm 7.3 psia	1.0 atm 14.7 psia	2.0 atm 29.4 psia	3.0 atm 44.1 psia	5.0 atm 73.5 psia	10.0 atm 147.0 psia
275°K 35°F	.0996	.0706	.0500	.0408	.0316	.0224
298.1°K 77°F	.2565	.1844	.1315	.1077	.0836	.0529
300°K 80°F	.2744	.1978	.1412	.1157	.0899	.0637
325°K 125°F	.5695	.4399	.3273	.2721	.2140	.1531
350°K 170°F	.8280	.7223	.5940	.5163	.4231	.3136
375°K 215°F	.9435	.8957	.8184	.7582	.6692	.5372
400°K 260°F	.9808	.9626	.9291	.8989	.8464	.7470
425°K 305°F	.9929	.9859	.9724	.9594	.9350	.8812

effect of this second dissociation for the case p = 1 atm. This is, they treat the total system

$$N_2O_4 = 2NO_2 = 2NO + O_2,$$

and if α_1, α_2, and K_1, K_2 are the degrees of dissociation and equilibrium constants of the two reactions (the number of moles of NO formed per mole of undissociated N_2O_4 is $2\alpha_2$), then the equations relating them at p = 1 atm are

$$\alpha_1 = \frac{\alpha_2 (8-K_1) + [\alpha_2^2 (8-K_1)^2 - 4(4+K_1)(4\alpha_2^2 - \alpha_2 K_1 - K_1)]^{1/2}}{2(4+K_1)}$$

$$K_2 = \frac{\alpha_2^2}{(\alpha_1 - \alpha_2)^2 (1 + \alpha_1 - \alpha_2)} .$$

Values of K_2 at various temperatures were also given by Giauque and Kemp; using the values of both K_1 and K_2 from Giauque and Kemp, Fan and Mason calculated the values of α_1 and α_2 given in Table 3.1.4. The small differences between these values for α_1 and those in Table 3.1.3 are the result of computational differences - probably a slight difference in the value chosen for the enthalpy of reaction - rather than the very small values of α_2 at these temperatures. At higher temperatures, the second dissociation becomes important.

TABLE 3.1.4

DEGREES OF DISSOCIATION AT ONE ATMOSPHERE (14.696 psia)

FOR $N_2O_4 \rightleftharpoons 2NO_2$ (α_1)

AND $NO_2 \rightleftharpoons NO + \frac{1}{2}O_2$ (α_2)

(From Fan and Mason, J. Chem. Eng. Data, Vol. 7, p. 183.)

T		α_1	α_2
300°K	(80°F)	.2007	3.24×10^{-5}
350°K	(170°F)	.7256	7.54×10^{-4}
400°K	(260°F)	.9642	4.882×10^{-3}
450°K	(350°F)	.9947	1.790×10^{-2}
500°K	(440°F)	.9989	4.910×10^{-2}
550°K	(530°F)	.9997	.1100
600°K	(620°F)	.9999	.2083
700°K	(800°F)	1.0000	.488
800°K	(980°F)	1.0000	.7388
900°K	(1160°F)	1.0000	.8752
1000°K	(1340°F)	1.0000	.938
1100°K	(1520°F)	1.0000	.965

3.2 RECOMMENDATIONS FROM OTHER SOURCES

The manufacturer of nitrogen tetroxide, Hercules Inc. of Wilmington, Delaware, recommends: "Transfer to salvage vessel. Neutralize with soda ash or lime. Keep from sewer or streams."[1] They further advise that they could "possibly rework N_2O_4 to reduce water content and adjust oxides content. Some contaminants, however, may not be acceptable in our plant. Each rework would probably require prior submission of an analysis showing impurities and a sample for our verification."[2]

The JANNAF Hazards Handbook contains the following recommendations: "Small quantities of N_2O_4 or mixed oxides of nitrogen can be disposed of by permitting them to evaporate and disperse in the atmosphere. Pit neutralization of N_2O_4 with limestone or soda ash is used but is not very effective. Large quantities can be burned in a controllable manner with a fuel such as kerosene. The disposal area should be well isolated and the perimeter cleaned of all combustibles. Spray the N_2O_4 or mixed oxides of nitrogen onto the surface of a burning pit partially filled with fuel. Repeat the procedure after burned out area has cooled. Firefighting equipment should be nearby during burning and disposal operations, and persons engaged in the operation should wear suitable protective equipment."[3]

The TRW Report did not refer to nitrogen tetroxide.

Nitrogen tetroxide combines with water to form nitric acid and nitric oxide; recommendations regarding the disposal of nitric acid are presented in the following chapter.

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[1] "Material Safety Data Sheet SOS-26." February 20, 1973.

[2] Written communication dated October 24, 1973, in response to our inquiry.

[3] "Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation." Prepared by the Liquid Propellant Handling and Storage Committee assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD 870259, May 1972.

3.3 CHEMICAL NEUTRALIZATION

3.3.1 Introduction

By far the most common means of disposing of nitrogen tetroxide is dilution with water followed by neutralization. Substances used for neutralization include sodium carbonate (soda ash), $Na_2 CO_3$; sodium bicarbonate, $NaHCO_3$; sodium hydroxide (caustic soda), NaOH; calcium oxide (lime) CaO; and calcium hydroxide, $Ca(OH)_2$. Other alkaline compounds, such as magnesium hydroxide, $Mg(OH)_2$, and calcium carbonate(calcite, aragonite, limestone, marble), $CaCO_3$, could also be used. In at least one instance, triethanolamine, $N(CH_2CH_2OH)_3$, has been used. It is also common to dilute the N_2O_4 and add it to the same disposal pond used for hydrazine fuels; these ponds are then usually neutralized using sodium hydroxide or hydrogen peroxide with copper sulfate catalyst, or both.

3.3.2 Chemical Description

The first step in the typical dilution/neutralization process, the mixing of N_2O_4 and water, itself involves a chemical reaction:

$$\frac{3}{2} N_2O_4 + H_2O \longrightarrow 2HNO_3 + NO$$

$$3\ NO_2 + H_2O \longrightarrow 2HNO_2 + NO$$

Some nitrous acid, HNO_2, will also be formed.

Nitric oxide, NO, is an insoluble gas that is also toxic, albeit colorless. The Threshold Limit Value is 25 ppm by volume in air, or 30 mg/m^3. Once in the atmosphere, the NO slowly oxidizes to NO_2. Thus the water dilution process is a very critical one from an environmental point of view, normally involving the release of large quantities of NO_x. Even if performed inside a reaction vessel, a normal water scrubber on the vent will not be able to remove the NO from the vent stream.

The nitric and nitrous acids are then neutralized by the alkaline materials added, as for example:

$$HNO_3 + NaHCO_3 \longrightarrow NaNO_3 + H_2O + CO_2$$

$$HNO_2 + NaHCO_3 \longrightarrow NaNO_2 + H_2O + CO_2$$

$$HNO_n + \frac{1}{2}Na_2CO_3 \longrightarrow NaNO_n + \frac{1}{2}H_2O + \frac{1}{2}CO_2$$

$$HNO_n + Ca(OH)_2 \longrightarrow Ca(NO_n)_2 + H_2O$$

$$HNO_n + Mg(OH)_2 \longrightarrow Mg(NO_n)_2 + H_2O$$

$$HNO_n + NaOH \longrightarrow NaNO_n + H_2O$$

where $n = 2,3$. The results are summarized in Table 3.3.1. The products of all of these reactions involve insoluble nitrate and nitrite ions. These products are themselves corrosive and toxic, and present a secondary disposal problem of some magnitude. A means of disposing of them -- or actually of turning them to a useful purpose -- is the subject of Section 3.4.

TABLE 3.3.1
NEUTRALIZATION OF N_2O_4

Neutralizing Reagent	Products Formed	Safety of Reagent	Relative chemical cost per pound of N_2O_4
$NaHCO_3$	Solutions of $NaNO_3$ and $NaNO_2$, H_2O, CO_2	Innocuous	\$.165
Na_2CO_3	Solutions of Na salts, H_2O, CO_2	Innocuous	\$.15
$Ca(OH)_2$	Solutions of Ca salts, H_2O	Skin irritant - Inhalation hazard	\$.08
NaOH	Solutions of Na salts	Corrosive to all tissues	\$.025
$Mg(OH)_2$	Solutions of Mg salts	Innocuous	\$.57

3.3.3 Comparative Evaluations

The most important considerations in evaluating the neutralizing agents are effectiveness, safety, and environmental impact. All the neutralizing agents are essentially equally effective but the strong basis $Ca(OH)_2$ and NaOH are a hazard in that they can cause severe burns if accidental skin contact occurs. Calcium and magnesium salts increase the "hardness" of water and thus present an environmental disposal problem if present in large quantities. The combined weight of NO_3^- and NO_2^- ions will be approximately the same for all reagents and present equivalent problems.

In order to obtain some sort of comparative evaluation of these five essentially similar alkaline reagents, each neutralizing agent was given a rating of 1 through 3 in each of three categories: safety and effectiveness, environmental hazard, and cost. Weighting factors of 3, 2, and 1, respectively, were given to the categories, so that a maximum total of 18 points were possible. The results are shown in Table 3.3.2. The "Total Points" column is the result of multiplying the rating in each column by the weighting factor for that column (in parentheses). For example, a rating of 3 in safety and effectiveness means the agent poses no hazard to people handling it, and the reaction with N_2O_4 is fast, complete, and reliable. A rating of 2 or 1 means the agent has important disadvantages in this category. A rating of 3 in the environmental hazard category means the product of reaction with N_2O_4 is as harmless to the environment as can be expected. A rating of 2 or 1 means that the product constitutes a more serious environmental hazard. A rating of 3 in cost means the price ranges from $0.01 to $0.10 to neutralize one pound of N_2O_4 (as of the March 1974 costs listed in Table 3.3.1). A rating of 2 indicates the cost range of $0.11 to $0.20. A rating of 1 is anything above $0.20. Two additional neutralizing materials not included in Table 3.3.1, urea (NH_2CONH_2) and triethanolamine ($N(CH_2CH_2OH)_3$), have been included in Table 3.3.2 for completeness.

It is seen that the result of this evaluation is that the two "household products", sodium carbonate (washing soda) and sodium bicarbonate (baking soda), receive far higher ratings than any of the other compounds.

TABLE 3.3.2

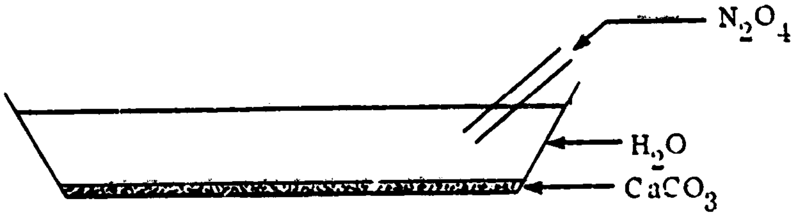
RATINGS OF N_2O_4 NEUTRALIZING AGENTS

Neutralizing Agent	Safety & Effectiveness (3)	Environmental Hazard (2)	Cost (1)	Total points
$NaHCO_3$	3	3	2	17
Na_2CO_3	3	3	2	17
$Ca(OH)_2$	1	1	3	8
NaOH	1	3	3	12
$Mg(OH)_2$	2	1	1	9
Urea	1	3	2	11
Triethanolamine	1	3	1	10

3.3.4 A Neutralization Method Using an Insoluble Reactant

All of the chemicals discussed in the preceding subsections are highly soluble in water; to our knowledge, insoluble neutralizing agents have not been used for N_2O_4 waste disposal. A possible advantage of the use of an insoluble compound is the fact that there would be no possibility of accumulattion of excess neutralization agent in the disposal pond waters - such accumulation could pose a problem in terms of final disposal, especially if a need should arise for immediate withdrawal of liquid from the pond. A laboratory scale experimental program was performed to evaluate the possibility of using a water-insoluble neutralization agent.

The cheapest and most readily available neutralizing agent in this category is calcium carbonate, $CaCO_3$, which can be purchased as limestone or marble chips. The basic operating principles are shown in the sketch below. A layer of $CaCO_3$ chips is established on the bottom of the pond, and N_2O_4 is fed to the aqueous layer. As time proceeds, only that amount of $CaCO_3$ is taken into the pond waters as is required for neutralization of the N_2O_4. After neutralization, the solution would be very near neutrality (ph 7).



A receiver vessel layered with $CaCO_3$ and water was prepared in the laboratory. To this solution was added N_2O_4. The water temperature and pH were monitored and the time and dilution necessary to safely dispose of given quantities of N_2O_4 without seriously raising temperatures were determined.

In the first experiment, the receiver contained two liters of tap water, and 250 gm. of finely powdered $CaCO_3$ was layered on the bottom to a depth of 5 mm. In a separate flask 25 ml. of N_2O_4 was placed. A 1/8" glass tube was inserted into a rubber stopper which was fitted to the flask. The other end of the glass tube was inserted into the receiver to a level just above the $CaCO_3$ (Figure 3.3.1). The flask containing the N_2O_4 was heated to 35°C with a water bath and N_2O_4 vapor and liquid proceeded into the receiver for

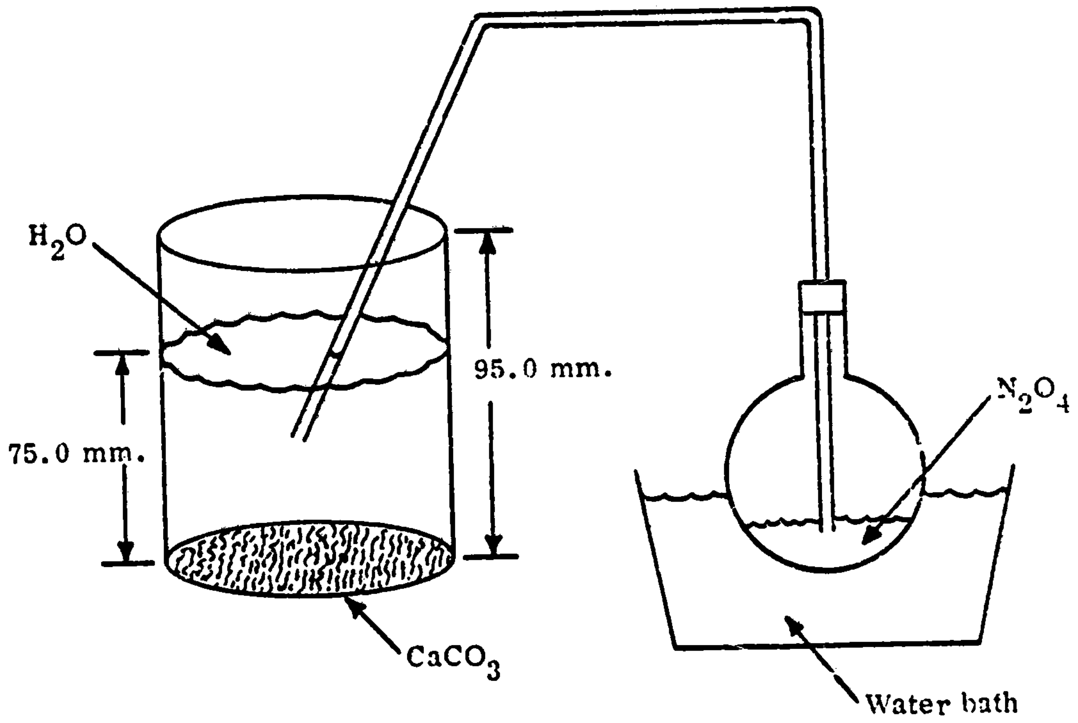


Figure 3.3.1 Addition of N_2O_4 to water over calcium carbonate.

15 minutes. The pH of the receiver solution dropped from 8.0 to 1.0 over this period of time while the temperature varied slightly from 21 to 22°C. The bubbles of NO_2-N_2O_4 were large, however, and a red cloud was observed over the receiver.

A second experiment was performed in which the only change made was a decrease in the rate of N_2O_4 addition. The amount of red gas over the receiver was considerably diminished; time required to feed the N_2O_4 was 30 minutes.

A third experiment was conducted similar to the preceding, but with an important exception. Limestone chips 0.75 inches in diameter were used in place of the finely powdered $CaCO_3$. The other parameters were as follows:

Weight of $CaCO_3$	400 g.
Volume of H_2O	1.8 l.
Volume of N_2O_4 added	25 ml.
Time for N_2O_4 addition	20 minutes.

Again, large bubblies of NO_2 - N_2O_4 were observed and a small amount of red gas (NO_2) was observed over the receiver. Additional data are presented in Table 3.3.3.

TABLE 3.3.3

RESULTS OF EXPERIMENT 3
CALCIUM CARBONATE NEUTRALIZATION

Time Mins.	pH	Receiver Temperature	Comment
0	3.5	21°C	Contact of N_2O_4 vapor with water
10	1.0	21°C	
15	1.0	21°C	
20	1.0	21°C	Vigorous CO_2 evolution
24 hr.	4.0	19°C	End of CO_2 evolution

The data indicated that a greater dissolution rate of NO_2-N_2O_4 would have to be obtained before this disposal approach could be considered. A further series of experiments was therefore conducted in which the N_2O_4 was delivered to the receiver using spargers with 10 to 15 micron porosity, to facilitate the production of small bubbles and thus allow a greater rate of dissolution.

A 500 ml. r.b. flask was filled with 50 ml. of N_2O_4. Two glass tubes were inserted in a rubber stopper and the stopper in turn inserted in the opening in the flask. These tubes were attached to two spargers (3 cm. in diameter) containing fritted glass outlets. These spargers were in turn inserted into a receiver bath containing two liters of tap water in a crystallizing dish 10 cm. high and 19 cm. in diameter. Five hundred gms. of marble chips were layered on the bottom of the crystallizing dish. The N_2O_4 was allowed to vaporize, pass through the tubes and spargers and into the water in the receiving vessel. All 50 ml. of N_2O_4 were added over five hours and the pH dropped from 8.1 to 1.2 with essentially no change in temperature. At the end of eight hours, the solution was essentially-neutralized (Table 3.3.4).

In Experiment 5, the N_2O_4 was heated in a water bath to 35°C to speed passage of N_2O_4 into the receiver. This time the pH changed from 8.1 to 1.1 in two hours and twenty minutes and again no rise in temperature was noted. At the end of three hours and twenty minutes, the pH was neutral (Table 3.3.5). At no time in these experiments was a red gas observed above the liquid in the receiver. Only clear bubbling CO_2 was observed.

A third experiment was conducted in which the marble chips were removed and 50 ml. of N_2O_4 was added to plain tap water through the same previously described system. At room temperature, the addition was complete in 400 minutes and the pH was less than 0. A slight rise in temperature was noted, and again no red gas indicating NO_2 was observed emanating from the water in the receiver flask (Table 3.3.6).

A final experiment was conducted in which a water bath at 35°C was used to heat the flask containing 50 ml. of N_2O_4. This treatment resulted in a faster flow of N_2O_4 into the receiver vessel. The data are shown in Table 3.3.7. Again, no red gas indicating NO_2 was observed above the water level in the receiver.

TABLE 3.3.4
RESULTS OF EXPERIMENT 4
CALCIUM CARBONATE NEUTRALIZATION

Time Mins.	pH	Receiver Temperature (°C)	Comment
0	8.1	23.5	Start
10	8.0	23.5	NO_2, N_2O_4 contacts water in receiver
20	3.0	23.0	CO_2 evolution starts
60	1.5	23.0	
300	1.2	23.0	End of N_2O_4 addition
480	6.6	23.5	End of CO_2 evolution

TABLE 3.3.5
RESULTS OF EXPERIMENT 5
CALCIUM CARBONATE NEUTRALIZATION

Time Mins.	pH	Receiver Temperature (°C)	Comment
0	8.1	23.0	Start
10	6.5	23.0	NO_2, N_2O_4 contacts water in receiver
30	1.2	22.5	CO_2 evolution starts
60	0.8	22.0	
120	0.8	22.0	
140	1.1	23.0	
200	7.1	23.0	End of CO_2 evolution

TABLE 3.3.6

ADDITION OF N_2O_4 VAPOR TO WATER

Time Mins.	pH	Receiver Temperature	Comment
0	6.5	23.5	Start
15	2.5	23.5	
30	1.8	23.5	
60	1.5	23.5	
120	0.5	24.0	Receiver water has blue tint
400	<0	25.0	End of N_2O_4 addition

TABLE 3.3.7

ADDITION OF N_2O_4 VAPOR AT 35°C TO WATER

Time Mins.	pH	Receiver Temperature	Comment
0	6.5	23.5	Start
15	1.5	24.0	
30	1.8	25.0	
120	<0	26.5	End of N_2O_4 addition

TABLE 3.3.8

ADDITION OF 10% HYDRAZINE SOLUTION TO 2.5% AQUEOUS SOLUTION OF N_2O_4

	Experiment 6	Experiment 7
Addition time	2.5 minutes	3.0 minutes
Temperature increase	20°C	25°C
pH after addition	6.6	6.5

After completion of addition of N_2O_4 in these two experiments, each solution was neutralized with 500 ml. of 10% aqueous hydrazine. The results are shown in Table 3.3.8. During neutralization vigorous gaseous effluence was noted but no brown gas was seen. After neutralization the solution had an amber color.

3.3.5 Conclusions

In terms of evaluating chemical means of destroying N_2O_4, a brief quantitative example is probably in order. We have estimated that approximately 135 pounds of N_2O_4 will be vaporized during the loading of the Space Shuttle oxidizer tanks.[1] To dispose of this amount of N_2O_4 in aqueous solution by neutralization with $NaHCO_3$, 165 lbs. of the neutralizing agent would be required at a cost of roughly $22. The cost figure seems reasonable but the storage and handling of such large quantities of chemical render this method unattractive. Also, this neutralization would produce approximately 166 lbs. of sodium nitrate and sodium nitrite. In order to maintain the same environmental standards as a sewage plant, this material would have to be diluted with approximately 6.7×10^9 gallons of water before being discharged from the pond.

Thus we have seen that there are three primary difficulties with chemical neutralization:

1. The evolution of large quantities of NO during dilution of liquid N_2O_4 with water.
2. The quantities of neutralization chemicals required.
3. The problem of ultimate disposal of the soluble nitrates and nitrites.

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[1] Final Report, Phase 5, Contract NAS 10-8399. Florida Institute of Technology Report No. ME-76-1, February 1976.

The first problem might be resolved by diluting the N_2O_4 with water that has already been treated with an excess of the neutralization chemical, and our work on vapor scrubbers reported in Section 3.9 showed that NO generation could be avoided in that case by addition of sufficient caustic soda to the scrubbing solution. An excess of these chemicals in the disposal pond might aggravate the ultimate disposal problem, however. Additional work on this problem is strongly indicated.

The second problem is unavoidable with this disposal method.

The third problem is an especially interesting one. The nitrates and nitrites are potentially valuable as plant nutrients, but not especially useful in the form that would be found in the pond. There is no known way that they can be precipitated out of the pond waters, and to discharge the pond waters to any lake or stream without removing these high nutrient concentrations would be environmentally unacceptable. One approach would be to transfer the pond water to large evaporation trays, and then either dispose of the residue in a land fill or attempt to use it as fertilizer. In this form it is still not a very useful fertilizer, however. Another approach is to grow water plants in the pond itself, where they would use the nutrients and purify the water. These plants would be periodically harvested, dried, and either used as organic fertilizer or as feedstock for a small methane generator. This latter solution is the subject of the following section.

3.4 BIOLOGICAL PROCESSES

The most promising ultimate disposal method for the nitrates and nitrites that result when N_2O_4 is treated, or added to water and neutralized, is assimilation by growing plants. In this way the nitrogen is used in a controllable manner and the uncertainties associated with discharging a potentially harmful (and potentially beneficial) substance to open bodies of water, flowing streams, or groundwater are avoided. Especially attractive is the use of water plants, periodically harvested, in a carefully controlled disposal pond. Long term investigations on one such pond are being carried out by us as this Handbook is being written, and will be covered by future contract reports.[1]

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[1] Contracts NAS 10-8399 and NAS 10-9166.

3.5 GAMMA IRRADIATION

The irradiation of aqueous solutions to decompose chemical compounds in solution was described in Section 2.8, where the results of experiments involving MMH and N_2H_4 were presented. This method is also appliable to aqueous solutions of N_2O_4 (or actually HNO_3, which results when N_2O_4 and H_2O are combined).

The results are shown in Table 3.5.1. The NO_3^- concentrations were reduced 12-14% in 1 1/4 hours, from various concentration levels.

The decomposition products include N_2 and oxides of nitrogen. In a closed system, as in the screw-capped bottle, the evolved NO_x will collect in the gaseous phase and set up an equilibrium with the liquid. It may be assumed that complete destruction by continued gamma radiation will not be easily achieved due to this equilibrium. Sufficient irradiation of NO_x to form N_2 may require an uneconomically long period of time.

TABLE 3.5.1

GAMMA RADIATION EXPERIMENTAL RESULTS

Test	Dose in Rads	Time Irradiated	N_2O_4 ppm (as NO_3^-)	% Reduction from Control
2	0 (control)	0	18,480	
	1,000	74.5 min	16,280	11.9
4	0		1,925	
	10^4	45 sec	1,870	2.9
	10^5	7.5 min	1,760	8.6
	10^6	74.5 min	1,650	14.3
5	0	0	50,600	
	10^4	45 sec	48,400	4.3
	10^5	7.5 min	44,000	13
	10^6	74.5 min	Bottle leaked	

3.6 INCINERATION

3.6.1 Introduction

Nitrogen tetroxide can be consumed in combustion with a hydrocarbon fuel, usually in the presense of air. Currently, the main application of incineration for N_2O_4 disposal involves the use of flare burners on vent stacks. In these burners, propane and nitrogen tetroxide vapors mix at the exit plane of the burner and react; the burner is operated in a fuel rich mode and the atmospheric air surrounding the primary reaction zone apparently reacts with the excess fuel to prevent undesirable hydrocarbon emissions. These units are in use both in portable, trailer-mounted systems and in permanent facilities.

Aqueous solutions of N_2O_4 (HNO_3) have also been incinerated at various times in large incinerators such as the one in use at Cape Canaveral Air Force Station; see Section 2.9.2.

In addition to these units, the Marquardt Sudden Expansion (SUE) burner discussed in Section 2.9 has also been used experimentally for the destruction of raw liquid N_2O_4.

The JANNAF Propulsion Committee's recommendation for disposal of large quantities of N_2O_4 was open pit incineration; see Section 3.1.

3.6.2 Thermochemical Description

N_2O_4 decomposes relatively easily and supports combustion. With proper feed rates and the use of auxiliary fuels combustibility is readily controllable. Temperature can be controlled by varying the air/fuel ratio. A minimum temperature must be maintained for satisfactory decomposition of wastes; rates of reaction are increased rapidly by higher temperatures. Combustion at high temperatures, however, converts atmospheric N_2 to NO. This NO is oxidized, either slowly by O_2 or rapidly by O_3, to produce NO_2.

The degree of turbulence in the reaction zone significantly affects the incinerator performance. Intimate mixing of the fuel and NO_2 is required for completeness of combustion. Ideally, adequate destruction of waste propellant is the reduction of N_2O_4 to N_2 with minimum NO formation. Effectiveness is judged by the combustion results as indicated by stack effluent analysis.

Santoleri and Ross[1] have discussed a number of methods used to control NO_x emissions during combustion processes. An equilibrium burner with good internal recirculation characteristics produces low NO_x levels because the mixing at equilibrium leaves little oxygen for nitrogen oxidation. Another technique uses two stage combustion where the fuel is burned with less than theoretical air in the primary stage. Air is injected into the second stage to burn the remainder of the fuel. A third procedure is flue gas recirculation. The gas at the end of combustion is recirculated into the combustion chamber. The result is lower flame temperature and oxygen concentration because of dilution with relatively inert gas.

The theoretical compositions of the products of combustion of various combinations of N_2O_4, natural gas, propane and air have been computed by the Marquardt Company.[2] These computations were based on NASA SP-273, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations" by Sanford Gordon and Bonnie J. McBride. The results are reproduced in Figures 3.6.1 through 3.6.3 as useful guidelines for future equipment evaluation. Figure 3.6.2 indicates that satisfactory operation can be obtained at over-stoichiometric (fuel-rich) conditions with little excess air present. Thus, a mass ratio of propane to N_2O_4 which is somewhat less than 0.45 results in less than 200 parts per million of NO production.

Figure 3.6.2 also shows that hydrogen is produced from traces up to 4×10^5 ppm. Carbon monoxide (CO) is produced from traces up to 3.5×10^5 ppm; nitric oxide and nitrogen dioxide from traces up to over 2×10^4 ppm. At the stoichiometric ratio of propane to N_2O_4, 40,000 ppm H_2, 140,000 ppm CO, and 15,000 ppm NO_x are formed.

Operation of an incinerator at lean fuel/N_2O_4 ratios with high air/fuel ratios is not feasible due to the low temperature and consequent abundant NO_x gas release into the atmosphere. For this reason, under-stoichiometric

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1. Santoleri, J.J. and Ross, R.D.: "Fast Reaction Burner Designs Minimize NO_x Emissions." Report No. 73-303, Thermal Research and Engineering Corp., Conshohochen, Pa.

2. Hutson, Joel E.: "Toxic Waste Burner Evaluation." Final Report, AFRPL Contract No. F 04611-73-C-0007, November 1973. Marquardt Co. Report No. S-1271.

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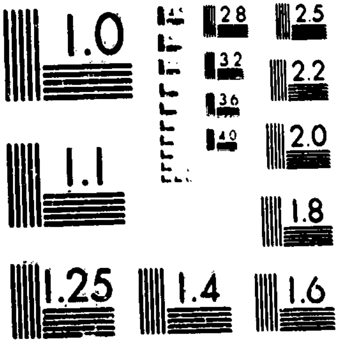

MICROCOPY RESOLUTION TEST CHART
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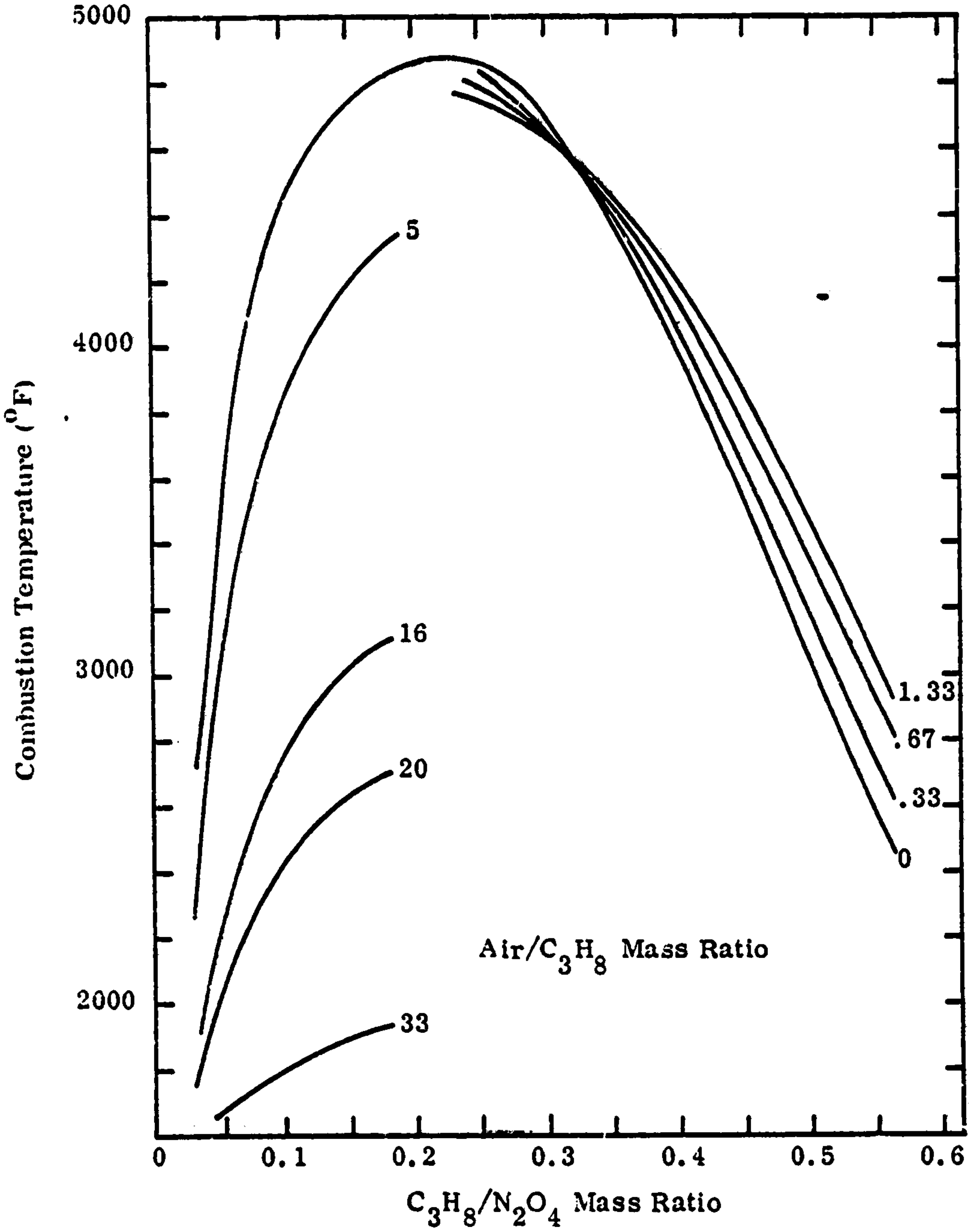

Figure 3.6.1 Adiabatic Flame Temperatures for N_2O_4/C_3H_8/Air Combustion (from Marquardt Co. Report S-1271).

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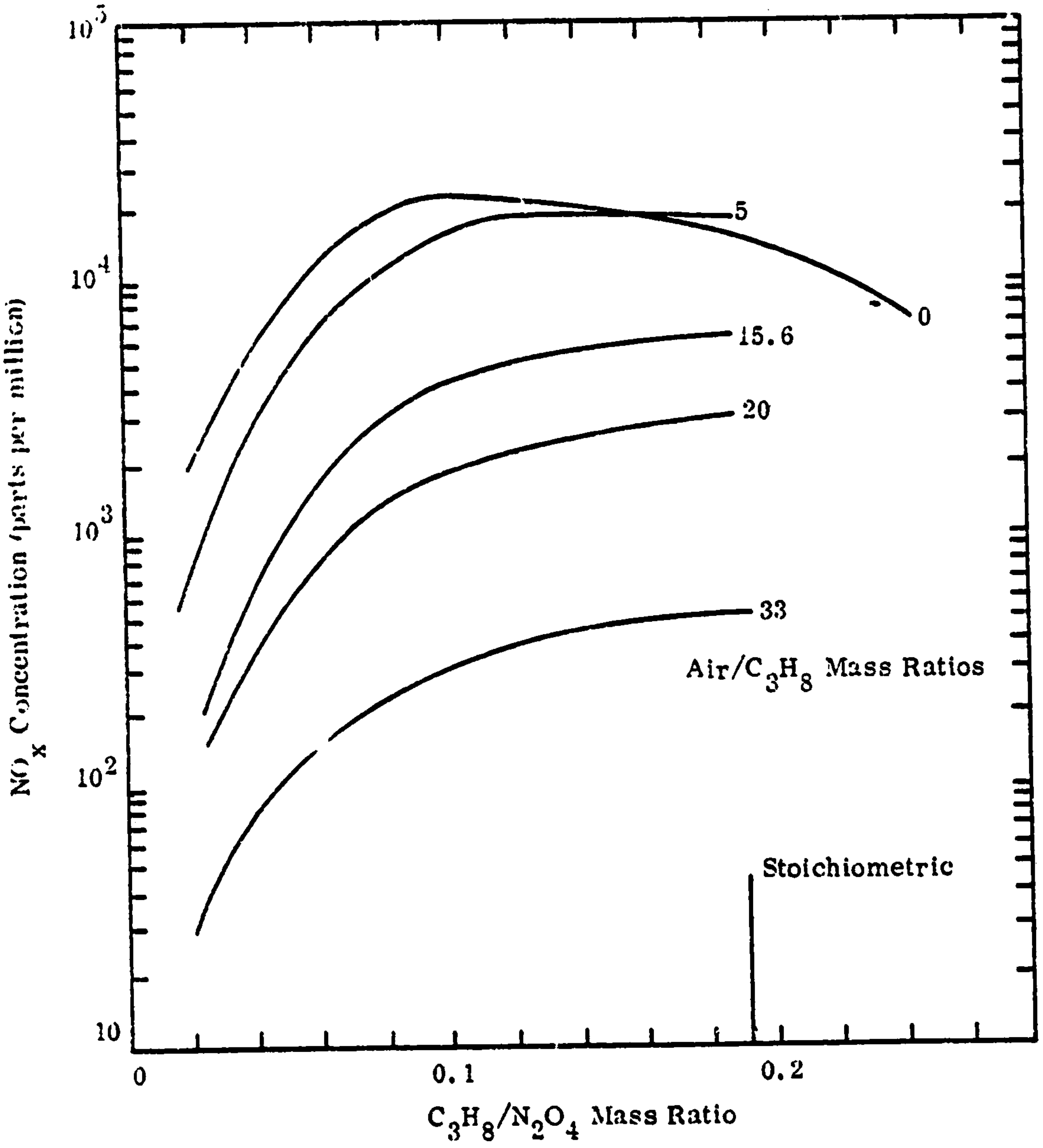

Figure 3.6.3 Equilibrium NO_x Concentrations for Under-Stoichiometric N_2O_4/C_3H_8/Air Combustion (from Marquardt Co., Report S-1271).

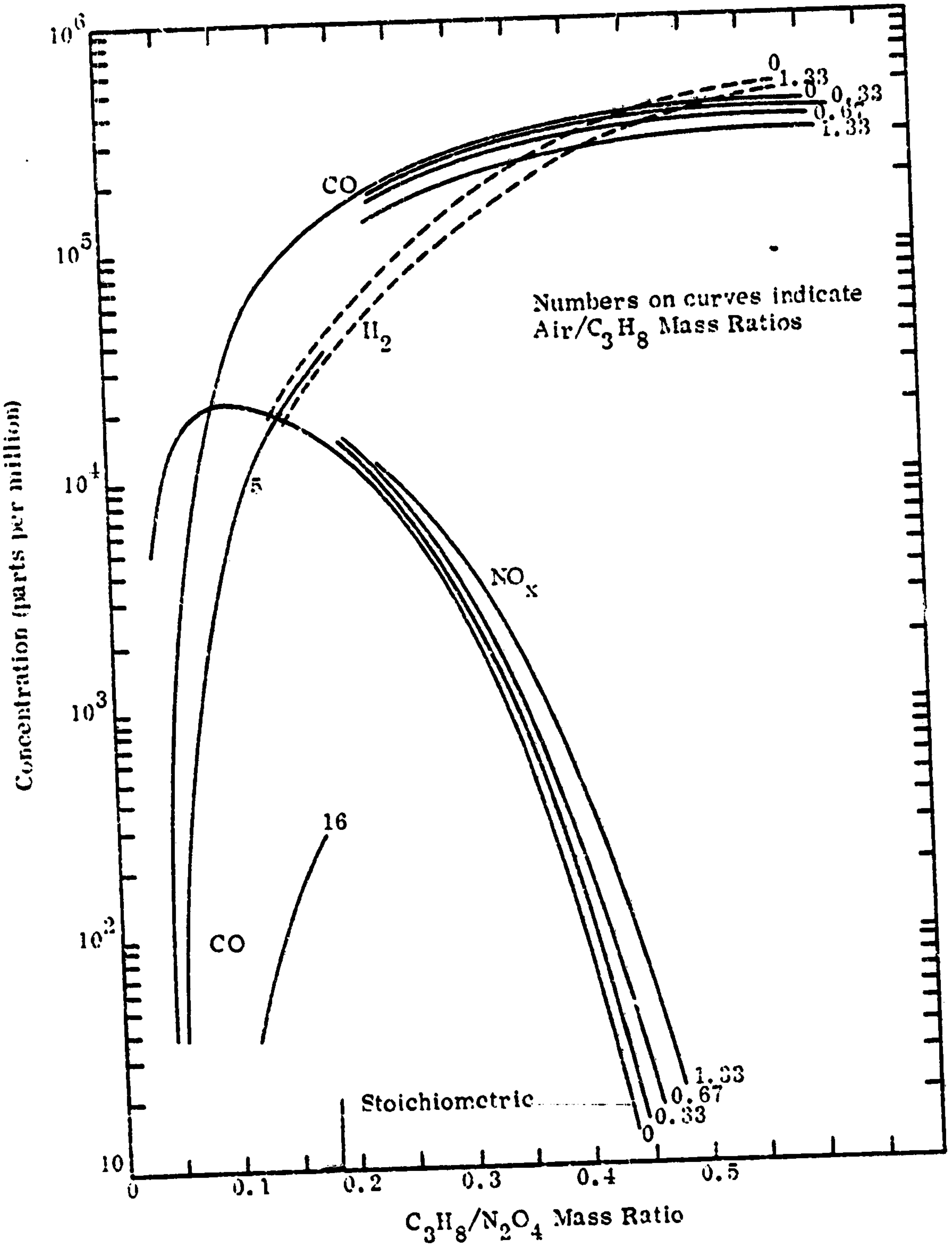

Figure 3.6.2 Theoretical Equilibrium Products for N_2O_4/C_3H_8/Air Combustion (for Marquardt Co. Report S-1271).

burning with N_2O_4 and air is not considered practical. (The results shown in Figure 3.6.3 seem to be primarily dilution effects rather than thermochemical effects.)

Operation at fuel/N_2O_4 ratios above stoichiometric, and with relatively high fuel/air ratio and higher temperature, is more desirable. Under these conditions more fuel is used and more CO and H_2 generated, but the amount of NO_x formed is considerably reduced.

Additional discussion of incinerators and formation of oxides of nitrogen was presented in Section 2.9. One aspect of combustion not discussed in that section might be especially significant in the case of destruction of an oxidizer, however: the possibility of formation of reactive hydrocarbons. For the complete destruction of an oxidizer, it is necessary for an incinerator to operate at fuel-rich conditions, which favor the formation of intermediate products that can be released to the atmosphere. The complete combustion of a hydrocarbon results in the formation of carbon dioxide and water,

$$C_nH_m + (n + \frac{m}{4})\,O_2 \longrightarrow n\,CO_2 + \frac{m}{2}\,H_2O\ ,$$

but the reaction of the same hydrocarbon with insufficient oxygen results in the formation of an aldehyde and an alkyl radical,

$$HC + O \longrightarrow RCHO + R^{\cdot}$$

The aldehyde, RCHO, is a smog-former, and the alkyl radical can react with another oxygen molecule to form a peroxyalkyl radical,

$$R^{\cdot} + O_2 \longrightarrow R\,O_2^{\cdot}$$

which in turn tends to oxidize nitric oxide to nitrogen dioxide,

$$RO_2^{\cdot} + NO \longrightarrow R\,O^{\cdot} + NO_2$$

Although the entire complex sequence of chemical and photochemical reactions that give rise to smog is still largely unknown, these reactions are thought to be some of the most important.[3] Their severity is somewhat diminished in our case by the fact that the reactivity of exhaust emissions is known to be very low in cases where propane or methane is the parent fuel.

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3. Obert, Edward F.: Internal Combustion Engines and Air Pollution. Intext Educational Publishers, New York, 1973. (Pages 363-373.)

The report by Hutson[4] also describes a short series of experiments on N_2O_4 destruction in the SUE burner. N_2O_4 flow rates in these tests were as high as 0.313 pounds per second. Although the overall results of these runs were deemed "inconclusive" by the author due to the small number of runs that were made, it was noted that colorless and odorless exhaust emissions were obtained in two ways.

1. "By ... achieving rich combustion with C_3H_8 and air only, then simultaneously bringing in N_2O_4, increasing C_3H_8, and decreasing air until sufficient fuel was available to theoretically provide over-stoichiometric burning of both air and N_2O_4."[5]
2. "at a constant C_3H_8/N_2O_4 ratio and decreasing amounts of air ... As air flow was reduced ... the exhaust cleaned up until no discoloration or odor was noticed."[5]

In neither case, however, was it possible to bring NO emissions within the range of the instrumentation. By way of explanation of the high NO readings, the author points out that "There are several possibilities such as instrument error in NO measurements or flow rate errors in propellant meters."[6] There are also other possibilities more closely related to the actual incinerator performance.

A comment is probably in order at this point regarding discrepancies between theoretical and observed products of combustion. There is no reason to expect that the equilibrium compositions of Figures 3.6.1 through 3.6.3 will necessarily be achieved in any particular incinerator. In particular, failure to achieve the desired results can be caused by the following:

1. Failure to achieve equilibrium, through poor mixing, short stay times, etc. The theoretical calculations are made on the basis of all reactions reaching completion.
2. Non-uniform incinerator flow conditions. Measured inlet flow rates give average values for mixture ratios; local variations could result in different product compositions at different points in the incinerator. In particular, local hot spots can result in large NO formation in almost any sort of air-breathing combustion chamber.

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[4] Op. cit., page 31

[5] Op. cit., page 32

[6] Op. cit., page 33

We are not presenting any conclusions regarding the SUE burner's performance in this respect, but merely recording some of the possibilities. Recommendations for further work made in the Marquardt report include "re-evaluation of the incineration configuration and injection system."

Measurements of NO_x emissions were also made by Pan American on the Thermal Research incinerator at Cape Canaveral Air Force Station. During combustion of aqueous solutions of N_2O_4, NO_x concentrations ranging from 250 ppm to 7990 ppm were measured.[7]

3.6.3 Flare Burners

A proprietary Martin-Marietta Corp. flare burner for destruction of waste oxidizer vapors, designed and developed during the late 1960's, has been installed at the Johnson Space Center, Vandenberg Air Force Base, and White Sands Test Facility, as well as at Martin-Marietta's Denver Division. The unit was originally designed for use at Titan II sites, and it seems likely that a number are also currently located at these installations.

This unit consists of a cylinder (one standard configuration is 8" diameter by 3' long) containing a plenum into which propane and waste N_2O_4 vapors are injected, and a burner head. The plenum is designed in such a way that the propane and oxidizer don't come into contact with each other until they reach the exit plane of the burner. A wind shroud protects the head from flame out. A continuous pilot is provided at the top of the burner head to ignite the gas mixture. Approximately 10 pounds per minute of N_2O_4 can be destroyed in the case of the 8 inch configuration.

The unit is basically similar in its principles of operation to the incinerators discussed in the preceding subsection and Section 2.9. Fundamental differences are that the combustion zone is external, rather than internal; there is no control over the air supply; and there is less latitude for refinement of the design (combustion chamber parameters, nozzles, secondary air, etc.). Testing is complicated by the fact that combustion is accompanied by uncontrolled

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[7] A series of internal reports of the Guided Missile Range Division, Pan American World Airways, dated 8 October 1970, 26 February 1971, and 3 January 1972, regarding operation of the Hypergolic Propellants Incinerator at Cape Kennedy Air Force Station.

dilution, and that the effluent is unconfined, giving rise to problems regarding where samples should be taken. On the other hand, the characteristic of a central C_3H_8/N_2O_4 flame, with an unlimited quantity of air available surrounding the flame, might well constitute a faborable environment for N_2O_4 destruction that would be difficult to duplicate in an internal combustion incinerator.

The stoichiometric equation for reaction of N_2O_4 with C_3H_8 is

$$5\ N_2O_4 + 2\ C_3H_8 \longrightarrow 6\ CO_2 + 8\ H_2O + 5\ N_2$$

The limitations of this sort of equation have been discussed extensively in earlier sections on incineration, including the need for fuel-rich operation to assure complete destruction of N_2O_4. In addition to reaction, however, dissociation is of prime importance in discussing N_2O_4 destruction.

At atmospheric pressure, the dissociation of N_2O_4,

$$N_2O_4 \longrightarrow 2NO_2,$$

is essentially complete at 200°C. At temperatures in this range and higher, the NO_2 in turn dissociates

$$2NO_2 \longrightarrow 2NO + O_2$$

$$2NO_2 \longrightarrow N_2 + 2O_2$$

If other constituents are predominantly oxidizing, the first equation is most important, but if they are strongly reducing the second dissociation predominates. In other words, fuel rich combustion favors the desirable NO_2 dissociation, as opposed to the formation of NO. (These dissociation considerations were implicit in the theoretical predictions discussed in the preceding subsection.)

The only published data on effluents from these flare burners resulted from a test program conducted at White Sands Test Facility several years ago.[8] "Samples were obtained simply by holding an inverted funnel connected ... to an evacuated 3-liter pressure bottle over the most dense portion of the flame," and were analyzed in an infrared spectrophotometer having detection limits of 1.0 ppm NO, 0.04 ppm NO_2, 1.0 ppm CO, 0.1 ppm CO_2, 0.1 ppm HC, 100 ppm

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[8] Smith, Irwin D.: Nitrogen Tetroxide Disposal Unit Combustion Products. NASA TN D-3965, May 1967.

H_2O. Results reported were simply that in a lean operating mode, NO and NO_2 were detected, whereas in the proper fuel-rich mode only H_2O, CO_2 and HC were detected. No carbon monoxide was detected in any of the samples. An interesting statement was that "No attempt was made to obtain samples that could be quantitatively analyzed to determine the exact output of the unit. Since wind conditions at the White Sands Test Facility are very erratic, sampling for precise quantitative analysis would be difficult and impractical."

We believe that these results illustrate our earlier statements regarding the difficulty of collecting meaningful data from this sort of external combustion device. The absence of both CO and NO from the same sample seems somewhat unlikely, except as a result of very considerable dilution. Perhaps, however, these results can be taken as evidence that the flare burner does not have any particularly severe NO problems in the fuel-rich mode.

While this result seems unlikely it is certainly not inconceivable, and could be a result of the more or less stratified nature of the burner's combustion zone, with fuel and waste oxidizer in the center and a second oxidizer (air) surrounding this region. It is possible that combustion here is sequential in nature, involving first N_2O_4 and excess fuel with air entering after complete N_2O_4 destruction but not too late to effectively oxidize the large amount of CO that must certainly form during primary combustion. Even so, however, some amount of nitric oxide formation seems inevitable.

3.6.4 Conclusions

In spite of the rather widespread application of incineration as a means of disposing of nitrogen tetroxide, it is still an extremely difficult method to evaluate. Theoretical considerations show that it should be possible to achieve very low NO_x concentrations in the exhaust of such an incinerator. However, fuel-rich combustion is necessary if formation of NO is to be prevented. Fuel-rich combustion is almost always less environmentally acceptable than lean combustion because of the formation of partial products such as CO, ketones, aldehydes, olefins, etc., although use of methane as the fuel will eliminate or minimize most of these problems.

It seems possible that air could be introduced downstream of the primary combustion zone in such a way as to react with these partial products to form harmless (CO_2, H_2O) final products, yet without formation of NO due to excessive heating of the air itself; both the SUE burner and the MMC flare burner are configured such as to perhaps be capable of achieving this goal. Experimental programs carried out with both units have been inconclusive, however. The SUE test program was terminated before low NO emissions were achieved; the flare burner measurements were made on samples that had been diluted by undetermined quantities of air, and the analyses performed on the samples were rather minimal.

We need hardly mention, however, that open methane flames have been used for residential heating and cooking for generations without causing air pollution problems even at the point of application, and hence concern with fuel-rich combustion in open methane flames is probably not of great importance.

It does seam clear that both the flare burner and the SUE burner, as well as large incinerators, are capable of producing colorless (no NO_2) effluents, and hence are at least comparable to water scrubbing, water dilution of liquid N_2O_4, and other processes where the chief problem is formation of quantities of NO.

3.7 CATALYTIC DECOMPOSITION

The basic principles of catalytic decomposition were discussed in Section 2.10. This method is applicable to nitrogen tetroxide as well as to the hydrazine fuels.

In the course of trying to learn more about the practicality of catalytic decomposition, we contacted two manufacturers who were willing to discuss catalytic decomposition of nitrogen tetroxide. W.R. Grace and Co. of Baltimore, Maryland, wrote that "N_2O_4 and HNO_3 pose the most difficulty in decomposition. A catalyst containing platinum or palladium used in a reducing atmosphere of hydrogen or carbon monoxide would probably do the job."

Engelhard Industries, Murry Hill, New Jersey, suggested that catalytic decomposition using a palladium catalyst would be feasible. Similar methods are in use at many nitric acid plants throughout the country to "decolorize" the nitric acid tail gas and reduce the NO_x concentration. In the manufacture of nitric acid, the first step is the catalytic air oxidation of ammonia to form NO, which reacts with residual oxygen to form NO_2 which is subsequently absorbed in water to form nitric acid and additional NO. The gases leaving the top of the column consist of mixed nitrogen oxides, oxygen, and nitrogen. These high pressure gases are passed through an expander for power recovery before discharge to the atmosphere, and quite commonly palladium or platinum catalysts have been added upstream of the expander to decompose the NO_2 to NO and O_2, thus increasing the power recovery as a result of the energy release during decomposition. An added benefit is the elimination of the characteristic red plume often associated with nitric acid plants. With the edvent of air polution laws, these systems were modified by the addition of "abaters" in which fuel - usually methane - is added to the gas stream upstream of the catalyst bed, as shown in Figure 3.7.1. The fuel reacts with the remaining O_2, with enough excess fuel to create reducing conditions so that decomposition of NO_2 to N_2 and O_2 is favored. With this scheme, total NO_x emissions are reduced to the 100 - 1000 ppm range. Engelhard has developed an improved version of this scheme, described by Gillespie et al[1], which is said to overcome problems of

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[1] Gillespie, G.R.; Boyum, A.A.; and Collins, M.F.: "Catalytic Purification of Nitric Acid Tail Gas: A New Approach." Presented at the AI ChE Annual Meeting, San Francisco, December 2, 1971.

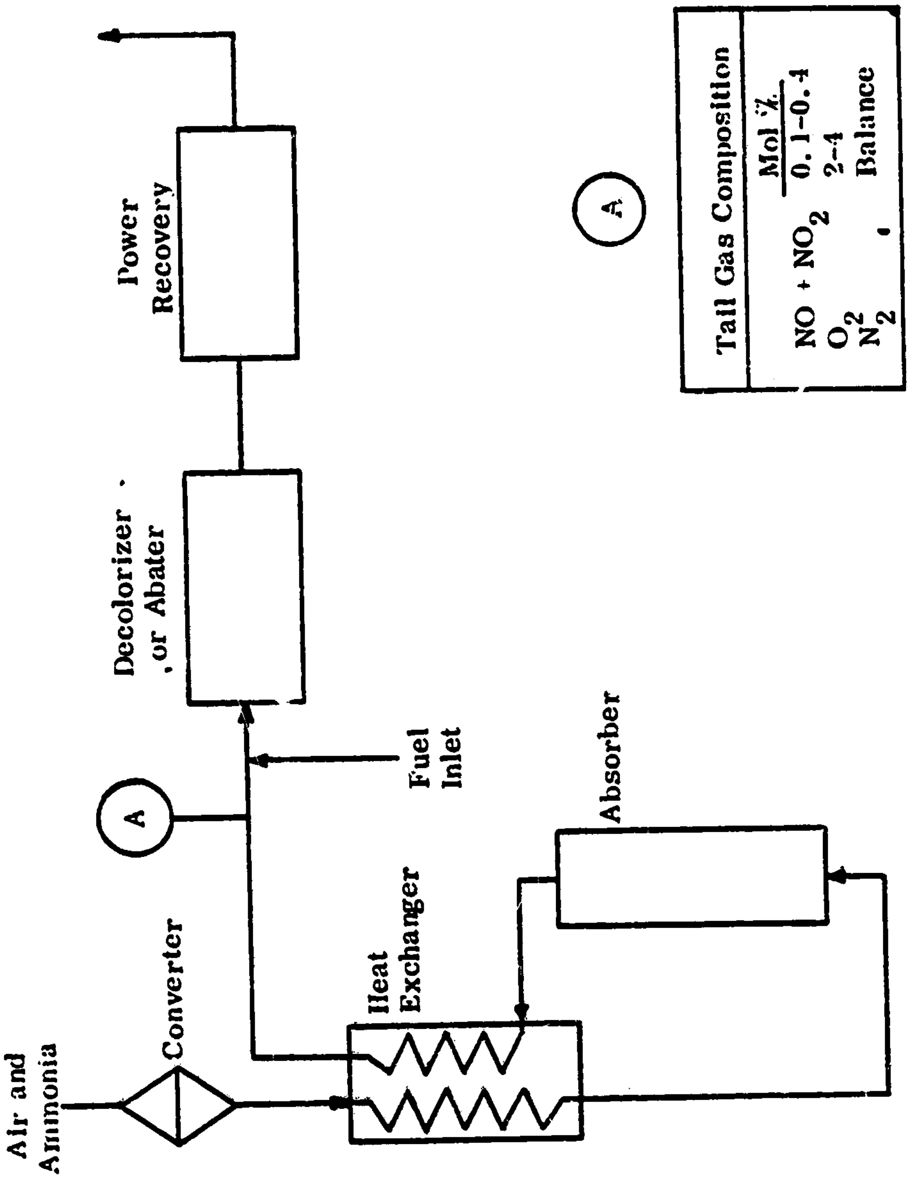

Figure 3.7.1 Flow diagram for typical nitric acid plant with abater. From Gillespie et al, 1971.

catalyst poisoning, rate limitations, thermal limitations, poor mixing, and excessive fuel/O_2 ratios that existed with earlier systems. The system, shown in Figure 3.7.2, uses a spherical palladium catalyst and relies on fuel desulfurization, abater bypass for start-up and shut-down, and careful control of temperatures and flow rates. Reliable operation with total effluent NO_x concentrations below 200 ppm is claimed.

The use of processes involving dry, catalyzed reaction to "scrub" oxides of nitrogen from nitric acid plant emissions has also seen considerable development in Japan, where regulations regarding atmospheric releases of NO_x are also quite stringent. Two dry catalytic processes using ammonia to reduce the oxides of nitrogen, in the presence of proprietary catalysts, have come to our attention. The Hitachi Zosen process is said to reduce the stream from 350 ppm to 10 ppm "and less", while the Sumitomo process is said to accomplish an 80-90% reduction in a stream initially at 200-500 ppm - a reduction to about 40 ppm. Cost of a Hitachi-Zosen system for 200,000 M^3/hr total flow is about $5 million, with an operating cost of about $2.5 million per year, based on 8,000 hours per year operation. Cost of the Sumitomo system is $270,000 - $330,000 per 10,000 M^3/hr. capacity.[2] It is not known at this time whether this approach is being developed by anyone in this country, or how the costs would scale to a smaller system.

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[2] Ushio, S.: "Japan's NO_x Cleanup Routes." Chemical Engineering, July 21, 1975, pages 70-71.

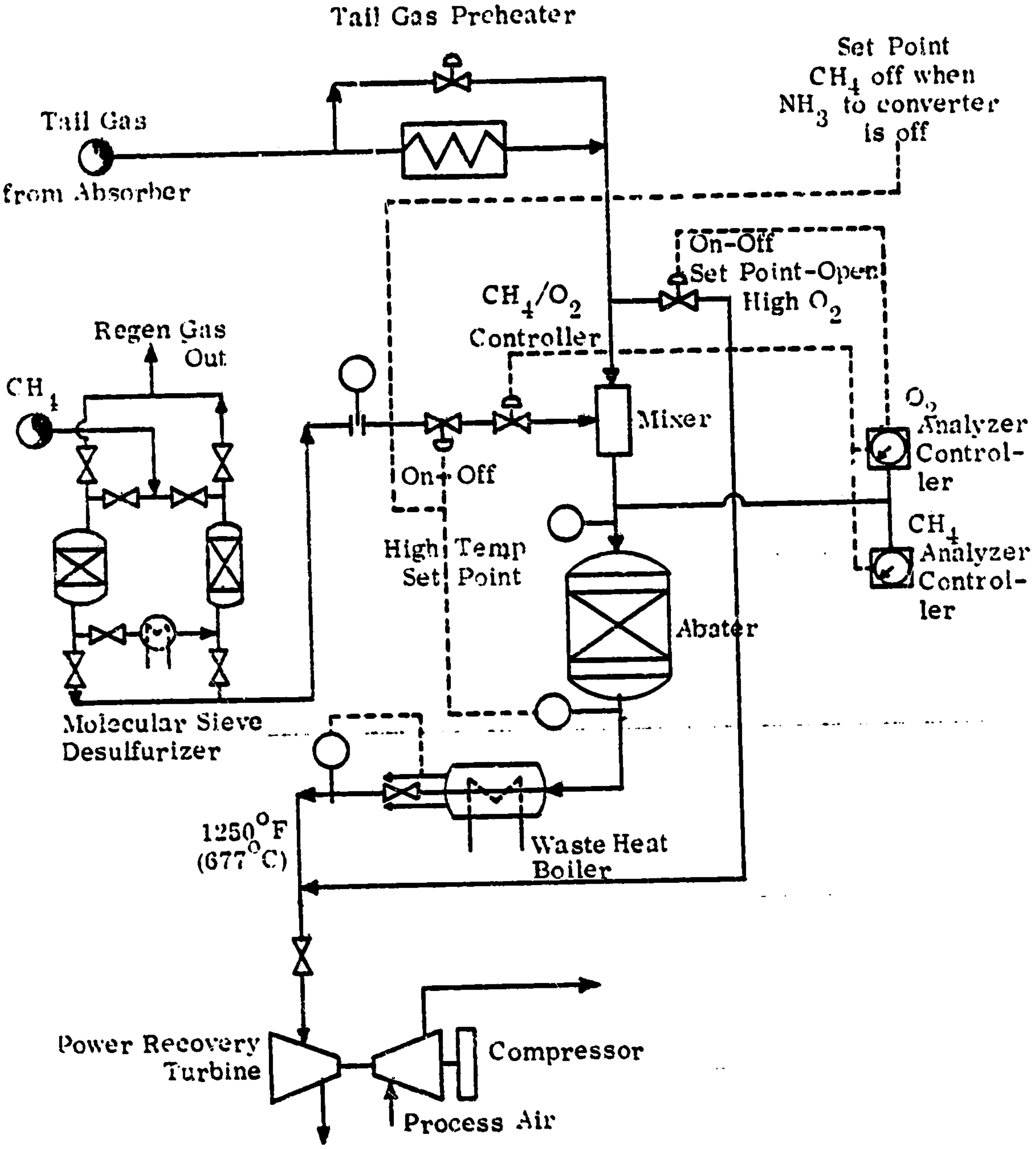

Figure 3.7.2 Schematic of Engelhard's NO_x abater system. From Gillespie et al, 1975.

3.8 PLASMA ARC AND MICROWAVE PLASMA DECOMPOSITION

These methods were described in Section 2.11 with regard to the decomposition of hydrazine fuels. They should be equally as applicable to nitrogen tetroxide. We are not aware of any experimental work having been performed to date that actually involved either hydrazine fuels or nitrogen tetroxide.

3.9 ABSORPTION OF VAPOR

3.9.1 Introduction

In cases where nitrogen tetroxide vent streams are treated rather than being discharged directly to the atmosphere, the most common treatment to date has been water scrubbing, in which the N_2O_4 vapors are absorbed in water in a packed column scrubber of some sort. In some cases, a solution of sodium bicarbonate ($NaHCO_3$) or other alkali has been used in place of water. Some of the scrubbers that have been used, along with theoretical aspects and design considerations, are presented in Appendix D.

Scrubbing of NO_2 - N_2O_4 presents formidable problems because of the low solubility of these agents in water, and also because NO is formed during the absorption of NO_2 and N_2O_4 in water according to the following equation:

$$3\ NO_2\ (\text{or } 3/2\ N_2O_4) + H_2O \longrightarrow 2HNO_3 + NO$$

As nitric oxide is only sparingly soluble in water, oxidation to NO_2 must take place in the gas phase before significant absorption of the evolved nitric oxide can occur whenever more than a few ppm of NO_2 are being absorbed. The oxidation of NO (the rate controlling step in the absorption of low concentrations of nitrogen oxides) is concentration-dependent, as seen in Table 3.9.1, which shows the time required for half the NO present in air at various concentrations to be oxidized to NO_2 at standard temperature and pressure.

TABLE 3.9.1

OXIDATION RATE OF NO IN AIR

NO conc. in air, ppm	Time for half NO to be oxidized to NO_2, min
20,000	0.175
10,000	0.35
1,000	3.5
100	35
10	350 (5.84 hr)
1	2500 (58.4 hr)

Whereas it takes 10 seconds for half the NO to be oxidized to NO_2 when the concentration is 2% by volume in air, it takes nearly 60 hours for half the NO to be oxidized when the original concentration is 1 ppm. The oxidation rate for all concentrations increases at higher pressure.

It may be concluded from these facts that, for cases in which water is used for scrubbing:

1. multistage absorption equipment with long gas retention times for oxidation of NO between absorption stages is required for high efficiency absorption of nitrogen oxides from flowing air streams;
2. it is impossible to reduce effluent concentrations below a few hundred parts per million NO_x in single stage absorption equipment of practical dimension when the entering concentration is in the percent range;
3. the effluent NO_x concentration in multi-stage equipment tends to be insensitive to increases in inlet concentration because of the greatly decreased oxidation times associated with higher concentrations of NO.

Experiments conducted in 8.5 inch diameter counter current tower packed with 5 feet of 1/2 inch Berl Saddles indicated that no permanent improvement in NO_x removal results from recirculating an alkaline scrubbing solution because of the inhibitory effect of accumulations of $NaNO_2$ on the absorption efficiency of the resulting mixture.[1]

The slow oxidation of NO in air can be improved by adding an oxidant such as $KMnO_4$ to the absorption liquid so that NO formed during the hydration of NO_2 can be oxidized in the liquid phase (and made water soluble) before it escapes from solution because of its limited solubility. When $KMnO_4$ was added to the alkaline scrubbing liquor, absorbability increased by a factor of 20% for the operating conditions employed.[2] The principal problem associated with the use of $KMnO_4$ in absorber scrubbing liquor, in addition to the high cost of the chemical, is the formation of an insoluble MnO_4 precipitate which can cause fouling of the absorber packings.

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[1] First, N.W., and Viles, J.J., Jr.,: "Cleaning of Stack Gases Containing High Concentrations of Nitrogen Oxides." Journal of the Air Pollution Control Association, Volume 21, 122-127 (1971).

[2] Ibid.

A $KMnO_4$ process that is being used on a commercial basis in Japan is the Mitsubishi Kakoki Kaisha process. The system is quite complex, consisting, in addition to the absorption tower, of thickener, filter, evaporator, crystallizer, separators, dryer, and electrolytic cell. It is said to reduce NO_x concentrations from 200 ppm to 50 ppm, at a system cost of $5 million and operating costs of $1.1 million per year for a 200,000 M^3/hr. system.[3]

Other chemicals can also be used in the scrubber liquor to prevent NO formation during the absorption of N_2O_4 vapors. Some of these chemicals - especially sodium hydroxide, ammonium hydroxide, and triethanolamine (TEA) - were the subject of an extensive test program that is described in later portions of this section.

Still another approach involves the use of a strong gaseous oxidant between the stages of a multistage scrubber. Ushio reported that the Chiyoda Chemical Engineering and Construction Company in Japan is working on an ozone process that converts NO effluent to NO_2, which can then be scrubbed in a second absorption stage.[4] A conceptual design of a system based on this concept is presented in subsection 3.9.3.

3.9.2 Water Scrubbing Experiments

First and Viles described the results of a series of tests performed on a 16-stage cross-flow NO_x gas absorber containing 37 micron diameter curled glass packing.[5] Details of the unit are shown in Figure 3.9.1.

The manufacturer was the Buffalo Forge Company, and the overall configuration is quite similar to that of the Hamilton Standard Gemini and Saturn scrubbers, which were also fabricated by Buffalo Forge. (See Appendix D.) Each absorption stage had a face area of 1.25 sq. ft. and contained a 4 inch depth of Owens-Corning K-115 curled glass fibers packed to a density of 2.3 pounds per cubic foot. Fifteen stages were wetted with nozzles having an

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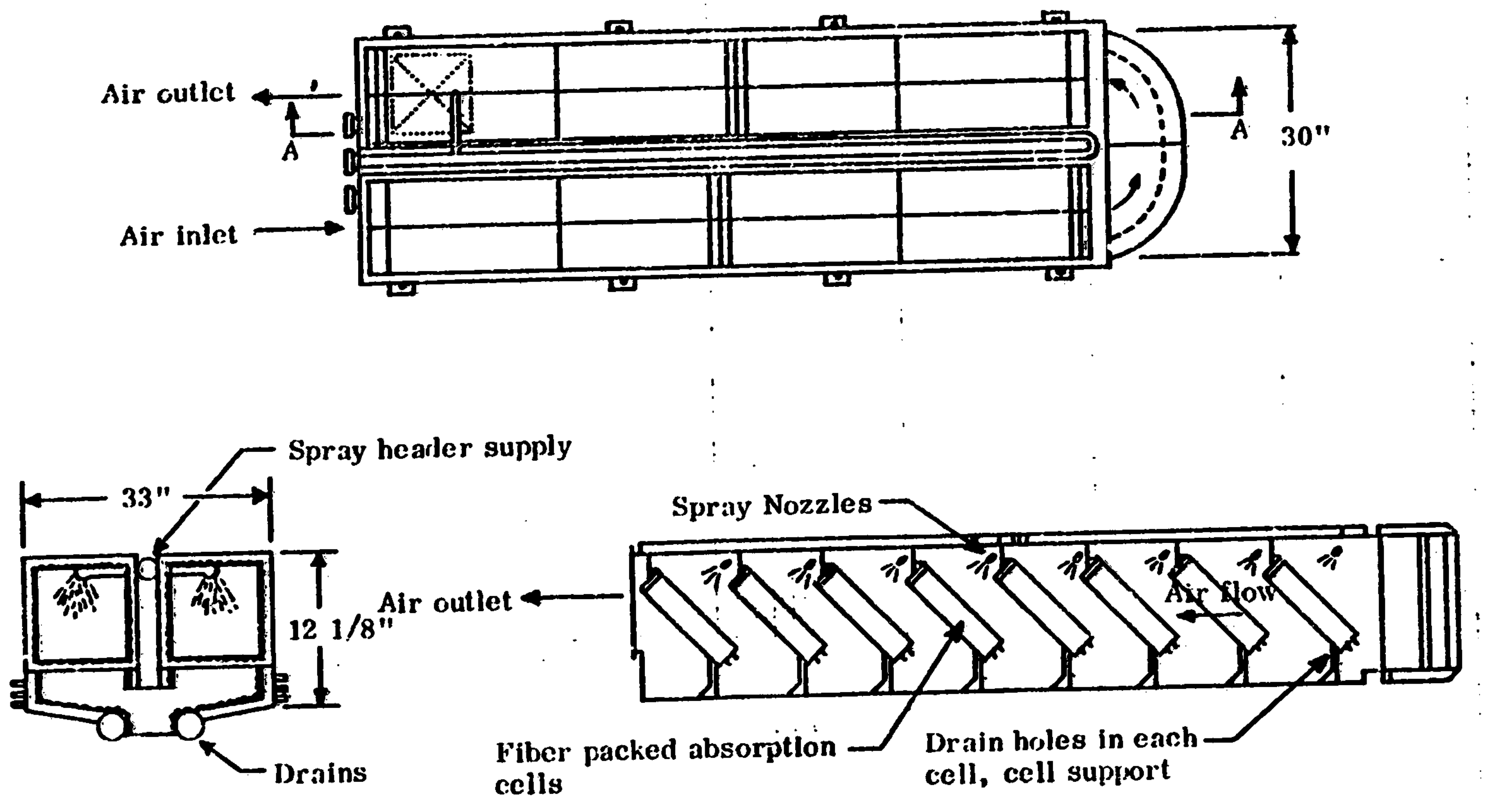
3. Ushio, S.: "Japan's NO_x Cleaning Routes." Chemical Engineering, July 21, 1975, pages 70-71.

4. Ibid.

5. Loc. cit.



Section A. A

Figure 3.9.1 The Buffalo Forge 16-stage gas absorber tested by First and Viles.

orifice diameter of 0.170 inches and delivering 2.5 g/minute at 8 psi. The sixteenth stage was operated dry and served as an eliminator to prevent emission of airborne droplets. The nozzles were serviced from a fresh water supply and waste water drained from the sumps connecting the cells to the bottom of the absorber casing. It was intended that the liquid would rise in the sumps to a level well above the drainage holes leading from the compartments and thereby provide effective air seals between the stages.

Performance tests were conducted under a variety of conditions. Provisions were made to measure temperature, flow rate, and the composition of gas and liquid streams entering and leaving the absorber. The following results were obtained:

1. Pure N_2O_4 - NO_2 mixtures at gas temperatures from 78 to 123° and scrubbing water temperatures from 40 to 74° were reduced to 30 ppm at exit from the scrubber because with little or no inert gas present, the gas absorber approximated an infinite-retention-time reactor after the flowing gas volume shrank to very small values.
2. In tests in which conditions were held constant except for NO_2 inlet concentration, outlet concentration appeared to be largely unaffected by very large changes in inlet concentration; e.g., in one series of tests a thirteen-fold increase in NO_2 inlet concentration (2000 to 26,700 ppm) produced no significant increase at the outlet. When outlet concentration was plotted on log paper against average gas velocity through the scrubber, the residual concentration appeared to be approximately proportional to the square of the gas flow velocity.
3. The outlet NO_2 concentration increased with a rise in water temperature.
4. Pressure of several atmospheres would be required to produce a marked improvement in absorption at low concentrations of NO_2.

We concluded from the First and Viles paper, and other sources, that multistage gas absorption of 1 - 50% nitric oxide, nitrogen dioxide, and nitrogen tetroxide from air with water or caustic solutions can produce colorless stack discharges. The rate at which NO is oxidized to NO_2 in the gas phase and the solubility rate of NO_2 in water or solution are highly concentration dependent so that reduction of emissions of nitrogen oxides below approximately 200 ppm appears to be impractical using current methods.

3.9.3 Multistage Absorption with Interstage Oxidation

The following paragraphs briefly describe a concept which we believe should be capable of reducing NO_x concentration from 10,000 ppm to below 70 ppm, without undue complexity or expense.

The system consists of four stages. In Stage I a jet type scrubber with plain H_2O, part of which may be recirculated, will reduce the initial 10,000 ppm NO_x concentration approximately 70%. Most of the NO_2 in the NO_x mixture will dissolve in the water according to:

$$3\,NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

(if all the NO_2 takes part in this reaction, the 10,000 ppm initial concentration would be reduced to 2500 ppm.)

The gaseous effluent from Stage I, assumed to contain 3,000 ppm NO_x, will be conveyed to Stage II, an absorption unit in which O_3 gas and ozonated water are recirculated. A chemical oxidation occurs with the insoluble constituent, NO, as follows:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

This newly formed NO_2 and the uncaptured NO_2 existing in the feed gas, being soluble, will dissolve in the scrubbing liquid. As before, 1 mole of NO will be formed from 3 moles of NO_2. The presence of O_3 in the absorption unit provides highly oxidizing conditions and thereby increases the efficiency of absorption to about 90%. The NO_x concentration is thus reduced to 300 ppm in Stage II.

A choice can be made to either recirculate the gases in the absorption unit until the NO_x concentration is reduced to the desired level, or alternately to go to a third stage. In Stage III, fresh ozonated H_2O and O_3 are contacted in an absorption unit with the gases from Stage II. The NO_x concentration is reduced to 60 ppm assuming only an 80% efficiency.

Finally, in Stage IV the gaseous effluent is freed of O_3 residuals by thermal decomposition in a gas heater and then vented to the atmosphere, with air dilution as required. The NO_x concentration in the exhaust is less than 70 ppm.

The liquid wastes from the three scrubbing stages are combined, neutralized with a suitable alkali to desired pH, and transferred to the waste disposal pond.

It should be emphasized that this system has only been described in a very preliminary conceptual form. Additional calculations, laboratory scale experimental work, and prototype development and testing would be required before a thorough evaluation of the efficacy of this system could be performed.

Two preliminary tests were performed in the laboratory to provide some verification of the concept. The results, shown in Table 3.9.2, were quite positive.

TABLE 3.9.2
RESULTS OF NO_x SCRUBBING TESTS

	Test 1	Test 2	
	PPM NO_x in Gaseous Effluent	PPM NO_x in Gaseous Effluent	PPM NO_3/NO_2 In Scrubber Liquor
System 1 (No Off Gas Treatment)	168*	200*	2,500
System 2 (Ozonation of Off Gases)	74	48	6,250

* Brown fumes visible in gas sampling container.

3.10 ADSORPTION OF VAPOR

Molecular sieves can be used to remove a wide variety of contaminants, including nitrogen dioxide and nitrogen tetroxide vapors, from gaseous effluent streams. In these systems, the contaminant molecules are adsorbed on the surface of the sieve material, which might be, for example, activated carbon, activated alumina, or silica gel, with a very high surface area to volume ratio.

A commercial system that has seen successful application in removing nitrogen dioxide from the tail gas of nitric acid plants is manufactured by Union Carbide and uses zeolite as the adsorbent; the adsorbent concentrates the NO_2, which is then desorbed by heating and scrubbed in a closed loop fashion. This system is quite expensive, and as far as we know has been applied to large, continuous contaminant flows; it does not seem to be economically feasible for small, intermittent contaminant sources typical of aerospace applications.

An extensive series of tests were performed by us to evaluate the practicality of using other adsorbents for removing N_2O_4/NO_2 vapors from nitrogen and helium streams - adsorbents that would be inexpensive enough to allow disposal of the contaminated adsorbent to a solid land fill, for example. Both laboratory scale and large scale (up to 9.1 SCFM GN_2 and 1.6 liters/minute (liquid) N_2O_4) were performed. Adsorbents investigated included charcoal briquets, dry ice, aluminum cuttings, alumina, activated carbon, silica gel, and various mixtures, both at ambient and elevated temperatures. Detailed results were not available in time for inclusion in this Handbook, but are available as a separate report.[1]

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[1] Sivik, H.; Thomas, J.; Cohenour, B.; Wiederhold, C.: "Hypergolic Propellants - Liquid and Vapor Disposal: Final Report, Phase VI, Task 8, Dry State Scrubbing Systems for N_2O_4 and MMH." Florida Institute of Technology, Melbourne, FL 32901, March 1977.

3.11 CONDENSATION OF VAPOR

3.11.1 Analysis

The method of analysis presented in Appendix E was applied to the case of N_2O_4/NO_2 condensation, as well as to the cases of fuel condensation of Section 2.13.2. In this case an empirical equation for the vapor pressure of liquid nitrogen tetroxide in the range 261.90 to 294.9°K was presented by Giauque and Kemp:[1]

$$\log_{10} p = -1753.000/T + 7.00436 - 11.8078 \times 10^{-4} T + 2.0954 \times 10^{-6} T^2.$$

This equation is plotted in Figure 3.11.1. It refers to the equilibrium mixture of N_2O_4 and NO_2 at any value of (p,T).

The latent heat of vaporization, h_{fg}, at 294.25°K was presented by Giauque and Kemp[2] as 9110 ± 9 cal/mole, based on a series of several experiments. This value was compared with a theoretical value (based on empirical equations of state and degree of dissociation) of 9223 cal/mole. The value 9110 was used for this study. In using this value, "per mole" actually means per 92.016 grams, as if none of the N_2O_4 were dissociated. The value is nevertheless the actual equilibrium value. It should be noted that the equilibrium at the boiling point is not altered by the phase change - it is the same in the liquid and the vapor phases.

$(\partial h/\partial T)_{SAT}$ was approximated by c_p, as in the hydrazine cases. Fan and Mason[3] have developed equations for the equilibrium heat capacity of the N_2O_4-NO_2-NO-O_2 system, taking account of the equilibrium reaction heat capacity. Numerical solutions were also presented; at 300°K, 1 atm, the result was

$$c_p = 1.309 \text{ calories/gram } ^\circ K,$$

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[1] Giauque, W.F., and Kemp, J.D.: "The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $N_2O_4 = 2NO_2 = 2NO + O_2$." J. Chem. Phys., Vol. 6, pp. 40-52 (1938). The equation used here was modified to yield p in mm Hg, for consistency with the hydrazine equations. T is in °K.

[2] Op. cit., p. 45.

[3] Fan, S.S.T., and Mason, D.M.: "Properties of the System $N_2O_4 = 2NO_2 = 2NO + O_2$." Journal of Chemical and Engineering Data, Vol. 7, pp. 183-186(1962).

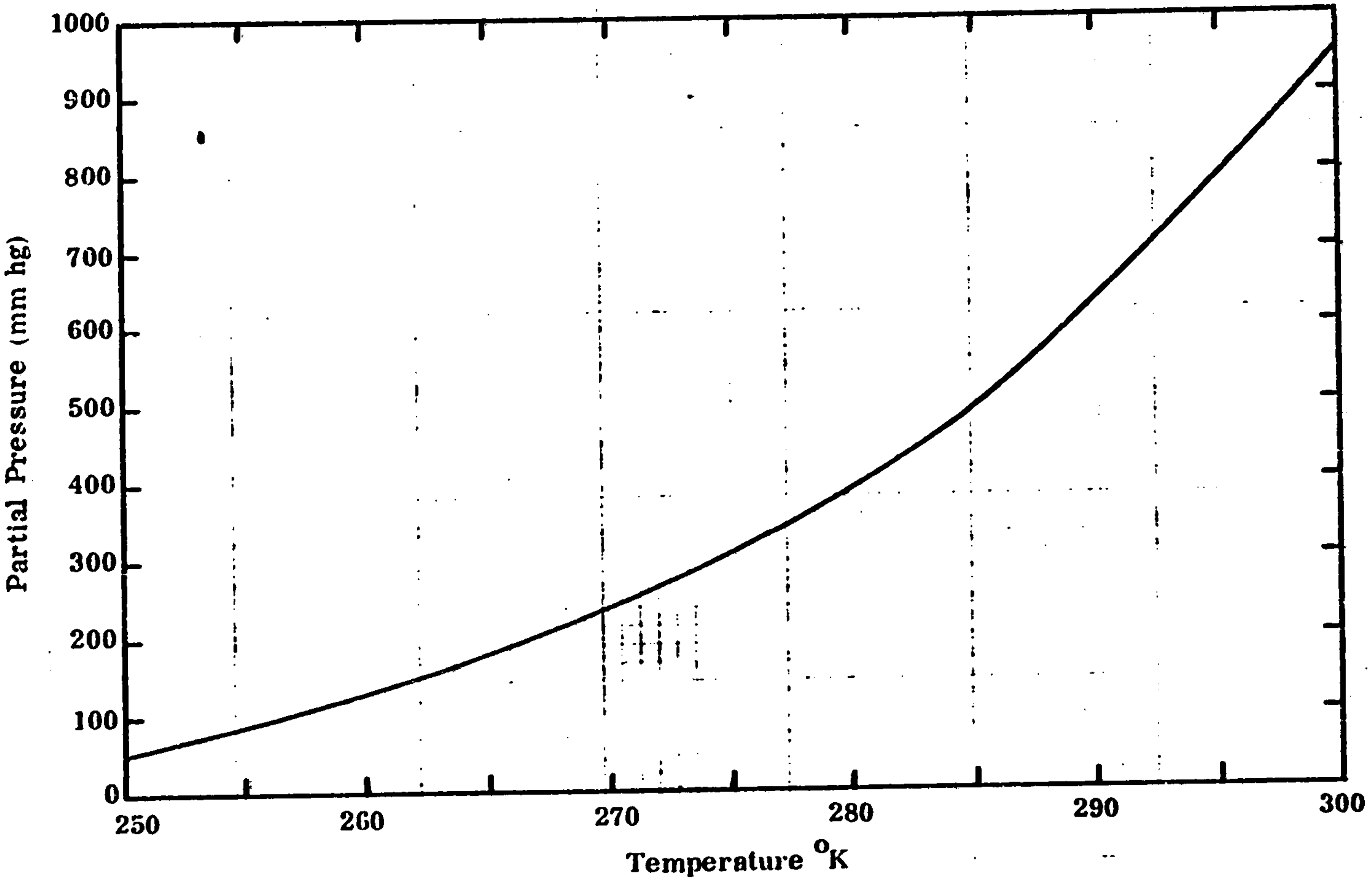

Figure 3.11.1 Liquid-vapor saturation curve for N_2O_4

the value used in this study. (It should be noted that this value is quite different from the frozen equilibrium heat capacity, calculated by Fan and Mason to be 0.2033 cal/g-°K.) Whether equilibrium or frozen equilibrium is closer to reality in our situation is difficult to determine and of course depends on rates, etc. The equilibrium value was chosen as being the more conservative.

The molecular weight of the equilibrium mixture is found from the molecular weights of the two constituents and the degree of dissociation:

$$M = (46.008) + (1-\alpha)\,(92.016)$$

where data for α as a function of temperature and pressure were given in Section 3.1. For the sake of obtaining an algebraic relationship between α and T, we used the equation (see Section 3.1)

$$K = \exp\left(\frac{-1}{R}\left[\Delta\left(\frac{F^{o}-H_{o}^{o}}{T}\right) + \frac{\Delta H_{o}^{o}}{T}\right]\right)$$

where ΔH_{o}^{o} = 12,875 cal/mole for the reaction $N_2O_4 = 2NO$, and $\Delta\left(\frac{F^{o}-H_{o}^{o}}{T}\right)$ was assumed linear over the temperature range of interest, using the data points at 275°K and 300°K:

$$-\Delta\left(\frac{F^{o}-H_{o}^{o}}{T}\right) = 36.18 + 0.01044\,T \text{ cal/mole}$$

Thus we have

$$K = \exp\left(\frac{0.01044\,T + 36.18 - 12.875\,T^{-1}}{1.986}\right)$$

where T is in °K. The degree of dissociation, α , at 3.0 atmospheres (44.09 psia) was then calculated, using this value of K, from the equation

$$\alpha = \left(\frac{K}{12 + K}\right)^{1/2} \qquad \text{(see Section 3.1)}$$

The values thus obtained are plotted in Figure 3.11.2.

The values used for c_{pN} were 6.95 cal/mole-°K for nitrogen and 5.00 cal/mole-°K for helium, as in Section 2.13. The computer code described in Appendix E was used, with these values, to investigate cases in which saturated mixtures of N_2O_4/NO_2 vapor in nitrogen or helium, initially at 300°K (80.33°F), are progressively cooled to the freezing point of the N_2O_4/NO_2, 262°K (-11.8°F). The pressure was held constant at 2300 mm Hg (44.47 psia). The slight discrepancy between this value and the pressure used in calculating α was unfortunately

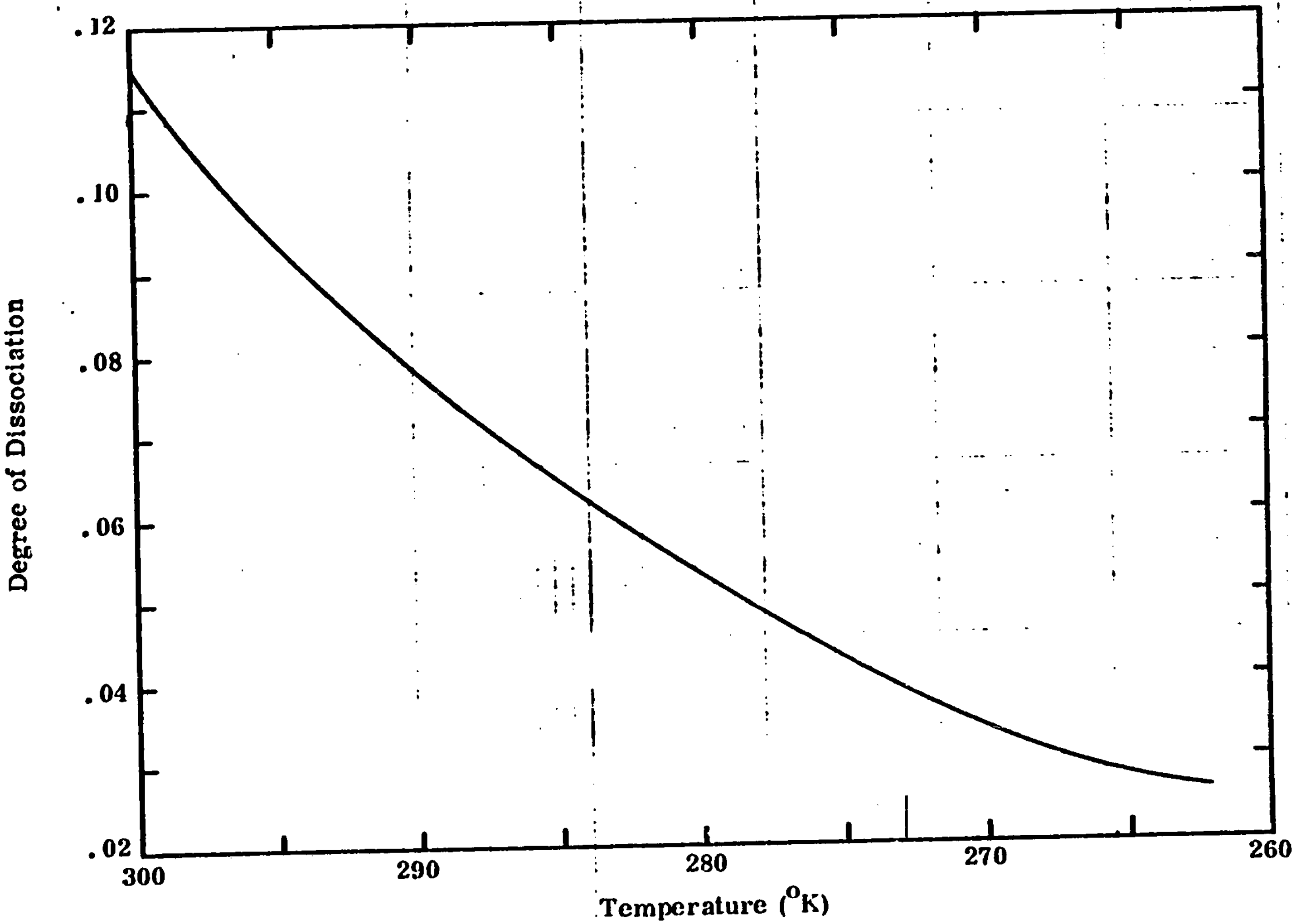

Figure 3.11.2 Degree of dissociation for $N_2O_4 \rightleftharpoons 2NO_2$, at three atmospheres

overlooked at the time this work was performed; the error introduced thereby is regarded as insignificant.

Figures 3.11.3 through 3.11.7 present the results for the case of a nitrogen carrier stream. The curves follow the same general format as those in Section 2.13. The results are even more favorable for N_2O_4 than for the hydrazine fuels.

Figure 3.11.3 shows the actual amount of N_2O_4/NO_2 condensed, as a function of temperature. Figure 3.11.4 presents the same information, but in terms of percentages of the initial mass of oxidizer in the vent stream, rather than total mixture. Figure 3.11.5 shows the total heat removal required to achieve any given temperature. This information is combined with the results for mass condensed in Figures 3.11.6 and 3.11.7, which show the heat removal per unit mass condensed. Figure 3.11.6 is a plot of total heat removal divided by total mass condensed at each temperature, while Figure 3.11.7 is a plot of the incremental heat removal divided by the incremental mass condensed.

Similar results are presented in Figures 3.11.8 through 3.11.11 for the case of a helium carrier stream. The plot of grams condensed per gram of initial mixture is omitted, since this result is virtually the same as the percent condensed result when the other constituent is helium.

In our Phase 5 Final Report,[4] we presented results of a computational exercise that showed N_2O_4/NO_2 vent flow rates of up to 14 grams per second (1.85 pounds per minute) during Space Shuttle loading, for a total oxidizer discharge of 60,600 grams (in a helium carrier stream). It is interesting to use this case as an example to which to apply our condensation results. Figure 3.11.8 shows that if we were to cool the vent stream to -11.8°F, at which point solid particles of the oxidizer would just begin to form, we could liquefy 92% of the oxidizer, at a total "cost" of 121 calories (removed) per gram condensed. Hence the highest oxidizer vapor flow rate would be reduced to about 1.1 grams per second (8.9 pounds per hour), the total mass of oxidizer vented would be reduced to 4850 grams (10.7 pounds), and the peak heat removal would be about 1600 calories per second: 22,500 Btu/hr, or about two tons of refrigeration.

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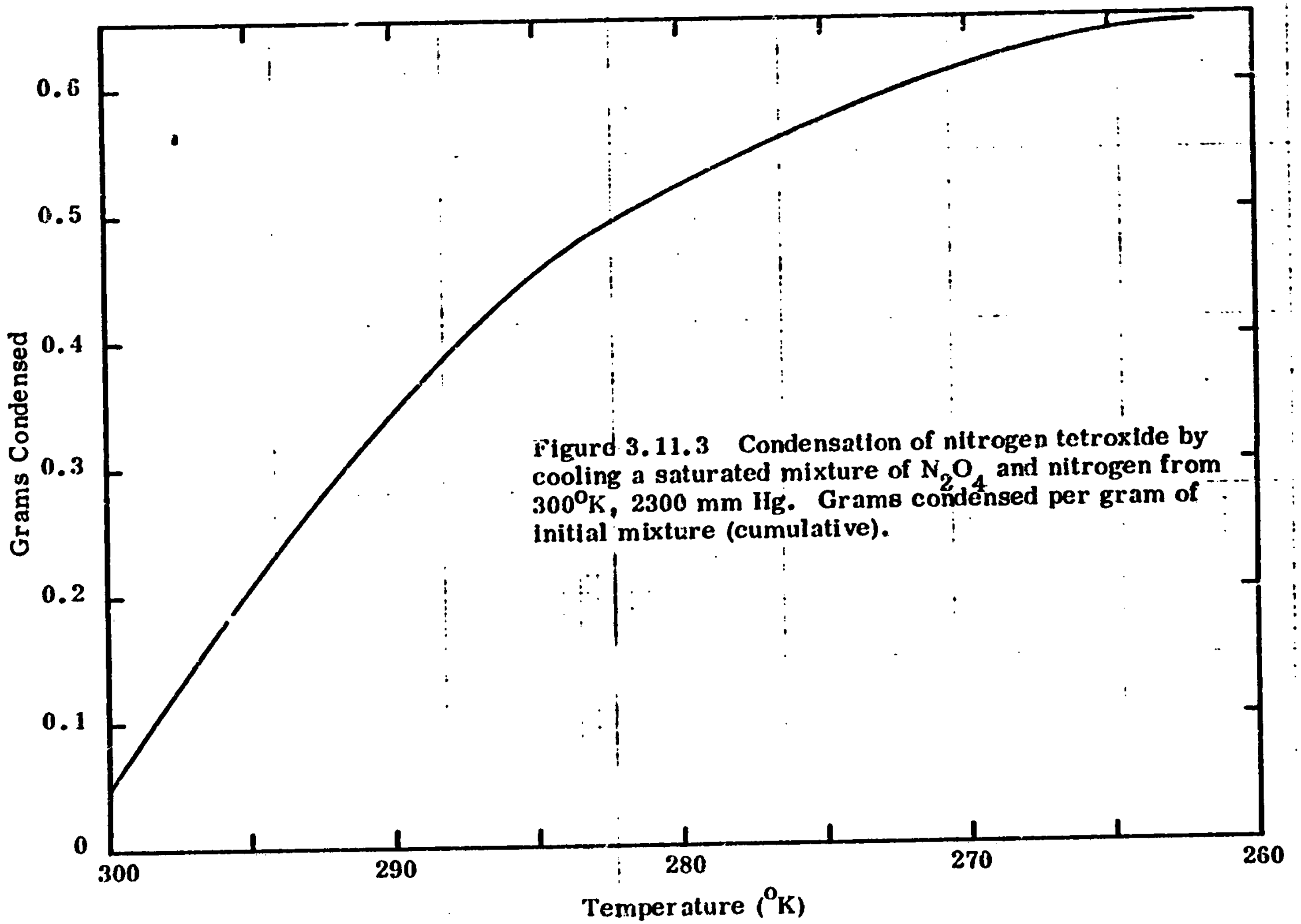
[4] Report Number ME-76-1, Florida Institute of Technology, Melbourne, Florida, 32901 (February 1976).



Figurd 3.11.3 Condensation of nitrogen tetroxide by cooling a saturated mixture of N_2O_4 and nitrogen from 300°K, 2300 mm Hg. Grams condensed per gram of initial mixture (cumulative).

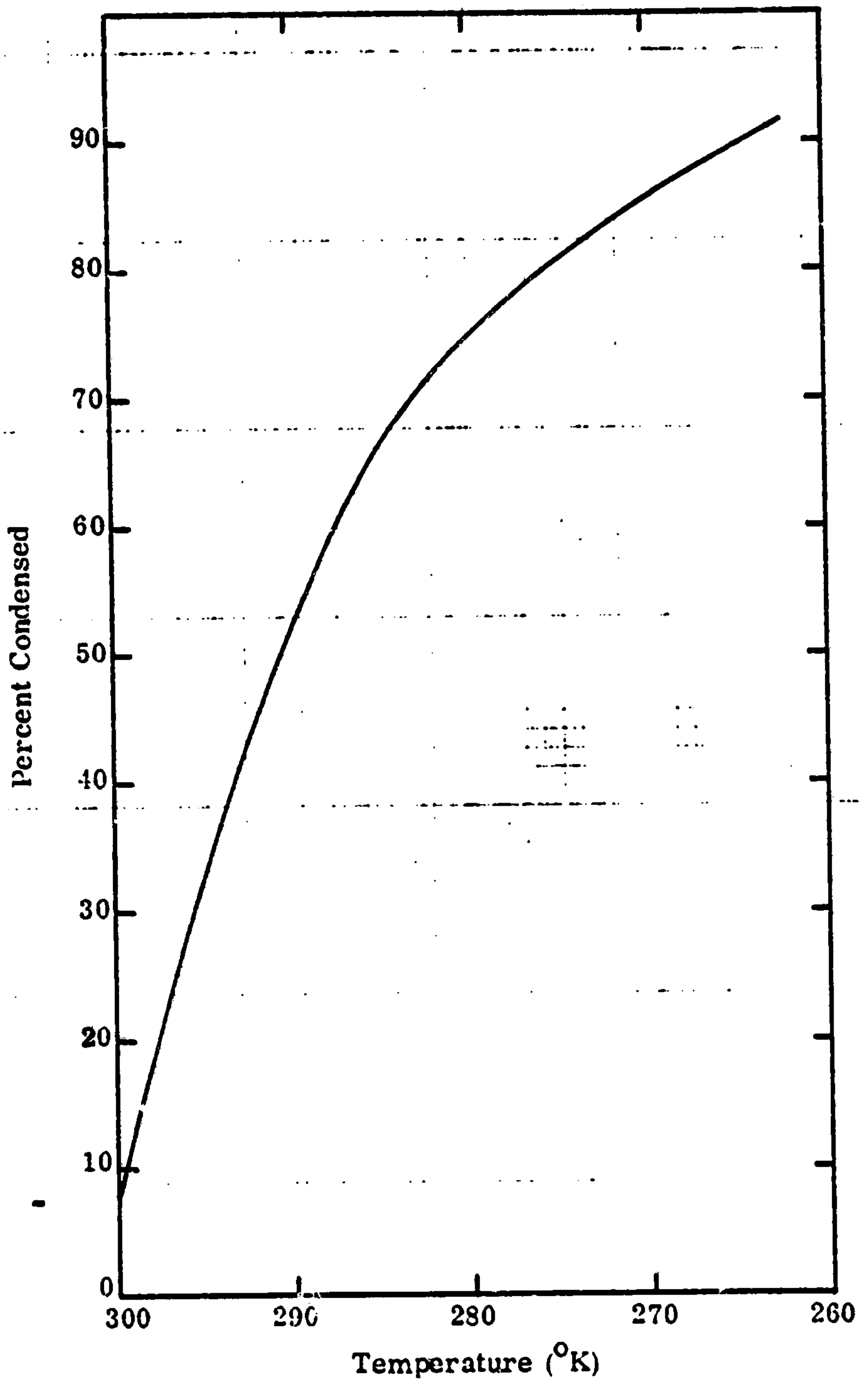


Figure 3.11.4 Condensation of nitrogen tetroxide from N_2 saturated with N_2O_4 vapor at 300°K, 2300 mm Hg.

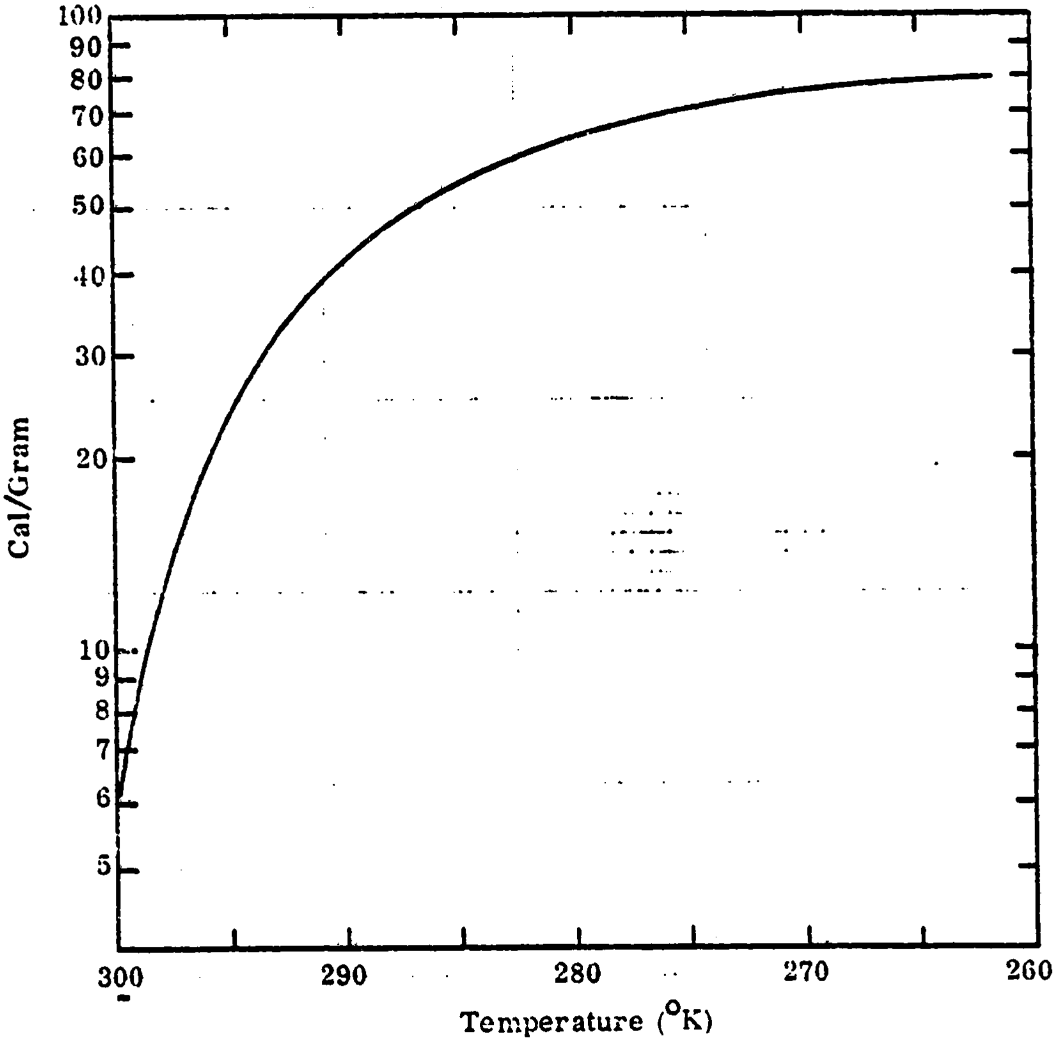


Figure 3.11.5 Required heat removal to cool and condense a saturated mixture of N_2O_4 and nitrogen from 300°K at 2300 mm Hg. Cal per gram of original mixture.

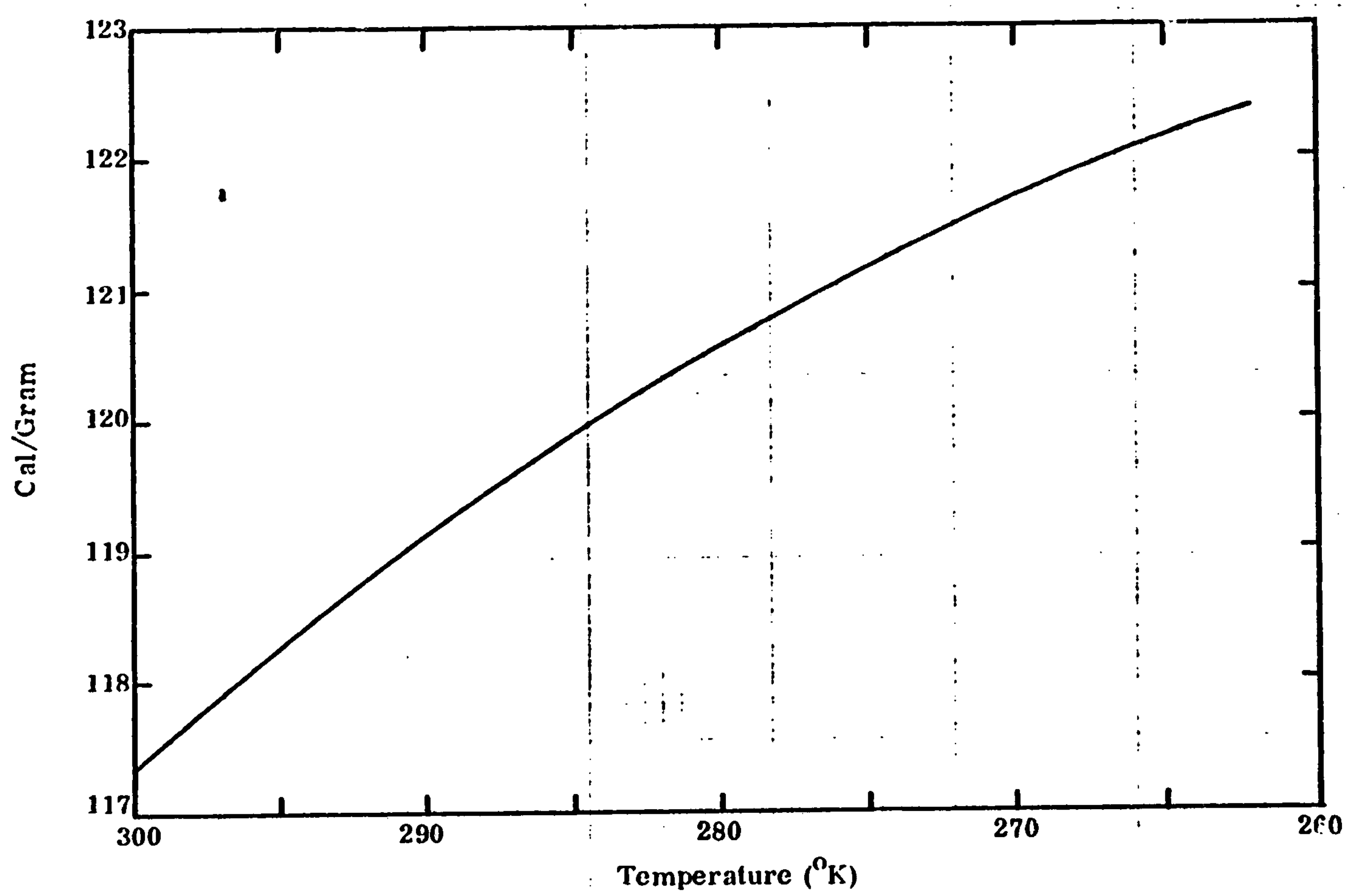


Figure 3.11.6 Condensation of nitrogen tetroxide by cooling a saturated mixture of N_2O_4 and nitrogen from 300^{o}K at 2300 mm Hg. Cal per gram condensed (cumulative).

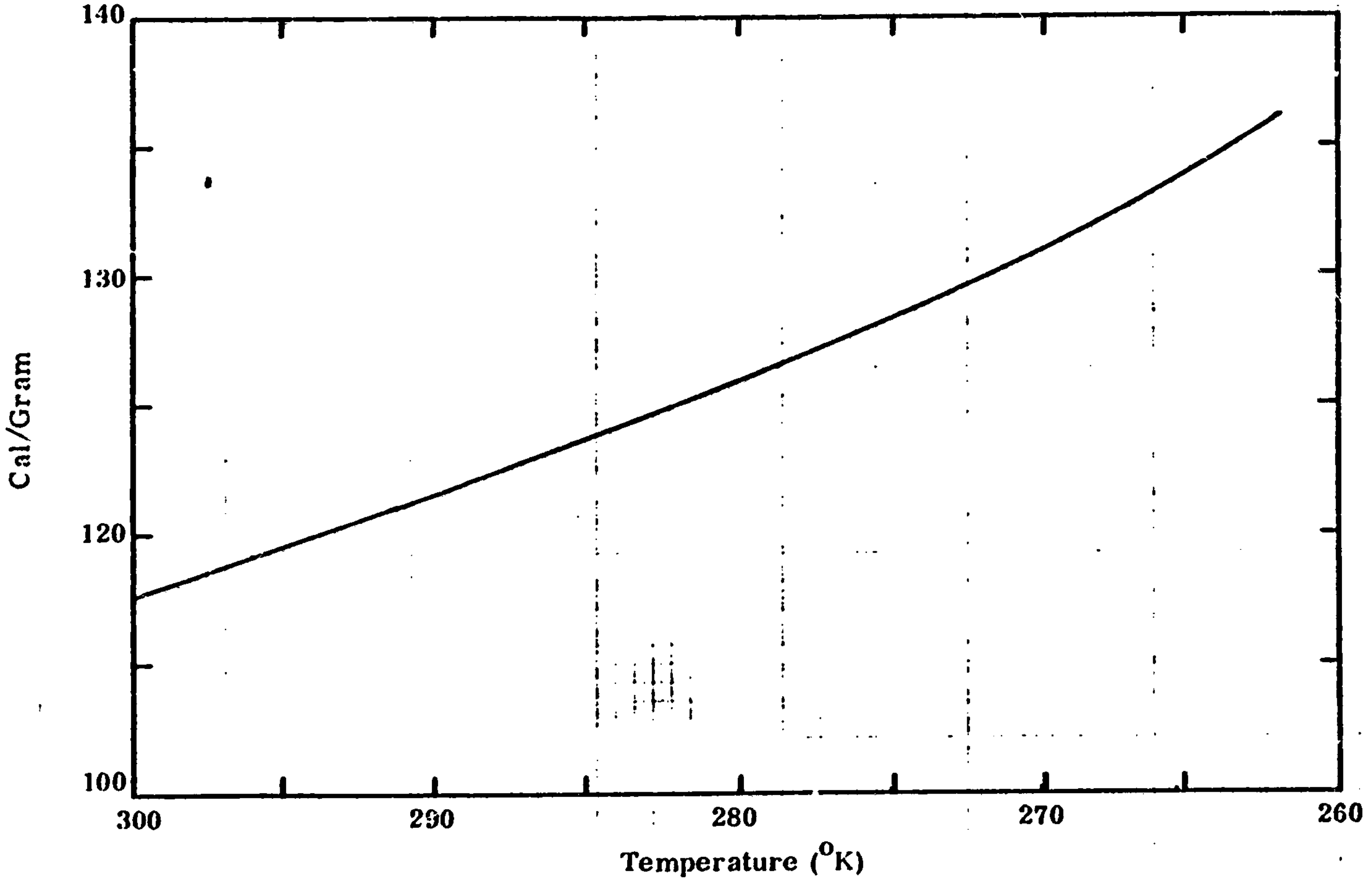


Figure 3.11.7 Condensation of nitrogen tetroxide by cooling a saturated mixture of N_2O_4 and nitrogen from 300^{o}K at 2300 mm Hg: cal per gram condensed (incremental).

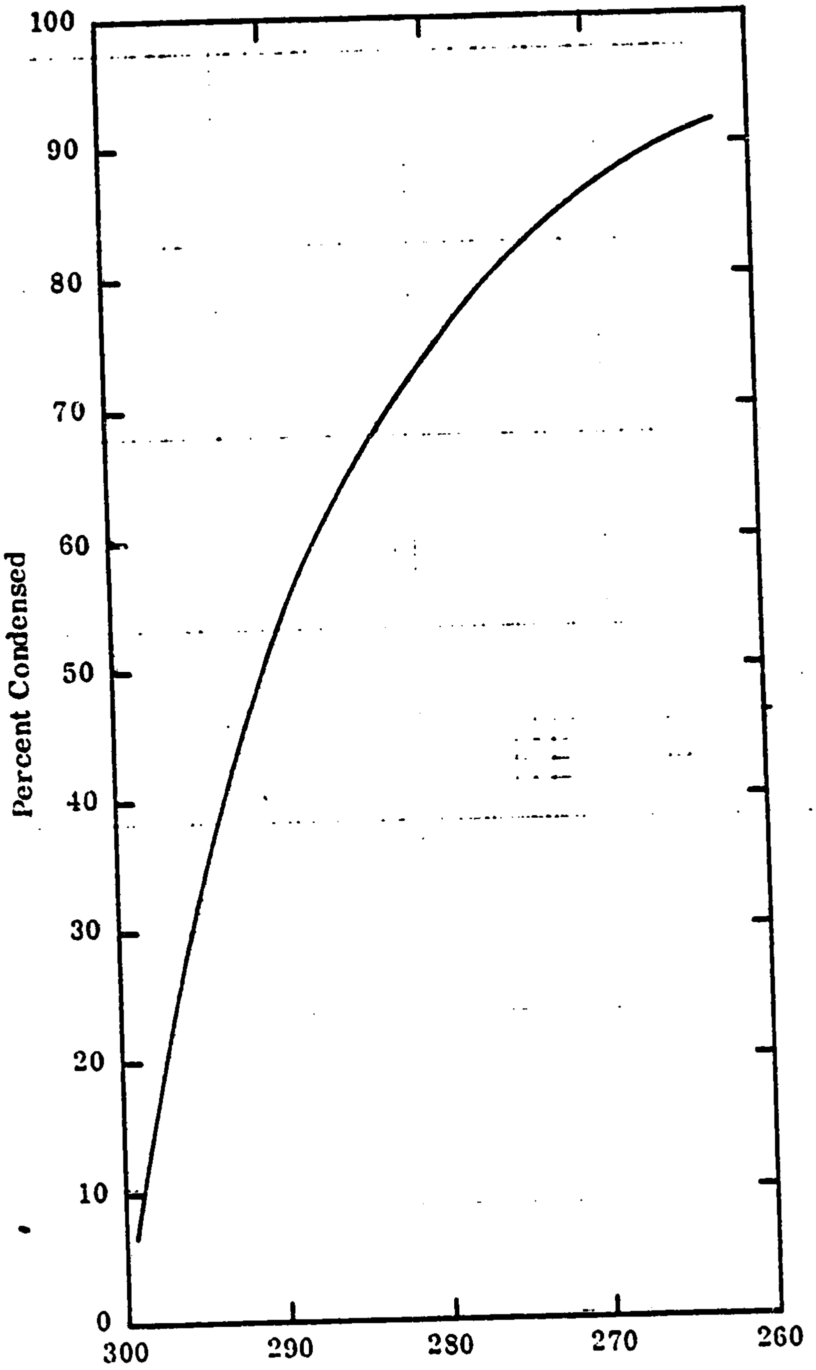


Figure 3.11.8 Condensation of nitrogen tetroxide from helium saturated with N_2O_4 vapor at 300°K, 2300 mm Hg.

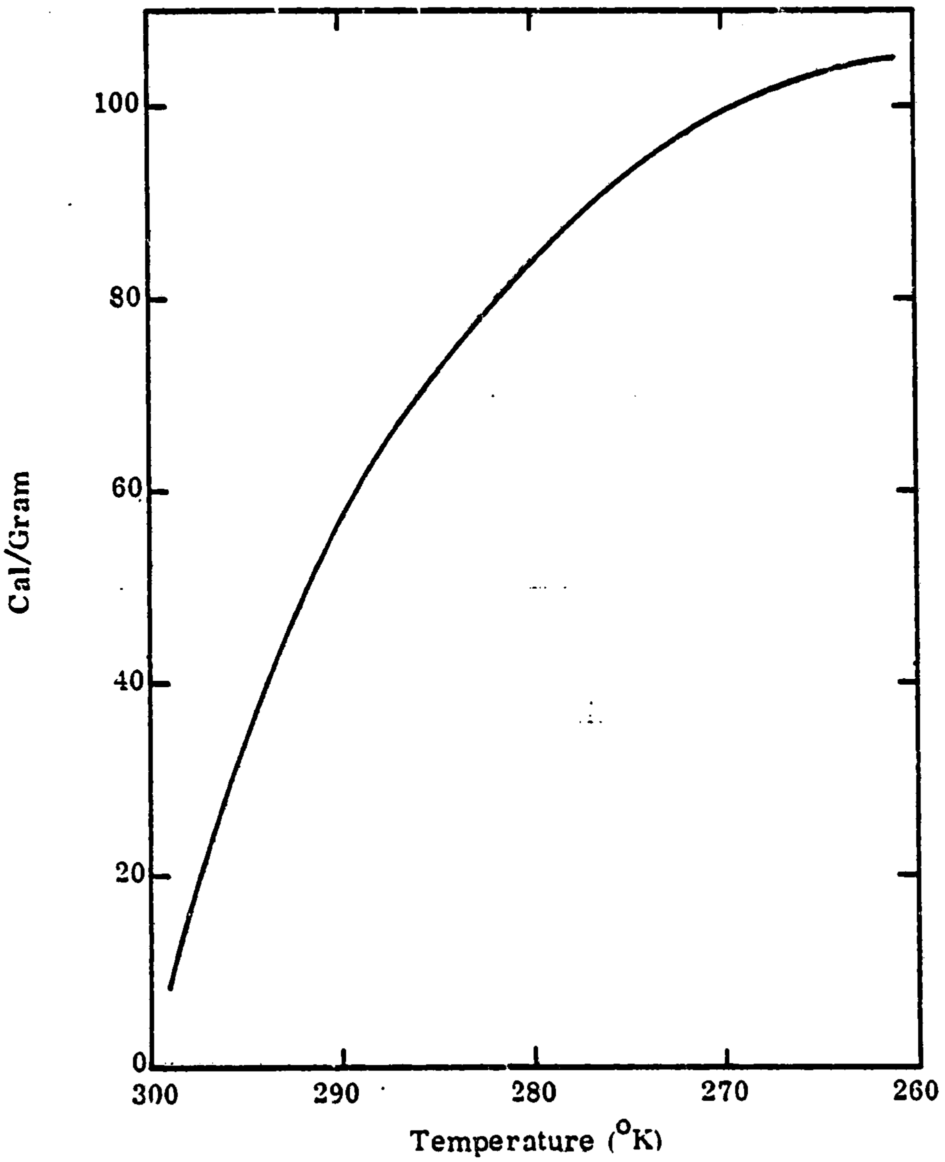


Figure 3.11.9 Required heat removal to cool and condense a saturated mixture of N_2O_4 and helium from 300°K at 2300 mm Hg. Cal per gram of original mixture.

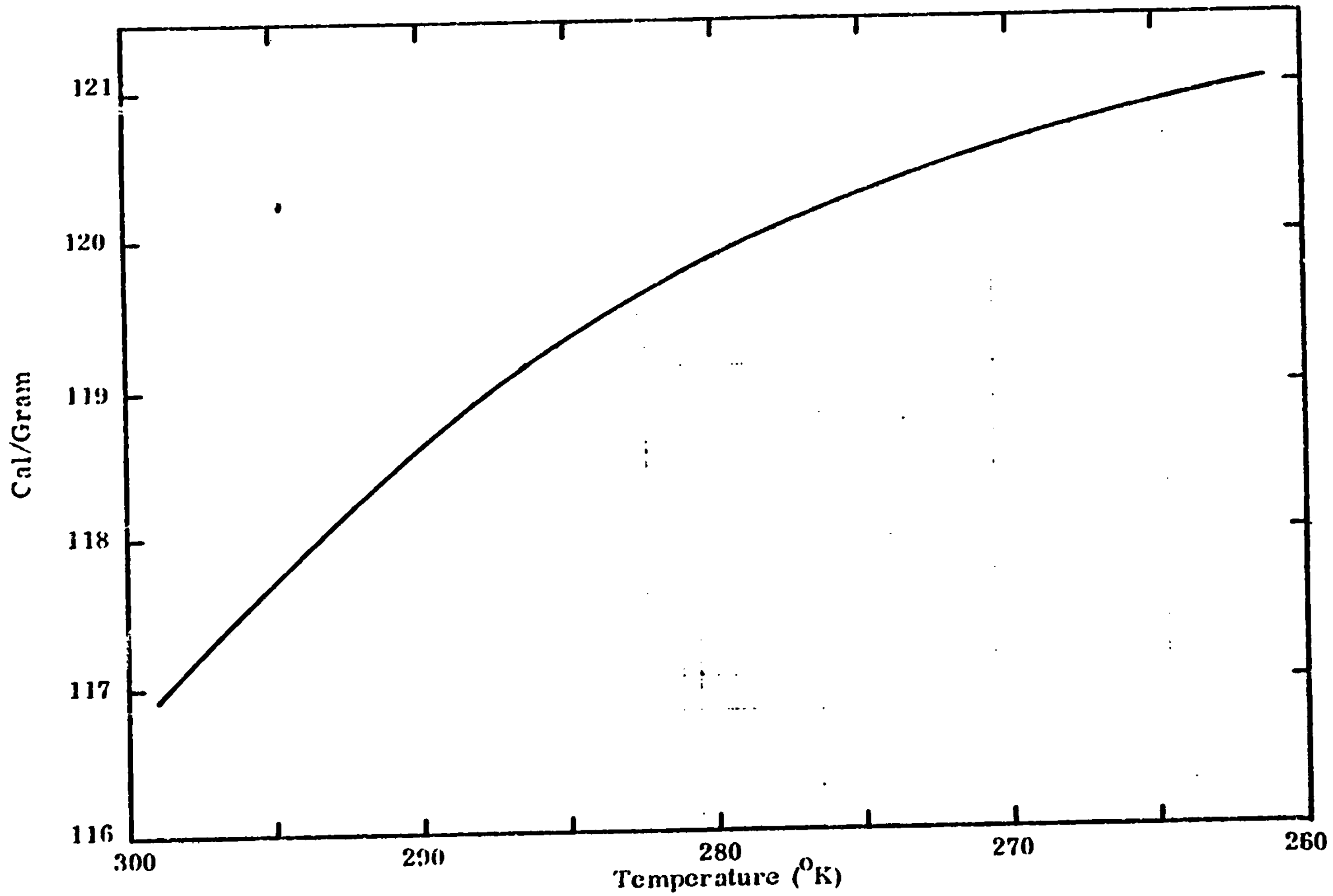


Figure 3.11.10 Condensation of nitrogen tetroxide by cooling a saturated mixture of N_2O_4 and helium from 300°K at 2300 mm Hg. Cal per gram condensed (cumulative).

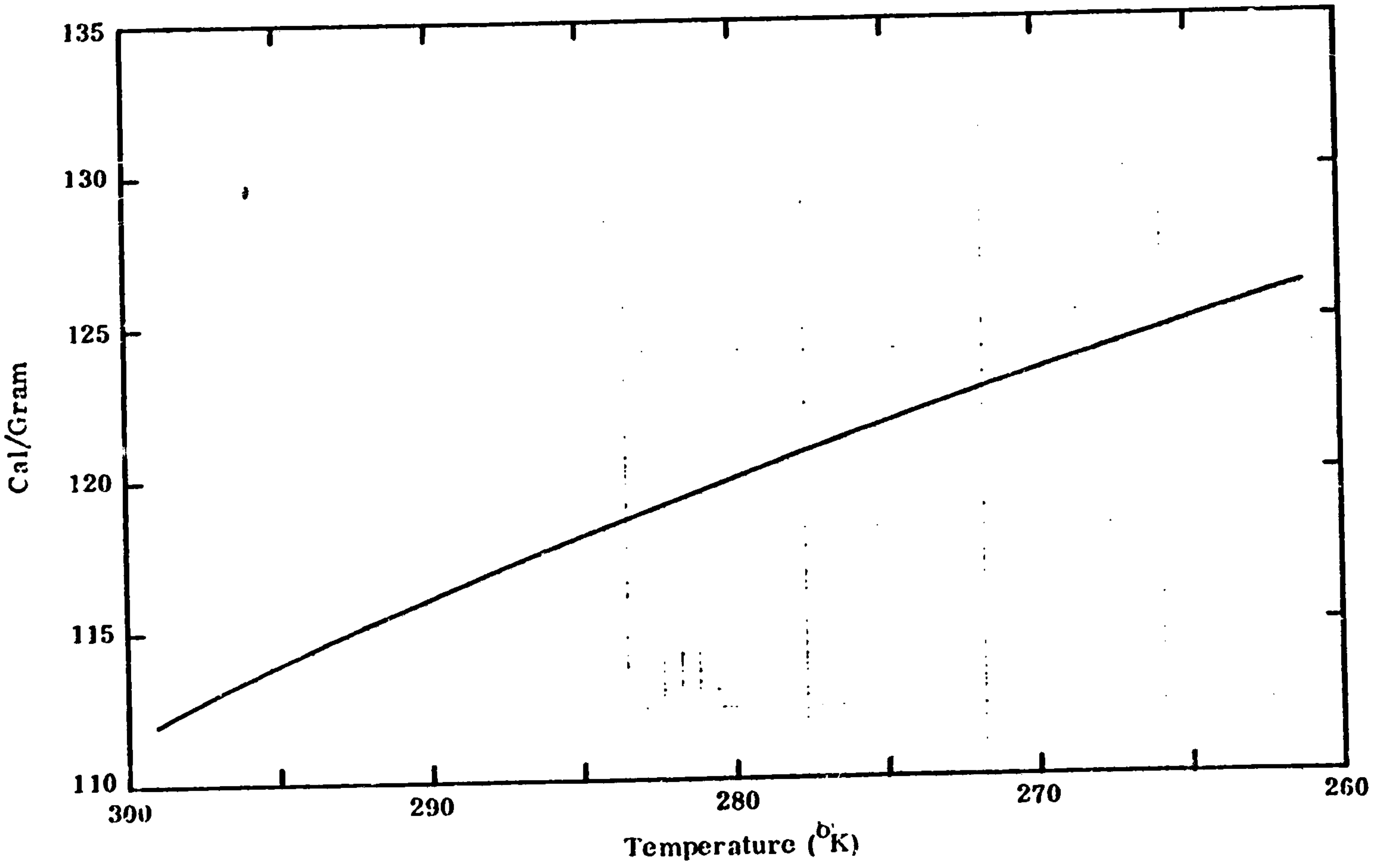


Figure 3.11.11 Condensation of nitrogen tetroxide by cooling a saturated mixture of N_2O_4 and helium from 300°K at 2300 mm Hg. Cal per gram condensed (incremental).

3.11.2 Experiments

A 500 ml. r.b. flask containing 50 ml. of N_2O_4 was connected to the top of a conventional reflux condenser, as shown in Figure 3.11.12. The condenser was cooled with water at various temperatures produced in a portable bath and circulator containing a refrigeration unit and a small water pump. The bottom of the condenser was equipped with a receiver flask and a side arm which led to a sparger and which in turn was inserted into a small beaker of water. The submersible pump used to circulate the cooling water was 1/150 horsepower, and produced a circulation of 10 liters per hour.

The N_2O_4 was heated to 35°C and the vapors condensed in the receiver flask. The cooling water temperatures, the percent of N_2O_4 recovered and the time required for recondensation are listed in Table 3.11.1.

TABLE 3.11.1

CONDENSATION OF N_2O_4

Cooling Water Temperature, °C	% Recovery of N_2O_4	Recondensation Time
-2.5	97%	10 minutes
0	88%	10 minutes
+5	80%	20 minutes

These results, obtained at one atmosphere rather than the higher pressure assumed in obtaining the analytical results, seemed to provide reasonably good verification of the results of the preceding section, and to reinforce our conclusions that condensation can be an effective means of recovering a high percentage of N_2O_4/NO_2 vapors from vent streams.

Another set of experiments on removal of N_2O_4 from a flowing gas mixture by condensation, performed by United Aircraft Research Laboratories, has also been brought to our attention. Their conclusions were as follows:

"1. A condenser system can be built in which two temperature zones can be maintained with a single cryogenic.

"2. When the condenser system is operated at a total pressure of one atmosphere and at a minimum temperature of -68°C with an inlet

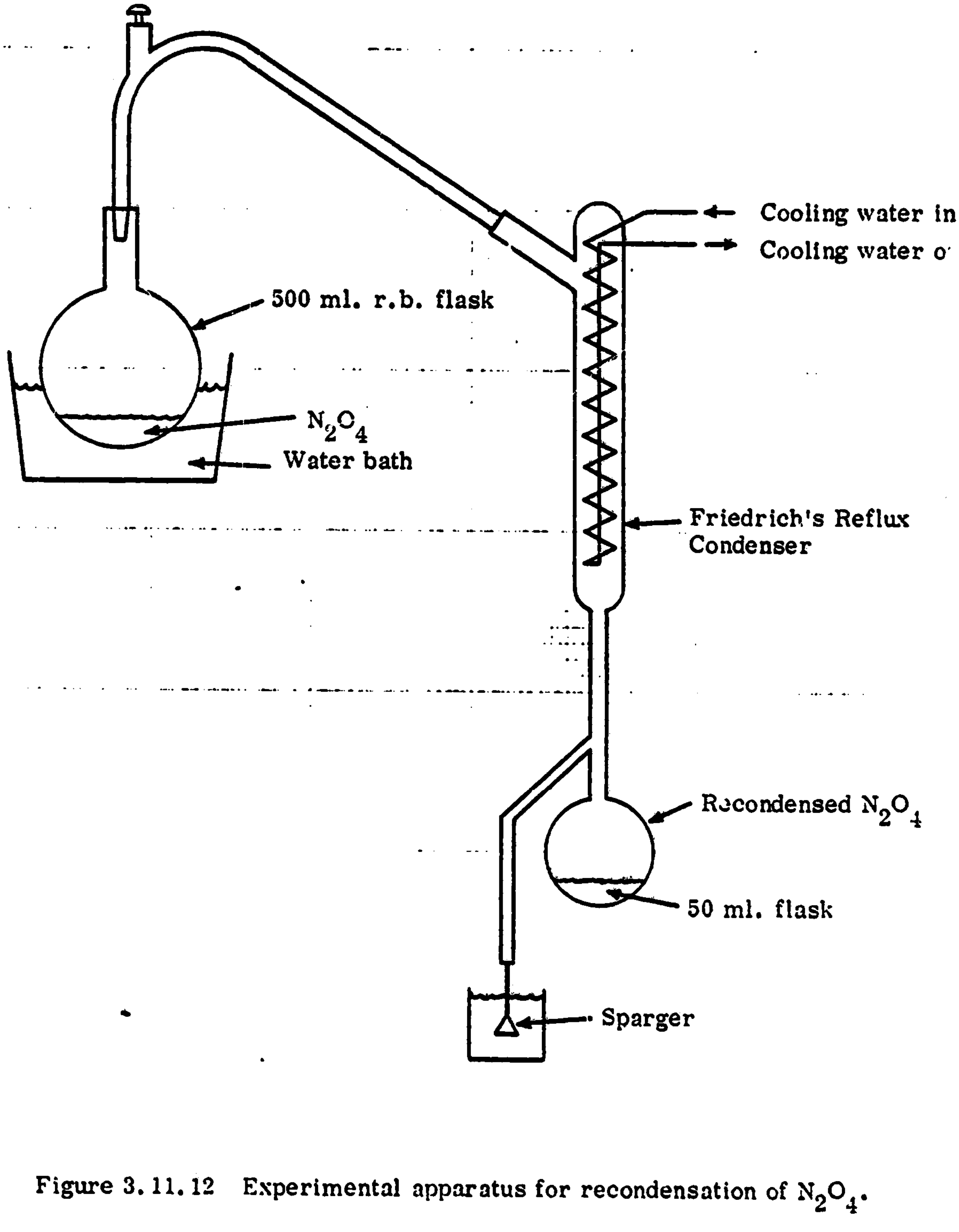


Figure 3.11.12 Experimental apparatus for recondensation of N_2O_4.

gas stream comprising an equimolar mixture of N_2O_4 and diluent, the minimum final concentration of nitrogen tetroxide will be about 750 ppm. Lower concentrations can be achieved by increasing the initial partial pressure of diluent, decreasing the final temperature of the condenser, or by air dilution of the gas stream emerging from the condenser."[5]

It is not clear from their description just how the N_2O_4 was ultimately recovered, or indeed whether the exposure of the N_2O_4 to these very low temperatures was such as to result in formation of solid particles. The topic of solidification, as opposed to simple condensation, is treated in the following section (3.12).

3.11.3 Condensation in Conjunction with Other Methods

It should be noted that a single vapor condensation stage could serve as both first stage and regeneration stage for a molecular sieve adsorption system. The molecular sieve would serve to achieve a low concentration effluent, but would not have to cope with the large quantities of N_2O_4 that would be necessary without the condensation stage. No scrubber/dryer system would be required during regeneration since the condensation stage would serve the same purpose if included in a regeneration loop. This combination is illustrated schematically in Figure 2.11.13. A scrubber could not be used in a similar fashion because of the intolerance of the molecular sieve for water.

A condensation stage could also be used upstream of a scrubber, to decrease the amount of solution required for scrubbing.

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4. Communication from David G. McMahon, Chief, Chemical Sciences, United Aircraft Corporation Research Laboratories, to H.H. Franks, DD-MDD-41, John F. Kennedy Space Center, dated February 10, 1975.

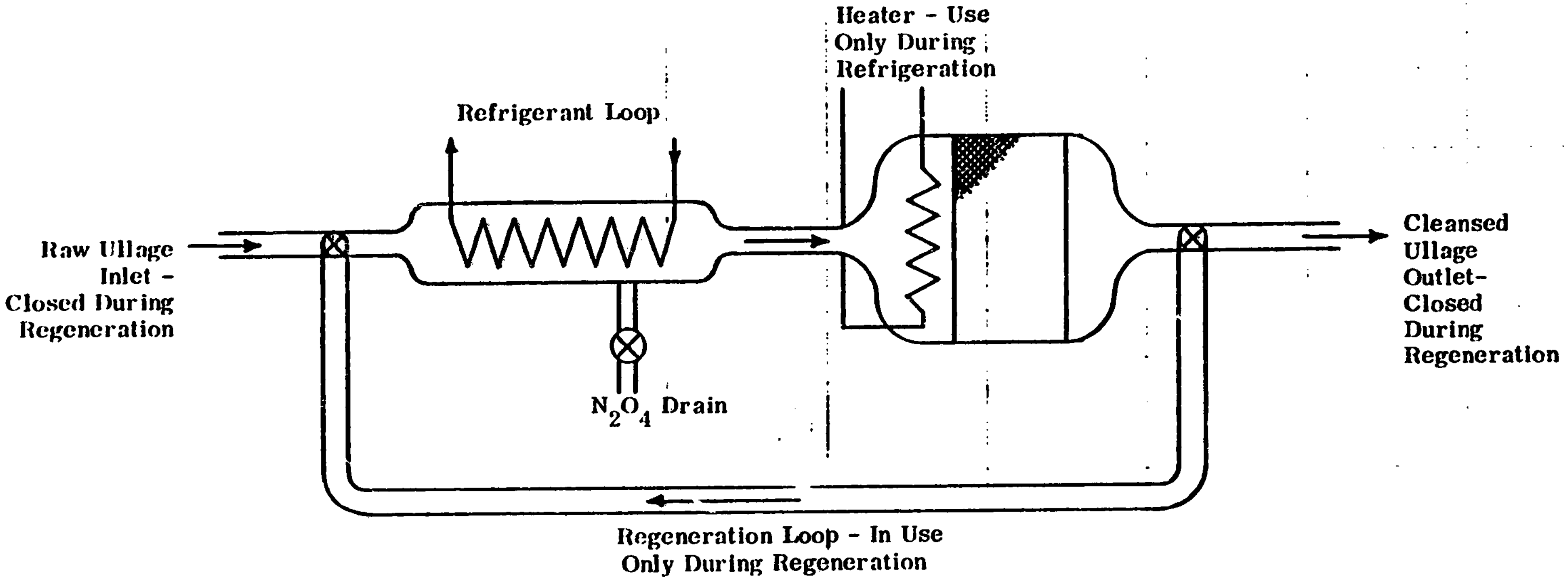

Figure 3.11.13 Schematic - vapor condensation unit followed by molecular sieve for cleaning of ullage. Condensation unit is used for regeneration of molecular sieve.

3.12 CRYOGENIC TRAPPING OF VAPOR

Cryogenic trapping refers to the use of liquid nitrogen systems in which gase gaseous effluent streams containing nitrogen dioxide and nitrogen tetroxide vapors are cooled to below the triple point of the oxidizer, resulting in accumulation of solid phase contaminant in a cold trap. This collected oxidizer than then be treated chemically and disposed of.

An intensive experimental program was performed by us to evaluate this means of cleaning gaseous effluents. The concept was not successfully demonstrated, although further development and testing might well establish the viability of this concept. Detailed results of our experiment program were not available in time for inclusion in this Handbook, but are available as a separate report.[1]

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[1] Thomas, John J.: 'Disposal of Hypergolic Propellants - Final Report, Task I, Phase VI." Florida Institute of Technology, Melbourne, FL August 1976.

3.13 UNTREATED DISPOSAL

3.13.1 Simple Dilution with Water

A fairly common disposal method for small quantities of N_2O_4 consists of simply diluting with water and transferring to the ground or a stream. The addition of water to N_2O_4 results in the formation of nitric acid and nitric oxide:

$$\frac{3}{2} N_2O_4 + H_2O \longrightarrow 2HNO_3 + NO$$

The State of Florida requires that when dumping an acid into a stream, the pH of the stream must not be changed by more than 1.0 pH unit. In the case of nitric acid, dilution to a normality of 1.0×10^{-6} would be necessary to obtain a pH of 6.0. This dilution requires about 1.6×10^{6} gallons of water per gallon of N_2O_4.

For disposal in significant quantities, attention would have to be given to means of assuring proper dilution prior to release. For example, a holding pond where pH could be monitored prior to release would be acceptable, as would a steady flow mixing apparatus.

Even with dilution to a safe level in terms of the strength of the acid, there remains the problem of generating large quantities of NO. Although the presence of NO is never so obvious as the presence of NO_2, it is itself a toxic gas, and eventually reacts with oxygen in the atmosphere to form NO_2.

3.13.2 Atmospheric Discharge

Probably the most common disposal method for N_2O_4 , up to the present time, has been direct release to the atmosphere. Vapors are vented to the atmosphere, usually via tall vent stacks or large air blowers and with some meteorological precautions (such as wind velocity and direction limitations). Liquids are allowed to simply evaporate or boil away due to the oxidizer's high vapor pressure at normal temperatures.

Vent stacks and blowers are both intended to move the toxic vapors away from the ground surface and to dilute the vapors, either by natural mixing or forced mixing with air. In the case of vent stacks, certain atmospheric conditions can result in concentrated vapors finding their way back to the surface. Blowers, in which the toxic stream is added to a large, high speed air stream, are a more positive means of achieving dilution. Both vent stacks and the blower units used in the Apollo program discharge highly visible, reddish brown plumes, however. Visible atmospheric discharges are of ever-increasing concern to the general public, and probably not without reason in the case of a highly toxic gas that can react with other trace contaminants in the atmosphere to form still more dangerous substances, including carcinogenic nitrosamines (see Appendix G).

Since the TLV for NO_2 is 9 milligrams per cubic meter of air, the evaporation of one gallon of N_2O_4 would require 6.1×10^5 cubic meters (2.2×10^7 cubic feet) of air to reduce the vapor concentration to a uniform level equal to the TLV throughout the air volume. Actually, of course, the concentration is never uniform and it is the peaks that we are concerned with; computational methods for prodicting peak concentrations for various vapor flow rates and atmospheric conditions are briefly discussed in Appendix G.

CHAPTER 4

INHIBITED RED FUMING NITRIC ACID (IRFNA)

4.1 MATERIAL DESCRIPTION

Inhibited Red Fuming Nitric Acid (IRFNA) (Fuming Nitric Acid Types IIIA and IIIB) is a highly concentrated nitric acid containing 81.6% to 84.8% nitric acid (HNO_3) by weight, with 13.0% to 15.0% disolved nitrogen dioxide (NO_2), 1.5% to 2.5% water, and 0.6% to 0.8% hydrogen fluoride inhibitor. It is a highly corrosive oxidizing agent that will vigorously attack most metals, and will react with many organic materials, spontaneously causing fire. It is hydroscopic, and will react with sea water, releasing large quantities of toxic oxides of nitrogen. It is soluble in water in all proportions, with an accompanying evolution of heat and oxides of nitrogen.

The fumes from IRFNA consist of HNO_3 vapor and NO_2, both of which are highly toxic. The Threshold Limit Values are 2 ppm and 5 ppm (by volume) in air respectively (5 mg/m^3 and 9 mg/m^3 by mass). NO_2, the monomer of N_2O_4, was discussed at greater length in the preceding chapter; see also Appendix G.

A few of the physical properties of IRFNA are given in Table 4.1.1.

TABLE 4.1.1
PHYSICAL PROPERTIES OF IRFNA[1]

Bubble Point (point at which liquid appears to boil) at normal atmospheric pressure	140°F (60°C)
Boiling Point of HNO_3	187°F (86°C)
Freezing Point	-61°F (-52°C)
Liquid Density at 77°F (25°C)	12.9 lb/gal (1.55 g/cc)
Critical Pressure	87.5 atm (1286 psia, 8.87×10^6 Pa)
Critical Temperature	520°F (271°C)
Vapor Pressure:	
0°F (-17.8°C)	0.2 psia (1.38×10^3 Pa)
77°F (25°C)	2.7 psia (1.86×10^4 Pa)
100°F (37.8°C)	5.0 psia (3.45×10^4 Pa)
148°F (64.4°C)	15.0 psia (1.03×10^5 Pa)

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[1] "Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation." Prepared by the Liquid Propellant Handling and Storage Committee assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD870259, May 1972.

4.2 RECOMMENDATIONS FROM OTHER SOURCES

The JANNAF Hazards Handbook contains a section on disposal of fuming nitric acids, which is quoted here in its entirety:

"Water is the most easily used and the most readily available decontaminating agent. Laboratory and field tests on reactions at 77°F between fuming nitric acids and aqueous 5 percent NaOH (caustic soda, sodium hydroxide), 5 percent $NaHCO_3$ (bicarbonate of soda), 5 percent Na_2CO_3 (sodium carbonate) and limestone indicate that approximately 50 percent more NO_2 fumes evolve during the treatment with the foregoing alkaline materials than are given off during water dilution. Concrete and asphalt contaminated with fuming nitric acids retain small amounts of acid in surface pores even though flushed with large quantities of water. The most practical decontamination procedures, therefore, are as follows:

"a. When fuming nitric acid is spilled on concrete or other hard surfaces having a proper drainage system and neutralizing pit and an adequate supply of water, complete washing down with water is sufficient. In enclosed areas, flush with large quantities of water, then spray entire working surface with a 5 percent solution of Na_2CO_3 (sodium carbonate).

"b. For spills on concrete, asphalt or other hard surfaces in the field where an adequate water supply is not available and where drainage is impossible, it is recommended that the surface be sprayed with a 5 percent solution of $NaHCO_3$ (sodium bicarbonate) or Na_2CO_3 (sodium carbonate) until bubbling ceases."[1]

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[1] "Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation." Prepared by the Liquid Propellant Handling and Storage Committee assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD870259, May 1972.

The TRW report[2] covered nitric acid along with a number of other widely used acids and other inorganic chemicals. The following excerpts from their "Evaluation of Waste Management Practices" for these substances refer to nitric acids in general, and not specifically to IRFNA:

"Waste streams containing acids, acidic oxides, or bases can be treated by neutralization (1) to form a neutral solution which can then be discharged safely, or (2) to yield an insoluble precipitate which can be removed by filtration."

"For the acids, acidic oxides and halides, soda ash-slaked lime solution is most commonly used. In the case of nitric and hydrochloric acids, the neutral solution of nitrate or chloride of sodium and calcium is formed and can be discharged after dilution with water."

"Ammonium hydroxide may be neutralized by nitric acid to form a solution of ammonium nitrate which can be used as fertilizer."

"Nitric acid forms a constant-boiling azeotrope with water (68% HNO_3 + 32% H_2O). The normal boiling point of the azeotrope is 120.5°C. Hence, under certain conditions, spent nitric acid can be recovered by steam distillation to yield concentrated acid."

The provisional limits for nitric acid recommended by the TRW study were 0.05 mg/m^3 as a contaminant in air and 0.25 mg/l in water and soil. These "Maximum Exposure Limits" are specifically related to release into the environment as a result of disposal, as opposed to the TLV's, which are concerned with worker safety. As a general rule, TRW's recommended provisional limits for atmospheric contamination are two orders of magnitude lower than the TLV's. TRW's overall recommendations for disposal of nitric acid was:

"Soda ash-slaked lime is added to form the neutral solution of nitrate of sodium and calcium. This solution can be discharged after dilution with water."[3]

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[2] Ottinger, R.S.; Blumenthal, J.L.; Dal Porto, D.F.; Gruber, G.I.; Santy, M.J.; and Shih, C.C.: "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste." Report No. EPA-670/2-73-053-1 (August 1973). NTIS PB-224 591. Volume XII, pages 106-108.

[3] Ottinger, et. al., op. cit., Volume I, page 173.

The manufacturing Chemists' Association recommendation for disposal of nitric acids in general is:

"Dilute and neutralize before disposal. Do not flush down drains where the acid will eventually polute streams, city sewage systems, etc."[4]

Hercules, Inc., a major manufacturer of nitric acids, also recommends neutralization with soda ash or lime.[5]

Allied Chemical Corp., a manufacturer of IRFNA, provided us with a recommendation for disposal of this substance in particular:

"Unwanted material may be disposed of by addition to a large volume of water containing an alkali such as caustic soda or soda ash to neutralize the acid and calcium chloride to precipitate the fluoride. The mixture should be settled and checked to be sure the pH is 7 or higher before decanting to waste. The sludge should be taken to a landfill area for disposal."[6]

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[4] Chemical Safety Data Sheet SD-5 (Revised 1961), page 15. Manufacturing Chemists' Association, 1825 Connecticut Avenue, N.W., Washington, D.C. 20009.

[5] Material Safety Data Sheet SOS-4, May 23, 1972. Synthetics Department, Hercules Incorporated, Wilmington, Delaware 19899.

[6] Communication dated October 9, 1973, from W.H. Weed, Supervisor, Chemicals Technical Service, Industrial Chemicals Division, Allied Chemical Corporation, P.O. Box 6, Solvay, New York 13209.

4.3 SIMILARITIES BETWEEN IRFNA AND NITROGEN TETROXIDE DISPOSAL

In most respects, IRFNA presents the same disposal problems as nitrogen tetroxide, and the various disposal methods are the same as those discussed in the preceding chapter. The vapors given off by IRFNA at low temperatures are primarily NO_2, and hence essentially the same as N_2O_4/NO_2 vapor. The addition of water to N_2O_4 results in the production of nitric acid, and hence aqueous mixtures containing N_2O_4 or IRFNA are virtually the same. The addition of water to either N_2O_4 or IRFNA results in the evolution of oxides of nitrogen in significant quantities, as well as increased temperature.

For these reasons, this chapter will concentrate on areas where there is some difference between the two oxidizers, and will not attempt to be a comprehensive discussion of disposal methods for IRFNA. Methods not discussed here, such as condensation, catalytic decomposition, plasma arc decomposition, etc., should all be appropriate for IRFNA as well as for N_2O_4/NO_2, and the discussions of Chapter 3 should in general apply. The chief exceptions will be in those cases where HF, present in small amounts in IRFNA, causes problems.

4.4 CHEMICAL NEUTRALIZATION

Water dilution followed by neutralization has in the past been the most common means of disposing of IRFNA; at the present time, the usage of IRFNA is practically nonexistent in this country. The waste IRFNA is typically diluted with water in the proportion 100:1 or so in a suitable tank or pond. The solution is then treated with one of a number of reagents, such as those in Table 4.4.1. The reagents are added slowly to allow heat dissipation, and in slight excess. A soluble calcium salt may be used with any of them, if desired, to precipitate the fluoride used as inhibitor. If fluoride removal is desired a filtration or settling step is required. The pertinent equations are:

1. $2HNO_3 + Na_2CO_3 \longrightarrow 2NaNO_3 + CO_2 \uparrow + H_2O$
2. $HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$
3. $HNO_3 + NH_4OH \longrightarrow NH_4NO_3 + H_2O$
4. $2HF + Ca(OH)_2 \longrightarrow CaF_2 \downarrow + 2H_2O$

   Filter, to Solid
   Waste Disposal

There are only minor differences in the three methods shown in Table 4.4.1 for performing the chemical treatments. For example:

1. The care required in mixing and handling the strongly caustic NaOH solution is a slight disadvantage for method (2).
2. The odor of NH_3 may be objectional for method (3).
3. The Na_2CO_3 method has an advantage with respect to ease in handling.

Use of other neutralizing agents than those shown in Table 4.4.1 is also possible. In particular, calcium carbonate (limestone) would have the advantage of accomplishing both the neutralization and the precipitation of CaF_2 without need for a second reagent. This insoluble compound could be used in a packed bed, either in the pond itself (see Section 3.3) or in a separate treatment loop.

The effectiveness of the neutralization disposal method for IRFNA has been amply demonstrated over the years. The major disadvantages are the high chemical and equipment cost incurred in disposing of the waste IRFNA,

TABLE 4.4.1
NEUTRALIZATION REAGENTS FOR IRFNA

Method	Neutralizing Reagent	Products Formed	Chemical cost per lb IRFNA*
1.	Na_2CO_3	Solution of $NaNO_3$, $Ca(NO_3)_2$, CO_2, trace of HF	\$.055
2.	NaOH	Solution of $NaNO_3$, trace of HF	\$.020
3.	NH_4OH	Solution of NH_4NO_3, trace of HF	\$.185
4.	$Ca(OH)_2$ (in addition to any of the 3 reagents above.	CaF_2 precipitate	-----

and the NO_x evolution that may occur during dilution. Means of precluding this NO_x evolution should receive further study.

Further dilution with water is necessary before the solution can be pumped to a stream or other body of water because of the nitrates (NO_3^-) formed. To dilute to the provisional limit of 45 mg/l (as NO_3^-) recommended by the TRW report[1] for ammonium nitrate and sodium nitrate requires approximately 1.7×10^5 liters (28,000 gallons) of water per gallon of IRFNA. This amount of water would reduce the HF concentration to about 0.4 mg/l which is somewhat higher than the 0.1 mg/l provisional limit recommended in the TRW report,[2] thus indicating the need to precipitate the fluoride.

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[1] Ottinger, et al, op. cit., Vol XII, p. 78

[2] Ibid., page 105.

4.5 INCINERATION

Insofar as we have been able to ascertain, incineration has never actually been used as a means of disposal for IRFNA. There seems to be no reason why it could not be used, however, with results quite comparable to nitrogen tetroxide (see Section 3.6.) In the case of the Thermal Research incinerator used at Cape Canaveral Air Force Station, IRFNA is included in Pan American's "Standard Practice Instruction No. 41-26-013", dated April 29, 1971, and hence could be incinerated as a routine matter; to our knowledge, none has actually been disposed of in this manner.

The presence of HF in IRFNA presents an added difficulty relative to N_2O_4. A scrubber on the exhaust stack of the incinerator will probably be necessary to remove the HF and any fluorine compounds formed during the combustion process.

The higher boiling point of IRFNA, relative to N_2O_4, might require some modification of the injection system used to atomize or vaporize the waste oxidizer as it enters the combustion chamber.

4.6 ABSORPTION OF VAPOR

The scrubbing technique with plain water, solvent or dissolved reagent has been used successfully for years by industry as a disposal method for many gases, mists and particulates, including nitric acid vapors and oxides of nitrogen associated with the production and use of nitric acid (Section 3.9). For small installations, either plain water or alkaline solution scrubbing may be used to reduce NO_2 and HNO_3 emissions. The usual problem exists (see Chapter 3) of formation of insoluble NO when NO_2 and water combine, and hence considerable NO emission is to be expected using this method. It is likely that this problem can be eliminated by proper use of a NaOH scrubbing solution, in view of the results we obtained in the case of nitrogen tetroxide, as reported in Section 3.9. No tests of this method using IRFNA have been performed, however.

Regardless of the method used, water alone or alkaline solution, the amount of nitrate released will be the same, but the pH of the effluent solution is controlled in the case of alkali addition.

4.7 REMOVAL OF FLUORIDES FROM EFFLUENT STREAMS

IRFNA contains approximately 0.7% HF (on a mass basis) as a decomposition inhibitor. HF and the fluorides that will be formed as products of reaction of HF with neutralizing reagents are toxic substances whose release into the atmosphere or water streams must be controlled to low limits.

One method for removing fluorides from waste liquid effluents is addition of a soluble calcium salt under controlled pH. Insoluble CaF_2 will precipitate out. This precipitate may be separated by filtration, settling or other suitable unit operation. A residual amount of CaF_2 will remain in solution due to its slight solubility in water. It is only by further dilution with H_2O that the residual CaF_2 may be reduced to an acceptable level.

To evaluate the effectiveness of this method, a series of experiments was performed. The solubility of CaF_2 in pure water is 17 ppm; our objective was to determine whether the solubility in a solution of treated IRFNA would be sufficiently close to this figure to give reasonable levels of fluoride precipitation.

Samples of IRFNA were diluted with water and neutralized using sodium carbonate, Na_2CO_3. The dilution yielded a working solution with nitrate concentrations between 2.2 and 2.6%, and fluoride concentrations of approximately 200 ppm. The sodium carbonate was added to yield a pH between 9.5 and 9.8 except for one run, where only enough was added to reach approximate neutrality.

Solutions of soluble calcium salt, $CaCl_2$ or $Ca(OH)_2$, were added in excess to provide the Ca^{++} ion in at least 2 to 5 times the stoichiometric quantity required for precipitating the contained fluoride ion. After standing from 1 to 24 hours to allow reaction or crystallization of CaF_2, the treated solution was filtered through a millipore apparatus using a 0.45 micron pore size filter. Analyses were performed on original and filtered solutions for NO_3^- and F^-. The results of the five tests are presented in Table 4.7.1.

These results were quite disappointing in terms of the effectiveness of this method for removal of fluorides from treated IRFNA effluent streams. The solubility of CaF_2 in these streams is just too high - on the order of 100 ppm or higher, as opposed to the 17 ppm obtained in pure water - to allow good yields of the solid precipitate.

In an attempt to achieve better results, a number of other experiments were performed in which the pH was adjusted at levels all the way from 1.2 to 12.5, and other calcium salts - $Ca_3(PO_4)_2$ and $Ca(H_4PO_4)_2$ - were used. The results were not substantially different from those presented in Table 4.7.1. Our conclusion at this time is that the problem lies with the nitrate concentration - that the only way to decrease the solubility of CaF_2 is to decrease the concentration of NO_3^- ions in the treated solution. Since the nitrate concentration is not affected by neutralization or other chemical treatments, the only means of achieving a lower concentration of nitrates is by dilution. This dilution would probably result in lower fluoride concentrations - final as well as initial - but it is not at all certain that the absolute quantities of fluoride in the final solution would be reduced.

TABLE 4.7.1

DATA ON REMOVAL OF FLOURIDE FROM DILUTED IRFNA

Run #	Initial Concentration		Final Fluoride Concentration	% Fluoride Removed	pH
	Nitrate ppm	Fluoride ppm			
1		205	150	27	9.8
2	26,400	195	115	40	9.7
3	26,400	150	80	46	9.7
4	22,000	170	105	38	9.5
5	26,400	205	125	39	7.2

Average ~ 38% fluoride removed.

At this time, then, we know of no really effective means of removing fluorides from treated (or diluted) IRFNA liquid effluent streams. Dilution is the only means of achieving the "Provisional Limit", 0.6 to 1.7 ppm in water, recommended in the TRW report[1] for disposal of fluoride-containing effluents.

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[1] Ottinger, R.S., et al, op. cit., Vol XII, pages 12, 196.

In cases where some of the fluoride is precipitated as CaF_2, disposal of the precipitate should follow the guidelines established in the TRW report in connection with formation of the same waste product during treatment of plating, wash and tin recovery wastes from halogen tin lines used in tin plating:

"To allow economic recovery, the discharged, alkaline CaF_2 slurry should be lagooned . . . The separated CaF_2 should then be dried, and re-used as metallurgical grade CaF_2 in steel mill operations. Where economic recovery is not feasible, the sludge should be added to a landfill."[2]

It should be mentioned that calcium compounds, such as calcium carbonate (limestone), could probably be used economically for the initial neutralization step itself. The precipitation of a portion of the CaF_2 formed would then be an added benefit albeit a minor one associated with this choice of alkaline material.

The presence of HF in gaseous effluent streams also presents a problem. The Threshold Limit Value is 3 ppm by volume in air (2 mg/m^3), and the Maximum Exposure Limit for atmospheric disposal recommended in the TRW report is two orders of magnitude smaller.[3]

Removal from the waste stream can be readily accomplished by means of either absorption (scrubbing) or adsorption. One operational scrubbing system was described for us by Dr. Ottinger:

"The HF laser system exhausts its gases through a steam ejector system which acts very similar to a venturi scrubber. The water ejected in the latter stages of the ejector is alkaline, forming soluble salts with the absorbed HF. The liquid effluent from the ejector is passed through a limestone packed bed which fixes the fluoride ion as highly insoluble calcium fluoride. The water from the process, which is virtually free of fluoride ion, is put into a holding pond and used as process water."[4]

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2. Ottinger, R.S., et al, op. cit., Vol XII, page 13.

3. Ottinger, R.S., et al, op. cit., Vol XIII, page 104.

4. Ottinger, R.S., TRW Systems Group, One Space Park, Redondo Beach, California 90276. Written communication dated 25 October 1974.

In our applications, the problem of CaF_2 solubility would arise in cases where the scrubber effluent contained significant nitrate concentrations.

Adsorbents mentioned in the TRW report as potential means of recovery of HF from gaseous effluent streams are "activated carbon, alumina, silica gel, and various molecular sieves."[5] Our work using these adsorbents for hydrazine and nitrogen tetroxide vapors was described in Sections 2.15 and 3.10.

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5. Ottinger, R.S., et al, op. cit., page 109.

4.8 UNTREATED DISPOSAL

Far more water would be required to dilute untreated IRFNA to a normality of 1.0 x 10^{-6}, as required to achieve an effluent with a pH of 6 (see Section 3.13.1), than the 28,000 gallons H_2O per gallon IRFNA needed to reduce the nitrate concentration in a chemically treated solution to the 45 mg/l provisional limit (Section 4.4). In cases where it is feasible to use such large quantities of water, there is probably some advantage to the fact that additional ionic species - sodium, ammonium, calcium, etc. - are not introduced into the effluent. The problem of evolution of oxides of nitrogen during dilution is a problem, as always.

Untreated atmospheric discharges present the same problems as those discussed in Section 3.13.2 with regard to N_2O_4/NO_2, with the added problems of HNO_3 and HF vapors, both of which have much lower TLV's than nitrogen dioxide (3 ppm for HF and 2 ppm for HNO_3, versus 5 ppm for NO_2). In view of the ease of scrubbing the HNO_3 and HF, and at least the major part of the NO_x, from these gaseous streams, there would seem to be no justification for ever discharging IRFNA vapors directly to the atmosphere.

CHAPTER 5

HYDROGEN PEROXIDE

5.1 MATERIAL DESCRIPTION

Propellant grade hydrogen peroxide is a clear, colorless liquid, slightly more viscous than water, containing from 90% to 98% H_2O_2, the remainder being water. It is an active oxidizing agent, and can initiate the combustion of more organic materials. It also decomposes rapidly on contact with many inorganic compounds, yielding water, oxygen and heat. The amount of heat released is normally such that all of the water formed will be superheated steam.

Hydrogen peroxide is miscible with water, alcohols, glycols, acetates, acids, and ketones. It is nearly insoluble in petroleum ether, toluene, styrene, carbon tetrachloride, chloroform, kerosene, fuel oil, and gasoline. Its reactivity can be quickly reduced by dilution with water. On the other hand, it can form explosive mixtures with many organic liquids, both soluble and insoluble.

As long as contamination is avoided and containers are passivated, hydrogen peroxide is relatively stable, decomposing at a rate of 1% per year, or less, at 70°F. The decomposition rate approximately doubles for each 15°F increase in temperature. Small quantities of contamination - especially alkaline material or heavy metals - can cause runaway decomposition. The tendency toward rapid decomposition in the presence of contaminants can be counteracted to some extent by certain organic and inorganic stabilizers. Once underway, accelerating decomposition can be brought under control by the addition of phosphoric acid.

Vapor concentrations of hydrogen peroxide above 26% by volume (40% by weight) in air become explosive at atmospheric pressure in a temperature range below the boiling point, and can be ignited by a spark.

Health hazards associated with concentrated hydrogen peroxide result from its strong oxidizing properties. Irritation of the eyes and respiratory tract, burns, and delayed but severe eye damage can occur. The TLV is 1 ppm by volume in air (1.5 mg/m^3).

Some of the physical properties of hydrogen peroxide are given in Table 5.1.1.

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1. The material in this section is based on Chapter 13 of "Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation", prepared by the Liquid Propellant Handling and Storage Committee assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD 870259, May, 1972.

TABLE 5.1.1

PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE[2]

Property	90% Concentration (by Wt.)	98% Concentration (by Wt.)
Boiling Point at One atmosphere	286°F (141°C)	299.5°F (148.6°C)
Freezing Point	12°F (-11°C)	27.5°F (-2.5°C)
Liquid Density at 68°F (20°C)	11.6 lb/gal (1.387 g/cc)	11.95 lb/gal (1.436 g/cc)

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[2] "Chemical Safety Data Sheet SD-53." Manufacturing Chemists Association, 1825 Connecticut Avenue, N.W., Washington, D.C. 20009. Revised 1969. There seems to be considerable disagreement over the exact properties of hydrogen peroxide, which are strongly dependent on the water content, and are all approximately linear at H_2O_2 concentrations above 90%. The data quoted here are in close agreement with those given by one manufacturer, FMC Chemicals, Inorganic Chemicals Division, 633 Third Avenue, New York, N.Y. 10017 (Bulletin No 46). There is somewhat more discrepancy relative to the data in the JANNAF Hazards Handbook (see footnote 1).

5.2 RECOMMENDATIONS FROM OTHER SOURCES

The JANNAF Hazards Handbook[1] recommends that "Containers of propellant grade hydrogen peroxide should be taken to an isolated place, uncapped, tipped over, and emptied, washing the peroxide away with large quantities of water."

The MCA states that "Hydrogen peroxide is an exceptionally pure product and contains no contaminants that would cause surface water pollution, or interference with sewage. Its decomposition products are pure water and oxygen. However, strong hydrogen peroxide should be diluted with copious quantities of water before disposal to prevent strong reaction with organic materials and to prevent injury to fish life since there is some evidence that high concentrations of hydrogen peroxide are harmful to certain fish."[2]

The TRW Report[3] recommends that "Wasted concentrated hydrogen peroxide can be disposed of by dilution with water to release the oxygen. Agitation would accelerate the decomposition. After decomposition, the waste stream may be discharged safely."

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[1] "Hazards of Chemical Rockets and Propellants Handbook, Volume III: Liquid Propellant Handling, Storage and Transportation." Prepared by the Liquid Propellant Handling and Storage Committee assisted by the Committee on Environmental Health and Toxicology, JANNAF Propulsion Committee, Hazards Working Group. AD 870259, May 1972. Pages 13-14.

[2] "Chemical Safety Data Sheet SD-53." Manufacturing Chemists Association, 1825 Connecticut Avenue, N.W., Washington, D.C. 20009. Revised 1969. Page 30.

[3] Ottinger, et al, op. cit., Volume XII, pages 107-108.

5.3 DISCUSSION AND CONCLUSIONS

The choice for disposal of liquid hydrogen peroxide is basically one of whether to decompose the material before adding it to a water stream or large body of water, or not. In either case, dilution with water to safer concentrations is a necessary first step; a ratio of five parts water to one part H_2O_2 is probably more than adequate in most cases. In cases where harm to fish life is of concern, either dilution with copious quantities of water or prior decomposition will be necessary.

The table below shows adiabatic decomposition temperature and active oxygen content as a function of H_2O_2 concentration, as a guide in dilution.

Concentration		30%	50%	70%	90%
Adiabatic Decomposition	°C		100	233	740
Temperature	°F		212	451	1364
Active Oxygen Content	(Wt %)	14.1	23.5	32.9	42.3

Decomposition of the hydrogen peroxide prior to disposal may be hastened by use of a catalyst; platinum and silver screens have been used for this purpose. W. R. Grace and Co. of Baltimore, Maryland, recommended the use of their Grade 908 manganese catalyst when we contacted them. Many other materials could also be used. Alternatively, alkaline material such as sodium hydroxide (NaOH) can be added. One organization that we contacted dilutes the H_2O_2 to between 25 and 40 weight percent and then adds NaOH to a concentration between 0.5 and 1.0 weight percent. At 100°C decomposition is 95% complete in one hour.

Addition of alkaline material has the disadvantage that any material that could be added is going to be more harmful to the environment, in the long run, than the hydrogen peroxide itself. Although the small quantities involved may render any associated problems insignificant, it still seems a shame to contaminate a material that is non-toxic and an excellent oxygen source just for the sake of disposal.

If the H_2O_2 is diluted with water containing quantities of organic material, the organic material will likely serve as a catalyst and also be oxidized by the oxygen produced during dissociation, forming CO_2 and N_2O. In this case, the water will be returned to the environment in a more pure condition than its "natural" state.

The use of H_2O_2 as a source of supplemental oxygen has been successfully demonstrated by DuPont for several prevalent problems in both industrial and municipal waste treatment systems.[1] Special emphasis has been placed on its use as a substitute source of oxygen that can be intimately mixed with the water and organisms, without requiring elaborate equipment.

In general, it would seem that the best disposal method for H_2O_2 is dilution followed by direct addition to a stream or other body of water where its high active oxygen content will be beneficial in increasing the dissolved oxygen (D.O.) content of the water, converting organic material to CO_2 and H_2O and killing anaerobic bacteria, which are a major source of infectious disease.

Exceptions to this rule would occur in cases where harm to aquatic life might be a significant problem, or where chemical contaminants in the water might be expected to react with the H_2O_2 to form undesirable products. In these cases, decomposition of the H_2O_2 prior to discharge would be indicated. This decomposition can be hastened by addition of appropriate catalysts - preferably catalysts that will not themselves enter the solution in any significant quantities. It is possible in many cases that naturally occurring organic materials will do an adequate job of catalyzing the decomposition of the H_2O_2.

Disposal of the H_2O_2 in an existing sewage treatment plant is an alternative that is well worth investigation, as the two disposal operations would be mutually beneficial - if the H_2O_2 were added to untreated sewage as it enters the plant, its decomposition would be hastened and the oxygen released could immediately be put to good use in reducing the load of organic material entering the plant.

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1. Haskins, James W., Jr.: 'H_2O_2 Looks good for Sewage Treatment". Innovation, Fall 1973, pages 6-9 (E. I. DuPont de Nemours and Company, Inc., Wilmington, Delaware 19898).

These methods might be inadequate in the case of contaminated H_2O_2 that has been stabilized with H_3PO_4 (phosphoric acid). Decomposition would leave phosphate residues requiring additional treatment before disposal into bodies of water. This would depend, of course, on the total content of phosphates in the dilute solution.

Pouring undiluted H_2O_2 on the ground would seem to us to be a potentially hazardous practice that should at least be limited to barren, sandy areas and followed with copious quantities of water. Disposal into streams or bodies of water is to be preferred wherever this option is available.

Atmospheric discharge of H_2O_2 vapors, which are non-toxic, would not seem to be harmful environmentally. There is, however, a serious safety consideration in the vicinity of the point of discharge, and attention is called to the TLV of 1 ppm in air - a value lower than that for nitric oxide, for example, a toxic gas that does cause atmospheric pollution when present in sufficient quantity.

A very rough approximation to the H_2O_2 vapor concentration over a quiet pond containing H_2O_2, as a function of H_2O_2 concentration in the pond, may be made by assuming that the H_2O_2 follows Raoult's law even at very low concentrations:

$$p_{H_2O_2} = p^{o}_{H_2O_2} \; X_{H_2O_2}$$

where $p_{H_2O_2}$ is the partial vapor pressure of H_2O_2 in solution, $p^{o}_{H_2O_2}$ is the vapor pressure of pure H_2O_2 at the same temperature, and $X_{H_2O_2}$ is the mole fraction of H_2O_2 in solution. For the mole fraction (volume fraction) of H_2O_2 vapor in air to be 1 ppm, the partial pressure of the vapor is 10^{-6} times atmospheric pressure, or 760×10^{-6} mm Hg. Taking the vapor pressure of pure H_2O_2 at 30°C (87°F) to be 2.8 mm Hg (Chemical Safety Data Sheet SD-53) gives $X_{H_2O_2} = 760 \times 10^{-6}/2.8 = 2.71 \times 10^{-4}$. The mass fraction of the H_2O_2 is related to the mole fraction according to

$$mf_{H_2O_2} = \frac{M_{H_2O_2} \; X_{H_2O_2}}{M_{H_2O_2} \; X_{H_2O_2} + M_{H_2O} \, (1-X_{H_2O_2})}$$

where M is the molecular weight. With $M_{H_2O_2} = 34$, $M_{H_2O} = 18$, we have

$$mf_{H_2O_2} = \frac{17X_{H_2O_2}}{8\,X_{H_2O_2} + 9}$$

Substituting $X = 2.71 \times 10^{-4}$ gives $mf = 5.13 \times 10^{-4}$, or 0.0513% by mass (513 mg per liter). This result is probably conservative since it assumes liquid-gas equilibrium (a still day) and a rather high pond temperature. It is very approximate, since it assumes a Raoult's law relationship in the absence of data on Henry's law constants for H_2O_2 solutions in water.

APPENDIX A

GENERAL DESIGN CRITERIA FOR DISPOSAL PONDS

A.1 CONSTRUCTION OF DISPOSAL PONDS

If holding ponds or lagoons are to be used for gathering, diluting, neutralizing, reacting, or otherwise processing waste hypergolic fuels, several problems and choices regarding the construction of the ponds present themselves. Choice of materials and the basic structure will be addressed in a general way here.

The combined factors of a high water table and the drainage advantage of placing the holding pond water level below ground level combine to limit the depth of a holding pond in many areas, barring extreme measures. A concrete pond or tank which is to be occasionally emptied cannot be considered to be stable if it extends in depth into the water table and is not ballasted - it is subject to floating up when empty. It is possible, depending upon the circumstances at specific locations, that it would be more economical to build holding ponds above the local surroundings.

Construction possibilities include reinforced concrete, reinforced concrete with sealing compounds, reinforced concrete with sealing interlayers, and simple excavation with a synthetic liner.

A simple excavation without a liner is unsuitable due to its permeability, and a lined excavation might be unsuitable in some applications due to its delicacy [1,2]. Leakage of fuel solutions from a concrete pond can result from seepage through the integral or undamaged concrete itself, and leakage through any splits or cracks which develop in the pond. The construction of a shallow holding pond that will retain its structural integrity and not split or crack is technologically routine if somewhat expensive. Consideration needs to be given to the sub-soil in the region of the pond. A foundation or pond-bed might have to be built, depending on the results of a sub-soil study. The design and installation of the reinforcement steel is of vital importance to the structural integrity of the holding pond. Freeze-thaw cycles, in areas where they occur, should obviously be taken into account by the designer. With proper

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1. Ewald, G.W.: "Stretching the Lifespan of Synthetic Pond-Linings". Chemical Engineering, October 1, 1973, pp. 67-70.

2. Kumar, J., and Jedlicka, J.A.: "Selecting and Installing Synthetic Pond-Linings." Chemical Engineering, February 5, 1973, pp. 67-70.

engineering design and construction, holding ponds can be constructed which will remain integral so that seepage through structural cracks in the pond wall need not be considered.

Many factors of materials, design, workmanship, and installation affect the permeability of integral concrete. Properly designed and constructed, an unlined and non-waterproofed concrete holding pond will be essentially watertight for our purposes. Quantitative data are given by several sources. Johnson[3] states (pp. 7-8): "Uncracked cement paste without continuous capillary pores has a coefficient of permeability of about 1 x 10^{-12} cm/sec, and so is less permeable than most rocks. Due to fissures in the paste and cracks at the paste - aggregate boundaries the permeability of concrete is from 500 to 1000 times as great, but even this is low enough for structurl concrete to be considered for most practical purposes to be completely impermeable, or 'waterproof'."

Assuming a permeability of 10^{-9} cm/sec, and a pond 80 feet long by 40 feet wide by 4 feet deep (24.4 m x 12.2 m x 1.22 m) yields a total seepage of a about 1/3 liter (1.4 cups) per day - an amount considered to be insignificant in almost all cases.

The attainment of a low permeability is dependent upon the choice of the concrete mix, the amount of water used in the mix, the density of the concrete as laid, and the curing of the concrete. The interplay of these variables is described, in part, by Moore and Moore:[4]

"It is not difficult to secure watertight concrete with portland cement without the use of special materials, if attention is paid to the control of the factors which influence watertightness.

"The same factors which influence strength and other properties of concrete also greatly affect watertightness. In order to produce watertight concrete it is essential that sound aggregates of low porosity be incorporated in an impervious cement-water paste. To secure an impervious paste a relatively low water-cement ratio must be used and the concrete must be

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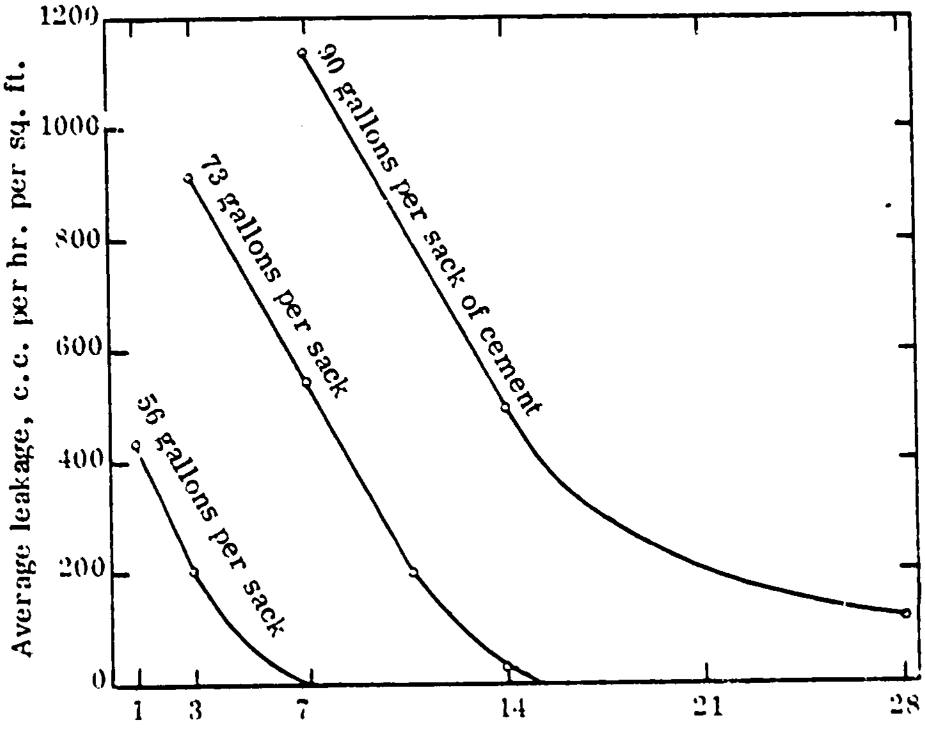
[3] Johnson, R. P.: Structural Concrete. McGraw-Hill, London, 1967.

[4] Moore, H. F., and Moore, M. B.: Textbook of the Materials of Engineering, 8th Edition. McGraw-Hill, New York, 1953.

sufficiently cured, since watertightness of the paste is greatly influenced by the extent to which the chemical reactions have progressed before it is subject to water pressure and this in turn is controlled by the kind and duration of the curing.

"The diagrams show in a striking manner how greatly the leakage at a given age is reduced by a reduction in the water-cement ratio. They also show that for a given water ratio the leakage rapidly decreases with duration of moist curing until it finally ceases entirely. These results emphasize how important it is, if watertightness is desired, to extend the curing period until the internal structure of the paste is built up to the point where it is impervious to water.



"In addition to the factors just discussed it is also essential that plastic, workable mixes be used so that they may be easily placed without segregation and also that the concrete be thoroughly mixed. Where possible, placing should be continuous and care taken to avoid undue accumulation of water on the surfaces of the layers. It is essential that cracking of the concrete due to settlement, or to shrinkage in settling and to temperature changes, be avoided in in watertight construction. Consequently, reinforcing steel and expansion joints must generally be provided to aid in preventing the formation or extension of cracks. Where settlement or contraction cracks are likely to occur, the use of a flexible membrane ... may be necessary."

It is concluded that, given proper care in design and installation, a reinforced concrete holding pond is quite adequate to the needs. A concrete surface can be designed to accept the loads of moderate sized materials handling equipment if necessary, and can be designed to neither crack and leak, nor to seep, dangerous amounts of hypergolic fuel or oxidizer solution.

It may be deemed either expedient or necessary to completely seal a holding pond for any of several reasons - to protect the environment from trace amounts of contaminant, or to protect the concrete itself from the holding pond contents. Means-of varying cost, reliability, and suitability-exist for the accomplishment of any or all of these goals, including coating an inside or outside surface with a crust concrete, with tar or bitumen, or with a polymer lining applied in sheets or sprayed or brushed on the finished survace. Polymers in use include PVC, bakelite, vinyls, polyethelene, Oppanol, silicones, and natural and synthetic rubbers. Synthetic polymeric additives may also be added directly to the mortar. Means also include membrane seals of polymers, sheet plastics or tar between concrete layers, requiring particularly careful structural design to avoid sheer stresses or large stress gradients across the membrane. While it is expected that these sealing techniques will prove to be unneeded, it is well to know that they are available. The concrete itself may prove to be chemically vulnerable and need protection. Concrete, for example, is known to be sensitive to sulfate salts. The foregoing review of techniques for protection and waterproofing of concrete is based largely on Biczok's encyclopedic text[5] on the technology and protection of concrete.

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[5] Biczok, Imre: Concrete Corrosion - Concrete Protection. Akademiai Kiado (Hungarian Academy of Sciences), Budapest, 1964.

A.2 FURTHER NOTES ON DISPOSAL PONDS

1. Allowance for rainstorm: it is necessary, with holding ponds, to allow sufficient dry volume above the holdings for the pond to accept a historic rainfall without overflow. The only alternative is to cover or partially cover the pond.

2. Animal and bird exclusion: it is desirable, and possibly environmentally necessary, to exclude animals from holding ponds. Those that walk and crawl can be excluded by use of peripheral fencing. Those that fly can be excluded by use of pond-top screening or netting. It should be noted that animals have senses, often keener in particular ways than man's, and these may be sufficient for exclusion. For example, the use of bright color dyes in the pond water may be sufficient to exclude birds. Odoriferous additives may yield a similar effect. Acidity is not a problem for pH greater than about 4, and probably even as low as 3, and at lower values the feet of birds are sensitive enough to the ions present that they would be warned away from the pond unharmed. Nitrate toxicity is probably a problem only in terms of birds drinking from the pond, unless the concentration is quite high. Any serious problem in terms of hazards to bird populations will probably be quite evident and remedial steps (such as screening) could be undertaken at the time. A screen mesh as large as 4" by 6" should be adequate.

3. Splash can be avoided by underwater liquid transfer -- easily acomplished by the use of vented hoses or other means. Some complication and expense, in terms of hardware and operational procedure, will result.

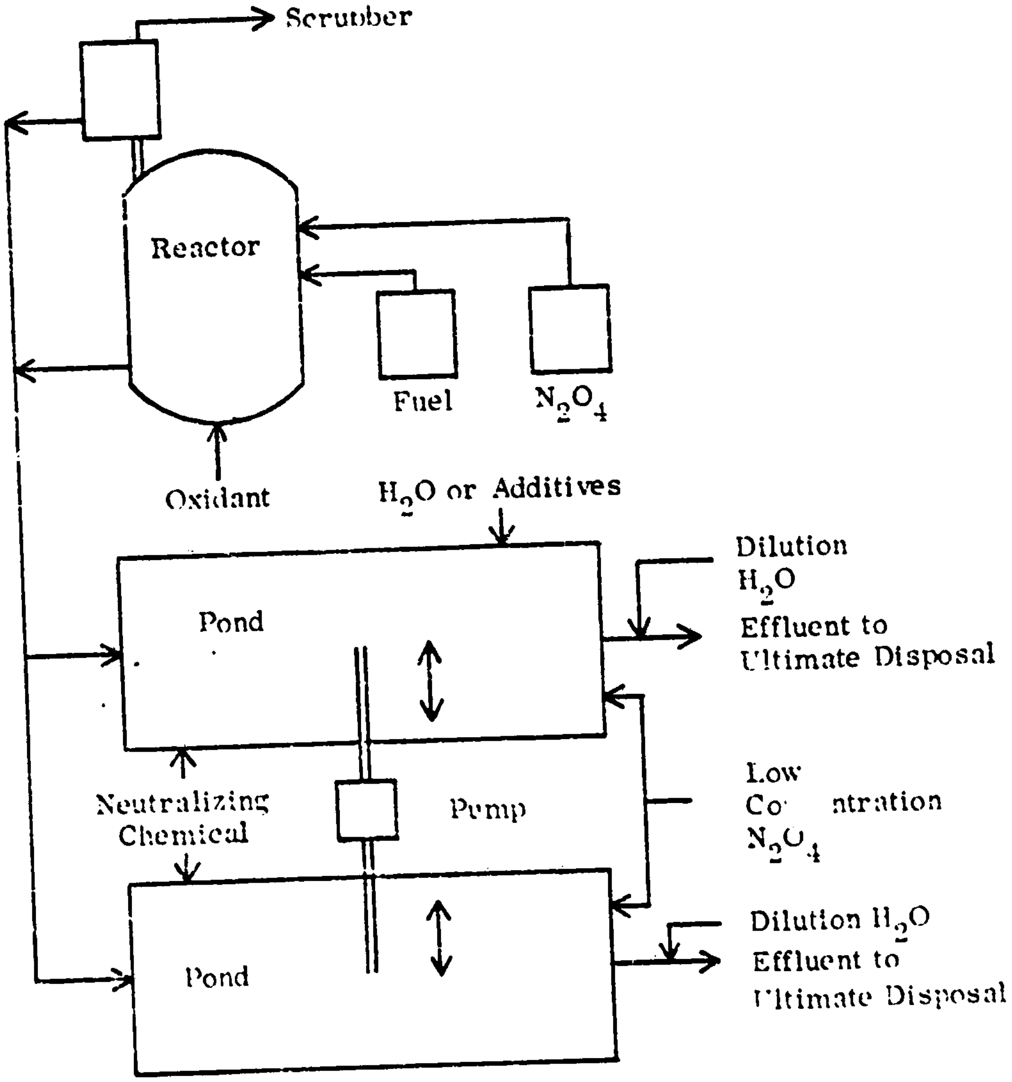
4. Dilution of N_2O_4 should be accomplished at low temperature under controlled conditions to minimize vaporization and NO_2 emission.

5. One product of dissolution of N_2O_4 in water is nitrous acid (HONO) which can combine with organic amines to form highly carcinogenic nitrosamines. Thus, chronic human exposure to ponds containing nitrous acid or its salts should be avoided.

A.3 LIQUID WASTE DISPOSAL CONCEPTS.

The purpose of the following pages is to present a number of different concepts for arrangements of disposal ponds and treatment tanks. Conceptual sketches and very brief discussions are presented, followed by a general discussion. No attempt has been made to select a "best" concept.

Preliminary Concept 1
Double Pond with Fuel/N_2O_4 Reaction Tank



Fuel and N_2O_4 are treated separately. Each is prediluted to a level that will ensure safe reaction.

Advantages (Concept 1)

Environmental impact is minimal due to closed tank treatment of fuel.

Allows use of a variety of oxidizing agents for fuel.

Hazardous vapor concentrations are easily controllable.

Permits alternate use of ponds at bimonthly intervals or as required for anomalies (one pond being serviced while the other pond is operating).

Closed system minimizes odor problem.

Ability to accomodate anomalies.

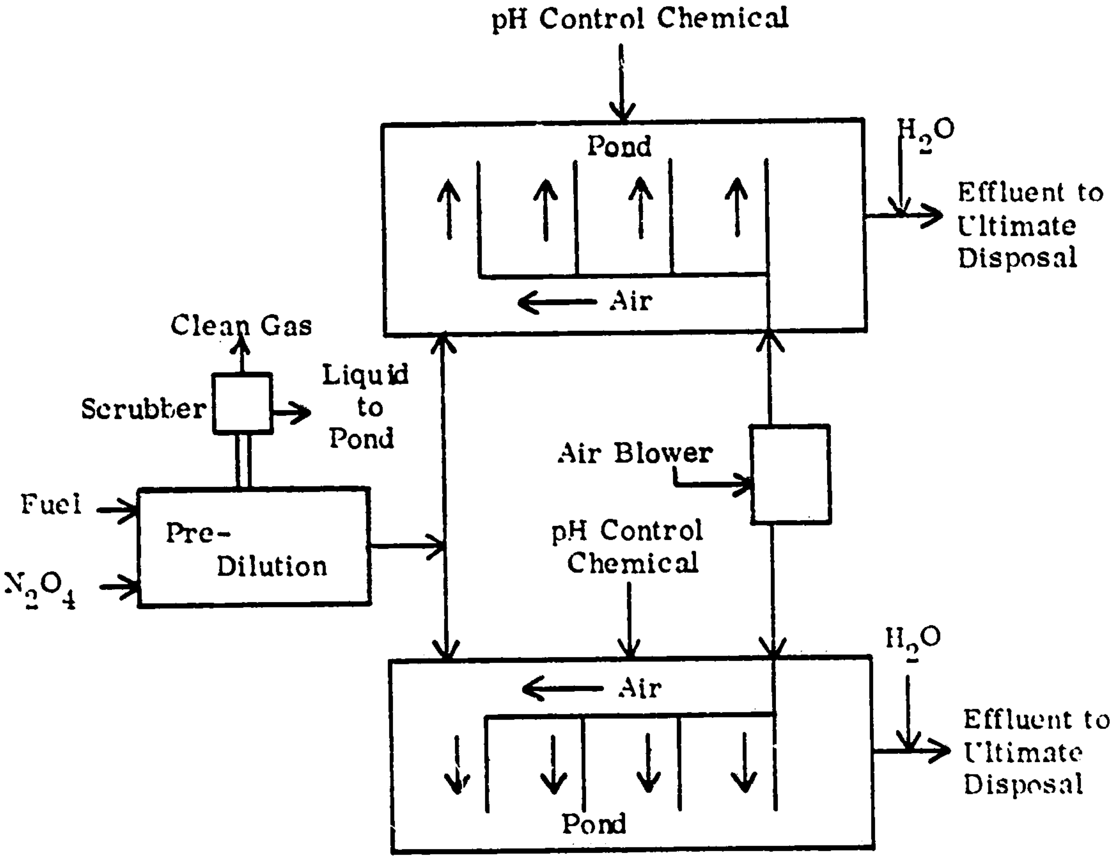
Disadvantages (Concept 1)

Spare liquid pump between ponds is on standby most of the time resulting in higher initial cost and maintenance costs.

If mixing in pond should be required during the neutralization step, pumping-recirculation will require considerable time (aeration would be faster).

A double pond requires additional fencing/screening, thereby increasing the initial cost.

Preliminary Concept 2
Aerated Double Pond Without Reaction Tank



Advantages (Concept 2)

Inexpensive design and construction.

Probably can be operated by lower-paid and less-skilled labor.

Disadvantages (Concept 2)

Toxic gas evolution (poor control of vapor).

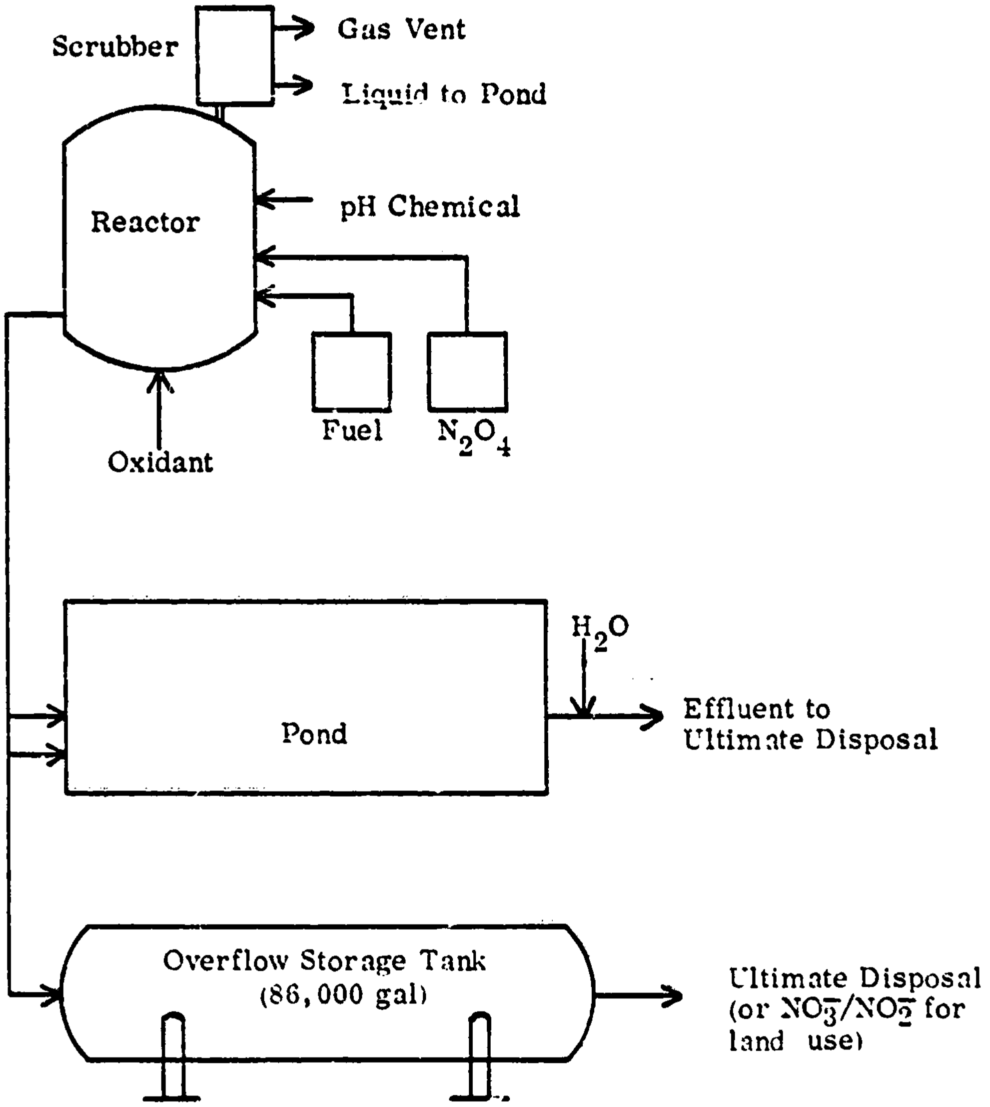
Aeration of a dilute solution requires a longer aeration period, as reaction rate drops with lower concentration of fuel as well as with presence of low pH from N_2O_4 dumping into pond.

Possible stagnant areas may form in pond resulting in increased aeration time. Plugging of diffusers is a distinct possibility.

If fertilizer value is to be saved, a higher concentration of NO_3^-/NO_2^- is advisable to save on transport/spreading cost. Higher NO_3^-/NO_2^- concentration in pond complicates destruction of fuel. The NO_2^- content may have to be oxidized to NO_3^- due to the higher toxicity of NO_2^- and lower permissible disposal levels (State & EPA regulations).

System lacks flexibility and substitute oxidants such as O_2, O_3, Cl_2, etc. cannot be used economically or for safety reasons.

Preliminary Concept 3
Single Pond, Reaction Tank, Storage Tank

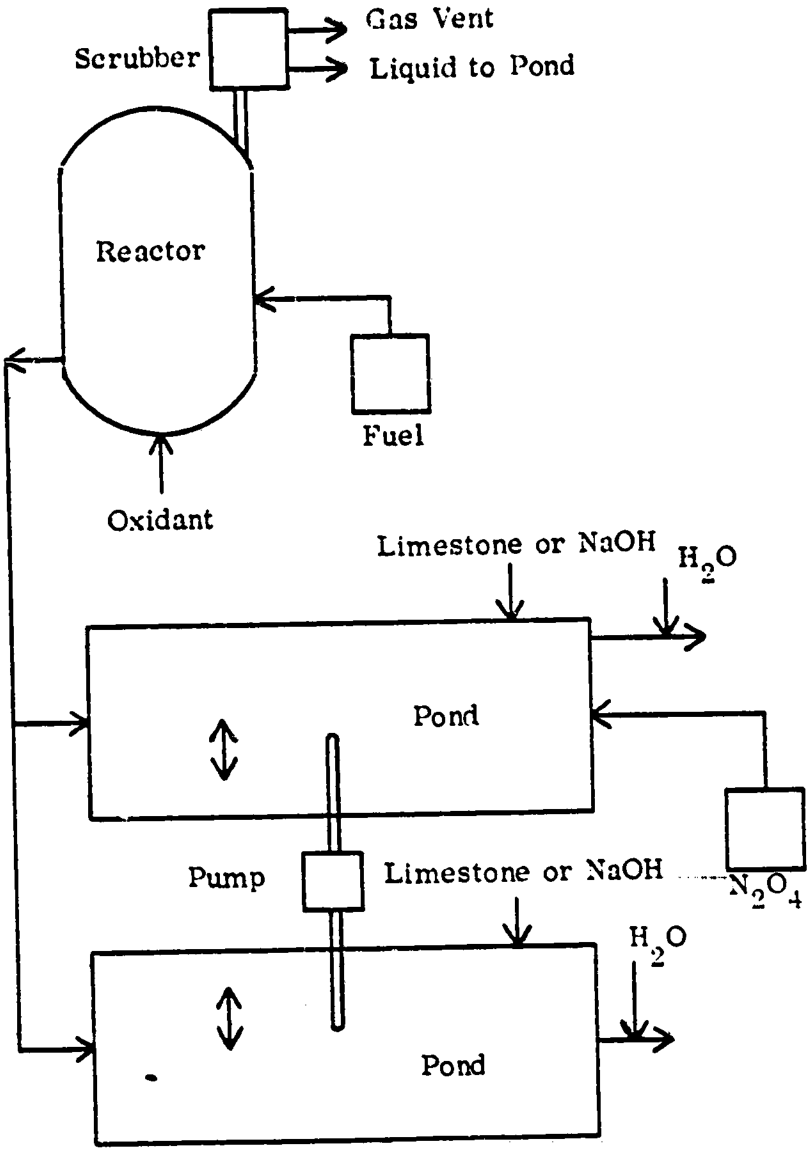


Advantage: Those listed for Concept 1.

Disadvantages: Less flexible than Concept 1.

An overflow tank generally requires more maintenance and is less useful than a second pond.

Preliminary Concept 4
Double Ponds, Fuel Reactor, N_2O_4 Neutralization in Pond



Advantages (Concept 4)

Those listed for Concept 1 except hazardous NO vapors are not controlled.

Good flexibility of operation, allowing simple addition of N_2O_4 to the pond.

Installation/construction costs are relatively low.

Double pond permits easy handling of anomalies (if prediluted).

Disadvantages (Concept 4)

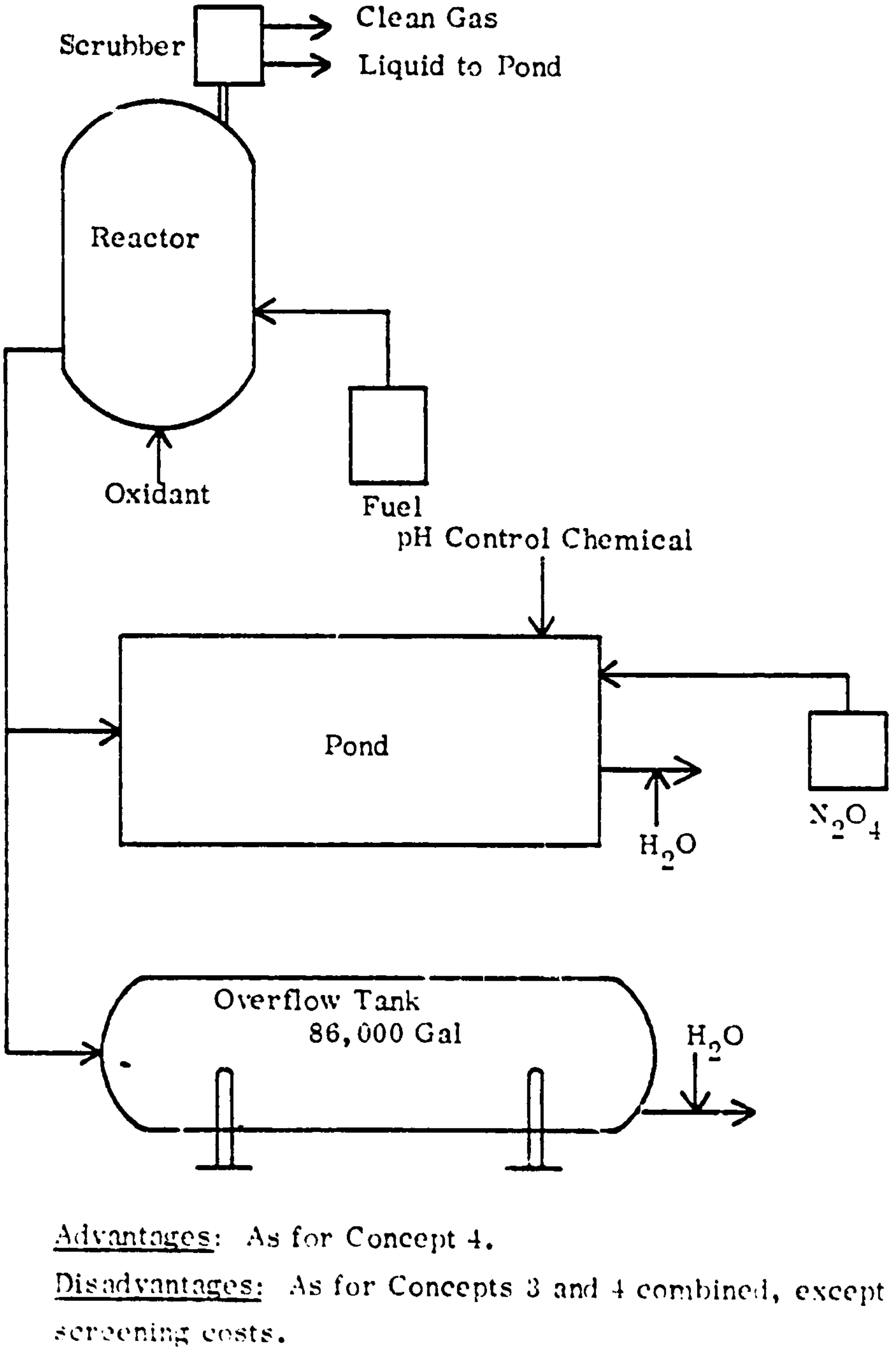
Possible NO_x vapor evolvement unless metering of N_2O_4 performed very slowly into pond and introduced near bottom of pond to allow NO gas maximum time to dissolve (limited solubility of NO is a problem). As concentration of NO_3^-/NO_2^- builds up NO dissolution drops off sharply and NO evolvement increases greatly, thus limiting amount of storage possible before saturation of NO occurs (oxidation of NO to NO_2 to increase solubility in H_2O is not feasible in pond).

Limestone creates solid waste handling and maintenance problems. However, NaOH or other neutralizer increases metallic ion content of pond water as well as cost.

Some form of agitation may be required to mix materials.

Fencing/screening costs increased due to larger perimeter.

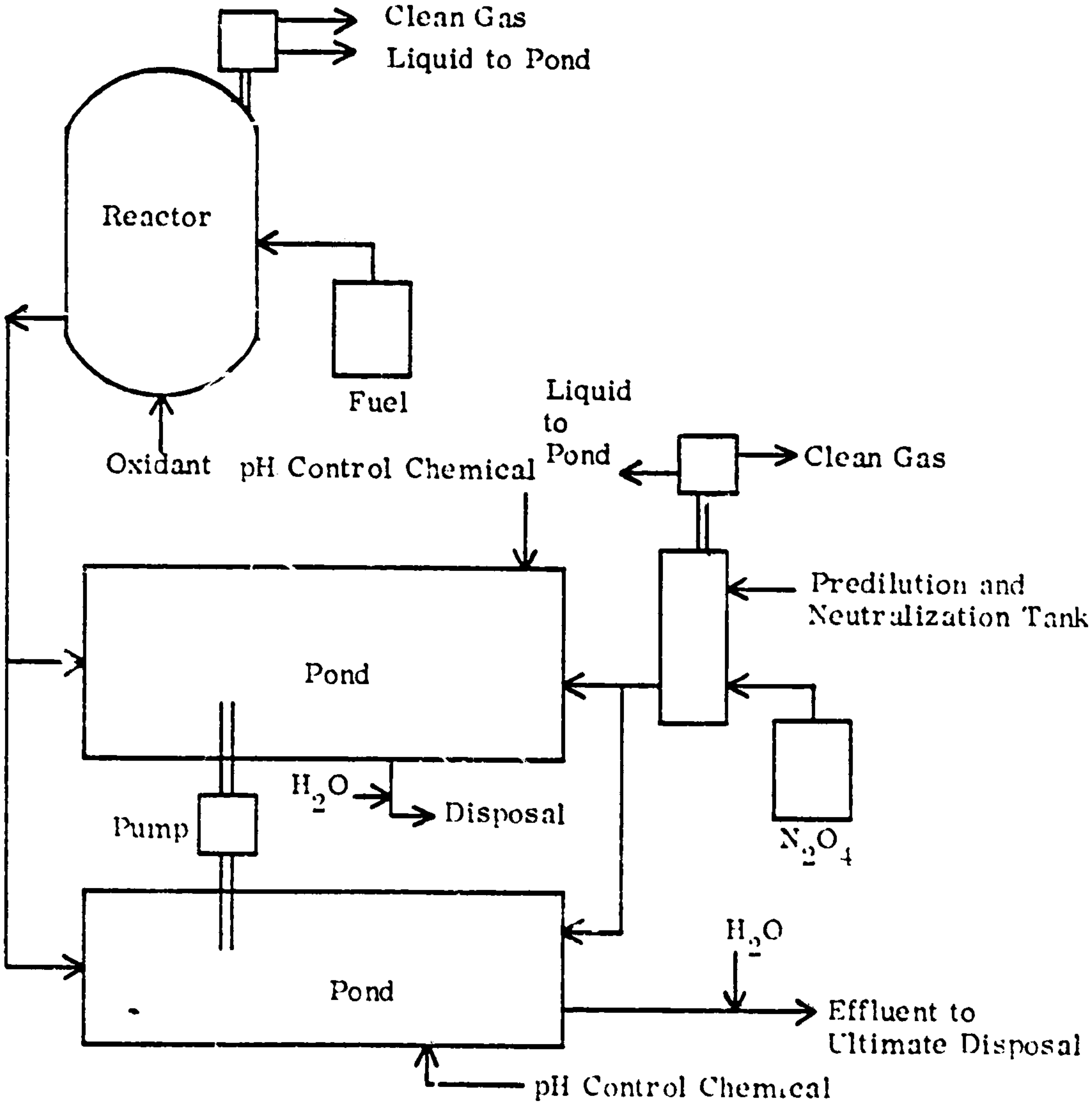
Preliminary Concept 5
Single Pond, Reactor for Fuel, Storage Tank



Advantages: As for Concept 4.

Disadvantages: As for Concepts 3 and 4 combined, except for fencing/screening costs.

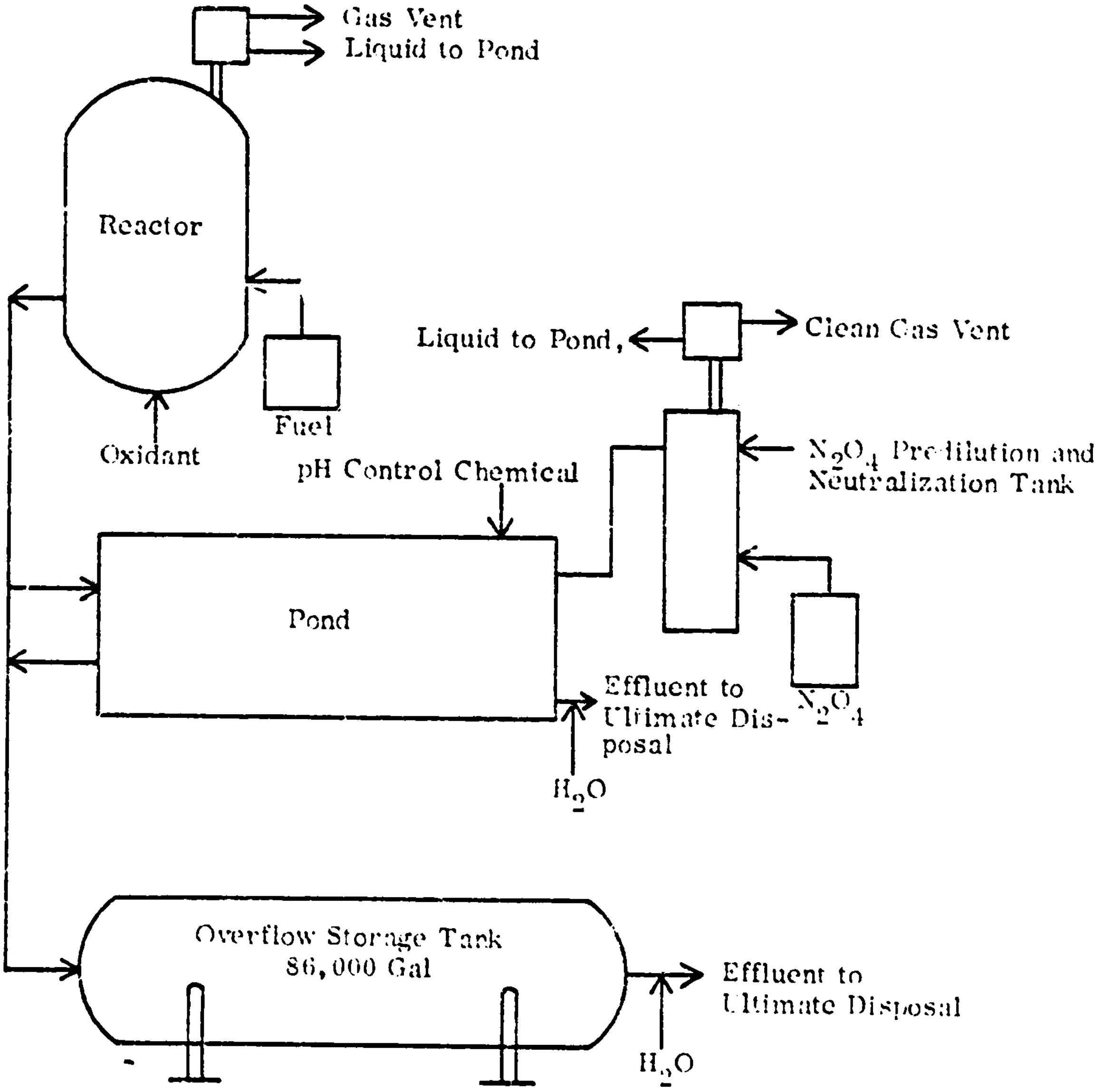
Preliminary Concept 6
Double Pond, Separate Fuel, N_2O_4 Treatment Tanks



Advantages: As for Concept 1. Allows maximally effective simultaneous treatment of N_2O_4 and fuel.

Disadvantages: More expensive to install and operate than any of the preceding concepts.

Preliminary Concept 7
Single Pond, Separate Reaction Tanks, Storage Tank



Advantages: As for Concept 6

Reduced land fencing/screening requirements relative to concept 6.

Disadvantages: Overflow tank will require more maintenance, and be less useful, than a second pond.

General Discussion

The preceding selection of "Preliminary Concepts" is not intended to be comprehensive. Other combinations of the basic components - treatment tanks, predilution tanks, aerators, ponds, overflow tanks, scrubbers, etc. - are possible. In particular, the ponds might be aerated (and probably would be) in any of the concepts.

In general, all the concepts can be regarded as consisting of the following stages:

Stage I, Predilution
Stage II, Treatment
Stage III, Temporary Storage
Stage IV, Ultimate Disposal

Figure A.1 shows schematically the four stages in a typical MMH destruction process.

The alternatives for fuel destruction were treated in Chapter 2. Whatever the actual process of choice, it seems almost imperative that it be performed in a closed vessel, with a scrubber, in view of the health factors involved (see Appendix G.)

The use of a closed vessel for N_2O_4 predilution and treatment is advantageous from the point of view of environmental protection, but just how advantageous -- how significant the NO release associated with N_2O_4 addition directly to the pond would be -- depends on a great many factors, including operational parameters and initial concentrations. Means of reducing NO release during dilution are well worth further study.

We actually regard Stage III as being considerably more than just a storage stage if an open pond is employed. In the open pond, water plants can be employed to remove nitrates and nitrites, heavy metals, and other contaminants from the water, leaving a product that should be essentially pure water, safe for disposal to a stream, open body of water, or the water table. Natural evaporation will eliminate the need for actual liquid discharge in many applications. In addition, sunlight and bacteria act together to bring about the biodegradation of trace quantities of fuel, solvents, and other contaminants.

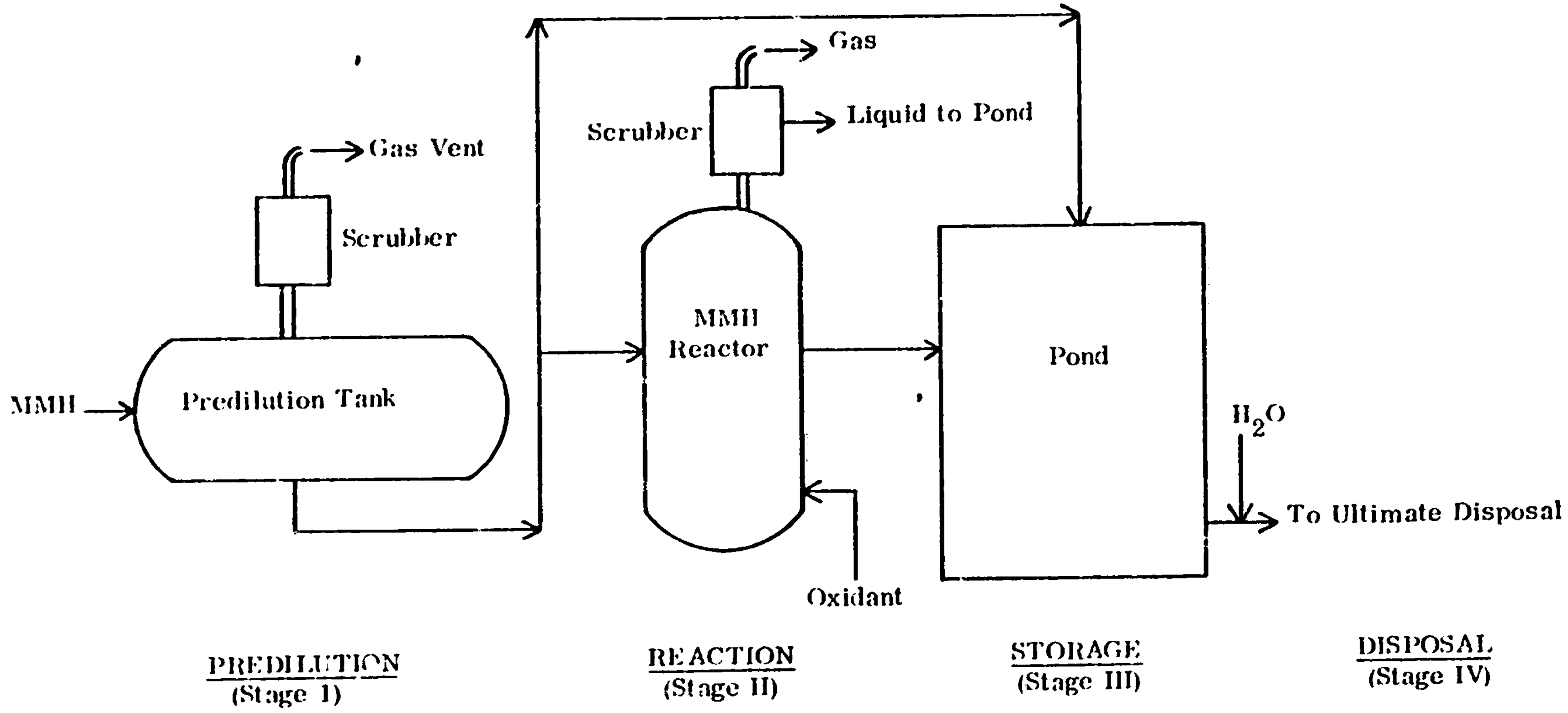


Figure A.1. Schematic of MMH destruction process

A need for disposal ponds was also identified in our study[6] of the disposal of six waste materials used primarily as solvents, and there is no reason that we can see why the same waste disposal pond could not be used for both propellants and solvents, provided the hydrazine fuels are adequately treated prior to addition to the pond. The essential storage function -- to contend with emergencies, and to spread out the discharge over a long period of time, await proper discharge conditions, etc. -- could of course be performed by a tank as well as by a pond. Because of the other functions performed by the pond, however, we regard the existence of at least one waste disposal pond as being highly desirable.

The need for a second storage reservoir -- either tank or pond -- is not well established. It would be essentially a redundancy, present in case of abnormally large disposal requirements, or abnormally large rainfall that might lead to an overflow problem with a single pond, or for use in case of maintenance -- routine or otherwise -- that might be required on the operational pond. Somewhat the same purpose could be served by a single pond with a partition to allow one side or the other to be pumped out. In addition, an emergency holding pond could probably be prepared very quickly using a bulldozer and large plastic liner. If a redundant storage capability is planned, the trade-offs between a second pond and a large overflow tank must be considered. The tank requires less land, less fence or screen enclosure, and might be cheaper. On the other hand, it requires more frequent inspection and maintenance, is less convenient for emergency dumping, and is more restricted in terms of both volume and the uses to which it could be put.

Ultimate disposal of the liquid and solid wastes directly as fertilizer is a possibility since nitrates will result as final products when N_2O_4 is neutralized. This method presents some problems, however. As a fertilizer, the final product leaves much to be desired. In addition, there is a toxicity problem associated with the nitrites that are also formed. There is also no practical method of chemically destroying or precipitating NO_2^- and NO_3^-, or converting them to elemental or less toxic forms. As a result, biological assimilation --

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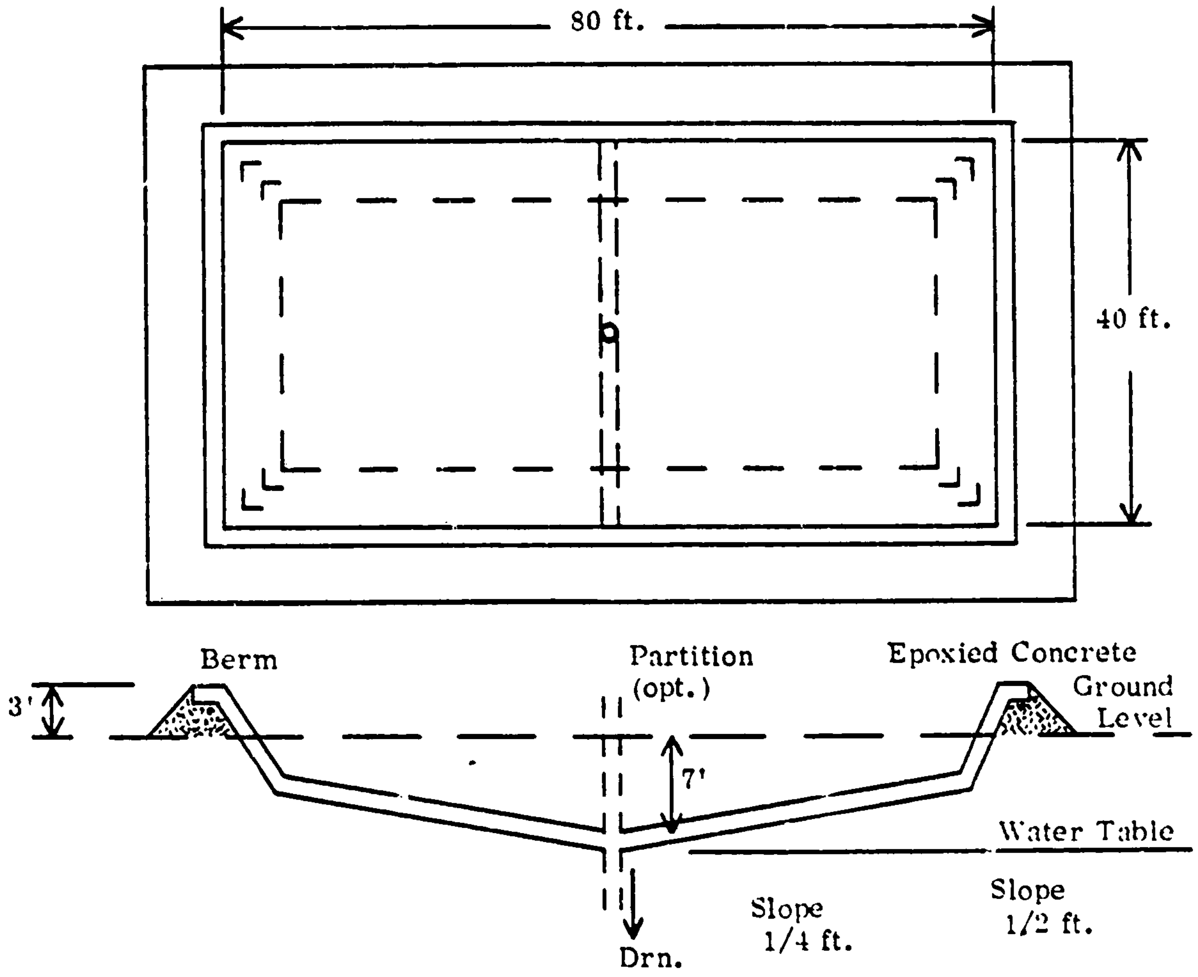
[6] Bowman, T.E.; Sivik, H.; Thomas, J.J.; and Tiernan, L.R.: Final Report, Phase Four, Contract NAS 10-8399, December 1975. Report No. ME/75/HP-1, Florida Institute of Technology, Melbourne, FL 32901.

in the pond itself -- looks increasingly attractive. In Florida and other parts of the Southeastern U.S., water hyacinths are an especially likely agent for this assimilation as this plant is a very hardy, fast-growing species that is known to remove toxic contaminants, including heavy metals in trace concentrations, from the water. Although extensive testing should be performed to verify this use of natural processes, we are quite optimistic that these plants will prove quite beneficial, both as a means of producing the purest possible effluent and as a potentially valuable end product in themselves in situations where they can be conveniently harvested.

Figure A.2 shows plan and elevation views of a simple aeration pond, of a size suitable for many typical applications. A rough estimate of the construction costs, exclusive of aeration equipment, pumps and piping, etc., is also shown.

Figure A.3 presents the details of a smaller pond to be used by Florida Institute of Technology for further experimentation. For quantities that will be involved with this pond, the fuel can be treated in a modified drum near the pond edge. Primary emphasis, at least in the early stages of prototype testing, will be on the operation of the pond itself rather than the treatment stage, which has already been studied extensively in the laboratory.



Volume at Ground Level	70,000 gals
Volume at Brim Level	140,000 gals
Concrete 400 yd. @ $60	$ 24,000
Reinforc. Stl. 12 Tons at $900	10,800
Wall Forms	10,000
Excavation	5,000
Engineering	5,000
Fencing/Screening	10,000
Misc.	12,000
Total estimated cost	$76,800

Figure A.2. Aeration pond schematic.

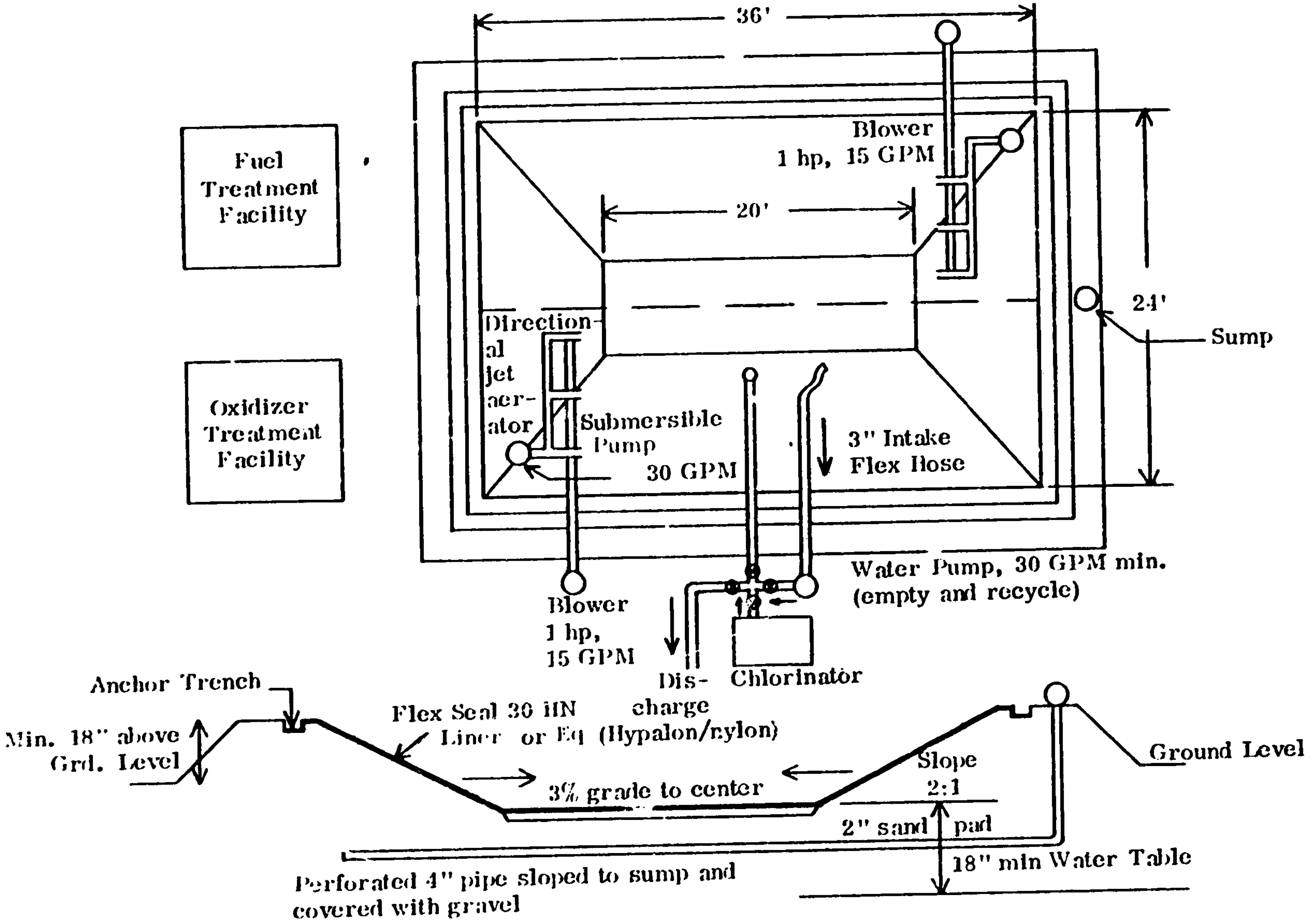


Figure A.3. Prototype disposal pond.

APPENDIX B

THERMAL ASPECTS OF REACTIONS IN DILUTE SOLUTIONS

B.1 ANALYTICAL CONSIDERATIONS

Questions of concern relative to fuel/oxidizer reactions in disposal ponds include thermal considerations: how rapidly fuel and oxidizer can be added to a pond without causing pond temperature to rise to a point that would be particularly hazardous, or causing significant amounts of toxic vapors to be evolved. These considerations are important in establishing minimum sizes of ponds for various applications.

A small rectangular pond, 30 meters (100 ft) long, 20 meters (66 ft) wide and 1 meter (3.3 ft) deep, was arbitrarily chosen for the purpose of calculations. In the pond, fuel and oxidizer can be mixed in the proper ratios to neutralize one another. The chemical reactions are exothermic and the temperature of the pond will increase. The heats of reaction for the various reactions of interest (for initial and final states at standard temperature and pressure) are as follows:

$N_2H_4 + 2H_2O_2 \longrightarrow$	$N_2 + 4H_2O$	153.6 Kcal/ Mole
$N_2H_4 + N_2O_4 \longrightarrow$	$N_2 + 2NO + 2H_2O$	85.9
$CH_3N_2H_3 + 5H_2O_2 \longrightarrow$	$N_2 + 8H_2O + CO_2$	345.5
$CH_3N_2H_3 + 2N_2O_4 \longrightarrow$	$\frac{3}{2}N_2 + 3NO + CO_2 + 3H_2O$	218.7
$(CH_3)_2N_2H_2 + 8H_2O \longrightarrow$	$N_2 + 12H_2O + 2CO_2$	535.9
$(CH_3)_2N_2H_2 + 3N_2O_4 \longrightarrow$	$2N_2 + 4NO + 4H_2O + 2CO_2$	350.0

A temperatu e increase of 30°C was arbitrarily chosen for purposes of calculation. If a large quantity of fuel and oxidizer is rapidly mixed in the pond, assuming for the time being that there is no heat loss, the amount of fuel plus oxidizer that would raise the temperature of the pond 30°C can be calculated using the heats of reaction, pond dimensions, and heat capacity of water to give the following results:

3750 kg (1010 gal) N_2H_4 + 7850 kg (1520 gal) H_2O_2

6500 kg (1700 gal) N_2H_4 + 18,600 kg (3420 gal) N_2O_4

2400 kg (735 gal) MMH + 8850 kg (1670 gal) H_2O_2

3800 kg (1150 gal) MMH + 15,200 kg (2800 gal) N_2O_4

2000 kg (685 gal) UDMH - 9060 kg (1750 gal) H_2O_2

3140 kg (1050 gal) UDMH + 14,500 kg (2640 gal) N_2O_4

Next we consider the propellant flow rates necessary to maintain a constant temperature difference of 30°C between the pond and its surroundings. For steady state, the energy released by the reaction of the propellants entering the pond will just equal the heat transfer from the pond to the surroundings plus the energy lost by the pond as a result of evaporation and the evolution of gaseous reaction products. For simplicity, we shall neglect the latter effects; the result of this simplification will be a conservative estimate of the energy transport from the pond.

The major portion of the heat transfer from the pond will be in the form of free convection from the surface to the air. For the pond dimensions we are assuming - or any realistic pond dimensions, for that matter - and a temperature difference on the order of degrees Kelvin or more, the convection will be clearly turbulent, and can be estimated using McAdams' approximate heat transfer coefficient for turbulent free convection in air from a horizontal, upward-facing heated surface:

$$h = .22\,(\Delta t)^{1/3},$$

where Δt is the temperature difference in degrees Fahrenheit, and h is in Btu/ft^2-hr. °F. For our case, taking $\Delta t = 30°C$ would lead to an unrealistically large answer in cases where the air itself might be quite hot. If we take the "normal" temperature of the pond to be 20°C (68°F) and the maximum allowable temperature to be 50°C (122°F) and the air temperature to be 35°C (95°F), then the Δt value for the convection equation will be 15°C (27°F), and the heat transfer will be

$$q_{conv} = hA\,\Delta t = (.22)(5.6786)(20)(30)(27)^{4/3} = 60{,}700 \text{ Watts}$$

The heat conduction through the ground should also be estimated. The conduction from an isothermal sphere of radius r buried in an infinite medium is simply

$$q_{cond} = 4\pi r\,k\,\Delta t$$

where Δt is the difference in temperature between the sphere and the medium far away, and k is the conductivity of the medium. We can approximate our pond as a hemisphere at the surface of a semi-infinite medium whose properties are those of sandy soil, and very crudely estimate the heat transfer as being half that given above:

$$q_{cond} = 2\pi r\, k\, \Delta t,$$

where r is an effective radius based on the surface area of our rectangular pond of length L, width W, and depth D:

$$r = \sqrt{\frac{LW + 2LD + 2WD}{2\pi}} = \sqrt{\frac{(20)(30) + (2)(30)(1) + (2)(20)(1)}{2\pi}}$$

$$= \quad 10.56 \text{ meters}$$

$$\therefore q_{cond} = 2\pi(10.56)(.6)(30) = 1200 \text{ Watts},$$

a figure sufficiently smaller than the convection figure that we can abide the very crude method of analysis rather than attempting a more refined analysis.

Using the estimated total heat transfer from the pond, $q_{total} = 61{,}900\text{W}$, we can now calculate the flow rates of fuel and oxidizer that will just maintain the 30°C temperature rise in the steady state. Letting H be the enthalpy ot reaction for any given reaction, in kcal per mole of fuel, and M be the molecular weight of the fuel (grams per mole), than the mass flow rate, $\dot{m}$, in kg/hr, is

$$\dot{m} = \frac{q_{total}\, M}{H} \left[\frac{3600 \text{ sec/hr}}{(1000 \text{ g/kg})\ (4186 \text{ watt sec/kcal})} \right]$$

and the mass flow rate of the oxidizer may be calculated in terms of the fuel in the usual manner. The results are as follows:

11.1 kg (2.92 gal) N_2H_4 + 23.6 kg (4.34 gal) H_2O_2 per hour

19.9 kg (5.22 gal) N_2H_4 + 59.5 kg (10.8 gal) N_2O_4 per hour

7.10 kg (2.14 gal) MMH + 26.2 kg (4.82 gal) H_2O_2 per hour

11.2 kg (3.38 gal) MMH + 46.7 kg (8.51 gal) N_2O_4 per hour

5.97 kg (2.01 gal) UDMH + 27.0 kg (4.97 gal) H_2O_2 per hour

9.14 kg (3.07 gal) UDMH + 43.8 kg (7.97 gal) N_2O_4 per hour

It should be noted that these figures would not increase significantly were the depth of the holding pond increased, but would rise in almost direct proportion to the surface area of the holding pond.

B.2 EXPERIMENTS

A brief series of laboratory experiments was also performed to obtain a better idea of the temperature rise involved in neutralization of small quantities of diluted hydrazines with diluted oxidizers. The concentration of reactants was from 1 to 20%. It was desired to determine if a prohibitively high temperature rise occurred on mixing fairly strong concentrations. If temperature rise was not excessively high, it was reasoned that reaction tank or pond volumes could be made smaller by designing for relatively high concentrations.

Solutions of MMH, N_2H_4, N_2O_4, IRFNA, urea and acetic acid were prepared in various concentrations. These generally included 20%, 10%, 7.5% and 1% by weight.

A volume of 50 ml of each reducer (MMH, N_2H_4 or urea) was poured into a beaker confined within a fume hood. The temperature of the solution was noted. The entire measured volume of diluted oxidizer (N_2O_4, IRFNA or acetic acid) corresponding to the stoichiometric requirement was poured <u>at once</u> into the beaker. The beaker was swirled by hand and agitated with a thermometer to mix the reactants. The peak temperature attained was observed and recorded as ΔT (peak temperature minus initial temperature). No allowance was made for heat absorption by the beaker or heat losses to the atmosphere.

The volumes of solutions used appear above each reactant in the following equations:

$$\overset{\text{50 ml}}{(CH_3)\,N_2H_3} + \overset{\text{100 ml}}{2N_2O_4} \longrightarrow \frac{3}{2}N_2 + 3NO + CO_2 + 3H_2O$$

$$\overset{\text{50 ml}}{(CH_3)\,N_2H_3} + \overset{\text{136 ml}}{2HNO_3} \longrightarrow N_2 + 2NO + CO_2 + 4H_2O$$

$$\overset{\text{50 ml}}{N_2H_4} + \overset{\text{144 ml}}{N_2O_4} \longrightarrow N_2 + 2NO + 2H_2O$$

$$\overset{\text{50 ml}}{N_2H_4} + \overset{\text{197 ml}}{HNO_3} \longrightarrow 1/2N_2 + 3NO + 3H_2O$$

$$\overset{\text{50 ml}}{(NH_2)_2\,CO} + \overset{\text{79 ml}}{N_2O_4} \longrightarrow NH_4NO_3 + CO_2 + N_2$$

$$\overset{\text{50 ml}}{(NH_2)_2\,CO} + \overset{\text{54 ml}}{HNO_3} \longrightarrow NH_4NO_3 + CO_2 + 2NO$$

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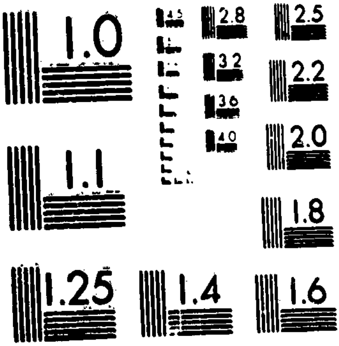

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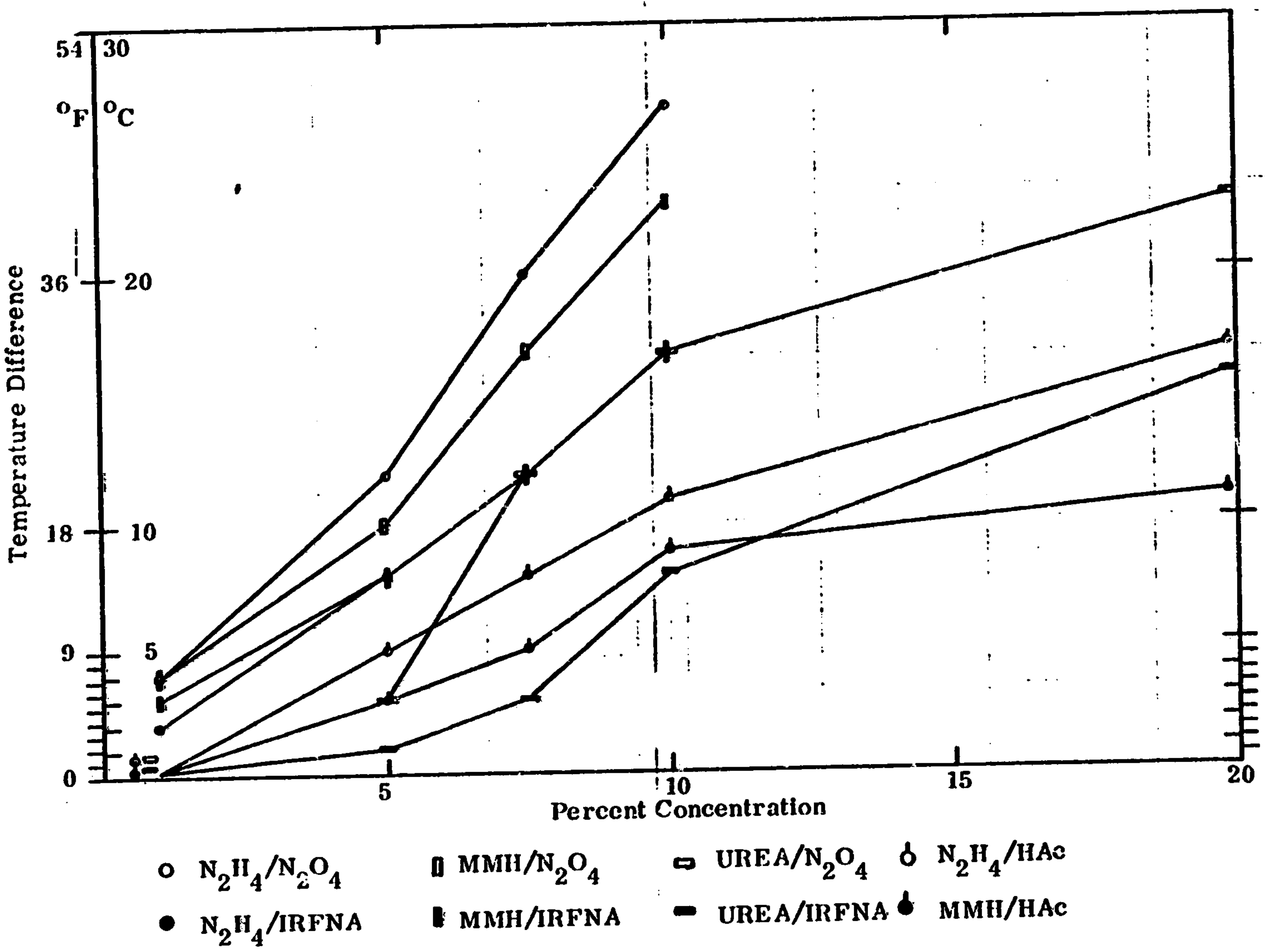


Figure B.1. ΔT vs. concentration for stoichiometric reactions in solutions.

C - 4

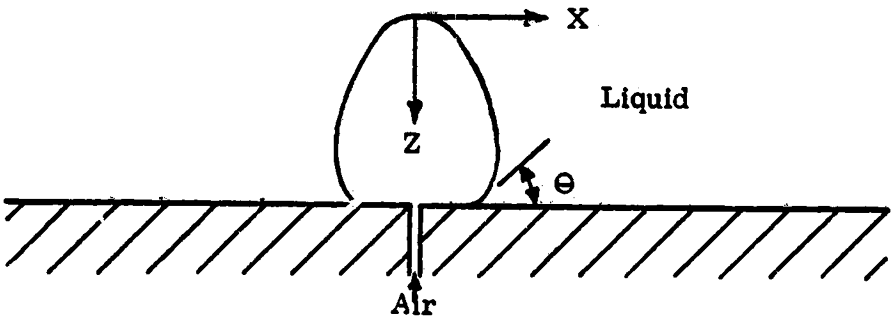
APPENDIX C

GAS BUBBLE GROWTH, DETACHMENT, AND RISE

C.1 INTRODUCTION

Engineering design considerations of aeration ponds must depend to a considerable extent on the size of bubbles formed. The purpose of this appendix is to present briefly the existing theories of bubble formation, growth, and detachment, and of the rise of small bubbles through bodies of liquid.

For simplicity, we shall begin by considering the formation of a bubble resulting from the introduction of air (or other gas) very slowly through a single, isolated, small hole. "Small" will mean smaller than the base of the bubble at the instant of detachment. If the hole is located in a horizontal surface, a side view of the bubble will be somewhat as shown below:



The Z-axis is an axis of symmetry. The contact angle, Θ, is defined as the angle between the solid boundary and the tangent to the bubble surface at its intersection with the solid boundary. The "base" refers to the portion of the bubble bounded by the solid surface rather than the liquid-vapor interface. In the case of static equilibrium, the bubble is subject to two external forces: the resultant of hydrostatic pressure on the water-air interface and air pressure on the base of the bubble, which is a buoyant-like force acting to remove the bubble from the surface; and the resultant of surface tension at the solid-liquid-gas intersection, acting to hold the bubble on the solid surface.

Simplified solutions based on assumptions regarding the bubble shape are tempting, but generally of little value and in fact simplified models are usually self-contradictory. One complication is the fact that Archimedes' Principle does not apply, since hydrostatic pressure does not act on all parts of the bubble surface. Therefore the relationship of base area to interface area and orientation, and the interrelationship of both with contact angle, is important. Considering that the liquid-gas interface in the vicinity of the solid surface becomes quite distorted just prior to detachment of the bubble, it is easy to understand why simplified models have not been successful in predicting the volumes of bubbles leaving solid boundaries.

This problem is an important one in boiling heat transfer, and at least in the static equilibrium case straightforward solutions exist, as discussed in the following section. In the case of aeration, considerations of bubble size are important in various ways.

1. The ratio of bubble surface area to volume is inversely proportional to diameter for similarly shaped bubbles, so that smaller bubbles have relatively more surface area for the air oxidation reaction to take place.
2. The air pressure in the bubble is inversely proportional to the curvature of the surface, and hence to diameter for similarly shaped bubbles, so that pumping requirements per unit volume of air in the pond are higher for smaller bubbles.
3. Assuming that the air always reaches pond temperature prior to leaving the aerator, the density of the air in the bubble is linearly proportional to the pressure, and hence inversely proportional to diameter, so that surface area per unit mass of air in the bubble is independent of size, and pumping requirements per unit mass of air or per unit surface area are higher for smaller bubbles (even more so if the smaller orifices required for the smaller bubbles are taken into consideration.)
4. Smaller bubbles rise more slowly through the pond, as discussed in a later section, and hence there is more time for the reaction to take place.
5. On the other hand, both the faster motion and larger size of larger bubbles help generate circulation in the pond, bringing the contents of the pond into contact with the air bubbles sooner and more frequently.

It therefore seems apparent that there is no obvious, easy answer to the question of best bubble size. A careful, detailed optimization would have to be performed, in terms of pond depth and other pond parameters. An exception would be a case where the bubbles contain N_2O_4 or other toxic vapors, so that the only important consideration would be complete reaction prior to the bubble reaching the pond surface, and selection of the smallest feasible bubble size is indicated.

C.2 ANALYSIS

The preceding section discussed the need for applying force equilibrium considerations at all points of the bubble surface, rather than trying to assume a shape and apply an overall force balance. Performing a force balance on a surface element results in the capillary equation[1]

$$\frac{1}{R} + \frac{\sin\phi}{X} = \frac{2}{b} - \frac{g(\rho_2 - \rho_1)Z}{\sigma} \tag{1}$$

where

X, Z are coordinates as shown in the sketch of the preceding section

R, $\frac{X}{\sin\phi}$ are principal radii of curvature, R in a plane containing the axis of symmetry

ϕ is the angle which the perpendicular from the interface makes with the axis of symmetry, measured from the apex ($\phi = 0$ at $S = 0$, $Z = 0$)

b is the radius of curvature at the apex (origin)

ρ_1, ρ_2 are the densities of the gas and liquid, respectively

σ is the surface tension at the interface

g is the gravitational acceleration

This equation has been treated by many authors, with most modern work patterned more or less after the work of Bashforth and Adams, whose book[2] reported the results of numerical calculations dating from 1855. This work is also believed to be the first application of Adams' predictor - corrector method, a numerical technique that is still useful for some types of problems. In essence, their work amounted to starting at the origin and numerically calculating the shape of the surface for a given value of b and the dimensionless constant

$$\beta = \frac{g(\rho_2 - \rho_1)}{\sigma} b^2$$

The results were families of possible surface shapes for each value of β con-

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[1] A detailed derivation, including more generality regarding orientation of the solid surface relative to gravity, has been presented by B.K. Larkin: "Numerical Solution of the Equation of Capillarity," Journal of Colloid and Interface Science, Vol. 23, pp. 305-312 (1967).

[2] Bashforth, F., and Adams, J.C.: An Attempt to Test the Theories of Capillary Action. University Press, Cambridge, England, 1883.

sidered. Boundary conditions would be applied by truncating a curve at a point where its slope corresponds to the desired contact angle.

These results were applied by Wark[3] to the specific calculation of sizes and shapes of air bubbles in water at 20°C. Of even more interest for our application is the work of Fritz,[4] who developed a technique for using the Bashforth and Adams results to find the maximum (detachment) sizes of bubbles as a function of contact angle and capillary constant. Fritz's results are reproduced in Figures C.1 and C.2. In figure C.1, the capillary constant is

$$a = \sqrt{\frac{2\sigma}{(\rho_2 - \rho_1) g}}$$

In figure C.2, Curve 1 is the case of primary interest: air bubbles in water at 20°C.

Modern investigators have used the digital computer to extend Fritz's results to other cases, and in the process have verified the validity of the Fritz and Bashforth and Adams calculations. In particular, Larkin[5] has developed a method of solution for nonaxisymmetric surfaces and gravitational accelerations that are arbitrary in both direction and magnitude, and Concus[6] has described liquid-gas interfaces in right circular cylinders. This last case might be applicable in the case of aerators with larger orifice sizes, since the interface inside the circular orifice might be of primary interest.

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[3] Wark, I.W.: "The Physical Chemistry of Flotation. I: The Significance of Contact Angle in Flotation." Vol. 37, p. 623-644, (1933).

[4] Fritz, W.: "Berechnung des Maximalvolumens von Dampfblasen" ("Calculation of the Maximum Volumes of Vapor Bubbles"). <u>Physik. Zeitschr.</u>, Vol. 36, pp. 379-384 (1935).

[5] Op. cit. See also McGrew, J.L., and Larkin, B.K.: "Cryogenic Liquid Experiments in Orbit, Vol. II: Bubble Mechanics, Boiling Heat Transfer, and Propellant Tank Venting in a Zero-Gravity Environment." NASA CR-652, December 1966.

[6] Concus, P.: "Static Menisci in a Vertical Right Circular Cylinder." <u>J. Fluid Mech.</u>, Vol. 34, pp. 481-495 (1968).

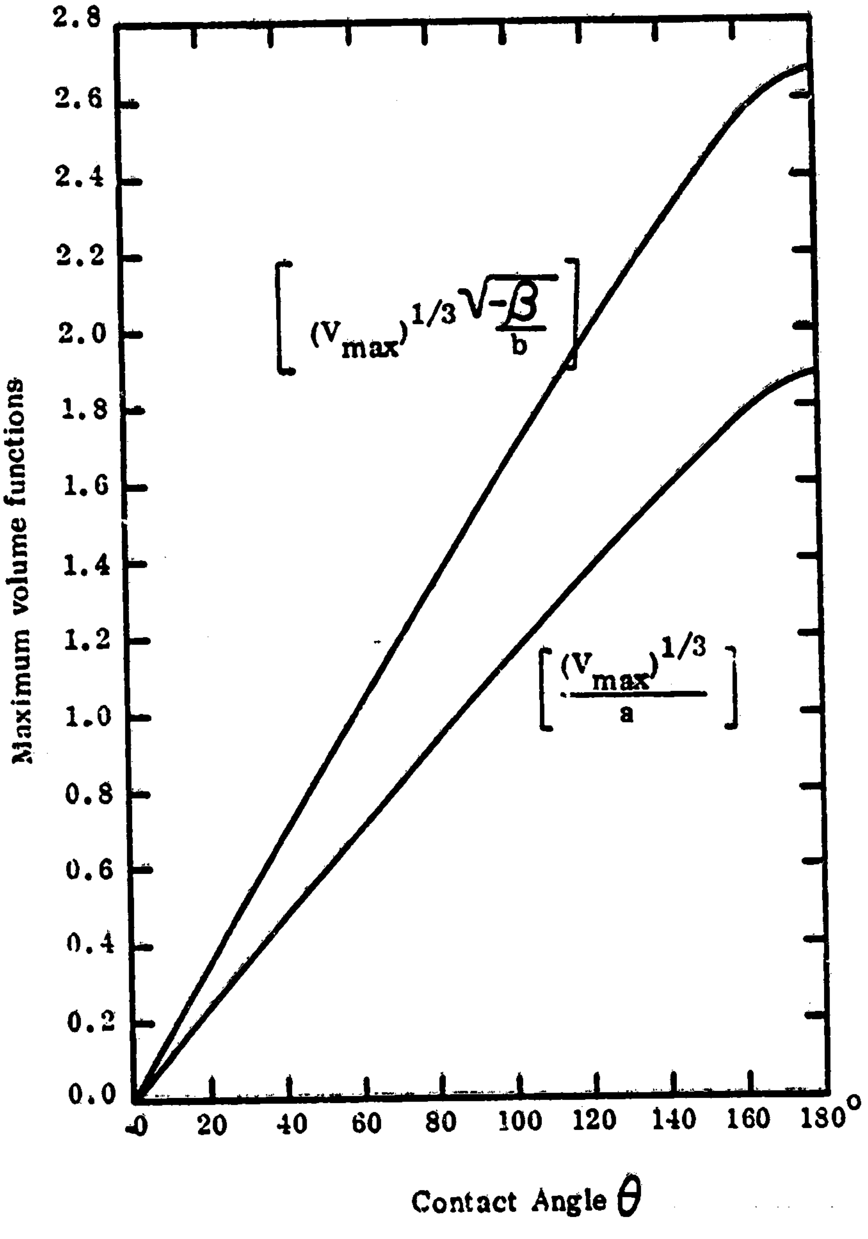

Figure C.1. Fritz's dimensionless presentation of the maximum volume V_{max} as a function of contact angle.

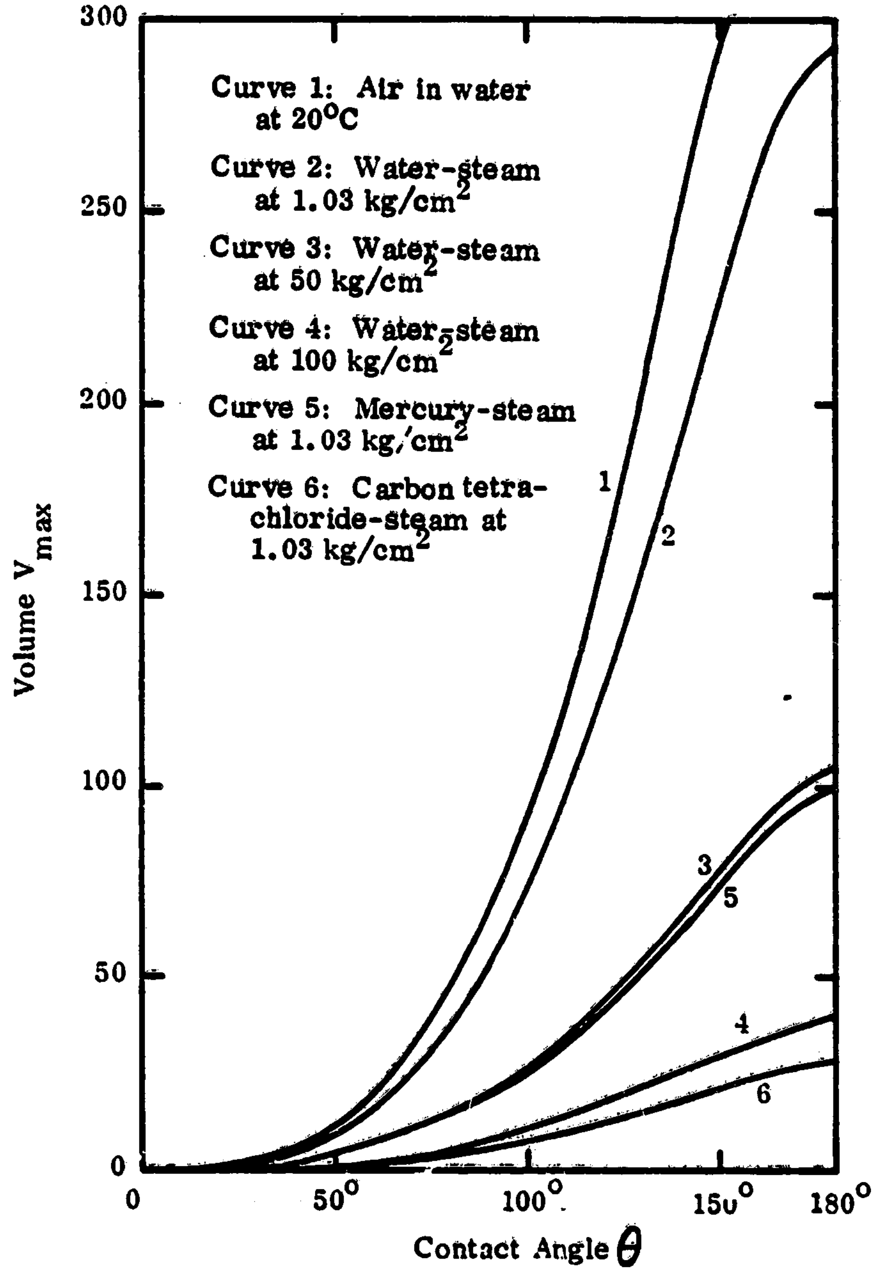

Figure C.2. Maximum volumes of various gas and vapor bubbles, from Fritz.

C.3 DISCUSSION

The results above show that small bubbles result from small values of either surface tension or contact angle - given of course, the essential prerequisite of a small pore size relative to the size of the bubbles being formed. Surface tension is a temperature-dependent property of the water-air system, but surface tension modifiers - detergents, for example - are readily available for water. The effect of these "surfactants" is to reduce the surface tension. Their effect on newly forming surfaces is unknown, however, at least to the present author. Contact angles, on the other hand, can be varied over a wide range.

The contact angle is a temperature-dependent property of a solid-liquid-gas system. Current knowledge of contact angles is due, in large part, to the work of William A. Zisman and various coworkers over a period of many years. Their results were summarized by Zisman[7] in 1964. One simple expression for contact angle that resulted from this work has proven useful in a great many cases:

$$\cos\theta = 1 - k(\sigma_L - \sigma_c), \qquad (3)$$

where k and σ_c are empirical constants, σ_c being referred to as the "critical surface tension" of the solid surface. σ_L is the actual surface tension of the liquid-gas interface. If $\sigma_L < \sigma_c$, the contact angle is near zero. Solid surfaces are characterized as being "high energy" or "low energy" according to whether their critical surface tension values are high or low, respectively. In general, metals are high energy surfaces, while the lowest values of σ_c are associated with highly fluorinated organic polymers and other organic compounds made up largely of CF_2 and CF_3 groups.

To achieve small values of θ, then, it is apparent that metallic surfaces with large values of σ_c are desirable. In the case of water, however, there is a particular problem that has been noticed by most researchers concerned with liquid surface phenomena.

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[7] Zisman, W.A.: "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution." In "Contact Angle, Wettability and Adhesion," Advances in Chemistry Series 43, R.F. Gould (Ed.), American Chemical Society Applied Publications, 1964, p.1.

Because of the unusually high surface tension of water, the contact angle between a water-air interface and a metal surface fluctuates over a wide range, as indicated by equation (3) when the term in brackets becomes the difference between two large numbers. An additional aspect of this problem is discussed by Frohnsdorff and Tejada[8] in the following terms:

> "The measurement of the true contact angles of high surface tension liquids such as water on high energy surfaces such as metals is difficult because of the strong tendency of the metals to adsorb organic vapors. Even a small fraction of a monolayer of organic molecules appears to be sufficent to increase the contact angle of water on many surfaces ..."

Perhaps the first extensive treatment of this problem was that of Trevoy and Johnson[9] in 1958. The problem became a persistent annoyance in connection with the zero-gravity experimentation of the early 1960's carried out in support of spacecraft propellant tank design efforts, and as a result the Lewis Research Center funded an extensive evaluation of procedures for cleaning metal surfaces to obtain "true" contact angles in laboratory work[10]. The conclusion was that the best procedure was vapor degreasing followed by immersion in an alkaline cleaner and thorough rinsing with water.

For cooling pond applications, if small bubbles are desired it seems likely that some benefit could be derived from using metal pipes for the actual aerator, degreasing them prior to installation, insuring that they remain submerged in a somewhat alkaline pond, and installing an oil trap on the compressed air line. For the sake of computation, however, it is probably prudent to assume the worst, which is a contact angle on the order of 80° to 100°. Contact angles reported by Frohnsdorff and Tejada for water at 20°C on cleaned and polished metal surfaces range from 8° to 12° for copper and aluminum, and from 16° to 20° for stainless steel.

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[8] Frohnsdorff, G., and Tejada, S.B.: "Measurement of Contact Angles and Evaluation of Surface Coatings." Final Report, Contract NAS3-13725, NASA Lewis Research Center. NASA CR 72975, August 1971.

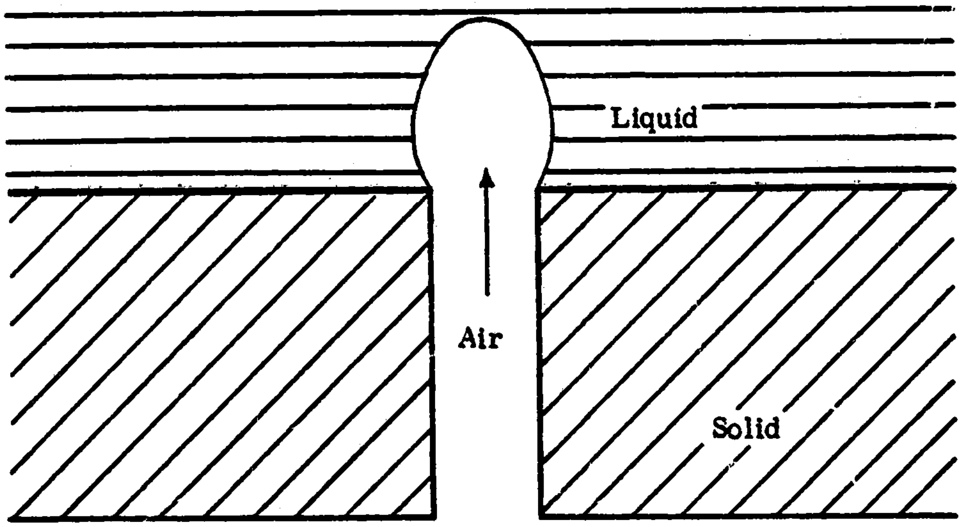
[9] Trevoy, D.J., and Johnson, H., Jr.: "The Water Wettability of Metal Surfaces." J. Phys. Chem., Vol. 62, p. 833 (1958).

[10] Schwartz, A.M., and Ellison, A.H.: "The Effect of Surface Contamination on Contact Angles and Surface Potentials." NASA CR 54708, 1966.

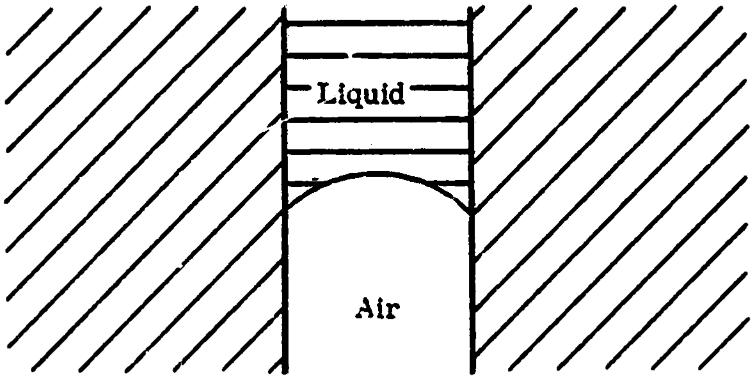
C.4 LARGER ORIFICE SIZES

One assumption in our discussion thus far has been an aerator orifice size much smaller than the bubble size. Curve 1 of Figure C.2 shows that, at $\theta = 100^{\circ}$, the maximum volume is about $90 mm^3$, corresponding to a sphere of 5.5 mm diameter. Hence this size bubble would not be expected to emanate from orifices larger than about this size. In the case of smaller contact angles, the restriction on hole size would be more severe.

If we consider the air hole to be sharp-cornered as shown in the sketch below, the contact angle ceases to be the controlling boundary condition if the interface is attached to the edges of the hole. Rather, the hole diameter predominates. A meaningful analysis would probably have to follow an approach similar to Fritz's, seeking in this case the largest member of the family of curves that can be spanned by the orifice diameter, rather than the largest member that will allow the requisite contact angle to be realized. (Note that the interface remains attached to the corner as its local orientation changes through 90°, for constant contact angle.)



Without attempting to actually solve the problem, we may surmise the following. If the hole is considerably smaller than the maximum bubble diameter calculated by Fritz, the bubble will reach the top of the hole, grow for a period while attached to the corner, and then spread across the horizontal surface as shown in the sketch at the beginning of this Appendix. Once it starts to spread across the horizontal surface, the Fritz analysis becomes applicable, and eventual detachment should come when it reaches the size predicted by Fritz. For increasingly larger hole sizes, a point is reached for which the bubble grows to Fritz's maximum volume while still attached to the corner, and hence cannot spread across the horizontal surface but detaches instead. For still larger holes, the bubble probably grows on the corner to a value somewhat greater than Fritz's maximum volume and detaches. As hole size increases, however, a point is reached for which a stable interface inside the hole is impossible.



This last case is entirely analogous to the well-known experiment in which water is picked up in a soda straw closed at the top by one's finger. The water in the straw is supported by air pressure, but only because the lower air-water interface is stable. The experiment cannot be repeated with a larger diameter tube, even though air pressure is equally capable of supporting the water, because of instability of the lower interface. It is also entirely analogous to the problem of liquid propellants in cylindrical tanks under low-gravity conditions, and hence the solution is by now well-known, and experimental verification is abundant.

The first comprehensive analysis was that of Reynolds, Satterlee, and Saad[11,12,13], results of which are presented in Figure C.3. The dimensionless

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[11] Satterlee, H.M., and Reynolds, W.C.: "The Dynamics of the Free Liquid Surface in Cylindrical Containers Under Strong Capillary and Weak Gravity Conditions." Tech. Rept. No. LG-2, Dept. of Mech. Eng., Stanford Univ., May 1964.

[12] Reynolds, W.C.; Saad, M.A.; and Satterlee, H.M.: "Capillary Hydrostatics and Hydrodynamics at Low-g." Tech. Rept. No. LG-3, Dept. of Mech. Eng., Stanford Univ., May 1964.

[13] Reynolds, W.C., and Satterlee, H.M.: "Liquid Propellant Behavior at Low and Zero G." Chap. 11 in The Dynamic Behavior of Liquids in Moving Containers, H.N. Abramson, ed., NASA SP-106, 1966.

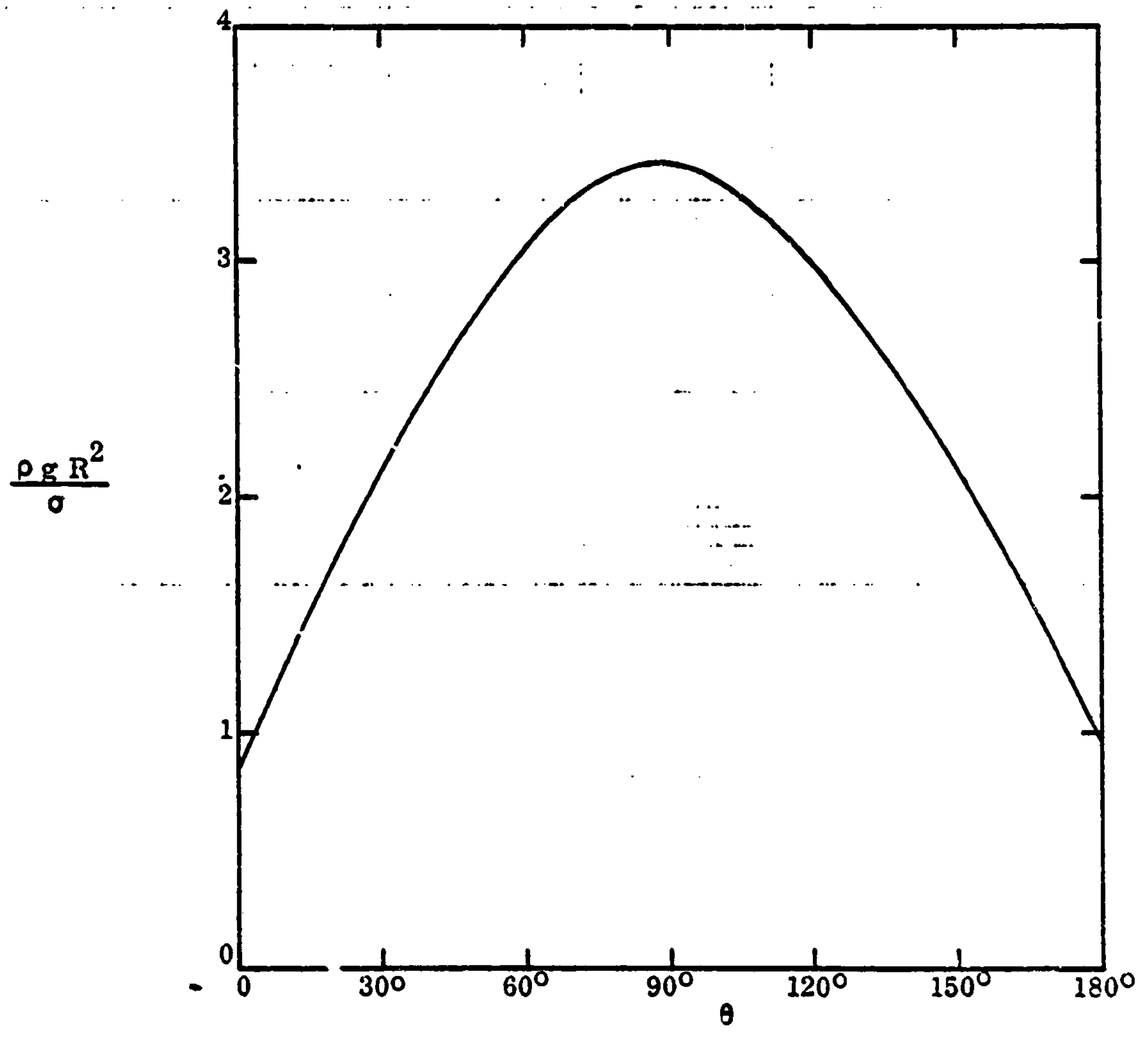

Figure C.3. Stability limit for an inverted meniscus in a cylindrical tube.

parameter $\rho gR^2/\sigma$ is known as the Bond number; ρ replaces the $(\rho_2 - \rho_1)$ density difference of earlier pages since $\rho_1 << \rho_2$ in most cases of interest. The critical Bond number for $\theta = 100^\circ$ is 3.33, giving a critical diameter of 10.0 mm, compared to Fritz's maximum bubble volume of 90 mm^3. The difference is more striking at smaller contact angles. At 50°, Figure C.2 gives a maximum volume of 11.7 mm^3, corresponding to a sphere of 2.8 mm diameter; the critical Bond number from Figure C.3 is 2.73, giving a critical hole diameter of 9.0 mm.

The conclusion is that these larger holes will produce larger bubbles up to the point where the hole diameter reaches the critical value calculated from the data of Figure C.3. For holes larger than this critical size, the aerator will presumably produce-bubbles whose size is governed by other factors besides hole size - flow rate and tube dimensions, for example - with a good likelihood that bubbles smaller than the opening size will be produced.

C.5 DYNAMIC EFFECTS

So far, we have assumed that static equilibrium conditions prevail at the time of bubble detachment. If the bubble grows rapidly, dynamic effects can be important in three ways:

1. If bubbles leave the aerator as a closely-spaced stream, due to rapid growth and detachment, they generate liquid motion away from the aerator in the vicinity of the bubble source. This liquid motion then tends to sweep newly-formed bubbles off the aerator surface before they reach their static equilibrium maximum volume.
2. The growth of the bubble itself might generate liquid motion away from the wall. If the volume changes linearly with time, then the linear dimensions of the bubble change rapidly at first, more slowly as time goes on. Therefore in the early stages of bubble growth, the rapid motion of its top surface away from the wall can generate liquid motion that then tends to drag the slowly growing bubble in a later stage of development off the wall.
3. Contact angle in the dynamic case is known to be a function of the velocity of the contact line, and also differs depending on whether the contact line is moving toward (advancing) or away from (receding) the gas phase - a phenomenon known as contact angle hysteresis. Investigations of dynamic contact angles to date have primarily been concerned with advancing contact angles, whereas the receding contact angle is the important one in the case of a growing bubble. The velocity dependence was demonstrated experimentally in 1962 by Rose and Heinz[14], who considered flow over a dry surface. The problem was then taken up by Friz [15], who analyzed the advance of a liquid over a previously-wetted surface. The numerical results led to the conclusion that contact angle depends on contact line velocity U_o according to

$$\tan\theta = 3.4\left(\frac{U_o\mu}{\sigma}\right)^{1/3}$$

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[14] Rose, W., and Heinz, R.W.: "Moving Interfaces and Contact Angle Rate-Dependency." J. Colloid Sci., Vol. 17, pp. 39-48 (1962).

[15] Friz, G.: "Uber den dynamischen Randwinkel im Fall der vollstandigen Benetzung." Zeit. fur Angew. Physik, Vol. 19, pp. 374-378 (1965).

μ being the viscosity. Ellison and Tejada[16] performed a series of experiments in which liquid advanced over a dry surface, and concluded that in this case the data could be correlated by the relation

$$\theta = A \tanh (CU_o) + D\ U_o^{1/3},$$

A, C, and D being empirical coefficients. The Fritz equation was found to give poor agreement with their results because of the difference in initial conditions. A set of experiments in which the situation analyzed by Fritz was carefully reproduced was carried out by Coney and Masica[17], who concluded that the Friz equation "is adequate." The results are shown in Figure C.4; the slight trend toward higher contact angles than predicted was thought to result from experimental error.

In summary, it appears that dynamic effects will result in smaller bubbles than predicted by static equilibrium considerations, except possibly for a dynamic contact angle effect in the case of rapidly growing bubbles. Even here, it is likely that just as advancing contact angles increase with velocity, receding contact angles should decrease with velocity, which would also result in smaller bubbles leaving the aerator.

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16. Ellison, A.H., and Tejada, S.B.: "Dynamic Liquid/Solid Contact Angles and Films on Contaminated Mecury." NASA CR 72441, July 1968.

17. Coney, T.A. and Masica, W.J.: "Effect of Flow Rate on the Dynamic Contact Angle for Wetting Liquids." NASA TN D-5115, March 1969.

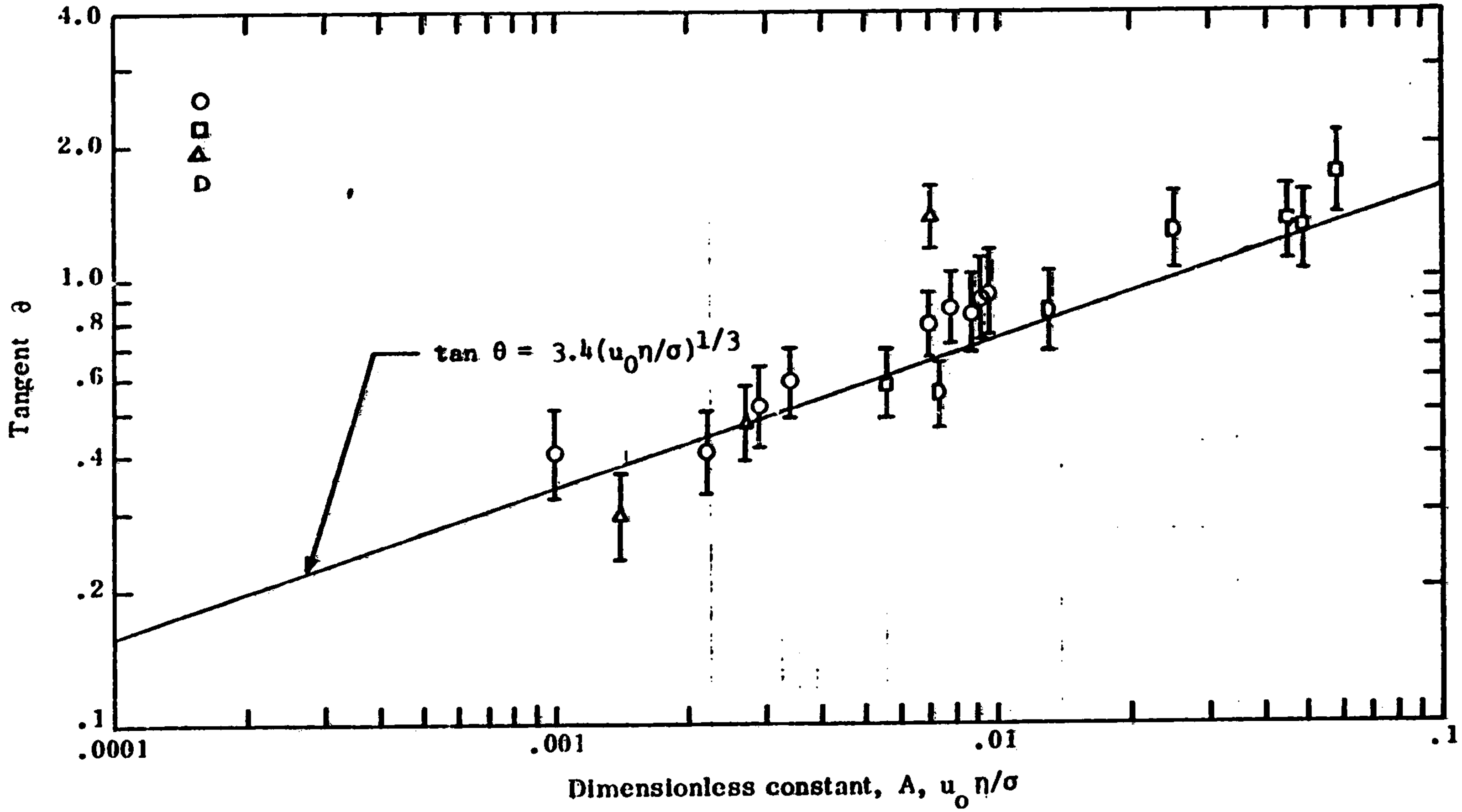

Figure C.4 Coney and Masica's experimental results for dynamic contact angle, compared to Friz's equation. Reproduced from NASA TN D-5115.

C.6 OTHER EFFECTS

In summary, we first considered the static equilibrium of a bubble assuming the hole to be too small to be a consideration, then looked at the effects of larger holes, defining essentially three regimes - hole to small to be significant, hole-dominated, and hole too large to be significant - and finally proceeded to consideration of dynamic effects. Of the other effects that might be important, the most significant is the proximity of other bubble sources, since we have always considered bubbles emanating from single, isolated holes.

Other nearby bubble sources can have at least two effects. By adding to the vertical fluid motion in the vicinity of the aerator, they tend to reduce the bubble size still more as bubbles are pulled away from the surface before reaching their static equilibrium maximum size. On the other hand, if the sources are very close there is a possibility of bubble coalescence, resulting in larger bubbles than predicted.

The potential energy associated with the surface of a free bubble is σA, the product of surface tension and surface area. If two spherical bubbles, each of radius R_1, coalesce to form one bubble of radius R_2, conservation of mass for the air within the bubble requires

$$2\,\rho_1 R_1^3 = \rho_2 R_2^3$$

and if we assume the process to be isothermal, the ratio of densities will equal the ratio of pressures,

$$\frac{\rho_2}{\rho_1} = \frac{p_2}{p_1} = \frac{p_a + 2\sigma/R_2}{p_a + 2\sigma/R_1}$$

yielding

$$R_2 = R_1 \left(2\,\frac{p_a + 2\sigma/R_1}{p_a + 2\sigma/R_2}\right)^{1/3}$$

The limiting cases, $(p_a R_1/\sigma) \rightarrow 0$ and $(p_a R_2/\sigma) \rightarrow \infty$ yield the result

$$2^{1/3} R_1 \leq R_2 \leq 2^{1/2} R_1$$

and hence if we compare the initial and final potential energies,

$$P.E._1 = 2(4\pi R_1^2)\sigma \quad , \quad P.E._2 = 4\pi R_2^2\sigma \quad ,$$

the result is

$$2^{-1/3} \leq \frac{P.E._2}{P.E._1} \leq 1 \quad .$$

The conclusion is two-fold. First, two bubbles that come into contact with each other will always tend to coalesce because of the resultant decrease in potential energy. Second, the resultant bubble will be at least twice the volume of each original bubble, and perhaps as large as $2^{3/2} = 2.83$ times the bolume of each original bubble.

C.7 BUBBLE RISE VELOCITIES

Once the bubble detaches from the aerator surface it rises through the pond at a velocity dependent on the size of the bubble. The study of bubble rise velocities was especially active in the 1950's, with particularly significant papers being those of Haberman and Morton[18] (experimental) and Moore[19] (theoretical).

Bubble rise velocity was found to depend on Reynolds and Weber numbers,

$$R = 2r_e U\rho/\mu$$
$$W = 2r_e U^2\rho/\sigma$$

and also on a third dimensionless parameter, M, defined as

$$M = g\mu^4/\rho\sigma^3,$$

where

r_e = equivalent bubble radius, $r_e = (3V/4\pi)^{1/3}$
U = terminal velocity
ρ = liquid density
μ = liquid viscosity
σ = surface tension
g = gravitational acceleration

A quote from Moore will serve to summarize the Haberman and Morton results very concisely:

"For low M liquids ($M \ll 10^{-8}$) the terminal velocity at first increases rapidly as r_e increases, achieves a maximum and after falling to a minimum rises gradually again. For high M liquids ($M \gg 10^{-3}$), the terminal velocity increases steadily with r_e, though the rate of increase falls off at a fairly well defined value of r_e.

"For low M liquids the shape is at first spherical, then increasingly oblate, then, at about the radius corresponding to the maximum velocity, the shape fluctuates rapidly about an oblate form until, for very large values

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[18] Haberman, W. L., and Morton, R. K.: David Taylor Model Basin Rept. No. 802, 1953.

[19] Moore, D. W.: "The Rise of a Gas Bubble in a Viscous Liquid." J. Fluid Mech., Vol. 6, pp. 113-130 (1959).

of r_e, the bubbles attain a striking umbrella shape which is quite steady at its frontal surface though the rear of the bubble fluctuates. These spherical cap bubbles were the subject of an important investigation by Davies and Taylor[20] (1950). For high M liquids the spherical cap shape is achieved without the bubble surface ever becoming unsteady.

"For low M liquids the bubble trajectory is at first rectilinear, then, at about the bubble radius for maximum terminal velocity, both planar zig-zag and spiral trajectories are observed. Finally, the spherical cap bubbles rise in very nearly linear trajectories. For low (sic) M liquids only rectilinear trajectories are observed."[21]

Figures C.5 and C.6 show the Haberman and Morton results in terms of the drag coefficient of the bubbles as a function of Reynolds and Weber numbers, with M as a parameter. The expression for terminal velocity in terms of drag coefficient, C_D, is

$$U = \sqrt{\frac{8r_e g}{3 C_D}} \quad .$$

Use of this information to find terminal velocity is of course complicated by the fact that R and W are defined in terms of this velocity. The present author can only quote without comment Moore's statement that "it is more illuminating to consider the drag coefficient C_D rather than U..."

These results show the Reynolds number variation is independent of M except in the range $10 < R < 10^3$, whereas the Weber number dependence varies greatly with M in terms of the location, but not shape or slope (in the log-log plot) of the curves.

Moore's analysis produced the significant result that the drag coefficient for a spherical bubble is given by

$$C_D = 32/R,$$

subject to the restrictions that R is large and W small, and showed that both conditions can be satisfied in low M liquids. Comparison with the experimental

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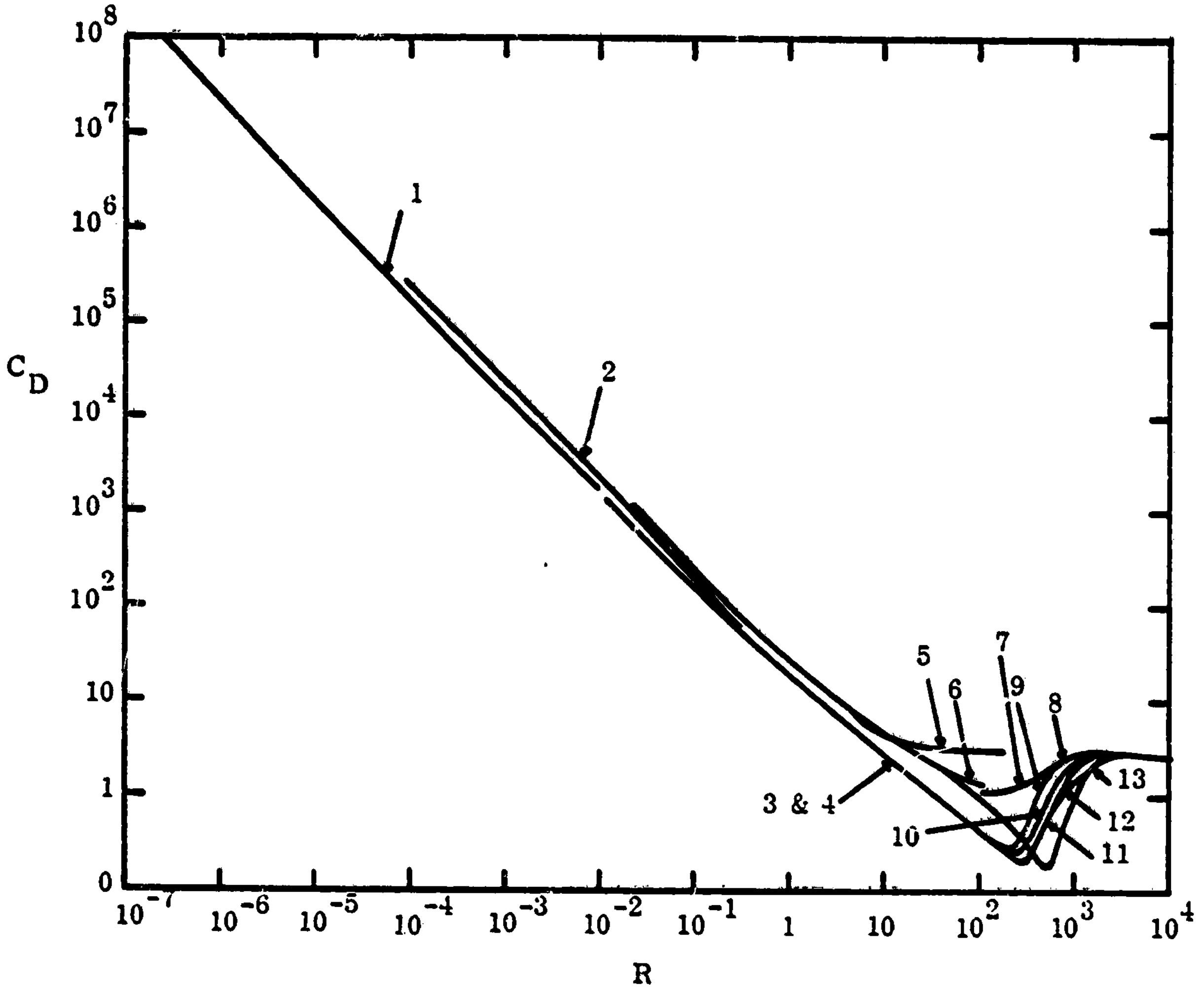
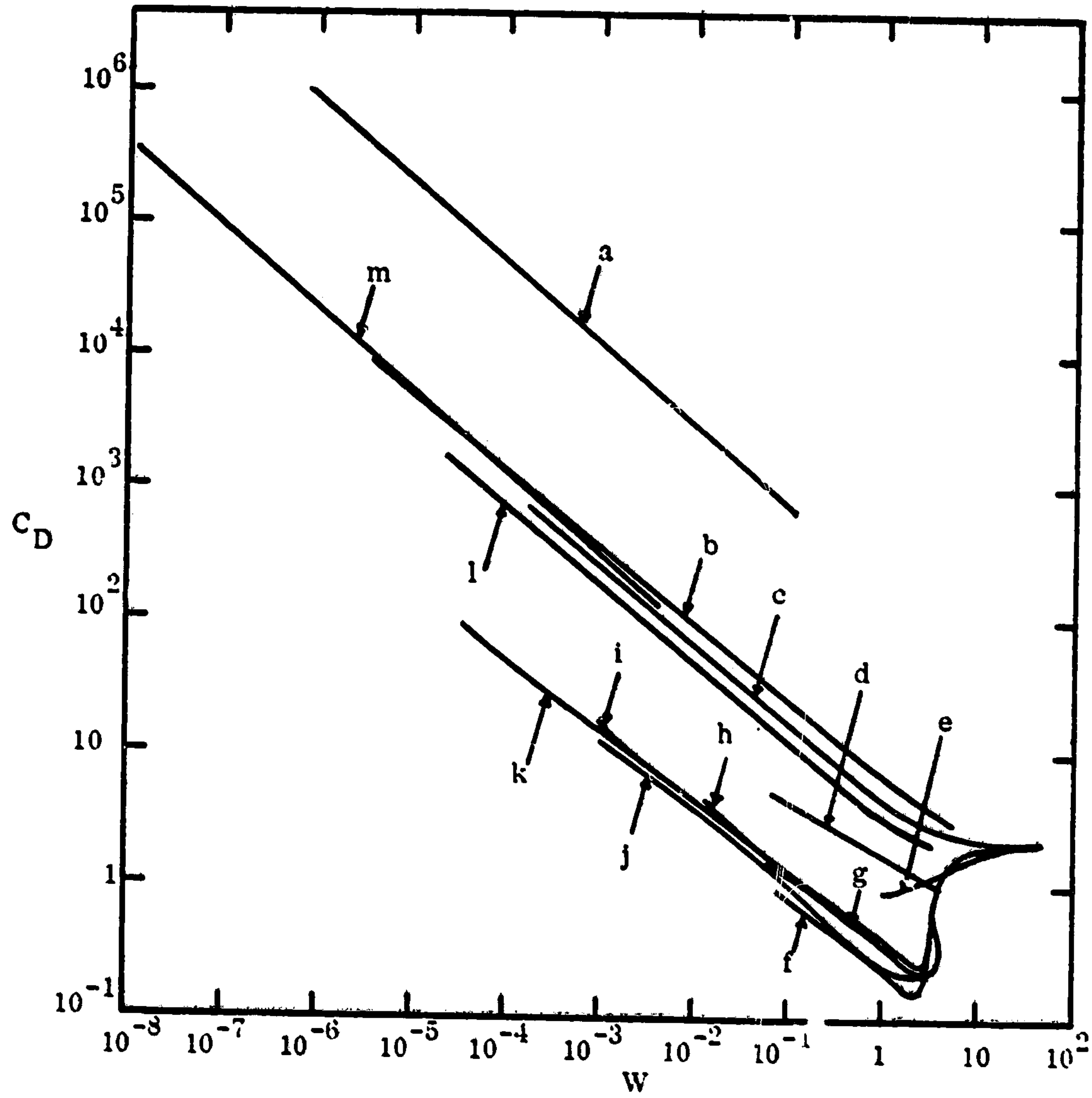
20. Davies, R.M., and Taylor, G.I.: "The Mechanics of Large Bubbles Rising through Extended Liquids and through Liquids in Tubes." Proc.Roy. Soc. A, Vol. 200, pp. 375-390 (1950).

21. Moore, D.W., op.cit.



1. Syrup (Bond), $M = 0.92 \times 10^{6}$.
2. Olive oil (Arnold), $M = 0.716 \times 10^{-3}$
3. Water + 62% corn syrup, $M = 0.155 \times 10^{-3}$
4. Water + 68% corn syrup, $M = 0.212 \times 10^{-2}$
5. Mineral oil, $M = 1.45 \times 10^{-2}$
6. Water + 56% glycerine (Bryn), $M = 1.75 \times 10^{-7}$
7. Water + 42% glycerine (Bryn), $M = 4.18 \times 10^{-8}$
8. Turpentine, $M = 24.1 \times 10^{-10}$
9. Water + 13% ethyl alcohol (Bryn), $M = 1.17 \times 10^{-8}$
10. Varsol, $M = 4.3 \times 10^{-10}$
11. Cold water (filtered), $M = 1.08 \times 10^{-10}$
12. Methyl alcohol, $M = 0.89 \times 10^{-10}$
13. Water (filtered), $M = 0.26 \times 10^{-10}$

Figure C.5. Moore's presentation of the Haberman and Morton results: Reynolds number dependence



(a) Syrup (Bond), $M = 0.92 \times 10^6$
(b) Water + 68% corn syrup, $M = 0.212 \times 10^{-2}$
(c) Mineral oil, $M = 1.45 \times 10^{-2}$
(d) Water + 56% glycerine (Bryn), $M = 1.75 \times 10^{-7}$
(e) Water + 42% glycerine (Bryn), $M = 4.18 \times 10^{-8}$
(f) Methyl alcohol, $M = 0.89 \times 10^{-10}$
(g) Water + 13% ethyl alcohol, $M = 1.17 \times 10^{-8}$
(h) Turpentine, $M = 24.1 \times 10^{-10}$
(i) Varsol, $M = 4.3 \times 10^{-10}$
(j) Water (filtered), $M = 0.26 \times 10^{-10}$
(k) Cold water, $M = 1.08 \times 10^{-10}$
(l) Water + 62% corn syrup, $M = 0.155 \times 10^{-3}$
(m) Olive oil (Arnold), $M = 0.716 \times 10^{-2}$

Figure C.6. Moore's presentation of the Haberman and Morton results: Weber number dependence.

results showed good agreement except for a slight displacement of the theoretical curve below experimental values.

Extension of the theory to non-spherical bubbles was also treated by Moore, but the results were less conclusive and are felt to be beyond the scope of the present discussion.

The expression $C_D = 32/R$ can be solved for U, giving

$$U = \sigma \frac{g r_e^2}{6\mu}$$

which gives, for water at 20°C,

$$U = 1.63 \ r_e^2 \text{ meters/second,}$$

if r_e is in mm.

ρ

APPENDIX D

ABSORPTION SCRUBBER FUNDAMENTALS AND DESCRIPTIONS

D.1 FLOW RATES AND SIZING OF ABSORPTION SCRUBBERS

The performance of a gas scrubbing operation involving only solution of a contaminant with no chemical reaction is limited by the equilibrium relation between the contaminated gas and the contaminated scrubbing liquid.

For scrubbing gases, the operating lines and initial and final points are constrained to lie on the side of the equilibrium line on which the contaminant concentration in the gas is greater than equilibrium concentration at any given concentration of contaminant in liquid. The slope of the operating line on a gas phase concentration vs. liquid phase concentration curve is given by the ratio of liquid flow rate (moles/area/time) to gas flow rate. Thus if the equilibrium curve is known, and the flow rate and degree of contamination of the entering gas is known, and the permissible degree of contamination of the leaving gas is given, the minimum liquid flow rate (liquid flow rate for an infinitely long scrubber) can be found.[1]

The foregoing obtains for cocurrent as well as countercurrent flow scrubbers, though we are here primarily concerned with the latter. The schematic diagram (Figure D.1) shows an example of an equilibrium curve and an operating curve for a countercurrent scrubber. As a very rough approximation, the length of a scrubber is inversely proportional to the distance between the equilibrium and operating lines. It is conventional that the equilibrium and operating lines be approximately parallel, as the equilibrium line permits. With the equilibrium line known, the gas flow rate and gas initial contamination concentration also known, and with the outlet gas contamination specified, the operating line for an infinitely long scrubber will be the straight line passing through the specified concentration points, tangent at one or more points to the equilibrium line, and elsewhere above the equilibrium line. Since the operating line and the gas flow rate are known, and the line's slope is the ratio of liquid and gas flow rates, the minimum liquid flow rate is determined. For a finite-length scrubber, the liquid flow rate is necessarily greater than for an infinitely long scrubber.

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[1] Calvert, Seymour: "Source Control by Liquid Scrubbing." Chapter 46 in Air Pollution, Vol. III, ed. by Arthur Stern, Academic Press, New York, 1968.

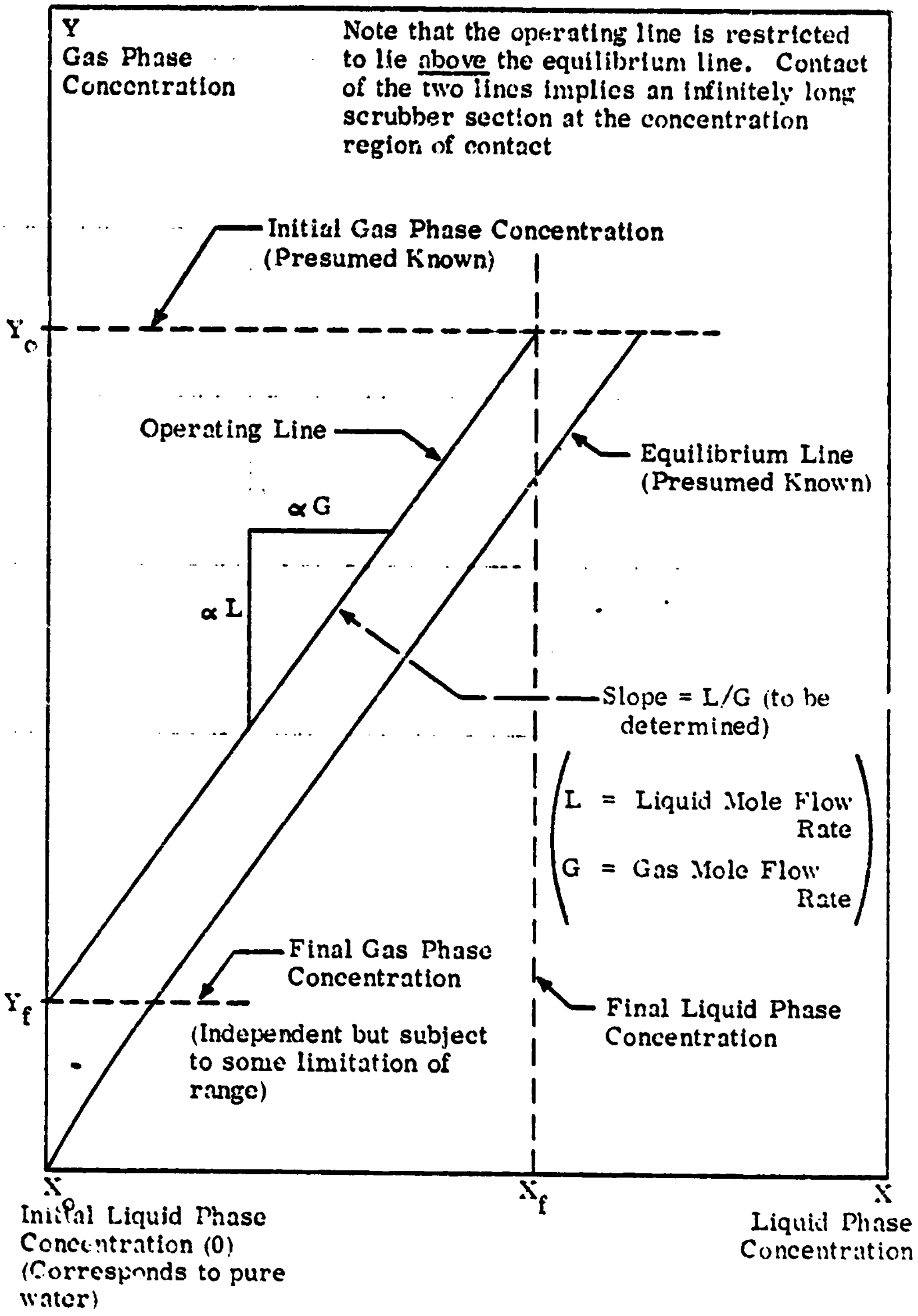

Figure D.1 Typical scrubber performance chart.

Equilibrium curves for air and water contaminated with N_2H_4, MMH, and NO_2, at room temperature, are presented in Figure D.2.

The concentration of noxious gases immediately over a solution is proportional to the vapor pressure of the liquid. The vapor pressure can be estimated from Raoult's law which states that the partial vapor pressure of any constituent of a solution is equal to the vapor pressure of the pure substance multiplied by the mole fraction of that constituent in solution. Figures D.3, D.4, and D.5 show the partial pressures in air for mixtures of the various propellants with water as calculated using Raoult's law, and also the vapor pressure for the solution. (This latter function varies linearly from the vapor pressure of pure water, on the left side, to the vapor pressure of pure propellant on the right side.)

Once the vapor pressure is calculated, the number of moles of each gas per liter can be approximated by the ideal gas law. The weights of the gases are then calculated and the weight concentrations can be found. The concentration of the vapor in air is a function of the concentration of the contaminant in water. The following results were calculated for 1 atm., 25°C:

For HNO_3,
wt conc in air $\approx$ .05 (wt conc in water), wt conc in water $<$ .1

For MMH,
wt conc in air $\approx$ .01 (wt conc in water), wt conc in water $<$ .1

For N_2H_4,
wt conc in air $\approx$ .025 (wt conc in water, wt conc in water $<$ .1

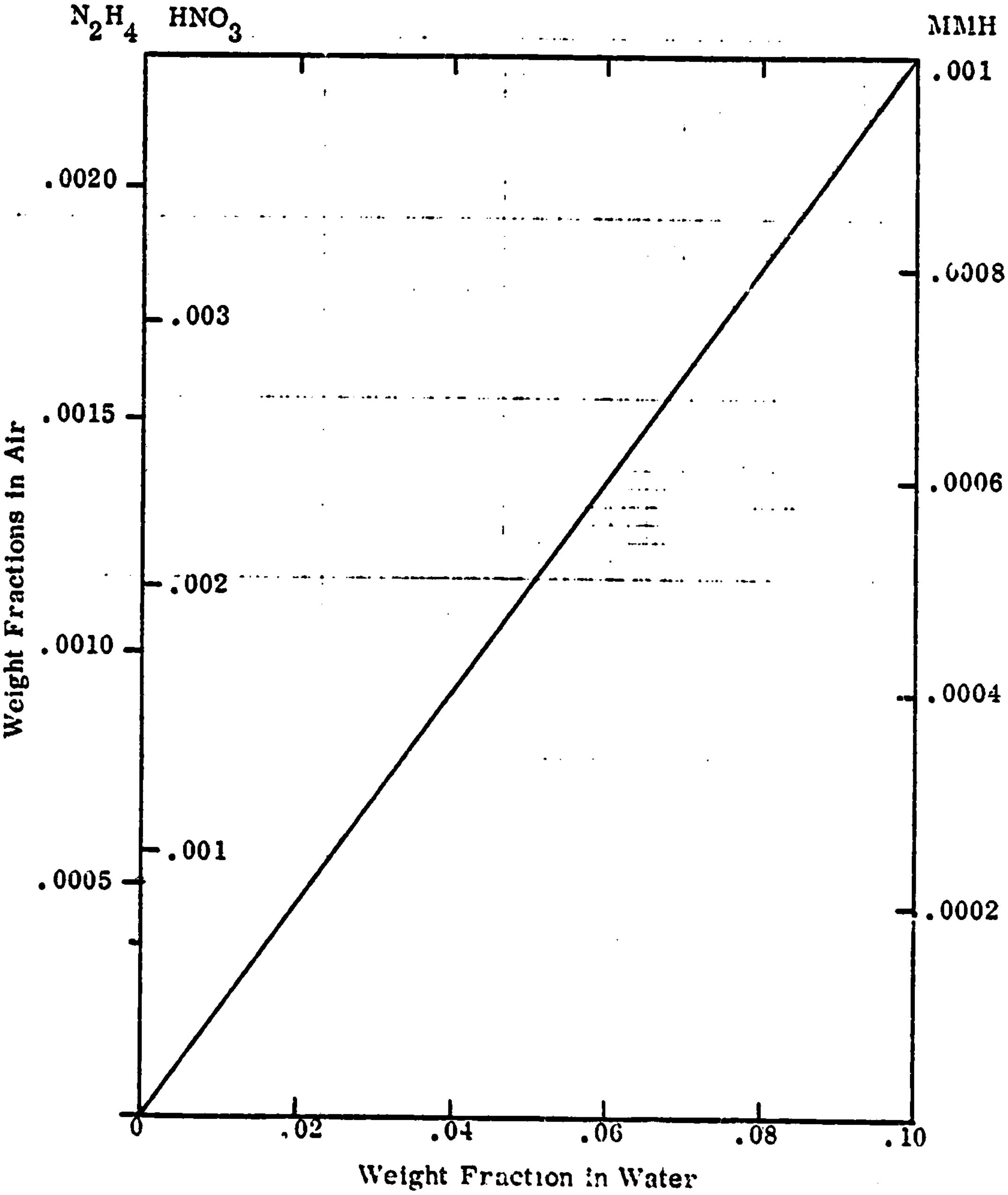

Figure D.2 Equilibrium curves for hypergolic propellants in air and water.

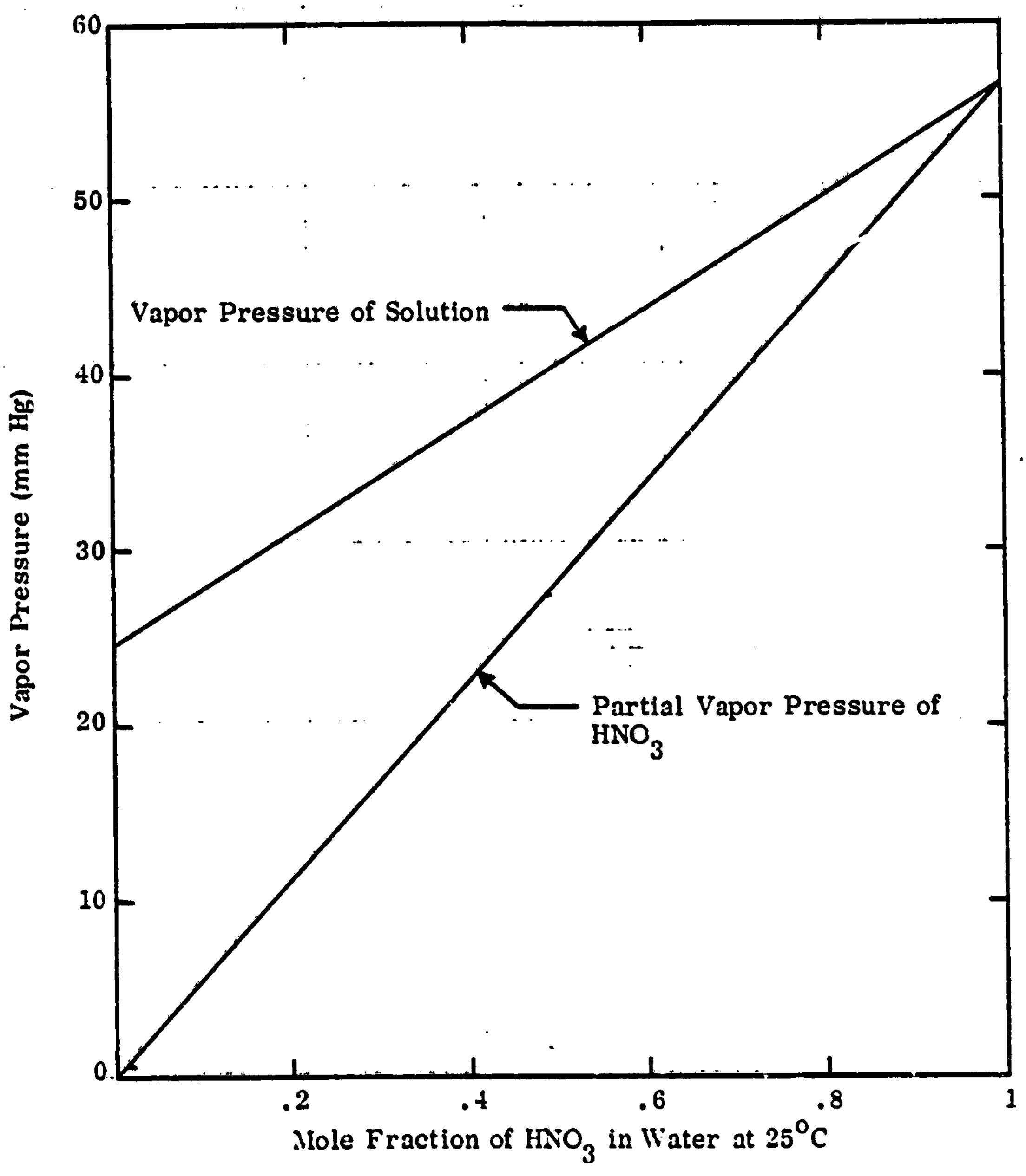

Figure D.3 Vapor pressures of HNO_3/H_2O mixtures.

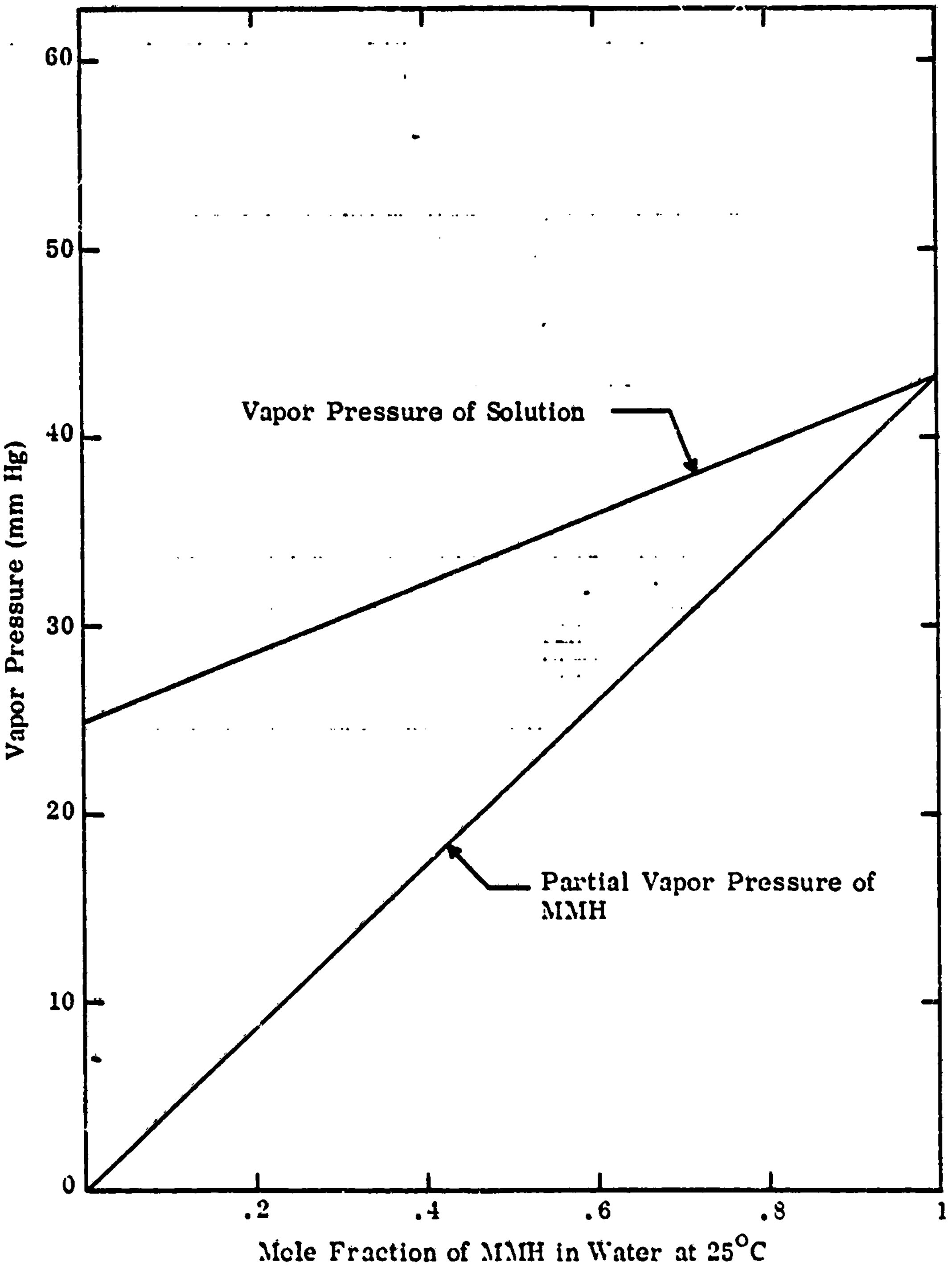

Figure D.4 Vapor pressures of MMH/water mixtures.

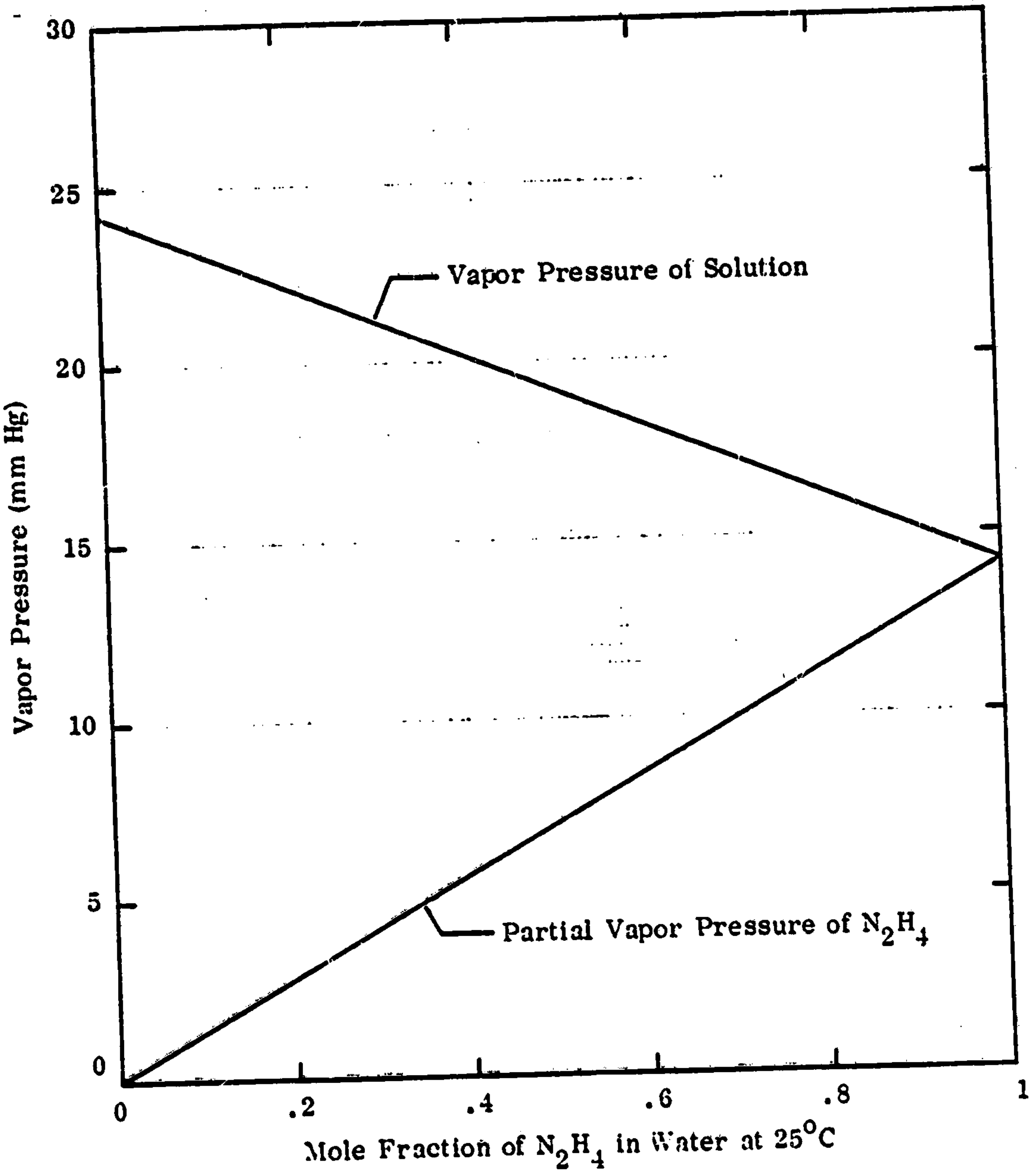

Figure D.5 Vapor pressures of N_2H_4/water mixtures.

D.2 DESCRIPTIONS OF SOME ABSORPTION SCRUBBERS

In the countercurrent packed scrubber, the gas stream moves upward in a direction opposite the liquid stream which is moving downward through a packed bed (Figure D.6). This method provides intimate contact between the liquid and gas streams within the packed beds and gives best results when the scrubber is operated at the maximum allowable pressure drop. At high pressure drops maximum turbulence is obtained, enhancing the quick absorption of the gaseous contaminants in the liquid stream.

A significant advantage of countercurrent flow is that the gas stream, rich in contaminants, comes into contact with the spent liquor at the bottom of the packed beds, while the fresh liquid coming in at the top of the scrubber is in contact with the least contaminated gas. This characteristic provides a fairly constant potential throughout the packed bed for driving the gaseous contaminants into the scrubbing liquid. There is also less chance that the dissolved gases will be stripped from the liquid.

Countercurrent flow scrubbers are more expensive to operate because of the high liquid consumption and high pressure drop. Since this design handles the tougher problem of removing gases, the higher cost of operation is balanced by the highly efficient absorption capability of removing gases with low solubility.[2]

A detailed presentation of the calculations involved in establishing scrubber size in terms of incoming and outgoing mole fractions of contaminant in the liquid and gas streams, and total contaminant quantities, is found in the chapter by Seymour Calvert cited previously. Among the concerns are contact surface area, packing density, number of transfer units, height and cross-sectional area of the tower. Packing density is the ratio of total surface area to volume for the packing. For example, one inch Raschig rings have a packing density fo 55 ft^{-1}.

Descriptions of some absorption scrubbers that have been used in the past for hypergolic propellants are presented on the following pages. More recent advances were covered in Sections 2.12 and 3.9.

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[2] "Countercurrent Flow Scrubbers". Ceilcote Technical Bulletin 12-3, February, 1974.

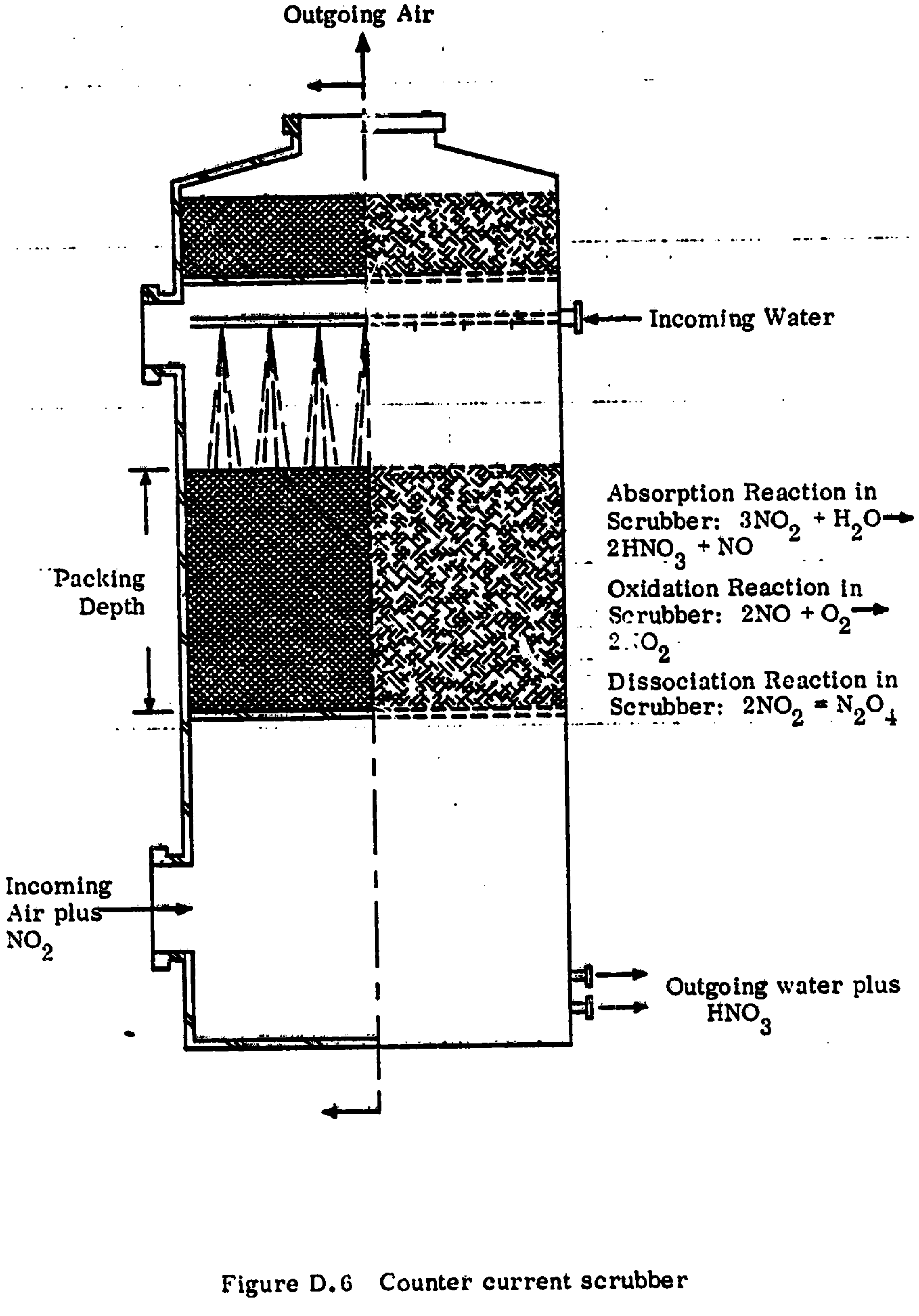

Figure D.6 Counter current scrubber

Hamilton - Standard's Gemini and Saturn Scrubbers

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 fuel or oxidizer vapors (different scrubbers of the same design were used for fuels and oxidizers) were put through the scrubbers, which met design specifications calling 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 is downstream of a dilution fan/mixing chamber where the scrubber effluent is mixed with fresh air in a 100:1 ratio, thus reducing contaminant concentrations by a factor of one hundred.

The scrubbers were designed to accept up to 10 SCFM at 10^6 ppm, up to 60 SCFM at 1500 ppm, of N_2O_4 - or MMH - contaminated nitrogen. One may infer that the scrubber, operating with a through flow of 60 SCFM, must reduce N_2O_4 concentration by at least a factor of 3 (67% removal) or must reduce MMH concentration by a factor of 15 (93% removal)

Scrubbing is accomplished by a cross-flow absorber which moves the gas across sixteen cascaded filters, each with an associated fresh water spray nozzle. The cross-section of the scrubber is about 2/3 ft^2, and of each filter, about 1 ft^2. The filters are of pyrex glass wool supported by stainless steel. The length of the scrubber is about 18 ft., folded once to a "U" form. Water flow rate is 40 GPM. The scrubber and associated dilution blower were manufactured by the Buffalo Forge Co. of Buffalo, N.Y. Schematic diagrams are shown in Figures D.7 and D.8. Details were also shown in Figure 3.9.1, and test results pertaining to the operation of this scrubber were described in Section 3.9.1.

Hamilton Standard's NASA-Goddard Hydrazine Scrubber

More recently, Hamilton Standard completed for NASA - Goddard a small scrubber-neutralization system to allow the indoor firing of monopropellant hydrazine reaction rockets. The system will accomodate a single 5 lb. thrust engine and two 1/2 lb. thrust engines simultaneously, representing a hydrazine flow rate of .025 - .030 lbs/min. The hydrazine concentrations in the system inlet and outlet are not known. Exhaust from the test engine(s) is drawn into a

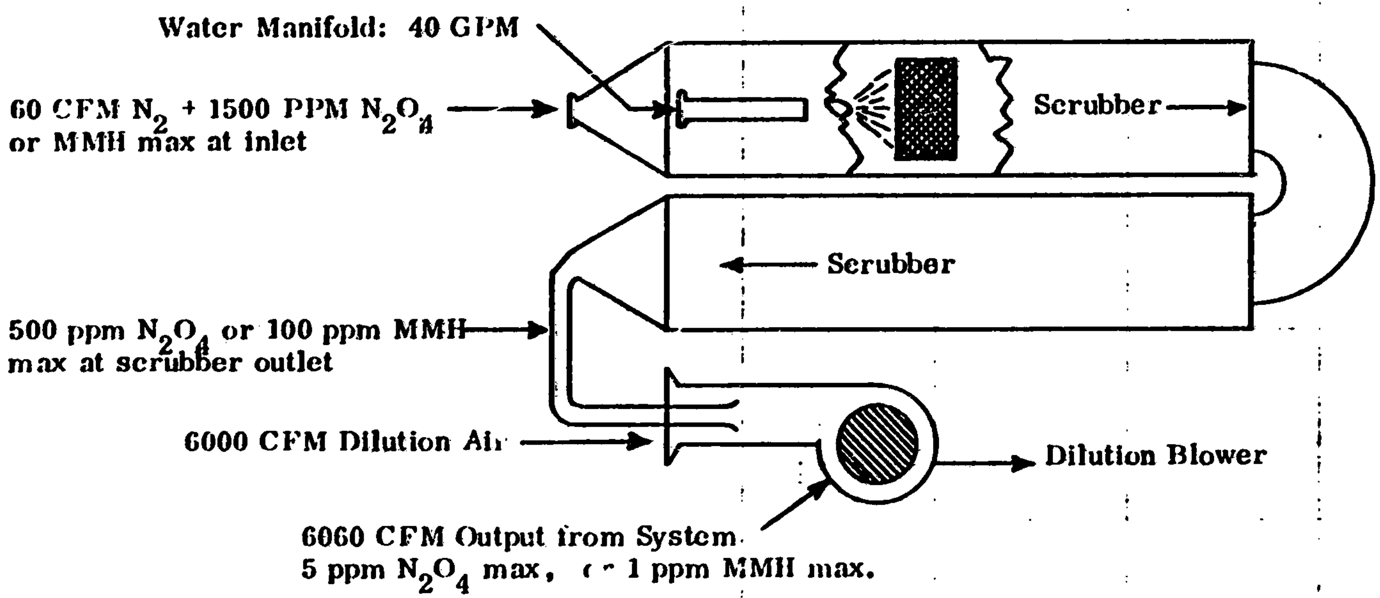

Figure D.7 Top View of the Hamilton Standard (Buffalo Forge) Scrubber

Scrubber Diagram

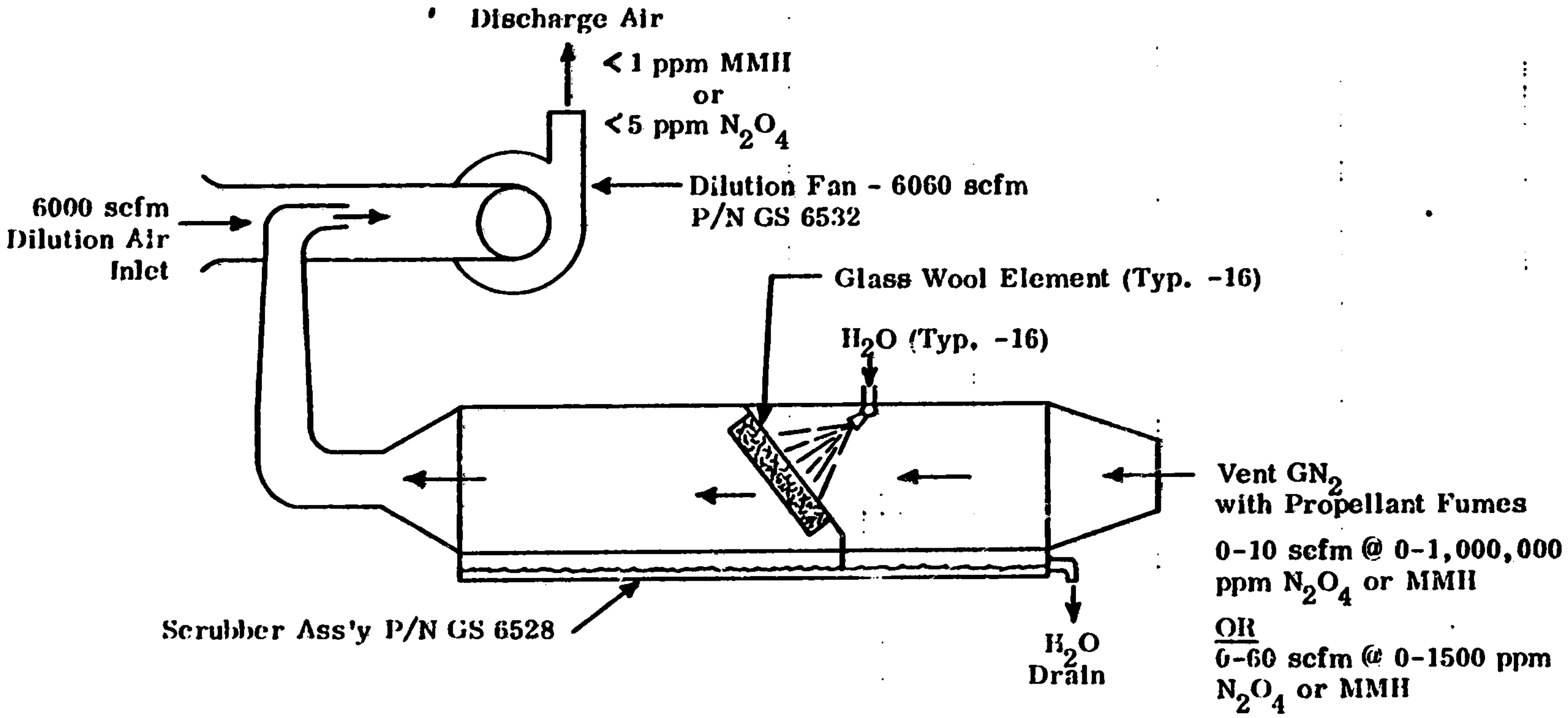

Figure D.8 Side view of the Hamilton Standard (Buffalo Forge) scrubber.

manifold along with a significant quantity ot room air, which has the purpose of diluting any free hydrogen which may present danger of explosion otherwise. The depression to draw the exhaust into the manifold is provided by coupling the manifold outlet to the inlet of a jet pump scrubber, which is a large water-driven jet pump. The scrubber exhaust impinges on the free surface of 100 gallons of liquid in an oversize water box; the liquid is a weak (pH 2.2) solution of hydrochloric acid (HCl). Gas and liquid are separated in this box and the cleaned gas is vented. The jet pump scrubber, drawing manifold gases, has an 8 in. (diameter) throat, or venturi, and the water jet which powers the scrubber uses about 50 GPM at 70 PSI, requiring a 15 HP motor to drive the water pump. The jet pump scrubber is supplied by Croll-Reynolds of Westfield, N.J., and is of a type commonly supplied by this company, if not actually "off-the-shelf". A diagram of the jet pump scrubber is shown in Figure D.9.

The Peabody Oxidizer Scrubber

Peabody scrubbers have been installed on the N_2O_4 vent lines at the Delta launch facilities at both Cape Canaveral and Vandenberg Air Force Base. This scrubber consists of a column, approximately 9 inches in diameter, mounted on a larger base, approximately 3 ft. in diameter, containing a 5% solution of $NaHCO_3$ which is recirculated during operation. Within the column are 5 impingement baffle plates located at different levels, a spray header in the upper part of the column, a spray nozzle in the lower part to saturate the incoming gases and to cool the bottom plate stage, and a stainless steel wire mesh water demister at the top of the column.

The liquor recirculating pump, gas control system, and the necessary regulating and safety valving and piping are located externally. The whole apparatus is mounted on a trailer for portability.

The recirculating pump capacity is 24 gpm; the GN_2 gas control regulates pressure within the system to smooth out pressure surges and partial vacuums and to control the operating pressure.

The base and piping hold about 190 gallons of scrubber solution, and a float-type liquid level controller adjusts the water level on the plates. The vent vapors enter near the top of the base of the scrubber where they encounter

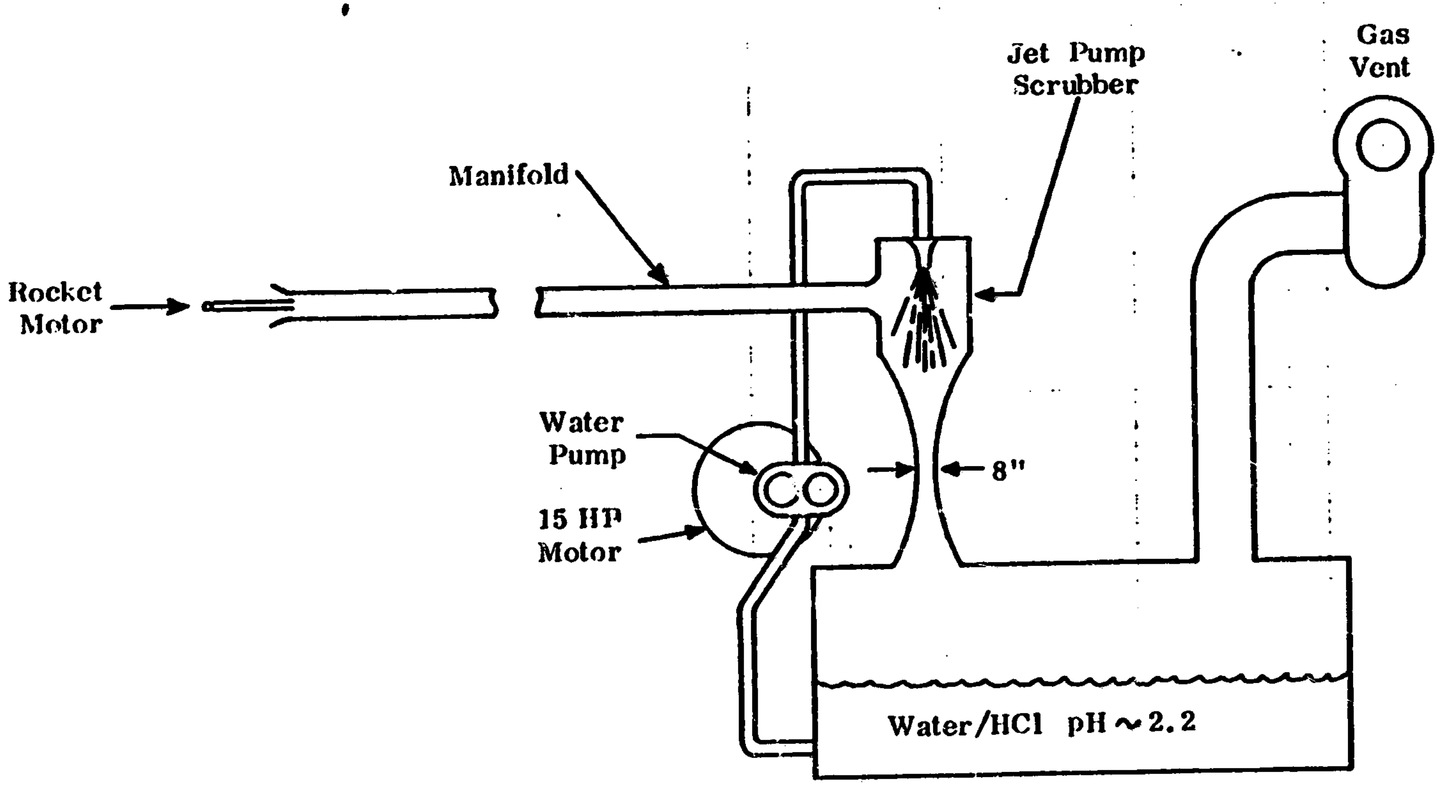

Figure D.9 The Hamilton Standard (Croll-Reynolds) jet pump scrubber.

the $NaHCO_3$ solution spray. The reaction begins here and continues as the gas proceeds through the 5 stages of baffles, as follows:

$$NO_x + \underset{\text{in solution}}{NaHCO_3} \longrightarrow CO_2\uparrow + H_2\uparrow + Na^+ + NO_3^- + NO_2^- + NO$$

with incidental NO formation:

$$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO\uparrow$$

The NO reacts with the HCO_3^- ion or is vented from the column.

The final products in the scrubber liquor are solutions of $NaNO_3$, $NaNO_2$, and unreacted $NaHCO_3$, with varying amounts of dissolved gases. Excess CO_2, H_2, H_2O-vapor, and NO_x are released to the atmosphere.

The water for scrubbing is supplied by the spray head located above the top plate stage. As the gases rise through the column they come into intimate contact with liquid flowing downward through the five stages of impingement baffles, utilizing a system of downcomers and seals. In the process, the gases are entrained as myriads of small bubbles, with an immense surface area, thus enhancing absorption into the water layers on the baffle plates.

As the water trickles down the column, it eventually reaches the enlarged base (reservoir) and is recirculated by the pump. Replacement of the scrubber liquor is performed as required.

The water demister captures entrained liquid droplets from the scrubber gas, forming larger drops which can fall downward.

The cleaned gas (usually N_2) exits through a pressure-reducing valve, located on the top of the column, to the atmosphere. A safety valve located atop the scrubber base prevents a buildup of excessive pressure within the system.

Except for the pump, this scrubber has no moving parts. The necessary maintenance reported by its users consists primarily of unclogging plugged spray heads and occasional replacement of the liquid solution.

The efficiency of this unit is not known. Only minor visible brown plumes were reported on rare occasions by the personnel involved.

The Nolte Hydrazine Scrubber

Nolte scrubbers have been installed on the Aerozine 50 vent lines at the Delta launch facilities at both Cape Canaveral and Vandenberg Air Force Base. The scrubber schematic is shown in Figure D.10, and the following brief description is quoted from an operating manual.

> "The Scrubber Water Supply Regulator feeds 30 psig, 3 G.P.M. tap water to the Scrubber through a motor-operated, normally closed ball valve. The Scrubber Water Supply Valve is opened at the beginning of every test by turning on S-5 at the electrical control panel. Water then flows through the Scrubber Flow Valve, and Scrubber Spray Valve. These valves control the scrubbing efficiency of the unit.
>
> "A standpipe in the bottom of the scrubber controls the liquid level for optimum system back pressure, and a Scrubber Drain Valve allows complete draining when required. Contaminated gas enters at the vapor inlet and rises through the water spray to the first scrubbing stage. As the gas flows through the 15 3/16"holes it comes in contact with the baffle and is deflected down against the water flooded plate. The water is thus aerated and subsequently absorbs and neutralizes the harmful propellant fumes in the vented gas. After the gas has passed through four successive scrubbing stages, 90% of the noxious vapors are removed; the water vapor is screened out with a stainless wire-mesh water eliminator, and the remaining gas is vented to atmosphere. To prevent high-pressure surge damage, each scrubbing stage has a 3/4 inch standpipe welded into it with a water cup on the bottom. When the pressure builds up, the water blows out of the cup and allows gas to flow straight to the vent without passing through the scrubbing holes. Water refills the cup after the pressure surge is reduced."

The Rockwell Scrubber System

A system of scrubbers for N_2O_4 vapors was designed and built at the Space Division of North American Aviation (now Rockwell International) in the late 1960's. The following paragraphs describe the system.

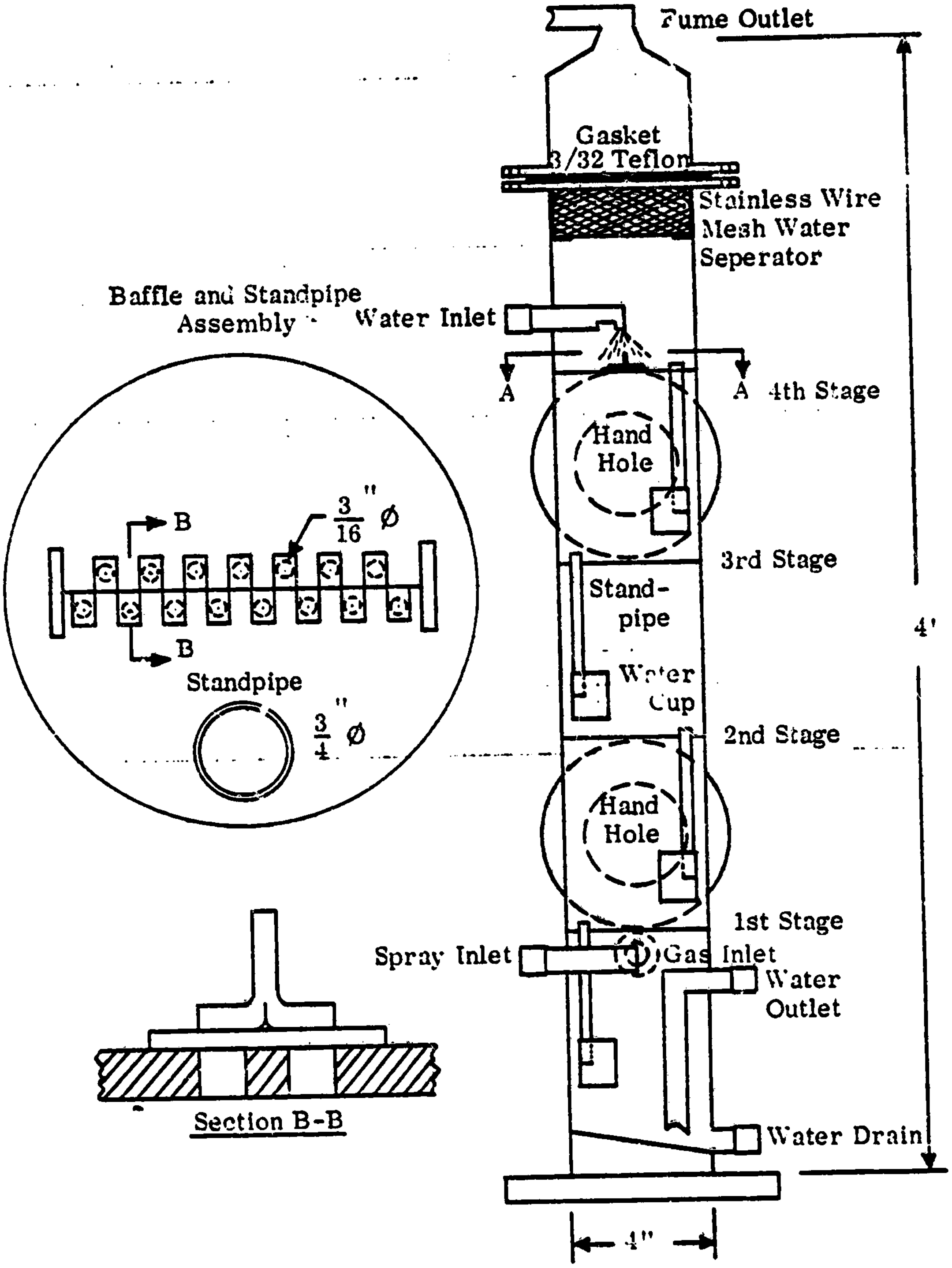

Figure D. 10 The Nolte hydrazine vent scrubber.

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"The RCS facility cell exhaust system employs three exhaust systems that can operate independently or in several combinations. Two of the systems, located adjacent to fuel and oxidizer test cells, have identical hardware. They employ 2000-cfm-rated exhaust fans, drawing approximately 1600 cfm from the test cell and 400 cfm from the 6 by 6-foot storage room at the corner of each propellant cell. The other system is serviced by one 6000-cfm-rated exhaust system.

"The ducting from the 6000-cfm scrubber is designed to draw exhaust gases from either the command module, service module, or both test cells. The fuel cell scrubber is interconnected to the fuel, fuel storage, service module, and command module cell. The oxidizer scrubber is connected to the oxidizer, oxidizer storage, and command module cells. All positions can be independently serviced.

"Each of the three exhaust systems consists of interconnecting ducting, a cyclone exhaust scrubber and a contaminants dilution unit equipped with an axial fan. The interconnecting ducting for the cells is equipped with remotely operated draft and isolation dampers, designed to the same principle as the forced air supply, i.e., selective isolation. In addition to the cell isolation capability, the scrubbers are equipped with dampers located in the ducting near the intakes to the exhaust fans; these dampers can be used to isolate the scrubbers from the cells or for selectively metering the exhausting from the cells.

"Each of the cyclone exhaust scrubbers consists of an intake fan and three water fog chambers (stacked). The fog chambers are separated by woven stainless steel screens and are equipped with separate air-water fog spray systems. The mechanism of the exhaust scrubber essentially involves forcing the contaminated air, exhausted from the cell, through the fog chambers, where they chemically react, and out to the contaminants dilution unit. In the contaminants dilution unit, the contaminated exhaust is diluted by mixing with uncontaminated air. It is exhausted through an outlet stack into the atmosphere at a high velocity, so that it is carried away from the vicinity of the facility roof top.

"The contaminants dilution unit consists of a high-speed (10,000-cfm-rated) axial fan installed in a cylindrical stack. The stacks are equipped with baffles; the baffles create eddy currents to provide ultimate mixing of uncontaminated air and air contaminated exhaust from the scrubber outlet before projecting them into the atmosphere. The contaminants dilution unit is installed adjacent to, and above, the exhaust scrubber unit. It is connected at the outlet of the scrubber unit and the inlet to the axial fans on a tee arrangement, so that the fresh air intake is not appreciably restricted, yet the exhaust gas exiting from the scrubber is entrained and accelerated.

"The water, used in the fogging system, is supplied by a pump and is drawn from a water-level-controlled reservoir. After the water is fogged into the chambers, it makes contact with the propellant vapors and chemically reacts. (Note: the exhaust from the scrubber fan is forced through the water fog in a swirling, cyclonic motion which, in conjunction with the three fog chambers, provides a large contact area for the reaction and scrubbing of the gases.) The residual falls to the bottom of the scrubber chamber and drains into the facility sump where it is later neutralized and loaded into the city sewage."[3]

"The chemical reaction of the propellants with water are second-order homogeneous reactions; the completion of the reactions depends solely on the length of contact time and assurance of excess water. However, since the first phase of the reaction is evolution of additional gas, care must be taken insure that the fumes are not pushed through the scrubber at a rate which does not allow sufficient reaction time.

"In the present scrubber design, the reaction time is assured by a design using three fog chambers. As the metered exhaust fumes are forced tangentially into the scrubber chamber, they come into contact with water fog in the first chamber. At the top of this chamber, approximately at the one-third level of the scrubber, is a core buster. After the primary reaction, the resultant enters the second fog chamber and

---

3. Freeman, B.: "The Reaction Control System Facility Operational Capabilities Evaluation and Analysis." Report No. SID 66-1905, North American Aviation, Inc., Space Division, Downey, California, May 1967, pp. 33-34.

further reacts. Fumes escaping the second chamber enter the chamber for further scrubbing action.

"The calculated efficiency of the first chamber is 50 percent provided that the correct metered level of intake is used. If necessary the total scrubber can be operated at an 87.5 percent efficiency. The escaping fumes are then diluted by mixing with uncontaminated air in the contaminated dilution unit and exhausted to the atmosphere."[4]

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[4] Op. cit., p. 46.

APPENDIX E

SEPARATION OF A PROPELLANT VAPOR FROM A MIXTURE OF GASES BY CONDENSATION

E.1 FORMULATION

Consider the transfer of heat away from a gas mixture for the purpose of condensing one constituent, "C". If the mixture is in equilibrium at each instant in time, with all constituents assumed to be perfect gases, then the mole fraction of C, χ_C, is related to its partial pressure according to

$$\chi_C = \frac{c}{p_m}$$

where p_m is the mixture pressure, assumed constant. Hence the change in χ_C resulting from a change in its partial pressure is

$$d\chi_C = \frac{dp_C}{p_m} \tag{1}$$

The mole fraction of constituent C is related to its mass and molecular weight, m_C and M_C, and the mass and molecular weight of the non-condensible fraction, m_N and M_N, according to

$$\chi_C = \frac{\dfrac{m_C}{M_C}}{\dfrac{m_C}{M_C} + \dfrac{m_N}{M_N}} \tag{2}$$

and solving for m_C gives

$$m_C = \frac{M_C}{M_N}\left(\frac{\chi_C}{1 - \chi_C}\right) m_N \tag{2'}$$

Since the molecular weight and mass of the non-condensible constituents are all constant, we have

$$dm_C = \frac{M_C}{M_N}\left[\frac{d\,\chi_C}{(1 - \chi_C)^2}\right] m_N$$

and substituting for χ_C, $d\,\chi_C$ from equations (1) and (2), with $p_C = (p_{SAT})_C$ for the case of a saturated mixture, gives

$$dm_C = \frac{M_C M_N}{p_m m_N}\left(\frac{m_C}{M_C} + \frac{m_N}{M_N}\right)^2 (dp_{SAT})_C \tag{3}$$

where p_{SAT} (T_m) for constituent C is assumed known, T_m being the mixture temperature. Equation (3) will be used as a difference equation to establish numerical relationships between m_C and T_m for various cases of interest. It describes the incremental mass condensed (the decrease in the mass of constituent C present as a gas, $-dm_C$) that will result from an incremental decrease in mixture temperature and hence saturation pressure, $-(dp_{SAT})_C$.

The amount of energy that must be removed from this mixture of gases to accomplish an infinitesimal temperature change dT_m is

$$dQ = - \left[m_N c_{p_N} + m_C \left(\frac{dh_C}{dT} \right)_{SAT} \right] dT_m - \left(h_{fg} \right)_C dm_C \qquad (4)$$

where the specific heat of the non-condensible fraction, c_{p_N}, and latent heat of constituent C, $\left(h_{fg} \right)_C$, are functions of T_m in the general case. $\left(\frac{dh_C}{dT} \right)$ is the rate of change of the enthalpy of C due to moving along the saturated vapor curve, and is also a function of T_m.

E.2 INITIAL CONDIT ION

Equation (2'), with $m_N = m_m - m_C$, becomes (after solving for m_C):

$$m_C = \frac{\frac{M_C}{M_N} \chi_C}{1 + \left(\frac{M_C}{M_N} - 1\right) \chi_C} \; m_m$$

where m_m is the total mixture mass, and

$$\chi_C = \frac{p_{SAT}}{p_m}$$

Similarly,

$$m_N = m_m - m_C = m_m \left[1 - \frac{\frac{M_C}{M_N} \chi_C}{1 + \left(\frac{M_C}{M_N} - 1\right) \chi_C} \right]$$

$$= \frac{1 - \chi_C}{1 + \left(\frac{M_C}{M_N} - 1\right) \chi_C} \; m_m$$

These values for m_C and m_N are used in Equation (3) as initial values at the beginning of the finite difference procedure.

E.3 SIMPLIFYING ASSUMPTIONS

The presentation thus far has been quite general. In our actual analyses, a number of simplifying assumptions were made, as described in the following paragraphs.

Data for the temperature dependence of the heat of vaporization, h_{fg}, and the derivative of enthalpy with temperature along the saturated vapor line, $\partial h_g/\partial T$, are not available, as far as we have been able to ascertain, except for a limited amount of data in the case of MMH. Theoretical approximations could certainly be obtained for the temperature dependence of h_{fg} using Clapeyron's equation and empirical equations of state; because of the relatively small temperature range of interest in this investigation, however, it was decided to treat h_{fg} and $\partial h_g/\partial T$ as constants.

The term $\partial h_g/\partial T)$ can be expressed as a function of more easily obtainable quantities using the expansion

$$\left(\frac{\partial h_g}{\partial T}\right) = \left(\frac{\partial h}{\partial T}\right)_p + \left(\frac{\partial h}{\partial p}\right)_T \left(\frac{dp}{dT}\right)_{sat}$$

where all terms are functions of position along the saturation line, and $(dp/dT)_{sat}$ can be obtained from the appropriate vapor pressure equation.

For the sake of this investigation, the perfect gas assumption was made so that

$$\left(\frac{\partial h}{\partial p}\right)_T = 0$$

and the expression for $(dp/dT)_{SAT}$ was not needed. In the more general case, $(\partial h/\partial p)_T$ could be calculated from a more sophisticated equation of state, or from published data, using the relation

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p ,$$

where v is the specific volume of the saturated vapor.

It was further assumed (as in the case of h_{fg}) that the specific heat, $c_p = (\partial h/\partial T)_p$, is constant throughout the temperature range of interest. Similarly, the temperature dependence of the specific heat of the non-condensible gas, c_{p_N}, is also neglected.

With these assumptions, equation (4) becomes

$$dQ = (c_{p_N} m_N + c_{p_C} m_C)\, dT_m + (h_{fg})_C\, dm_c,$$

with m_N, c_{p_N}, c_{p_C}, and (h_{fg}) all being constants. The equation in this form was used as a finite difference equation in the computer code for this investigation.

Listings of the computer code are presented on the following two pages. The application of this method of analysis to specific cases of interest is described in Sections 2.13 and 3.11.

```
      DIMENSION TITLE(10)
      DOUBLE PRECISICN T.C.ZASSC.DLCG10
    1 FORMAT (6F8.3)
    2 FCRMAT (3F8.3/4F12.6/9A4)
   11 FCRMAT (1H1.3CX.9A4///' INITIAL TEMPERATURE =',F4.0,' CEG K'//' IN
     2ITIAL PARTIAL PRESSURE =',F7.2,' MM HG'//' INITIAL VAPCR MASS FRAC
     3TICN =',F6.4//' INITIAL VAPOR MOLE FRACTION =',F6.4////18X,'HEAT',
     412X,'MASS CONCENSED',7X,'PARTIAL'/'  TEMP',11X,'REMOVEC',10X,'PCT
     5OF INITIAL',7X,'PRESSURE',10X,'CALORIES PER GRAM'/' (DEG K)',10X,
     6'(CAL)',10X,'MIXTURE   VAPCR',7X,'(MM HG)',8X,'MARGINAL     CUMULA
     7TIVE'/)
   12 FORMAT (F8.3,E18.4,F13.3,F9.2,F13.2,4X,3E14.4)
      IN=5
      IOUT=6
      READ (IN,1) EMMN,CPN,PMIX,TINIT,TSTOP,CELT
      CPN=CPN/EMMN
      READ (IN,2) EMMC,HLAT,CSATC,A,B,C,D,(TITLE(J) ,J=1,9)
      HLAT=HLAT/EMMC
      CSATC=CSATC/EMMC
      Q=C.
      T=TINIT
      PSAT=10.**(A+B/(T+C)+D*DLOG10(T))
      FRAC=PSAT/PMIX
      ZASSN=(1.-FRAC)/(1.+(EMMC/EMMN-1.)*FRAC)
      ZAN=ZASSN*CPN
      ZASSC=1.-ZASSN
      WRITE (IOUT,11) (TITLE(J),J=1,9),T,PSAT,ZASSC,FRAC
      ZAM=ZASSC
      KOUNT=0
   50 T=T-DELT
      PSAT1=10.**(A+B/(T+C)+D*DLOG10(T))
      DELM=EMMC*EMMN/PMIX/ZASSN*(ZASSC/EMMC+ZASSN/EMMN)**2*(PSAT-PSAT1)
      DELQ=(ZAN+ZASSC*CSATC)*CELT+HLAT*CELM
      Q=Q+DELQ
      ZASSC=ZASSC-DELM
      PSAT=PSAT1
      KOUNT=KOUNT+1
      IF (KOUNT.LT.10) GO TO 50
      HEAT=DELQ/DELM
      ZAP=ZAM-ZASSC
      TWEET=Q/ZAP
      ZAR=ZAP*100.
      ZANG=ZAR/ZAM
      WRITE (IOUT,12) T,Q,ZAR,ZANG,PSAT,HEAT,TWEET
      KOUNT=0
      IF (T.GT.TSTOP) GO TO 50
  100 CONTINUE
      STOP
      END
```

Listing E.1. Computation of N_2F_4, MMH,UDMH condensation.

```
      DIMENSION TITLE(10)
      DOUBLE PRECISION T,Q,ZASSC,DLOG10
    1 FORMAT (6F8.3)
    2 FORMAT (3F8.3/4F12.6/9A4)
   11 FORMAT (1H1,30X,9A4///' INITIAL TEMPERATURE =',F4.0,' DEG K'//' IN
     2ITIAL PARTIAL PRESSURE =",F7.2," MM HG"//" INITIAL VAPOR MASS FRAC
     3TION =',F6.4//' INITIAL VAPOR MOLE FRACTION =',F6.4////18X,'HEAT',
     412X,"MASS CONDENSED",7X,"PARTIAL"/"  TEMP",11X,"REMOVED",10X,"PCT
     5OF INITIAL',7X,'PRESSURE',10X,'CALORIES PER GRAM'/' (DEG K)',10X,
     6"(CAL)",10X,"MIXTURE   VAPOR",7X,"(MM HG)",8X,"MARGINAL     CUMULA
     7TIVE'/)
   12 FORMAT (F8.3,F18.4,F13.3,F9.2,F13.2,4X,3F14.4)
      IN=5
      IOUT=6
      READ (IN,1) EMMN,CPN,PMIX,TINIT,TSTOP,DELT
      CPN=CPN/EMMN
      READ (IN,2) EMMC,HLAT,CSATC,A,B,C,D,(TITLE(J) ,J=1,9)
      HLAT=HLAT/EMMC
      Q=0.
      T=TINIT
      QUAY=10.**(-11.585+.036*T)
      ALPHA=SQRT(QUAY/(12.+QUAY))
      EMMC=ALPHA*46.008+(1.-ALPHA)*92.016
      PSAT=10.**(A/T+B+C*T+D*T*T)
      PSAT=10.*PSAT
      FRAC=PSAT/PMIX
      ZASSN=(1.-FRAC)/(1.+(EMMC/EMMN-1.)*FRAC)
      ZAN=ZASSN*CPN
      ZASSC=1.-ZASSN
      WRITE (IOUT,11) (TITLE(J),J=1,9),T,PSAT,ZASSC,FRAC
      ZAM=ZASSC
      KOUNT=0
   50 T=T-DELT
      QUAY=10.**(-11.585+.036*T)
      ALPHA=SQRT(QUAY/(12.+QUAY))
      EMMC=ALPHA*46.008+(1.-ALPHA)*92.016
      PSAT1=10.**(A/T+B+C*T+D*T*T)
      PSAT1=10.*PSAT1
      DELM=EMMC*EMMN/PMIX/ZASSN*(ZASSC/EMMC+ZASSN/EMMN)**2*(PSAT-PSAT1)
      DELQ=(ZAN+ZASSC*CSATC)*DELT+HLAT*DELM
      Q=Q+DELQ
      ZASSC=ZASSC-DELM
      PSAT=PSAT1
      KOUNT=KOUNT+1
      IF (KOUNT.LT.10) GO TO 50
      HEAT=DELQ/DELM
      ZAP=ZAM-ZASSC
      TWEET=Q/ZAP
      ZAR=ZAP*100.
      ZANG=ZAR/ZAM
      WRITE (IOUT,12) T,Q,ZAR,ZANG,PSAT,HEAT,TWEET,ALPHA
      KOUNT=0
      IF (T.GT.TSTOP) GO TO 50
  100 CONTINUE
      STOP
      END
```

Listing E.2. Computation of N_2O_4 condensation.

APPENDIX F

SEPARATION OF A PROPELLANT VAPOR FROM A HELIUM STREAM BY PERMEATION

In the case of helium streams contaminated with hypergolic propellant vapors, one possible means of separating the helium from the contaminant is to simply utilize the low permeability of many materials to helium. Helium, a very simple monatomic gas with a low molecular weight of 4, will diffuse rather readily through many solids, whereas MMH (molecular weight 46) and N_2O_4 (molecular weight between 46 and 92 depending on degree of dissociation) are easily contained and will not readily diffuse through most solids. In a chamber, under internal pressure, containing a mixture of helium and either MMH or N_2O_4, the concentration of helium will decrease with time as the helium leaks out through the walls of the chamber. The helium which does leak out will be essentially 100% pure if the chamber walls are properly designed.

Polytetraflouroethylene (PTFE, or Teflon) was chosen as the basis for a crude calculation because of its compatibility with both fuels and oxidizers. Its permeability to N_2O_4 and MMH remain to be determined - we shall assume it to be impermeable, for our purposes, to both. At room temperature, 100 square inches of Teflon FEP film .001 inch thick and supporting a one atmosphere pressure difference will pass 1 gram of helium per day according to information provided to us by DuPont, the manufacturer. Hence approximately 2.4×10^6 square inches - 16,700 square feet - of Teflon at this thickness would be required to pass one kilogram of helium per hour. The total volume of Teflon would be 1.4 cubic feet, and because the flow per unit area is so small the sheet could be highly convoluted, in the manner of an air filter element, so that the actual volume of the chamber could be on the order of several cubic feet rather than the volume of $(16,700/6)^{3/2}$ cubic feet that would be indicated for a simple cube with the necessary surface area.

Such an extensive membrane would have to be carefully supported to enable it to contain the necessary pressure difference. As contaminant concentration in the gas box exceeds saturation and contaminant precipitates out as a liquid, it can be bled out of the gas box.

At this stage, it would seem that the possibility of an accidental opening or hole in the membrane (an intolerable situation) is the greatest potential difficulty to overcome. Many operational and mechanical problems remain unmentioned and unexplored and the idea is put forth only as a possible alternative that might warrant additional study.

APPENDIX G

ATMOSPHERIC EMISSION LIMITS

G.1 Existing Standards and Regulations
G.2 Carcinogenic Properties and Considerations
G.3 Analytical Methods for Predicting Atmospheric Concentrations

G.1 EXISTING STANDARDS AND REGULATIONS

The most commonly quoted standards for airborne concentrations of various substances are the Threshold Limit Values (TLV) established by the American Conference of Governmental and Industrial Hygienists (ACGIH), and the Emergency Exposure Limits (EEL), Short-Term Public Limits (STPL) and Public Emergency Limits (PEL) recommended by the Committee on Toxicology of the National Academy of Sciences - National Research Council (NAS-NRC).

Threshold Limit Values are airborne concentrations to which nearly all workers may be repeatedly exposed day after day without adverse effect, based on time-weighted concentrations for a 7- to 8-hour workday and 40-hour workweek. They permit excursions above the limit, provided they are compensated by equivalent excursions below the limit during the workday. Table G.1 presents the TLV's for hypergolic propellants and other chemicals typically found above liquid hypergolic propellants, or typically resulting from common hypergolic propellant disposal processes.

Short-Term Public Limits are defined as "limits for short-term exposure of the public to air pollutants in view of occasional repeated events in the same locality." The Public Emergency Limits apply to "accidental, unpredictable, and uncontrollable exposures of the public to toxic substances. These exposures are expected to be single events in the lifetime of the very few people who would accidentally be exposed. The PEL assumes that some temporary discomfort may accrue to the public but that any effect resulting from the exposure is reversible and without residual damage." The limits proposed by NAS-NRC in June 1974 for hydrazine propellants are presented in Table G.2.

Emergency Exposure Limits for military and space personnel have also been recommended by NAS-NRC, in 1971, and are presented in Table G.3.

An Emergency Exposure Limit for nitrogen dioxide is included along with the NAS-NRC hydrazine recommendations in the 'Hazards of Chemical Rockets and Propellants Handbook", as follows:

10 minutes	30 ppm
30 minutes	20 ppm
60 minutes	10 ppm

TABLE G.1

THRESHOLD LIMIT VALUES FOR CHEMICAL SUBSTANCES IN WORKROOM AIR, ADOPTED BY ACGIH FOR 1975

Substance	Concentration by Volume (ppm)	Concentration by Mass (mg/m^3)
Hydrazine	0.1	0.1
Monomethyl hydrazine	0.2	0.35
1, 1- Dimethylhydrazine (UDMH)	0.5	1
Nitrogen dioxide	5	9
Nitric acid	2	5
Hydrogen peroxide	1	1.4
Ammonia	25	18
Carbon monoxide	50	55
Chloroform	25	120
Methyl chloride	100	210
Methyl chloroform	350	1900
Methylene chloride	200	720
Nitric oxide	25	30

TABLE G.2
RECOMMENDED LIMITS FOR EXPOSURE[1]

	STPL's (25°C/760mm. Hg.)			PEL's (25°C/760mm. Hg.)		
	Time	Limit		Time	Limit	
	min	ppm	mg/m^3	min	ppm	mg/m^3
Hydrazine	10	15	20	10	30	39
	30	10	13	30	20	26
	60	5	7	60	10	13
Monomethylhydrazine	10	9	17	10	90	169
	30	3	6	30	30	56
	60	1.5	3	60	15	28
1, 1, Dimethylhydrazine (UDMH)	10	50	127	10	100	255
	30	25	64	30	50	127
	60	15	38	60	30	77

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1. "Guides for Short-Term Exposures of the Public to Air Pollutants. V. Guide for Hydrazine, Monomethylhydrazine, and 1, 1-Dimethylhydrazine." Prepared by the Committee on Toxicology of the National Academy of Sciences - National Research Council, for the Environmental Protection Agency. Report No. NAS/ACT/P-628.6 (June 1974). NTIS PB-244 337.

TABLE G.3

EMERGENCY EXPOSURE LIMITS FOR MILITARY AND SPACE PERSONNEL[2]

Compound	Time (min)	Limit (ppm)
Hydrazine	10	30
	30	20
	60	10
Monomethylhydrazine	10	90
	30	30
	60	15
1,1-Dimethylhydrazine	10	100
	30	50
	60	30

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[2] "Basis for Establishing Guides for Short-Term Exposures of the Public to Air Pollutants." Prepared by the Committee on Toxicology of the National Academy of Sciences - National Research Council (1971). NTIS PB-199 904.

The TRW study[3], which was performed for the Environmental Protection Agency (EPA) and will undoubtedly have a strong influence on future EPA standards, presents a "recommended provisional limit in air" of 0.01 ppm for N_2H_4. The basis for this recommendation is given as ".01 times TLV", and presumably this criterion would also be applied to MMH and UDMH. The same set of reports also recommends provisional maximum exposure limits for ammonia (0.02 mg/m^3) and carbon monoxide (0.55 mg/m^3) in air, both values again based on 1% of the TLV.*

A number of local standards also exist in the case of nitrogen dioxide (the monomer of nitrogen tetroxide), which is a very common pollutant. The standards for the State of Florida are as follows:

Alert Status	0.6 ppm	over period of one hour
Warning Status	1.2 ppm	over period of one hour
Emergency Status	1.6 ppm	over period of one hour
Alert Status	0.15 ppm	averaged over 24 hours
Warning Status	0.30 ppm	averaged over 24 hours
Emergency Status	0.40 ppm	averaged over 24 hours

Figure G.1 presents this multitude of NO_2 standards in visual form.

In addition to considerations of human exposure, there are other environmental effects associated with nitrogen dioxide. Continued exposure of plant life to NO_2 will change the flora of the environment. The sensitivity of selected plants to NO_2 has been categorized as follows:[4]

Sensitive: azalea, pinto bean, brittlewood, hibiscus, head lettuce, mustard, sunflower, tobacco.

Intermediate: Cheesewood, chickweed, dandelion, annual blue grass, orange, rye.

Resistant: asparagus, bush bean, carissa, Kentucky blue grass, heath, ixora, lamb's-quarters, nettle-leaf goosefoot, pigweed.

[3] Ottinger, R.S.; Blumenthal, J.L.; Dal Porto, D.F.; Gruber, G.I.; Santy, M.J.; and Shih, C.C.: "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste". Report No. EPA-670/2-73-053-1 (August 1973). NTIS PB-244 591.

* In the case of ammonia, there appears to be a discrepancy between the stated basis for recommendation and the actual recommended provisional limit.

[4] *Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas*, J.S. Jacobson and A.C. Hill, Eds., Air Pollution Control Association and National Air Pollution Control Association, Pittsburgh, Pa. (1970).

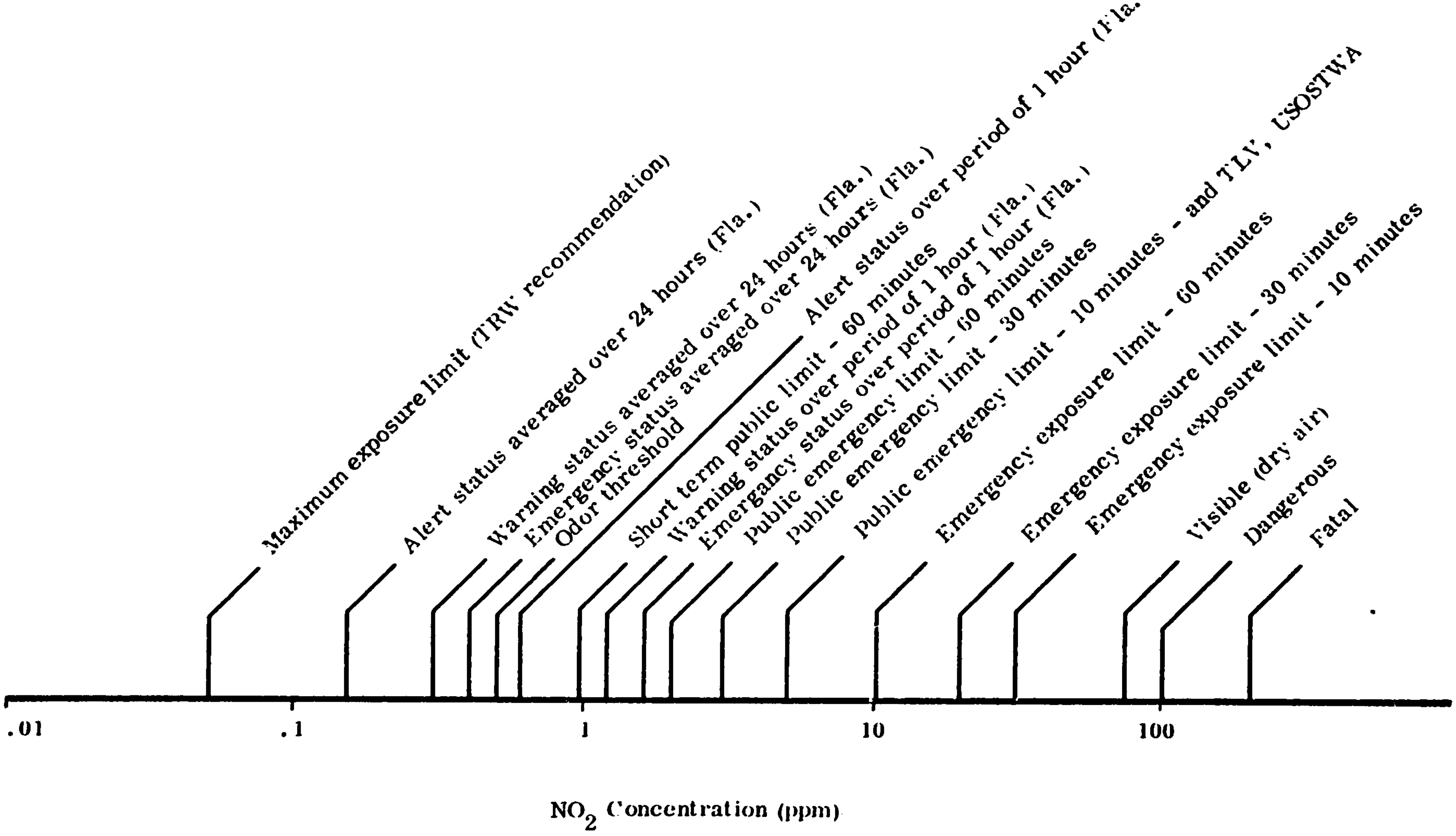

Figure G.1: NO$_2$ concentration limits

G.2 CARCINOGENIC PROPERTIES AND CONSIDERATIONS

The pathological effects of environmental carcinogens resemble those of other toxins in that the effect is proportional to dose. There is, however, an important fundamental difference. Cells surviving ordinary toxic agents usually show complete recovery or may even develop some sort of resistance to these species. However, cells exposed to the carcinogens retain the pathological carcinogenic burden representing the sum of such repeated carcinogenic imprints.

There is, moreover, no relation between acute toxicity of a chemical and its carcinogenicity. Chronic toxic action, often expressed in tissues by signs of chronic inflammation, has no direct relation or significance to the development of carcinogenic reactions in such tissue, although it may precede or accompany them. Such toxic reactions are not a part of the carcinogenic process.

Numerous competent scientists have testified that presently available evidence does not justify the adoption of a "safe dose", because such a safe dose does not exist scientifically, and moreover, cannot be demonstrated by any of the test methods available.

The Environmental Protection Agency has defined nine guidelines to be used with regard to suspected carcinogens. One in particular should be quoted here:

"The concept of a threshold exposure level for a carcinogenic agent has no practical significance because there is no valid method of establishing such a level."[5]

Further definition of EPA's approach to the carcinogen problem has been presented more recently. "According to EPA, a substance will be considered to be a presumptive cancer risk when it causes a statistically significant excess incidence of benign or malignant tumors in humans or animals. And the agency says that it holds by the concept that any exposure to a carcinogen, however small, will confer some risk of cancer on the exposed population."[6]

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5. Chemical and Engineering News, Nevember 3, 1975, page 16.
6. Chemical and Engineering News, May 24, 1976, page 4.

The NAS-NRC report quoted above treats questions related to the toxicity and carcinogenicity of the hydrazines at considerable length with very extensive references. A relatively very small number of the references are concerned with carcinogenicity studies, all with laboratory animals. Some of the data in the area of carcinogenicity, as presented, are contradictory and the report leaves one with the impression that carcinogenicity of hydrazine in particular is still an open question. It is our opinion that the evidence for hydrazine carcinogenicity is much stronger and that all the hydrazine fuels should be treated and handled as carcinogens, for the following reasons:

1. There is no reasonable doubt as to the mutagenic properties of hydrazine and there are extremely few chemical agents which are mutagenic and not carcinogenic. In fact mutagenicity of bacteria is now being used extensively in the chemical industry as a preliminary index of potential carcinogenicity.
2. Hydrazine sulfate is now used as an anti-tumor agent and there is no known anti-tumor agent which is not also a carcinogen with the possible exception of some steroids. It is also known that hydrazine reacts with oxygen in the presence of metals to produce hydroxyl radicals and hydrogen peroxide. These agents are known to be carcinogens.
3. A study of the available data in DHEW Publication No. (NIH) 75, "Survey of Compounds Which Have Been Tested for Carcinogenic Activity 1972-1973," revealed that Toth conducted studies on hydrazine itself as well as hydrazine sulfate. We quote from this document: "Author concludes hydrazine significantly increases the incidence of lung tumors in Swiss mice." Although Toth's negative finding in the case of hydrazine sulfate was quoted in the NAS-NRC report. the positive finding in the case of hydrazine itself was omitted, presumably because these results were not included in the journal article being referenced.

On the basis of these data, the conclusion that hydrazine is a carcinogen seems inescapable. The carcinogenicity of the methylated hydrazines is even more firmly established by both the available data and comparative considerations.

Results of Toth and Shimizu[7] and Toth[8] are quoted in the NAS-NRC report with regard to the carcinogenicity of monomethyl hydrazine. Not quoted in the NAS-NRC report, but included in DHEW Publication No. (NIH) 75, are other data by Toth taken in 1973 in which the incidence of tumors is also increased by ingestion of UDMH.

One consideration of particular importance in the case of the hydrazines in solubility. It has been shown that the very soluble and the least soluble of potential carcinogenic agents yield the lowest number of cancerous responses. Hydrazines, being very soluble, are probably less potent carcinogens than many others that are known. Hydrazines being vented in an effluent stream to the atmosphere may, however, undergo reactions which would cause the reaction product to be less soluble and therefore more carcinogenic.

For several years a correlation has been noted between high levels of NO_2 and the high incidence of urban cancer, yet NO_2,HNO_3, HNO_2, and NO are not in themselves carcinogenic. However, HNO_2 can combine in the atmosphere with certain amines to form nitrosamines which are highly carcinogenic. Amines, which are found almost everywhere,are produced in the decomposition of proteins and are used extensively in industrial processes.

Recent studies have shown nitrosamines including dimethylnitrosamine (DMN) to be present in Baltimore (0.02 to 0.01 $\mu g/m^3$), Charleston (0.7 $\mu g/m^3$), and New York City (0.8 $\mu g/m^3$).[9] Water and sewage samples at some of these locations also showed the presence of nitrosamines. Preliminary calculations have shown that a person ingests 0.5 μg of DMN if he eats four slices of cooked bacon and inhales 0.8 while smoking a pack of cigarettes. However, a person breathing air containing 1 $\mu g/m^3$ of DMN for 24 hours will inhale 10 to 14 μg of DMN. Animal studies have also shown that nitrosamines activate other relatively weak carcinogens such as benzo (a) pyrene.

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7. Toth, B.; and Shimizu, H.: "Methylhydrazine Tumorigenesis in Syrian Golden Hamsters and the Morphology of Malignant Histiocytomas." Cancer Research, Vol. 33 (1973), pages 2744-2753.

8. Toth, B: "Tumor Induction Studies with Substituted Hydrazines." Report No. AMRL-TR-73-125, Wright-Patterson Air Force Base, Ohio (1973).

9. Shapley, Deborah: "Nitrosamines: Scientists on the Trail of Prime Suspect in Urban Cancer". Science, Volume 191, pages 268-270, January 1976.

A 1970 study which correlated cancer in 38 U.S. cities with a great number of environmental chemicals found that NO_2 cross-correlated with seven out of eight categories of cancer and with heart disease. Thus nitrosamines are now being considered as the "defining factor in urban cancers".

A great deal of research remains to be done in this area, but at the present time the data strongly indicates that atmospheric nitrosamines present in minute concentrations pose a hazard to all continuously exposed personnel.

Another pertinent report appeared in the September 29, 1975 issue of Chemical and Engineering News, as follows:

> "Nitrosamines have been found in the air in two eastern U.S. cities and consumerist/environmentalist Ralph Nader wants the Environmental Protection Agency to start an all-out study.
>
> "In calling for EPA action, Nader sites a recent study by Samuel Epstein of Case Western Reserve University, Cleveland, and David Fine of Thermo Electron Corp., Waltham, Mass., that found as much as 0.96 ppb of dimethyl nitrosamine in the ambient air in Baltimore. Dimethyl nitrosamine is regarded as a powerful carcinogen, and this, the report says, 'gives rise to considerable cause for concern.'
>
> "In addition, levels of 0.014 to 0.051 ppb of the chemical were found in Belle, West Virginia, an industrial suburb of Charleston. However, in three other eastern cities - Philadelphia, Wilmington, and Waltham, Mass. - the researchers did not find detectable levels.
>
> "Commenting on the findings, Fine and Epstein caution that because their measurements were 'one shot' determinations, 'there is no knowledge as to whether the levels reported here represent average, high or low values.' But they say the data gleaned in the study 'confirm an earlier report (from West Germany) that nitrosamines may be present in urban air.'
>
> "Epstein says that he isn't sure where the nitromanines in ambient air come from, but he has several theories. One is that they originate directly from certain industrial processes that use them. Another is that they result from the reaction of atmospheric nitrogen oxides produced by industrial sources and automobiles with airborne amines from natural or industrial sources.

"For its part, EPA says that it is studying the data produced by Epstein and Fine, and that it plans to conduct studies to determine the extent of nitrosamines in urban air.

"Moreover, according to EPA, it is possible that nitrosamines also may be present in drinking water supplies, and the agency plans to expand current water supply studies to include these chemicals. Epstein and Fine also consider this in their study but say that the possible presence of nitrosamines in drinking water is 'tentative and speculative.' "[10]

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[10] Chemical and Engineering News, September 29, 1975.

G.3 ANALYTICAL METHODS FOR PREDICTING ATMOSPHERIC CONCENTRATIONS AS A FUNCTION OF EMISSION FLOW RATES AND CONCENTRATIONS

To apply any of the standards discussed in Section G.1, it is necessary to have a link between emission flow rates and concentrations, and atmospheric concentrations at any point downwind of the point of emission. In evaluating scrubber requirements, for example, a relation is needed between the postulated scrubber discharge parameters and atmospheric concentrations at various finite distances from the scrubber. It is obviously not necessary to apply atmospheric standards exactly at the scrubber exit, especially in the case of very small flow rates for which concentrations will fall rapidly within a short distance of the scrubber exit.

The best approach, in view of modern computational capabilities and the fact that the basic problem of atmospheric dispersion of identifiable species is a common one, is to use a computational model to predict downwind concentrations as a function of emissions for a wide variety of atmospheric conditions - wind velocity profile, lapse rate, humidity, etc.

The remainder of this section describes briefly the NASA effluent dispersion modeling capability and one of the simplified methods of analysis that is in common use.

NASA Dispersive Transport Prediction Capabilities

A significant NASA effort has been underway for several years, primarily at Marshall Space Flight Center and Langley Research Center, to develop computational models capable of predicting rocket exhaust effluent transport for air quality and environmental assessments. A major objective of this effort has been to minimize the environmental constraints on Space Shuttle launch operations. The end result of these efforts is a special purpose computer incorporating a set of mathematical models known collectively as REED (Rocket Exhaust Effluent Diffusion). This system recently became operational, and was flown to Kennedy Space Center for the two Titan III Viking launches that took place during Summer 1975. The system was used at KSC for operational predictions of the dispersion of the Titan exhaust plume. Its use is of course not limited to exhaust plume problems; almost any point-source or line-source effluent dispersion problems could be treated with some attention to the specification of the input parameters.

The REED system has been described quite thoroughly in a paper by Stephens and Stewart.[11] Important earlier descriptions of the diffusion models used in this program were given by Stephens et al[12] and Dumbauld et al.[13] A more recent report by Gregory and Storey[14] describes the measurement of rocket exhaust effluents at KSC and comparison with the NASA multilayer dispersion model. Excerpts from the Stephens and Stewart paper will serve to describe the REED capability in more detail:

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11. Stephens, J. Briscoe, and Stewart, Roger B.: "Rocket Exhaust Effluent Modeling for Tropospheric Air Quality and Environmental Assessments." Paper presented at NASA Space Shuttle Tropospheric Environmental Effects Meeting, Langley Research Center, Hampton, Va. 23665, February 24-26, 1975.

12. Stephens, J. Briscoe; Susko, Michael; Kaufman, John W.; and Hill, C. Kelly: "An Analytical Analysis of the Dispersion Predictions for Effluents from the Saturn V and Scout-Algol III Rocket Exhausts." NASA TMX - 2935, October 1973.

13. Dumbauld, R.K.; Bjorklund, J.R.; and Bowers, J.F.: "NASA/MSFC Multilayer Diffusion Models and Computer Program for Operational Prediction of Toxic Fuel Hazards." NASA CR - 129006, 1973.

14. Gregory, Gerald L., and Storey, Richard W., Jr.: "Effluent Sampling of Titan III C Vehicle Exhaust." NASA TMX - 3228, August 1975.

"The spatial description, in terms of concentration and dosage, of the dispersive transport of effluents from a discrete source is afforded by the NASA/MSFC REED description." (See Figure G.2). "This description, which represents an update in our technology and techniques, is composed of three models: the meteorological model, the rocket exhaust cloud rise model and the multilayer diffusion model.

"The NASA/MSFC meteorological model for the atmospheric conditions involves a number of techniques to model the thermodynamic and kinematic parameters measured in the atmosphere by rawinsonde and tetroon soundings that are used as the input for the cloud rise model. Since launch predictions involve a meteorological forecast, we normally limit our model to a first-order meteorological technique in which the surface mixing layer is treated as a homogeneous layer. This same first-order meteorological technique is also used in climatological assessments. In postlaunch analysis, a second-order meteorological technique is utilized, where the surface mixing layer is structured into a number of more nearly homogeneous layers. Here the term homogeneous layer means that the layer parameters can be modeled in terms of representative mean values. Options exist with both of these techniques to include precipitation effects and land-sea interfaces.

"The NASA/MSFC exhaust cloud rise model is designed to utilize the output of the meteorological model and define the source parameters for the multilayer diffusion model. This is the first-order gradient technique that uses two value differences to obtain thermodynamic parameters. The second-order statistical technique uses regression analysis to obtain the thermodynamic parameters. There is an option of instantaneous sources for solid rockets like the Titan III. In the case of vehicles like the Delta-Thor or the Space Shuttle a combination of options must be used that utilizes both the instantaneous and continuous source options to account for the combination of solid motors and liquid engines. Two options also exist to account for the thermodynamic lapse rate; namely, the adiabatic option and the stable option. These options are always combined with the source options.

"The NASA/MSFC multilayer diffusion model is designed to take the output of the exhaust cloud rise model and generate a mapping for the concentration levels of the exhaust constituents. This is accomplished by using one of two

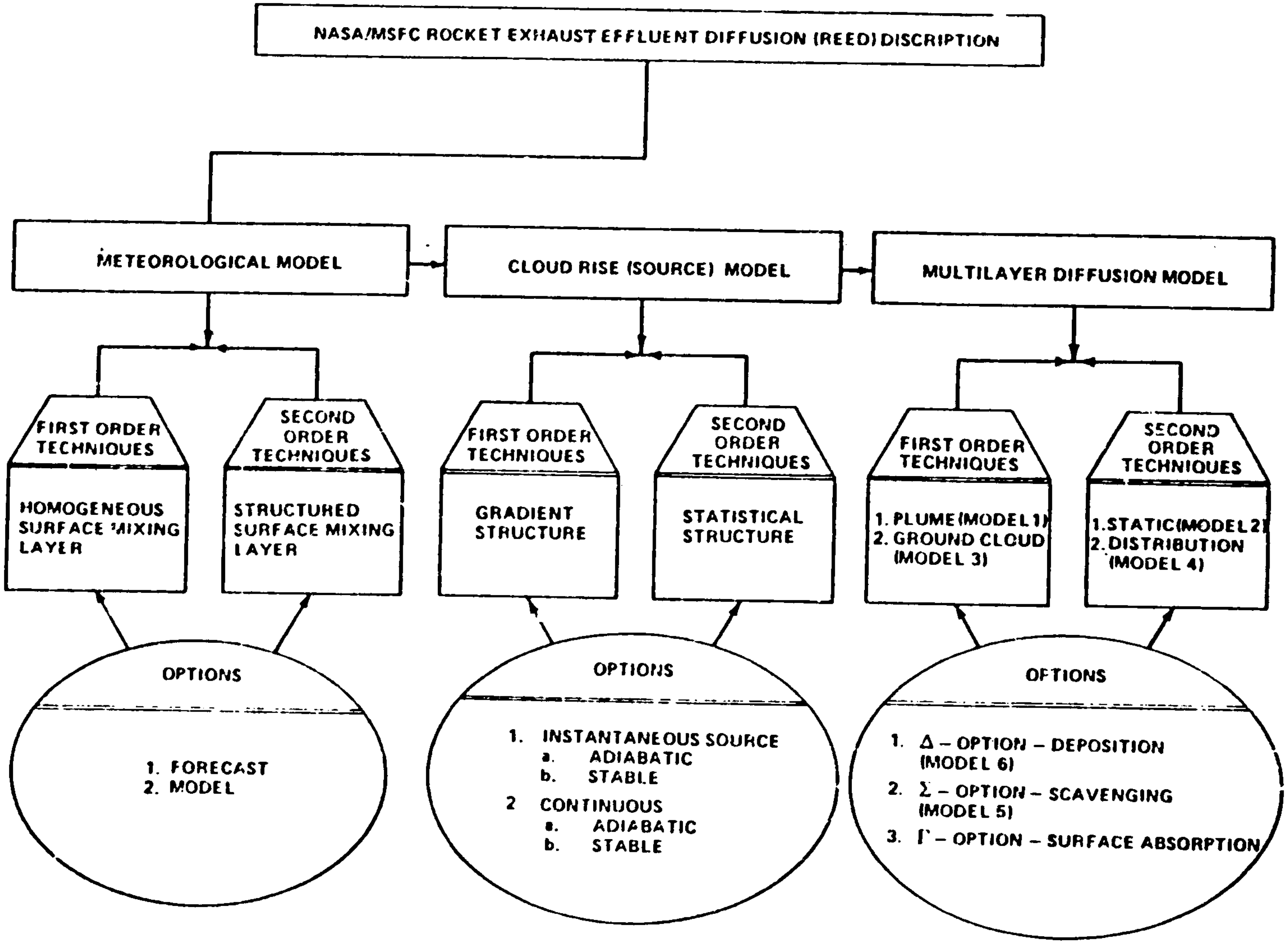

Figure G.2. REED description reproduced from Stephens and Stewart, "Rocket Exhaust Effluent Modeling for Tropospheric Air Quality and Environmental Assessments."

techniques, the unlayered first-order technique or the layered second-order technique. The two first-order techniques are the plume technique (model 1) where a cylindrical distribution is assumed and the ground cloud technique (model 3) in which an ellipsoidal distribution in a homogeneous surface mixing layer is assumed. The second-order techniques are the static plume technique (model 2) where it is assumed that there is a layer where no turbulent mixing occurs and the distribution technique (model 4) where the surface mixing layer is layered into statistically thermodynamically and kinematically homogeneous layers along with a well distributed source. The multilayer diffusion model has three options that can be used with either technique. There is a precipitation scavenging option (model 5), or Σ -option, to account for the depletion of an exhaust constituent during rain. There is a deposition option (model 6), or Γ -option, to account for gravitational settling. A new option, the Δ -option, has been added to account for surface absorption of a constituent. In addition, the diffusion model has provisions for cold spills and fuel leak calculations in the surface mixing layer."

Dispersion Calculations Using the Bosanquet and Pearson Equations

The preceding method, while very powerful, is not very accessible to people who don't work with it regularly. While similar methods will no doubt be available as programs for general purpose computers in the near future, we know of none that is currently available. Until such programs are available traditional "smokestack equations" will continue to see widespread use.

The mathematical expression of atmospheric concentration of a contaminant downstream from a source of constant emission is complicated because of the variation with time. The most frequently used formulas in stack meteorology are those giving average ground level concentrations downwind from an elevated source of constant discharge rate, such as the Bosanquet and Pearson[15] equations. Local topographic and microclimatic conditions, and other turbulence factors, are not considered in this first approximation.

The dilution of air contaminants is a direct result of atmospheric turbulence and molecular diffusion. The rate of turbulent diffusion is so much greater than the rate of molecular diffusion that the latter effect is also neglected.

The working formula used for calculating the maximum average ground level concentration, C_{max}, of contaminant issuing from the vent stack is

$$C_{max} = \frac{4Q}{\sqrt{2\pi}\; e^2 u H^2} \; \frac{p}{q}$$

where C_{max} = ground level concentration (by volume)

Q = emission rate at atmospheric temperature (cubic feet per second)

u = mean wind speed (feet per second)

H = effective stack height (feet)

p, q = Bosanquet diffusion coefficients

e = 2.718

For the purpose of an example, $\frac{p}{q}$ was taken to be 0.5, and the effective stack height, H, to be 100 feet. The highest NO_2 discharge rate during loading of the Space Shuttle oxidizer tanks has been estimated[16] to be about 0.04 cubic

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[15] Bosanquet, C.H., and Pearson, J.L.: "The Spread of Smoke and Gases from Chimneys." Trans. Faraday Soc. Vol. 32, pages 1249-1264 (1963).

[16] Sivik, H., et al: "Hypergolic Propellants - Liquid and Vapor Disposal." Report No. ME-76-1, Florida Institute of Technology, Melbourne, FL 32901 (February 1976).

feet per second. Using these values, the relation for C_{max} becomes

$$C_{max} = 4.319 \times 10^{-7}/u$$

$$\text{or } C_{max}(\text{ppm}) = 0.4319/u$$

This relation obviously gives very low maximum ground level concentrations, even for the scrubbed effluent. The results would of course be much less favorable in the case of the ground level discharge, because of the fact that C_{max} is inversely proportional to the square of H.

Under a strong inversion, it would be expected that the NO_x concentration would increase several-fold at the lower wind speeds (below 5 fps) but remain approximately the same at higher wind speeds (above 7 fps).

The location of the maximum ground level concentration is given by

$$X_{max} = \frac{H}{2p}$$

where typical values of the Bosanquet diffusion coefficient p range from 0.02 (low turbulence) to 0.10 (moderate turbulence). For our assumed 100 foot effective stack height this gives a range of values of X_{max} from 500 to 2500 feet. For ground level discharge, not only is the maximum ground level concentration much higher, it also occurs closer to the scrubber -- 50 to 250 feet for a 10 foot effective height, for example. The lapse rate (temperature profile) of the lowest layer of the atmosphere would of course also influence these results.