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BIOREMEDIATION OF HYDRAZINE:
A LITERATURE REVIEW

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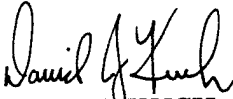TYNDALL AIR FORCE BASE, FLORIDA 32403-5323

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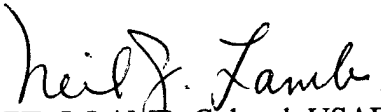
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Numerous industries utilize hydrazine on a daily basis. The highly toxic hydrazine fuels are utilized by the US Air Force as a rocket propellant and as an emergency power source on the F-16. Civilian industry requires hydrazine in the manufacture of agricultural chemicals and pharmaceuticals, in photography, and as a corrosion inhibitor (oxygen scavenger) in boiler rooms. This literature review was performed as our first step in addressing an USAF Environmental Safety and Occupational Health (ESOH) concerning hydrazine remediation. Large volumes of the fuels are shipped across the highways of the United States annually, increasing the probability of an accidental spill. Such inadvertent releases of hydrazines to the environment are extremely hazardous due to their mutagenic natures. Laboratory bench-scale research has been proposed to develop a more effective and predictable treatment technique. The treatment process needs to be developed to replace existing disposal options, and address the environmental contamination caused by hydrazine spills. Research conducted over the last 20 years has had little success in providing a hydrazine tolerant microbe. Although the use of biological mechanisms has been successfully applied to numerous chemical contaminants, the concentrations of hydrazine at a spill would prove toxic to conventional microbes.

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PREFACE

This report was prepared by Armstrong Laboratory Environics Directorate (AL/EQ), 139 Barnes Drive, Suite 2, Tyndall Air Force Base, Florida 32403-5323.

The purpose of this document is to provide a compilation of published literature concerning the bioremediation and fate and effect of hydrazine in order to avoid duplication of effort. The US Air Force needs an environmentally conscious and inexpensive remediation technique for hydrazine cleanup/treatment. Our proposed effort intends to devise a strategy for both routine and major emergency hydrazine spill treatment. The method will also have application in the bulk destruction of hydrazine.

The work was performed between 1 Dec 1993 and 1 Mar 1995. AL/EQW project manager was 2Lt David Kuch.

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EXECUTIVE SUMMARY

A.   OBJECTIVE

The purpose of this document is to provide a compilation of published literature concerning the bioremediation and fate and effect of hydrazine in order to avoid duplication of effort. This literature review was performed as our first step in addressing an USAF Environmental Safety and Occupational Health (ESOH) concerning hydrazine remediation.

B.   BACKGROUND

Numerous industries utilize hydrazine on a daily basis. The United States Air Force and the National Aeronautics and Space Administration (NASA) uses hydrazine as a rocket propellant. However, hydrazine usage is not isolated to the Department of Defense (DoD) and NASA. Civilian industry requires hydrazine in the manufacture of agricultural chemicals and pharmaceuticals, in photography, and as a corrosion inhibitor (oxygen scavenger) in boiler rooms.

The highly toxic hydrazine fuels are utilized by the US Air Force as a rocket propellant and as an emergency power source on the F-16. With world-wide deployment of the F-16 fighter, a remediation technique is currently being developed in the event of a hydrazine spill. Large volumes of the fuels are shipped across the highways of the United States annually, increasing the probability of an accidental spill. Such inadvertent releases of hydrazines to the environment are extremely hazardous due to their mutagenic nature.

C.   SCOPE

An understanding of the bioremediation of hydrazine and its fate in the environment was the focus of this paper. Also, the interaction between hydrazine and biological systems had to be established. The use of a biological remediation tool, a "popular" solution to industrial contamination, could provide a cost-effective alternative. Laboratory bench-scale research has been proposed to develop a more effective and predictable treatment technique. The treatment process needs to be developed to replace existing disposal options, and address the environmental contamination caused by hydrazine spills.

D.   CONCLUSION

An environmentally conscious and inexpensive treatment technique is required in the event of emergency hydrazine spill. Although the use of biological mechanisms has been successfully applied to numerous chemical contaminants, the concentrations of hydrazine at a spill would prove toxic to conventional microbes. Research conducted over the last twenty years has had little success in providing a hydrazine tolerant microbe.

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TABLE OF CONTENTS

LIST OF TABLES

SECTION I

INTRODUCTION

A.   OBJECTIVE

This literature review was performed to compile all published research that has been conducted concerning the both the environmental fate and biodegradation of hydrazine. It will support the funded research initiative, Bioremediation of Hydrazine, and ensure that we do not "reinvent the wheel." Because hydrazine has been studied for a hundred years, a great deal of literature is available.

B.   BACKGROUND

Numerous industries utilize hydrazine on a daily basis. The United States Air Force uses hydrazine as a high energy propellant and an auxiliary power unit on fighter aircraft. National Aeronautics and Space Administration (NASA) uses hydrazine as a rocket propellant. However, hydrazine usage is not isolated to the Department of Defense (DoD) and NASA. Civilian industry requires hydrazine in the manufacture of agricultural chemicals and pharmaceuticals, in photography, and as a corrosion inhibitor (oxygen scavenger) in boiler rooms.

The environmental fate of hydrazine and its alkyl-substituted derivatives is of considerable interest to the Air Force. the liquid missile fuels, which include hydrazine (Hz), monomethylhydrazine (MMH), unsymetrical dimethylhydrazine (UDMH), and Aerozine-50, are used extensively by the United States Air Force (USAF) and the National Aeronautics and Space Administration (NASA). These agencies utilize the fuel for fuel cells, rocket propellants, and auxiliary power units for the F-16 and the Space Shuttle Orbiter. The   F-16 carries approximately 6.5 gallons of 70% hydrazine - 30% water solution (McNaughton et al., 1979). The hydrazine solution is used to supply emergency electrical and hydraulic power to the aircraft. Substantial quantities of hydrazines are also used as propellants in the Titan ballistic-missiles and satellites. The use of hydrazine, MMH, and UDMH, especially as high energy propellants, has increased dramatically in recent years.

This increased usage and worldwide deployment of the F-16 fighter have raised concerns about the toxic properties and proper cleanup procedure for spilled hydrazines. Because the Air Force is a major user of hydrazine, it is concerned with health, safety, and environmental considerations. Consequently, most of the hydrazine research conducted in the past 25 years

The toxicity and, sometimes, unusually stable character of hydrazine contamination in the environment requires quick and thorough cleanup management to prevent serious environmental contamination (MacNaughton, 1981). Potentially, large volumes of hydrazine could spill from rail and truck transport containers, resulting in significant environmental damage. To protect soils and groundwater, hydrazine spills must be treated quickly and efficiently. The current method for hydrazine spill decontamination is the addition of oxidizers, such as sodium/calcium hypochlorite (bleach). Incomplete oxidative reactions may create more hazardous conditions and introduce unknown and possibly more toxic contaminants in the environment.

Over the years, the properties of hydrazine compounds have been defined and characterized. The hydrazine propellants, which are carcinogenic diamines, are used alone, mixed with water, or blended with UDMH (Aerozine-50). Hydrazine is a very strong reducing agent (i.e., easily oxidized) and exothermic fuel. The compounds are colorless, highly polar liquids, which are combustible at ordinary temperatures (Schmidt, 1984). The hydrazine fuels, like other low molecular weight amines, are quite soluble in water (Judeikis et al., 1992). Thermodynamically, the fuels are unstable, and are easily degraded, generating an energy release. Hydrazine has been known to catch fire when brought in contact with porous materials such as wood, asbestos, cloth, earth, and "rusty" materials. The fuel is not compatible with oxidizers, such as hydrogen peroxide, nitric acid, metal oxides, and strong acids (OSHA, 1978, p. 110). It was discovered, however, that the energetic fuel is unusually stable in the absence of an appropriate catalyst. Copper metal is an example of an ideal catalyst in the degradation of hydrazine. The N-N bonded compounds in nature are rare and, in general, toxic to living biological systems (LaRue, 1977).

More stringent environmental and Occupational Safety and Health Act (OSHA) regulations have been established to regulate hydrazine compounds. As a result, it is necessary to maintain closer control of releases and establish more comprehensive contingency plans dealing with accidents. Stricter compliance limits by federal, state, and local officials will increase the demand for an effective and controllable treatment technique for hydrazine.

The literature consistently establishes that hydrazine and its related derivatives are highly toxic to the environment (Lu, 1989) and that hydrazine is toxic to all forms of life (Moliner et al., 1989). The fuel is classified by the Environmental Protection Agency (EPA) as a Group 2B carcinogen; this defines it as a probable human carcinogen. The degradation of hydrazine is also important in terms of toxicity. Toxic intermediates, which could arise during the degradation process, can be potentially more hazardous than hydrazine itself. Because of this, the characterization of degradation and reaction products, determination of reaction pathways, and the development of a disposal technique which completely converts hydrazine fuels to nontoxic compounds are important.

C. SCOPE

An understanding of the bioremediation of hydrazine and its fate in the environment was the focus of this ~~paper~~ report. Also, the interaction between hydrazine and biological systems had to be established. The use of a biological remediation tool, a "popular" solution to industrial contamination, could provide a cost-effective alternative. Laboratory bench-scale research has been proposed to develop a more effective and predictable treatment technique. The treatment process needs to be developed to replace existing disposal options, and address the environmental contamination caused by hydrazine spills.

SECTION II
TREATMENT AND DISPOSAL TECHNIQUES

Over the past 25 years, the disposal methods for hydrazine have covered a wide range of techniques, ranging from ocean dumping to chemical oxidation. In the treatment of hydrazine fuels, the objective is to treat the wastewater in such a manner that the contaminants will not endanger human life or the environment. Potential treatment technologies can be classified as either thermal, physical, chemical, or biological treatment.

The thermal treatment of hydrazine can be seen in open pit burning, an early disposal technique that was utilized (Bowman et al, 1977). This method involves pouring the hydrazine fuels and/or wastewater into a large pit and igniting the fuel. The technique generates nitrogen oxides, methyl-substituted hydrazines, and carbon monoxide, making this disposal option environmentally undesirable.

A second thermal method of hydrazine disposal is by incineration (Bowman et al., 1974). This disposal method requires the transport of large quantities (~500,000 gallons per facility for 1 year) of hydrazine wastewater (Stollar et al, 1988) to the incinerator. Trailer-mounted or stationary incinerators can burn a variety of hydrazine dilutions. The disposal process has essentially 100 percent destruction of contaminants, producing N_2, water, carbon dioxide, and carbon monoxide. Minor products of this procedure include hydrogen gas, sulfur dioxide, hydrocarbons, and NO_x. This alternative effectively destroys 70% hydrazine solutions but is unfeasible with less than 50% solutions. This combustion process, while converting waste propellant to less toxic material, produces hydrocarbons/soot and a high energy requirement, making it an undesirable disposal technique.

The physical treatment of hydrazine, absorption/adsorption, has been conducted with little success. Activated carbon adsorption has been shown to be effective in the removal of organic compounds with large molecular weight (Stollar, 1988). However, research conducted by the Illinois Institute of Technology Research Institute (IITRI) showed that hydrazine related compounds, including nitrosomethylamine (NDMA), were poorly adsorbed onto activated carbon (EPA, 1979). Therefore, no further research was conducted on this treatment technology.

The disposal technique utilizing metal oxide adsorption was inspired by the studies conducted by researchers concerning the adsorption of hydrazine compounds in soils. Research was conducted by Hayes et al (1982) and by the research team of Braun and Zirroli (1983). Studies by these researchers revealed that the iron oxides and silicates were responsible for the disappearance of hydrazine and its related derivatives Rather than destroying the hydrazine fuels, the disappearance was attributed to the transfer of the hydrazine compounds from one

media (liquid) to another (solid), i.e., adsorption. Further consideration of this disposal technique was ceased because the contaminant was not destroyed, but rather transferred.

In the past, less concentrated hydrazine wastewater is treated by water dilution in untreated holding ponds (Bowman et al, 1977). Examples of hydrazine holding ponds can be found at the Kennedy Space Center, FL and Vandenberg AFB, CA, both of which rely on natural degradation of the hydrazine compounds. The hydrazine is mixed with copious amounts of water to form a very dilute hydrazine solution. While in the holding pond, the dilute hydrazine solution slowly decomposes by the combination of air oxidation and ultra-violet radiation followed by the biodegradation of decomposition products to nitrogen, carbon dioxide, water, and ammonia. The oxidation of hydrazine follows the reaction mechanism (Stone, 1978):

$$N_2H_4 \quad + \quad O_2 \quad ----^{h\nu}-----> \quad N_2 \quad + \quad 2H_2O$$
(Hydrazine)

Side reactions and the oxidation of MMH account for the production of ammonia in hydrazine oxidation.

$$2N_2H_4 \quad + \quad 0.5O_2 \quad ---^{h\nu}---> N_2 \quad + \quad 2NH_3 \quad + \quad H_2O$$

$$(CH_3)N_2H_2 \quad + \quad O_2 \quad ---^{h\nu}---> 2\,NH_3 \quad + \quad CO_2$$
(monomethylhydrazine)

$$(CH_3)N_2H_2 + \quad 2.5O_2 \,---^{h\nu}---> \quad CO_2 + H_2O + N_2$$
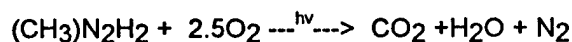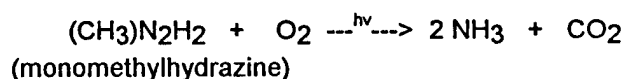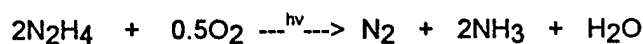
The benefit to this mechanism is that only naturally occurring chemicals react with hydrazine. Although this process has been shown to work, the process has many drawbacks. For low hydrazine concentrations that reaction rate is very slow (extended holding time). For initial concentrations of up to 1100 ppm, 90 percent of the hydrazine was auto-oxidized within 2 to 3 days (Bowman et al, 1977). However, when concentrations fall below 40 ppm, more time is required. Since the fuel is highly toxic and carcinogenic, a rapid and controlled disposal method is desired. This disposal process produces high, uncontrolled ammonia concentrations in the effluent. More recently (since 1987), the residual hydrazine in the holding ponds at Vandenberg AFB, CA has been oxidized with hypochlorite. After the concentration of hydrazine has been established in the holding pond, the corresponding amount of bleach is added to neutralize the residual hydrazine. Incomplete oxidation, however, results in the formation of environmentally toxic compounds (i.e., nitrosamines).

The holding pond method of hydrazine waste water disposal has been further enhanced by the addition of an aeration device. Aeration increases the oxidation rate in the pond. Bubbling of pure oxygen through the solution further enhances the oxidation rate in the holding pond. A requirement of this method is the need for a closed system. The addition of catalysts such as iron oxide, copper sulfate and/or charcoal can further enhance the decomposition of

hydrazine. The use of water hyacinth (phytoremediation) in the assimilation of dilute solutions of MMH has shown potential (Sivik and Wiederhold, 1977). Although improvements have been made on the technique, a more time efficient and cost-effective way of hydrazine waste disposal is still needed.

Hydrazine may also be treated by spray irrigation (Ebasco, 1987). This treatment relies on several natural mechanisms in the destruction of hydrazine similar to those previously discussed. The destruction can be attributed to the adsorption and oxidation by soils, the oxidation by air, the photolysis by sunlight, and biological degradation of reaction products by microbes. Although the technique has shown to be successful, the potential of groundwater contamination uncharacterized reaction products and slow uncontrolled reaction, are cause for concern. The possibility of process failure, which would result in further environmental contamination, limits this treatment technique. *In situ* treatment methods depend on the degradation of the reaction products by microrganisms which would be dormant in cold weather.

Hydrazine fuels and hydrazine-laden wastewater have also been treated by chemical means. Oxidation/reduction mechanisms for the treatment of hydrazine have been explored.

The reduction of hydrazine involves the conversion of hydrazine compounds to the corresponding amine. Research conducted by Lunn et al. (1983) showed the successful reduction of hydrazine, MMH, and UDMH. The method involves the addition of potassium hydroxide and an aluminum-nickel alloy powder, both of which produce optimum reducing conditions. The reaction results in the production of amines, ammonia, alcohol, and hydrogen gas. The reduction of UDMH generates dimethylamine, which is classified as a hazardous waste. Because of this, the reduction of hydrazine fuels is not desirable.

More recently, hydrazine waste water has been treated more successfully with oxidizing compounds. This technique of hydrazine waste treatment and disposal is currently the most common and popular. An oxidizing compound such as hydrogen peroxide, permanganate, chlorine, ozone, or oxygen is added to the hydrazine until in excess of stiochiometric ratio.

The oxidation of hydrazine can be seen in the UV-chlorination of hydrazine laden wastewater (Brubaker et al., 1985). The chlorination method of treatment can employ different forms of chlorine including chlorine gas, hypochlorous acid, hypochlorite, and chlorine dioxide. Hypothetically, if the chlorination process continued to completion, the reaction should yield hypochlorous acid, methanol, and nitrogen gas, all of which require only minor secondary treatment. However, in practical application, incomplete chlorination can produce unacceptable chlorinated by-products. These secondary wastes require additional treatment.

The use of ultraviolet light, in conjunction with chlorination, was studied to enhance the destruction of the undesirable chlorinated by-products associated with chlorination alone. Work conducted by Fochtman and Koch (1979) revealed that the UV-chlorinolysis treatment of hydrazine produced undetectable levels of chloroform, carbon tetrachloride, and chlorinated

amines. The treatment of a solution of 500 ppm hydrazine with UV-chlorination produced effluent that was not toxic to both stock culture and trickling filter heterotrophs (Wachinski et al., 1980). The addition of ultraviolet light to the chlorination process provided an effective disposal technique for hydrazine-laden wastewaters.

Permanganate and hydrogen peroxide, both strong oxidizing agents, have been examined in the treatment of hydrazine. The oxidation of hydrazine using permanganate, however, is limited by two factors (Castegnaro et al., 1986). First, the oxidative reaction involving UDMH and MMH yields nitrosodimethylamine, a known human carcinogen. Second, the reaction generates manganous oxide, requiring additional disposal. Hydrogen peroxide successfully destroyed 100 ppm hydrazine to limits below detection (Hager and Smith, 1985). The mechanism of the oxidative reaction resembles that of the reaction involving ozone and hydrazine.

Ozonation is the most popular oxidation process which can be applied in the treatment of hydrazine (Judeikis and Damschen, 1992). Ozone, a stronger oxidizer than hydrogen peroxide and chlorine, is less likely to be limited by the formation of harmful and more detrimental reaction products. However, following ozonation, the formation of miscellaneous byproducts can occur through incomplete oxidation. Thorough ozonation is required to completely convert hydrazine to carbon dioxide, water, nitrogen, and nitrates. The oxidative reaction can be enhanced by coupling the reaction with UV light. To date, the combination of ozonation and UV light has proven to be the most effective treatment method for hydrazine wastewater.

The aqueous-phase reaction, which involves the oxidation reaction between hydrazine and ozone, was observed as having the highest oxidative rate of reaction (Judeikis and Damschen, 1992). The aqueous-phase ozonolysis reaction between hydrazine and ozone produce primarily nitrogen gas and water. Small amounts of nitrates are also produced during the reaction. The aqueous-phase reaction between MMH and UDMH leads to the production of methanol, nitrosodimethylamine (NDMA), and tetramethyltetrazine (TMT). The formation of NDMA was of most concern because it is a known animal/human carcinogen. The reactions of UDMH and MMH with ozone were almost identical, except that the chemistry of the UDMH was more complex. Results of this research have already found industrial application in an ozone treatment facility, now being tested for the treatment of amine fuel wastes at Vandenberg AFB, California.

Although chemical oxidation is the most popular and most efficient method of hydrazine disposal, the cost of the chemicals is the major concern. For example, to completely destroy/treat 1pound of hydrazine requires 6.4 pounds of calcium hypochlorite. (Bowman et al, 1977). Although the reaction is effective, it is not efficient. The formation of insoluble salt deposits is another problem with some chemical means of treatment (i.e., calcium hyprochlorite

and sodium hyprochlorite). Although the hydrazine is gone, the resulting problem of cleaning the unwanted salts arises.

Incomplete reaction during the chemical treatment of hydrazine could create even more problems. Although the chemical reduction and oxidation reactions convert hydrazine to carbon dioxide, nitrogen, water, and nitrates, the reaction of MMH and UDMH is much more complex. Much of the oxidation involving MMH and UDMH is unknown, generating complex compounds. One of the known products of MMH and UDMH oxidation is nitrosodimethylamine, one of the most potent of all chemical carcinogens. The high energy requirement of the process also makes this disposal technique impractical.

To support worldwide deployment of the F-16 combat fighter, the Environics Directorate of Armstrong Laboratory studied the consequences of using 70% hydrazine in the aircraft's emergency power unit (EPU). MacNaughton, et al (1981) observed the behavior of hydrazine in the environment to be dependent on air and ground temperatures, wind speed, solar radiation, dimensions of the spill, and the evaporation rate of the hydrazine fuel. In the absence of the appropriate catalysts, hydrazine exhibited remarkable stability in the environment. The study focused on the development of spill management. Different chemicals were evaluated in the destruction of hydrazine. Unfortunately, it was discovered that massive amounts of chemicals would be required to completely detoxify a substantial hydrazine fuel spill. Neutralization of a spill created by a 55-gallon drum would require approximately 1000 kilograms (2200 pounds) of calcium hypochlorite. Through the research conducted, it was recommended that spill management include dilution and containment collection, followed by treatment with a neutralizing agent.

Not all of the hydrazine disposal techniques have been described. Other methods of disposal/treatment have also been explored. The catalytic decomposition of hydrazine using copper sulfate has recently shown promise. A significant amount of work remains before an effective and efficient treatment method for hydrazine spill cleanup can be demonstrated and fielded.

SECTION III

ENVIRONMENTAL INTERACTIONS

Due to the widespread use and distribution of hydrazine worldwide in the support of the F-16 fighter, numerous opportunities exist in which major amounts of hydrazine fuels could be released into the environment. In addition, past disposal practices, accidental spills or leaks from manufacture, storage, transportation, or final use have created soil and ground water contamination. Experimentation has shown that the interaction of hydrazine with the environment depends on many factors. Although hydrazine is an extremely reactive compound, the absence of catalysts enables the fuel to become remarkably stable (Christensen, et al., 1979).

The persistence of hydrazine in the soil-groundwater environment is clearly defined. Many factors determine the fate and transport of hydrazine in the soil environment. For example, soil pH and organic content of the soil have been found to have a large effect on its retention. The half-lives of hydrazine and its derivatives in soil and groundwater range from 8 to 12 days (Schmidt, 1984). The major concern of hydrazine spills in the environment is its migration to groundwater drinking supplies.

When introduced in pure or aqueous form, hydrazine is relatively mobile in the soil and groundwater system (IRP Toxicology Guide, 1989). Although hydrazine would be expected to be highly volatile and reactive in the environment, it has proven remarkably stable under the right conditions. The solubility of hydrazine is described as miscible with water and ethanol, with slight misicibility in hydrocarbons and halogenated hydrocarbons (IARC, 1974). The nature of hydrazine adsorption by soils is highly dependent on suspension pH and the functional groups present (Moliner et al., 1989). Quantities of the fuel can be transported through the unsaturated zone of soil. At pH 7, roughly 90 percent of the hydrazine will exist as the hydrazinium cation ($N_2H_5^+$), which is non-volatile (IRP Toxicology Guide, 1989). Under acidic conditions, all but 0.1% of the hydrazine was found as the protonated form (Moliner et al., 1989). Approximately half the hydrazine was protonated and half was uncharged under alkaline conditions. The unprotonated form of the fuel is a strong nucleophile which can participate in condensation reactions with carbonyl groups in humic substances (Schnitzer and Skinner, 1965). The nonvolatile, ionized form of hydrazine could account for its unusually stable character in the environment. The mobility of the hydrazinium ion in the soil depends on the pore water velocity and the concentration of this ion in the soil (Mansell and Bloom, 1988). However, hydrazine is exposed to numerous degradation pathways in the soil-groundwater environment.

Evaporation and volatilization are both important in the fate of hydrazine in the environment. The evaporation rate of a spilled liquid is a function of ambient air temperature, wind speed, solar radiation, size of spill, vapor pressure, and diffusion coefficients (Stauffer, 1977). The volatilization of hydrazine from soils and surface waters is a potential transport pathway of the fuel in the environment (MacNaughton et al., 1981). This transport mechanism depends on the ionic concentration (pH) of the soil or water matrix. The rate of volatilization is directly proportional to the amount of hydrazine which remains unprotonated.

In terms of soil and aqueous degradation of hydrazine, numerous aspects of the process have been explored. Early research by Slonim and Gisclard (1976) studied hydrazine degradation in aquatic systems. The organic content of the water and its effect on hydrazine degradation were the primary focus of their report. It was observed that the greatest breakdown of hydrazine occurred in the most organically rich water. This water was rich in organic material and was a nonsterile environment, both of which made a conducive environment for biodegradation. The concentration of hydrazine in the treated city drinking water (no organics) was unchanged. Research conducted by MacNaughton et al. (1978) found that hydrazine degraded much faster in natural waters than in distilled water. Therefore, it was concluded, that the degradation of hydrazine depended on the organic content, presence of minerals, and microbial presence of the water environment.

The effect of copper concentration , phosphate concentration, and ionic strength on the degradation of hydrazine in aquatic systems was studied by Moliner and Street (1989). The oxidation of hydrazine to nitrogen gas and water can be catalyzed by the addition of copper (II) and phosphate ions. The mechanism of the enhancement can be seen in the abstraction of a H+ from the hydrazine to form the hydrazyl radical. The dimerization of the hydrazyl radicals results in the formation of ammonia as one of the degradation products. Research has also shown that the rate of hydrazine autooxidation increases proportionally to the ionic strength of the matrix. These results suggest that one of the steps in the pathway involves a reaction of ionic intermediates with identical charges.

The environmental fate of hydrazine in water environments was studied by Braun and Zirrolli (1983). The fate of the fuel in an aqueous environment is dependent on chemical and biological degradation, volatilization, sedimentation, dilution, and/or dispersion. The rate of aqueous oxidation depended on the presence of metal ion catalysts the aeration, the organic matter, the ion concentration, and the temperature of the water. All these factors contribute to the "real world" situation. The aqueous half-life of hydrazine ranged from 10 to 14 days. The persistence of the fuel in the aqueous environment was directly correlated to the migration of the fuel. The aerobic biodegradation of hydrazine occurred in water having hydrazine concentrations less than 2 mg/L. Although hydrazine is extremely energetic, the fuel exhibited remarkable stability in uncatalyzed, aqueous solutions.

The sorption of hydrazine by different soil types was also assessed by the Braun-Zirrolli research group (1983). Through laboratory soil column studies, four soils were studied (cleaned sand, clay, organic, and soil from Vandenberg AFB). The results of their studies can be seen in the following table (Braun and Zirrolli, 1983):

Table 1. Soil Sorption Data.

Soil	Percentage of Hydrazine Recovered
Sand	89.1
Clay	7.6
VAFB	1.6
Organic	1.3

As one can see, nearly 90 percent of the hydrazine spilled on the sand was recovered. The percentage of fuel from the other soils was much lower. The researchers concluded that the interaction between the hydrazine and the natural soils was the result of chemical decomposition and/or fuel adsorption to soil components. The percolation studies showed that hydrazine migration through natural soils is slow and confined.

The pH of the environment has shown to be very important in the retention and degradation of hydrazine in the soil (Street et al., 1988). It was determined that pH 7 supported the optimum degradation of hydrazine. As the ionic concentration became more acidic, the oxidation rate of hydrazine slowed. At pH 2, the reaction stopped completely. The study also showed that copper metal proved to be the best catalyst in the oxidation of hydrazine.

Many transition metals are known to catalyze the degradation of hydrazine, acting as a one- or two-electron acceptor anaerobically (Cosser and Tompkins, 1971). In the presence of Cu^{2+} -montmorillonite degradation of hydrazine was rapid and vigorous. Degradation of hydrazine was much slower in suspensions containing Mn^{2+} and Fe^{2+}. Of the transition metals, copper proved to best catalyze the degradation of hydrazine.

The interaction between hydrazine and the colloidal constituents of soils is another instrumental factor in the fate of the fuel in the environment (Hayes et al., 1984). It has been shown that the degradation of hydrazine is proportional to the pH of the system, and enhanced in the presence of heterogeneous surfaces of K+, Na+, Mg+, and Ca+ through homoionic exchange (Hayes et al, 1984). As a result of high redox reactions, the degradation of hydrazine was further catalyzed by clays containing Cu^{2+} , Mn^{2+} , and Fe^{3+} . However, the degradation of hydrazine was most rapid in the presence of Cu^{2+} montmorillonite. The group believed that the soil sorption of hydrazine was largely dependent on not clays, but humic acids. Once bound, most of the hydrazine cannot be removed from the humic acids.

A slightly different aspect of the interaction between hydrazine and soils was studied by Hayes et al. The effect of the clay colloidal component of soil was studied relating to hydrazine
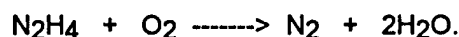
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degradation (Hayes et al., 1984). The soil clay constituents, which are the active surfaces in soil, are composed of various hydrous oxides of aluminum and iron, amorphous, organic humus colloids, and clay minerals. As predicted, the research revealed that the clay colloidal component in soil had a large influence on the fate of hydrazine in the soil and ground-water environment. The clay montmorillonites can sorb hydrazine, and sometimes catalyze the degradation of hydrazine. The sorption of the hydrazine by the montmorillonites was found to be highly dependent on the pH values of the solutions, and the amount of exchangeable metal cations held by the clay. Because of the polarity of the N-H bond, hydrazine has the potential to form hydrogen bonds with electronegative surfaces on clays and organics (Moliner et al., 1989). The amount of hydrazine sorption was found to be considerably greater at pH 4 than at pH 8. The sorption of hydrazine to humic acids and iron (II) was also observed in this study.

SECTION IV

MICROBIOLOGY AND BIOREMEDIATION OF HYDRAZINE

An effective treatment technique needs to be developed to confront environmental contamination in the event of an accidental spill and from past disposal practices. The use of biological treatment has been successfully applied to a number of organic and industrial chemicals. If feasible, the development of a biological treatment process for hydrazine spills would offer a cost-effective method for hydrazine contamination.

Auto-oxidation of hydrazine in the soil environment appears to be the principal factor contributing to the disappearance of the chemical fuel from soil (Ou and Street, 1987). The following stoichiometric equation describes the process of auto oxidation of hydrazine in soil:

$$N_2H_4 + O_2 \text{-------} > N_2 + 2H_2O.$$

Hydrazine fuels are inherently reactive in the presence of oxygen and in alkaline or neutral environment. However, it has been demonstrated that the fuels become stable under acidic and/or anaerobic conditions (Cuy and Bray, 1924).

Biological oxidation of degradation products (not pure hydrazine) has also been shown to be a factor in the hydrazine degradation process. However, biological oxidation of hydrazine, which accounted for 20 percent of the degradation process, was only a minor factor (Street and Ou, 1987).

The relationship between hydrazine and the soil microbiology is an important determinant in the bioremediation process. The goal of research in this area is to biodegrade hydrazine contamination in an efficient manner using bacteria, while the fuel is still present in the soil. Most of the hydrazine bioremediation bench work has been conducted aerobically, unless otherwise stated.

Much has been conducted in terms of the relationship between hydrazine and the bacteriology of the soil. Observations have shown that hydrazine and its derivatives are toxic to many types of bacteria (London, 1979). The activities of autotrophic nitrifiers Nitrosomonas and Nitrobacter, of denitrifying bacteria, and of Enterobacter cloacae were all inhibited by hydrazine fuels. The selection of a research microbe was based on the following criteria: (1) the constituent of a representative soil community, (2) the ability of aerobic growth in a glucose mineral salt medium, (3) the mean generation time of 30 to 60 minutes, and (4) the moderate sensitivity to hydrazine fuels.

Organisms, which tolerate hydrazine, develop mechanisms to endure hydrazine resulting in an extended lag period of growth (Mantel and London, 1980). One mechanism which can cause an increase in the lag time is a bactericidal effect. The time required for the microbe to degrade the toxic hydrazine to nontoxic, usable compounds is yet another mechanism for the

increase in lag time. Adaptive mechanisms are also used by the microbes to overcome the toxic effects of hydrazine.

The research conducted using Paracoccus denitrificans, found that an increase in ionic and organic content appeared to increase the rate hydrazine propellant decomposition (London, 1979). Although the addition of hydrazine produced a delay in the start of the log growth phase, the resultant growth yield was nearly identical to that of the control. It was concluded that the concentration of the hydrazine fuels was directly proportional to the growth of the microbes. At 0.05 ppm, the smallest concentration, the lag phase of the bacteria was about 45 minutes, while the a concentration near 10 ppm delayed the lag phase for 49 hours. High concentrations of hydrazine, ranging from 50 to 500 ppm, resulted in no visible microbial growth. Exposure of Paracoccus denitrificans to MMH and UDMH had results similar to that of hydrazine.

From the experimental results, London et al. (1979) postulated that the increase in the lag phase may be attributed to the initial killing effect. Following the killing, a bacteriostatic process, which may be due to an interference to a synthetic pathway, resulted in a depletion of an essential metabolite, inhibition of energy transfer, or transport mechanism. One solution to this problem would be the use of mixed cultures. Since bacteria exhibit a wide range of cellular compositions and catabolic activities, the selection of a single species is limiting. A more realistic test system would include the utilization of mixed bacterial cultures. The selection of compatible strains, growing under the same conditions, must be attempted.

Work performed by Kane and Williamson (1983) used Nitrosomonas, Nitrobacter, methanogens, anaerobic, and denitrifying bacteria, which were all inhibited in the presence of high concentrations of hydrazine. These bacteria were selected based on their involvement in the nitrogen cycle and their abundance in the environment. The results of their research can be summarized by the following table (Kane and Williamson, 1980):

Table 2. Effects of Hydrazine, MMH, and UDMH on Bacterial Metabolsim.

Bacteria	Concentration Causing 50% Reduction in Metabolism (mg/l)		
	Hydrazine	MMH	UDMH
Nitrobacter	15	15	1800
Nitrosomonas	165	>1	35
Anaerobic bacteria	100	75	2300
Denitrifying bacteria	100	10	12,500

Since hydrazine spills and wastewaters concentration levels normally exceed these levels, the use of biological systems seems unlikely. Possibly the combination of dilution and acclimation could overcome the toxicity of hydrazine, resulting in the successful biodegradation of hydrazine.

Hydrazine concentration levels typically associated with hydrazine wastewater would require a dilution of at least 100 to 1 in order for effective biological degradation (Kane and Williamson, 1980).

At low concentrations of hydrazine, the presence of bacteria doubled the rate of hydrazine oxidation. This increase of oxidation was attributed to cellular metabolism. The results of the toxicity studies showed that hydrazine was least toxic to Nitrosomonas. Because Nitrosomonas had the ability to survive at doses toxic to other bacteria, it was chosen for further study.

The research group, led by Kane and Williamson (1980), studied the hypothesis that Nitrosomonas could metabolize hydrazine. Nitrosomonas was shown to cometabolize hydrazine, with the major metabolic product being nitrogen gas in the presence of ammonium sulfate. Although Nitrosomonas was also found to metabolize hydrazine to nitrogen gas, it could only utilize hydrazine for a short period of time. Nitrosomonas was unable to acclimate to long-term doses of hydrazine. Because hydrazine seriously disrupts the natural bacterial balance in the aquatic environment, the researchers concluded that hydrazine contamination in a natural aquatic environment can be expected to seriously disrupt bacterial populations. Hydrazine was found to be inhibitory and toxic to Nitrobacter, Nitrosomonas, denitrifiers, and anaerobic bacteria (Kane and Williamson, 1980). It is believed that the inhibition occurs when hydrazine reacts with the proteins which cleave the C-terminal amino acids and release them as acylhydrazines and amines (Akabori et al., 1952). Therefore, the biological waste treatment of hydrazine laden wastewater was not recommended.

The mechanism of natural biodegradation of hydrazine contaminated soil was studied. Results from experimentation described the mechanism of hydrazine biodegradation in the soil. At low concentrations, hydrazine disappeared rapidly from soil. Hydrazine concentrations near 10 ug/g disappeared completely in 1 and a half hours. Hydrazine concentrations around 500 ug/g completely disappeared in 8 days. Microbial degradation of hydrazine in soil was only a minor factor, contributing to only 20 percent of the hydrazine removal (Ou and Street, 1987). Although biological degradation was a relatively minor factor, hydrazine consistently disappeared from sterile soil at a somewhat slower rate. Soil respiration rates and bacterial populations in hydrazine treated soils were initially inhibited. The inhibition was found to be directly proportional to the concentration of hydrazine. However, this effect was only temporary. The bacterial populations exposed to 100 ug/g hydrazine quickly recovered. The hydrazine in this situation was completely gone within 24 hours. The bacterial population exposed to hydrazine at concentrations of 500 ug/g were 10 times smaller in number than the bacterial count in the control after 21 days. The fungal populations, which were not affected by hydrazine, in all the hydrazine treated soils were larger than the populations in the control.

Ou and Street, along with Johnson, Mansell and Bloom (1988) discovered that Achromobacter sp., Bacillus sp., and Psuedomonas sp. all had the ability to tolerate, and degrade hydrazine in dilute solutions. Of the three bacteria, Achromobacter sp. had the shortest lag period of growth. It was also the only microbe which had the ability to tolerate and degrade hydrazine in concentrations larger than 100 ug/mL. It was shown experimentally, using ^{15}N-hydrazine, that the Achromobacter sp. oxidized hydrazine to nitrogen gas (Street, Ou, 1987). A Pseudomonas sp. also was to degrade MMH. Through the work completed in this research effort, it was determined that Achromobacter sp. had the most potential for use in hydrazine bioremediation, and was chosen for further research.

Achromobacter sp. was unable to utilize hydrazine as its sole source of metabolism. The enzymatic system of the Achromobacter sp. was dependent on the co-metabolic need for an external nitrogen source. This species of bacteria also enhanced the degradation of hydrazine in water. The researchers concluded that Achromobacter sp. could have the potential for use in the detoxification of hydrazine from contaminated soils and groundwater systems.

Similar results between monomethylhydrazine and the soil microbiology were found. Achromobacter sp. and Pseudomonas sp. rapidly degraded hydrazine found in soil. Both, however, required an alternate carbon source and a second nitrogen source. When the paper was published in 1988, efforts were being made to isolate a microbe from soil which would be able to utilize hydrazine and its derivatives as a sole source of growth.

Mantel and London (1980) studied the mechanism of adaptation of soil bacterium to hydrazine propellants. Studies, using Enterobacter cloacea, would determine the mechanism of survival as inductive, selective, or mutative. The three fuels were shown to exert both a bacteriostatic and bactericidal relationship to the bacteria. At concentrations near 10 ppm, it was discovered that the bacteria were able to survive the hydrazine through both an inductive process and a selective process. During the inductive mechanism, hydrazine acted as the inducer, which activated a normally latent metabolic pathway. Once activated, the new metabolic pathway had the ability to counteract the inhibitory effects of hydrazine. These induced pathways allowed the organism to continue growing. Once the hydrazine, the inducer, was removed, the gene no longer was expressed and the organism lost only a part of its resistance. A selective process is also believed to be involved in the In the adaptive mechanism of the microbe to 10 ppm hydrazine. The selective process involves the growth of variants in the culture. When the variants were "selected out," they maintained their characteristic lag time while grown on 10 ppm hydrazine. At concentrations between 20 ppm and 50 ppm of MMH and UDMH, the bacteria showed just the selective mechanism. Only the MMH and UDMH resistant variants were permitted to grow, and therefore, were selected out.

Further investigations include the effects of hydrazine, MMH, and UDMH on the utilization of compounds involved in the intermediary metabolism (Mantle and London, 1983).

The organism used was <u>Enterobacter cloacae</u>. The bacterium's ability to utilize different substrates as a sole energy and carbon source was influenced by the presence of the hydrazine compounds. The effects, which ranged from reduction in final cell concentration to total inhibition of growth, were related to the specific hydrazine compound. Hydrazine had the greatest impact, while UDMH had the least (London, 1979). There did not appear to be any correlation between the substrate structure and the effect of hydrazine on the utilization of the saccharides studied. None of the hydrazines affected the utilization of pyruvate, malate, or succinate, while citrate or acetate were not metabolized by hydrazine and MMH exposed cells.

Stiefel et al (1977) found an enzyme in heterotrophic nitrogen fixing bacteria capable of degrading hydrazine. At pH values between 7.2 and 7.4, which are normal assay conditions, nitrogenase can catalyze the reduction of hydrazine at only a very slow rate. In all respects, the reduction of hydrazine behaves like that of other substrates, with ATP and $S_2O_4^{2-}$ being required and dihydrogen evolution being decreased by the amount commensurate with the amount of hydrazine added (Bulen, 1976). Thus, hydrazine is reducible by the nitrogenase, and although there is still no direct evidence, the result establishes the potential of a bound intermediate in the overall process of dihydrogen reduction.

Ironically, <u>Azotobacter agile</u> has been found to produce hydrazine through the process of nitrogen fixation (IARC, 1974). UDMH and MMH, however, do not occur naturally in the environment.

SECTION V
CONCLUSION

An environmentally conscious and inexpensive treatment method is required to replace existing disposal and treatment techniques. When released into the soil environment, hydrazine should undergo rapid autooxidation, because it is subject to chemical (autooxidation) and microbial (naturally occurring bacteria) soil degradation in the soil environment. However, in soils absent of necessary catalysts, such as organics or metals, hydrazine is remarkably stable.

In theory, biological treatment can offer the most cost-effective alternative for environmental contamination and disposal of hydrazine. Unfortunately, the research that has been conducted show the toxicity of hydrazine makes the biological treatment of emergency hydrazine spills impractical. Biodegradation of hydrazine spills has shown to be possible at the very low concentration levels. Researchers continue the search for a soil microbe isolate which will tolerate, and then, hopefully, degrade hydrazine. If one cannot be found, possibly microbial-adaptive mechanisms, including environmental selection, mutation, and the induction of specific enzymatic systems could be used to counteract the effects of the toxic fuels. The use of fungual populations in the degradation of hydrazine must also be fully explored and understood.

Data "gaps" exist in the research concerning hydrazine degradation chemistry performered to date. No comprehensive work has been performed to establish the reaction mechanisms and reaction products of hydrazine, MMH, and UDMH as a function of soil and atmospheric parameters (i.e., soil type, organic/inorganic contaminants, presence of metals, aerobic/anaerobic conditions, etc.).

This literature review was performed as our first step in addressing an USAF Environmental Safety and Occupational Health (ESOH) concerning hydrazine remediation.

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