An Evaluation Study Of The Effectiveness Of Using A Reaction-based Process For Hydrazine Waste Remediation

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AN EVALUATION STUDY OF THE EFFECTIVENESS IN USING A REACTION-BASED PROCESS FOR HYDRAZINE WASTE REMEDIATION

by

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B.S. University of Central Florida, 2004

A dissertation submitted in partial fulfillment of the requirements For the degree of Doctor of Philosophy in the Department of Chemistry in the College of Sciences at the University of Central Florida Orlando, Florida

Fall Term

2011

Major Professor: Christian A. Clausen III
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ABSTRACT

Hydrazine (HZ) and monomethylhydrazine (MMH) are used extensively as hypergolic propellants at Kennedy Space Center. These highly reactive fuels are considered highly toxic, and potentially carcinogenic. Consequently, the transport, handling, and disposal of hydrazines is strictly regulated to protect personnel and the environment. Currently, KSC generates large volumes of hydrazine-laden wastewater for disposal. This waste is contained and shipped on public highways for subsequent disposal by incineration presenting a potentially catastrophic threat to the environment and the general public in the event of an accidental release. Other existing remediation methods include oxidative and reductive pathways as well as biodegradation in fixed film reactors. Each of these methods has associated drawbacks and limitations that make them unsuitable for industrial use. Recently, hydrazine neutralization by reaction with alpha-ketoglutaric acid (AKGA) to form the stabilized pyridazine derivatives PCA and mPCA has been explored. The applicability of this technique for use at KSC has been established and procedural considerations for implementation have been addressed.

Experimental evidence based on worst case scenario decontamination processing simulations and reaction characterization has suggested that AKGA can cost effectively function as a drop-in replacement for current neutralizers with minimal modification to existing infrastructure and operating procedures. Further work will be necessary to satisfy permitting
requirements and verify that the reaction product stream is non-hazardous in light of limited toxicity data.
ACKNOWLEDGMENTS

I would like to thank Wiltech and Chuck Davis of NASA for providing the opportunity, to conduct this research. Without their faith and funding, this dissertation would never have come to fruition.

I would also like to show my appreciation to Tim Griffin for his unwavering support over the years. As well as to my committee members: Seth Elsheimer, and Delbert Miles for making themselves available and providing meaningful direction and support.

Additionally, I am eternally grateful to my advisors Christian A. Clausen III and Cherie Geiger for their patience, guidance, and support throughout my academic career. Without which, I would never have come this far.

Most importantly, I would like to thank my husband for being my rock. And, thank you to my friends and family for their constant love and encouragement.
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACGIH</td>
<td>American Conference of Governmental Industrial Hygienists</td>
</tr>
<tr>
<td>ADL</td>
<td>Acceptable Detection Limit</td>
</tr>
<tr>
<td>AKGA</td>
<td>Alpha-ketoglutaric acid</td>
</tr>
<tr>
<td>APU</td>
<td>Auxiliary Power Unit</td>
</tr>
<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
</tr>
<tr>
<td>DOT</td>
<td>Department of Transportation</td>
</tr>
<tr>
<td>EAA</td>
<td>Ethyl Acetoacetate</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FDEP</td>
<td>Florida Department of Environmental Protection</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>GSE</td>
<td>Ground Support Equipment</td>
</tr>
<tr>
<td>Hazmat</td>
<td>Hazardous Materials</td>
</tr>
<tr>
<td>HWWTS</td>
<td>Hydrazine Waste Water Treatment System</td>
</tr>
</tbody>
</table>
HZ    Hydrazine

IDLH   Immediately Dangerous to Life and Health

KSC    Kennedy Space Center

L      Liter

µg/g   micrograms per gram

µg/mL  micrograms per milliliter

mg/m³  milligrams per cubic meter

mg/L   milligrams per liter

MMH    monomethylhydrazine

mPCA   1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid

MS     Mass Spectrometer

m/z    mass to charge ratio

NASA   National Aeronautics and Space Administration

NDMA   N-Nitrosodimethylamine

NIOSH  National Institute of Safety and Health

NMHU   New Mexico Highlands University
NPD  Nitrogen Phosphorus Detector
NVR  Non-Volatile Residue
OMS  Orbital Maneuvering System
OSHA Occupational Safety and Health Administration
PCA  6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid
PEL  Permissible Exposure Limit
ppb  parts per billion
ppm  parts per million
RCRA Resource Conservation and Recovery Act
RCS  Reaction Control System
REL  Recommended Exposure Limit
%RSD Relative Standard Deviation
SCAPE Self Contained Atmospheric Protective Ensemble
STEL  Short Term Exposure Limit
STP  Sewage Treatment Plant
TLV  Threshold Limitation Value

xvi
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIC</td>
<td>Total Ion Chromatogram</td>
</tr>
<tr>
<td>TVD</td>
<td>Toxic Vapor Detector (Interscan® Series 4000 Portable Gas Analyzer)</td>
</tr>
<tr>
<td>TWA</td>
<td>Time Weighted Average</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible</td>
</tr>
<tr>
<td>WHPU</td>
<td>Waste Hydrazine Processing Unit</td>
</tr>
<tr>
<td>% (wt/wt)</td>
<td>Percent by weight</td>
</tr>
<tr>
<td>WWTU</td>
<td>Waste Water Treatment Unit</td>
</tr>
</tbody>
</table>
CHAPTER ONE: INTRODUCTION

Hydrazine Use

Hydrazine (N$_2$H$_4$) and monomethylhydrazine (N$_2$H$_3$(CH$_3$)), termed collectively throughout this document as “hydrazines”, have been used extensively as propellants in rockets and spacecraft including the Space Shuttle Orbital Maneuvering System (OMS), Reaction Control System (RCS) and Auxiliary Power Units (APUs). As monopropellants, hydrazines cannot compete with hydrocarbon fuels in terms of heating value, handling safety, or availability. However, these highly reactive and flammable fuels are strong reducing agents that react hypergolically in the presence of strong oxidizers such as dinitrogen tetroxide, fuming nitric acid, hydrogen peroxide, or fluorine. The result is spontaneous combustion. In comparison to hydrazines as monopropellants, hypergolic bipropellant combinations are advantageous in that they produce combustion in the absence of external ignition sources. For this reason, hypergols are used widely in rocket engines that require frequent restarting, such as those responsible for attitude control. Hypergolicity can minimize the tendency toward destructive resonant instabilities in liquid rocket engines. And, from a launch facilitation perspective, hypergols can be stored at room temperature without boil-off losses or refrigeration as required by cryogenic propellants. Another advantage presented by hydrazine bipropellant combinations is that a loaded, bipropellant rocket can be stored in a state of instant readiness for years. Moreover, they are relatively lightweight, which is beneficial in terms of payload minimization.
Aside from their use as propellants, hydrazines and hydrazine derivatives are used in polymer synthesis as building blocks, cross linkers, and chain extenders. Hydrazine is used as an oxygen scavenger in boiler feed water to prevent corrosion. And, the reducing properties of hydrazines are utilized in metallurgical applications such as metal plating, metals reprocessing, and ceramics. In addition, hydrazine is used in pesticides, as blowing agents in plastics processing, and as an intermediate in pharmaceutical drug synthesis (Schmidt, 2001).

**Hydrazine Toxicity and Exposure Limits**

Hydrazines are considered highly toxic and potentially carcinogenic. Human occupational data and laboratory studies indicate that people exposed to hydrazines may develop adverse systemic health effects or cancer. The U.S. Environmental Protection Agency, the U.S. Department of Health and Human Services, the International Agency for Research on Cancer, and the World Health Organization have classified hydrazines as possible cancer-causing environmental contaminants (Choudhary, 1997). Symptoms of acute (short-term) exposure to high levels of hydrazine may include irritation of the eyes, nose, and throat, dizziness, headache, nausea, pulmonary edema, seizures, and coma in humans. Acute exposure can also damage the liver, kidneys, and central nervous system in humans. Hydrazines are corrosive liquids and caustic burns are the immediate result of contact with the liquid. Chronic (long-term) exposure has resulted in effects to the lungs, liver, spleen, and thyroid of animals exposed via inhalation. And, increased incidences of lung, nasal cavity, and liver tumors have been observed in exposed rodents (Environmental Protection Agency Web site, 2007).
To protect the public from exposure, governmental agencies have established exposure limits. The Occupational Safety and Health Administration (OSHA) issued exposure limits based on recommendations from research conducted by the National Institute of Safety and Health (NIOSH). The OSHA enforced permissible exposure limit (PEL) for HZ is 1.0 ppm (defined as 1.3 mg/m³) in air. This limit is a time weighted average (TWA) for an 8-hour workday. Meaning, a worker may be continually exposed to HZ vapors no greater than 1.0 ppm for 8 hours per day. OSHA also notes that absorption of HZ vapor through skin, mucous membranes, and eyes may contribute to overall exposure. More cautiously, the NIOSH recommended exposure limit (REL) is 0.03 ppm (defined as 0.04 mg/m³). This is the lowest detectable concentration by NIOSH methods and is considered the ceiling exposure concentration over any 120-minute sampling period. NIOSH also advises a 15-minute short-term exposure limit (STEL) of 50 ppm, which they consider immediately dangerous to life and health (IDLH). From an independent perspective, the American Conference of Governmental Industrial Hygienists (ACGIH) suggests a threshold limit value (TLV) of 0.01 ppm (defined as 0.01 mg/m³) for HZ in the workplace. This recommendation, like the OSHA PEL, is a TWA for continuous exposure over an 8-hour workday/40-hour workweek. Table 1 summarizes the current exposure limits for HZ and MMH. Individual industry standards vary within the legal range of exposure limits, but are generally more conservative.
Table 1: Summary of MMH and HZ exposure limits as issued by Federal and independent agencies

<table>
<thead>
<tr>
<th>Organization</th>
<th>Exposure Duration</th>
<th>HZ, ppm</th>
<th>HZ, mg/m³</th>
<th>MMH, ppm</th>
<th>MMH, mg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSHA PEL</td>
<td>TWA (8 hrs/day; 40hrs/ week)</td>
<td>1.0</td>
<td>1.3</td>
<td>0.2</td>
<td>0.35</td>
</tr>
<tr>
<td>NIOSH REL</td>
<td>120 minute period</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>NIOSH STEL (IDLH)</td>
<td>15 minutes</td>
<td>50</td>
<td>50</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>ACGIH TLV</td>
<td>TWA (8 hrs/day; 40hrs/ week)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Environmental Fate**

The use of hydrazines as propellants and in the agricultural and pharmaceutical industries has resulted in the inadvertent release of the chemicals into the environment and the accumulation of large volumes of industrial wastewater containing hydrazine fuels at toxic levels. The carcinogenic effects on laboratory animals in conjunction with the determined and potential hazards to humans and surroundings have led to the concern for their fate in air, water, sediment, and soil.

**Air**

Hydrazines degrade rapidly in air on reaction with ozone, hydroxyl radicals, and nitrogen dioxide. The major fate of hydrazines released into the atmosphere is likely reaction with ozone. The second order reaction rate constant based on degradation of hydrazine in the presence of excess ozone to yield hydrogen peroxide is $3 \times 10^{-17}$ cm³molecule⁻¹sec⁻¹. Based on this data, the estimated atmospheric half life ranged from less than 10 minutes for hydrazine during an episode of ozone pollution to 2 hours under normal conditions. Atmospheric hydrazine half life based on
the reaction with hydroxyl radicals ranged from less than 1 hour in polluted urban air to 3-6 hours in less polluted atmospheres. Hydrazine also leaves the atmosphere via autoxidation. Experimental half-lives determined in a dark reaction chamber ranged from 1.8 to 5 hours with the former measured at higher humidity (Choudhary & Hansen, 1998).

Water

Hydrazine degradation in aqueous systems is dependent on several variables including pH, hardness, temperature, oxygen content, and the presence of metals or organic matter. Oxidation and biodegradation are the major mechanisms of removal. Metal ions catalyze the reaction of hydrazine with dissolved oxygen (Choudhary & Hansen, 1998).

One study followed hydrazine degradation in seven water samples of varying origin with differing hardness, pH, and dissolved oxygen levels. These samples were used to make 5 mg/L hydrazine solutions which were monitored for the next 4 days. They found hydrazine was most rapidly removed from the dirty river water with the initial concentration decreased by two-thirds after 2 hours. Both the pond and the filtered, chlorinated county water contained 10% of the original hydrazine content after 1 day. In contrast, the chlorinated, filtered, and softened city water still contained 4.5 mg/L after 4 days. In summary, organic matter and water hardness were found to increase hydrazine degradation rates (Slonim & Gisclard, 1976).

Biodegradation is an effective means of hydrazine removal at low hydrazine concentrations in ambient water. However, higher hydrazine concentrations were toxic to the bacteria population. Spills of these fuels into the aquatic environment can be expected to seriously disrupt natural bacterial populations. For example, the *Achromobacter* bacteria.
efficiently degraded hydrazine at concentrations up to 50 µg/mL in Santa Fe river and Lake Alice water samples, but the same bacterium declined in capacity to degrade hydrazine at 25 µg/mL in other waters such as Newmans Lake, Prairie Creek, tap water, and distilled water (Ou & Street, 1987). Another study found low levels of HZ and MMH decreased *Nitrosomonas* populations (Kane & Williamson, 1983).

**Soil and Sediment**

Hydrazine degrades more rapidly in soil than water. Just as in water, oxidation and biodegradation are the major processes in hydrazine depletion. Hydrazine applied to fine (Arrendondo) sand at concentrations of 10, 100, and 500 µg/g was degraded in 1.5 hours, 1 day, and 8 days respectively. This study found oxidation to be the dominant process with about 20% attributed to biodegradation (Ou & Street, 1987).

**Environmental Regulation**

Although the environmental persistence of hydrazines is low by comparison to other toxicants such as polychlorinated biphenyls (PCBs), or dioxin, they do pose a significant threat based on their corrosive, flammable, and toxic nature. Consequently, legislation is in place to regulate the transport and disposal of hydrazine waste.

At the federal level, the Resource Conservation and Recovery Act (RCRA) issues general guidelines for controlling hazardous waste from point of generation to disposal. RCRA Subtitle C directs the Environmental Protection Agency (EPA) to develop comprehensive regulations to regulate commercial businesses, as well as federal, state, and local government facilities that generate, treat, store or dispose of hazardous waste from generation to disposal. These
regulations can be found in 40 CFR (Code of Federal Regulations). HZ and MMH are specifically identified under waste codes U133 (reactive, toxic waste) and P068 (acute hazardous waste) respectively in 40 CFR §261.33. Generally, the EPA encourages the State hazardous waste regulatory agency to assume primary responsibility for implementing a hazardous waste program through State adoption, authorization, and implementation of the regulations. Therefore, hydrazine-laden waste streams generated at Kennedy Space Center (KSC) are regulated at the state level by the Florida Department of Environmental Protection (FDEP) (Environmental Protection Agency Web site, 2007).

**Current Neutralization and Disposal Techniques**

Many processes in the use of hydrazines as propellants generate hydrazine-laden waste waters for disposal including: vapor scrubbing, system level testing of hydrazine tanks in missiles and satellites, rinsing of hardware and transfer hoses before storage and reuse, and hydrotesting of MMH and HZ tank cars to meet Department of Transportation requirements. In light of the potential hazards associated with flammability and inhalation of HZ and MMH vapors, the practice at KSC is to “neutralize” these waste water streams by solubilization and dilution. Citric acid is added to waste water streams to lower the vapor pressure and minimize off-gassing of hydrazine vapors. Similarly, a 14% (wt/wt) citric acid solution is utilized as a scrubber liquor to entrap hydrazine vapors. In process cleaning operations, a glycolic acid solution containing anti-foam and wetting agents is used to rinse or soak hydrazine contaminated hardware and soft goods. Noteworthy is that in these scenarios the term “neutralize” refers to entrapment rather than destruction of the hydrazine molecule. This action is reversible and pH dependent. And, the end result is conversion of an air pollution problem into a more manageable
water pollution problem (Schmidt, 2001). Ultimately, most hydrazine-laden waste streams generated at KSC are combined into a “fuel soup” wastewater mixture containing citric acid, HZ, MMH, and isopropyl alcohol. The final solution is adjusted to contain less than one percent HZ and MMH by weight with a target pH of five to six. Under these conditions, the waste water can be held onsite for up to ninety days before shipping for off-site disposal. Currently KSC generates approximately fifteen thousand gallons of hydrazine-laden wastewater for disposal at a cost on the order of $120K per year. The wastewater is transported to Illinois for offsite incineration in three thousand gallon tankers that travel on public highways (Chuck Davis, personal communication, March 21, 2011). Transportation costs are included in this estimate and can be expected to escalate with increasing fuel prices. Per RCRA regulations, the generator is responsible for the waste stream from cradle to grave. Therefore, in the case of an inadvertent release, the generator is liable for any damages to personnel, the general public, and the environment. It is difficult to project a dollar amount on these potential punitive damages, but from a cost analysis perspective, the possibility must be weighed.

Various methods of safe and cost-effective disposal of hydrazines have been explored including incineration, chemical oxidation, chemical reduction and biodegradation. Each of these techniques has its own associated drawbacks and limitations that make them impractical for use on an industrial scale. The current state of the art technologies are discussed here.

Off-site incineration of the citric acid “fuel soup” mixture is the disposal method currently utilized by NASA/KSC and the United States Air Force. As mentioned previously, one significant drawback to this method is the shipping requirement and its associated liabilities. In
addition, combustion of HZ and MMH results in emission of mono-nitrogen oxide (NOx) gases, which are regulated greenhouse gases.

Oxidation by hypochlorite is an effective method for waste streams containing only hydrazine. Hypochlorites are most economically available as sodium hypochlorite or calcium hypochlorite. These neutralization reactions proceed as follows:

\[
\begin{align*}
\text{N}_2\text{H}_4 + 2\text{NaOCl} & \rightarrow 2\text{NaCl} + 2\text{H}_2\text{O} + \text{N}_2 \\
\text{N}_2\text{H}_4 + \text{Ca(OCl)}_2 & \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} + \text{N}_2
\end{align*}
\]

**Equation 1: Chemical equations relevant to the neutralization of hydrazine by hypochlorites**

Although this oxidation approach efficiently destroys MMH as well, its usefulness is compromised by the production of carcinogenic \(N\)-nitroso compounds, alkylchlorides and/or other unknown mutagenic species as degradation products. The same is true for oxidation by potassium iodate and potassium permanganate in sulfuric acid. Therefore, these treatments are not recommended for degrading bulk quantities or solutions of hydrazines (Castegnaro, et al., 1986) (Schmidt, 2001).

Chlorinolysis at pH 4 was found to effectively degrade HZ without by-product formation. However, chlorination of MMH yielded significant quantities of chloromethane, and small quantities of nitrogen trichloride, \(N,N\)-Dichloromethylamine, \(N\)-chloromethylamine, dichloromethane, and chloroform. Thus, one stage chlorination is unsuitable for destruction of alkylhydrazines because of the environmental hazards presented by the by-products of degradation (Schmidt, 2001).
Chlorinolysis at pH 5 with simultaneous ultraviolet (UV) illumination is effective at destroying all types of propellant hydrazines in contaminated water. This process requires UV lamp power input and sodium thiosulfate to remove excess chlorine. It was field tested in 30 gallon test vessels with solutions containing up to 500 ppm hydrazines. Design data was obtained to scale up to treating 7500 liters (L) of waste water a day (Schmidt, 2001). However, this process is not currently in use by NASA/KSC presumably due to permitting issues or budgetary constraints.

Oxidation of hydrazines by hydrogen peroxide proceeds as follows:

\[ \text{N}_2\text{H}_4 + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{N}_2 \]

**Equation 2: Neutralization of hydrazine by hydrogen peroxide**

This reaction is markedly slow in the absence of a catalyst (Zhong & Lim, 1989). However, greatly improved performance is attained by addition of UV radiation and inorganic iron (Fenton’s reagent) or organic (ferrioxalate) to the aqueous reaction mixture in a commercial UV/oxidation unit known as Rayox®. After successful field testing of the Rayox® technology, an effective permitting strategy was devised to conform to regulatory compliance. FDEP sanctioned the Rayox® process as satisfying the treatment standards pursuant to 40 CFR 268.40 and meeting the RCRA definition of a Waste Water Treatment Unit (WWTU). The treatment rendered the hydrazine-based waste acceptable for discharge and final treatment by the microbial process at STP-1 (Sewage Treatment Plant-1) in lieu of off-site disposal. Consequently, a functional second generation unit was built at KSC in close proximity to STP-1 in 1998 (Tierney). The major limitation of the Rayox® process is that it could only treat dilute waste
streams containing ≤ 3500 ppm or 0.35% hydrazine and MMH (Divina LeClair, personal communication, November 13, 2009). In practice, this proved a formidable limitation. Moreover, replacement parts for the damaged components are no longer available due to the age of the system. Therefore, the Rayox® system is no longer in use at KSC (Rob Ouellette, personal communication, March, 30 2011).

The ozone oxidation of hydrazine occurs as:

\[ \text{N}_2\text{H}_4 + 2\text{O}_3 \rightarrow \text{N}_2 + 2\text{O}_2 + 2\text{H}_2\text{O} \]

**Equation 3: Neutralization of hydrazine by ozone**

Ozonation of MMH does lead to production of the suspected human carcinogen N-nitrosodimethylamine (NDMA) intermediate, but it is destroyed by extended treatment (Schmidt, 2001). A Hydrazine Waste Water Treatment System (HWWTS) that utilized oxidation of hydrazines by ozone in conjunction with UV radiation was built at the water treatment facility at Vandenberg Air Force Base (Judeikis & Hill, 1991). Public data on the system performance is limited. The HWWTS was not implemented at KSC.

Another treatment option explored at KSC was the Waste Hydrazine Processing Unit (WHPU). This system utilized electrochemical means to oxidize HZ to nitrogen and water and MMH to nitrogen and carbon dioxide. Hydrogen ions generated by oxidation of hydrazine in the anode travelled through an electrolytic membrane to the cathode where they were converted to hydrogen atoms and subsequently oxidized to water using atmospheric oxygen. Electrocatalytic materials were selected to promote selective oxidation of HZ and MMH (NASA Tech Briefs website, 2007). Field testing rendered the WHPU inefficient from a cost perspective based on
power and safety requirements. Because unattended operation was not authorized, round the
clock operation required at least two personnel in Self Contained Atmospheric Protective
Ensemble (SCAPE) which greatly increased cost. Also, the necessary flow regulation was
problematic (Chuck Davis, personal communication, March 21, 2011). Consequently, the
WHPU was not pursued for further use at KSC.

Reductive pathways to hydrazine destruction have also been explored. One study
evaluated the applicability of two different nickel-based catalytic reductions to the
decontamination of hydrazine-laden waste (Lunn, G et al). The first approach utilized
preformed Raney nickel, with and without an exogenous hydrogen source. The other involved
generation of hydrogen and spongy nickel by addition of powdered aluminum-nickel alloy to an
alkaline hydrazine solution. Both approaches were found to have potential for reliable
quantitative destruction of hydrazines. For large scale industrial applications the authors suggest
the use of preformed Raney nickel over the in situ generation system because the latter required a
strongly alkaline solution to achieve useful reaction rates. In cases where Raney nickel alone
could not quantitatively reduce the contaminant, addition of a hydrogen atmosphere was
recommended. This would be impractical in the field because of the associated safety
ramifications. All detected products were relatively non-toxic. However, up to 27% of the
starting hydrazine was unaccounted for in some of the reactions. Thus, a material balance with
emphasis on detecting any potentially harmful products must be established before these
reactions could be seriously considered for use in environmental protection applications.
The use of conventional biological treatment processes for hydrazine wastes is not recommended since serious toxicity was observed at low levels (Kane & Williamson, 1983). However, one study reported favorable results for enhanced bioremediation of NASA waste water containing HZ, MMH, and citric acid in fixed-film bioreactors over batch culture systems (Nwankwoala et al, 2001). Although, these laboratory scale results were favorable, NASA did not pursue design and operation of an industrial immobilized biofilm reactor.

**Proposed Treatment Technology**

New Mexico Highlands University (NMHU) recently patented the use of an aqueous solution of 2-ketoglutaric acid, also known as alpha-ketoglutaric acid (AKGA) for remediation of hydrazine-contaminated equipment and surfaces (Helveston et al U.S. Patent 7,074,959 B2). The patent expressly relates to the use of aqueous AKGA for remediation of hydrazines, but also mentions solutions of other dicarbonyl compounds, including dialdehydes, diketones, aldehyde-ketones, aldehyde-acids, aldehyde-esters, keto-acids, and keto-esters. The distinguishing characteristic of this technique over the prior art of treatment by solubilization and dilution is the exothermic conversion of hydrazine to a stable organic compound. Specifically, HZ reacts with AKGA to yield 6-oxo-1,4,5,6-tetrahydro- pyridazine-3-carboxylic acid (PCA), and MMH reacts to produce 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA) as follows:
Equation 4: Reaction of HZ with AKGA to form stabilized pyridazine derivative

Equation 5: Reaction of MMH with AKGA to form stabilized pyridazine derivative

Subsequently, the stable pyridazine product can be treated with a metal catalyst and hydrogen to produce glutamine or a derivative thereof as shown in Equation 6 for microbiological degradation without further remedial intervention.

Equation 6: Metal catalyzed reduction of pyridazine product to glutamine derivative
As an alternative to catalyzed reduction, NMHU suggested that the pyridazine products, PCA and mPCA, may be marketable in their own right as plant growth stimulants. This possibility was based on the findings of a 1979 article appearing in the Canadian Journal of Microbiology that found a species of soil bacteria and a mold that were able to utilize PCA as a C and N source to enhance growth (LaRue). As a precedent, Biagro Western has already successfully marketed a similar eco-friendly plant growth enhancer under the trade name “Take Off”. This analog of the metabolite 2-oxoglutaramate reportedly stimulates growth by increasing nitrogen uptake and use efficiency thereby leaving less nitrogen fertilizer in the ground (Los Alamos Laboratory website, 2010). The proposed AKGA treatment process is summarized below:

![Proposed hydrazine neutralization process flow diagram (Dibbern, 2008)](image)

**Figure 1: Proposed hydrazine neutralization process flow diagram (Dibbern, 2008)**

The AKGA remediation technique piqued the interest of NASA for use in hydrazine family fuel decontamination processing, waste stream treatment, and vapor scrubber applications. In conference, the patent holders suggested another dicarbonyl compound for
consideration: ethyl acetoacetate (EAA). The reaction of ethyl acetoacetate with HZ produces a stabilized pyrazoline product and ethanol as shown:

![Chemical Structure](image)

**Equation 7: Reaction of HZ with EAA to yield stabilized pyrazoline product and ethanol**

The patent holders advised that EAA had also performed favorably in the lab and recommended it in addition to AKGA for further evaluation by those skilled in the art of hydrazine processing operations for NASA.

**Applicability for NASA**

This hydrazine remediation technology is of interest to NASA if it can provide a cost-effective means for improved safety and lessened potential environmental impact. Although promising, several of the numerous and broad claims made in the patent have not been experimentally demonstrated or validated, and their practicable implementation remains to be proven.

For example, the patent claims that the reaction of AKGA with aqueous HZ is a rapid and quantitative conversion to PCA, but there is no evidence to support such a yield. To validate this claim Helveston et al cite the previously published work of Gene Kaupp and Jens Schmeyer’s investigation of the solid state reactivity of a 1:1 hydrazine-hydroquinone complex (2000). This study found the solid state hydrazine-hydroquinone complex to react with AKGA when ball
milled in a 2:1 ratio to produce PCA in 98% yield. However, this solid state data has little relevance to the proposed application. The reaction of AKGA with HZ in solution does appear in the literature as far back as 1945 when Evans and Wiselogle reported preparation of PCA in basic solution (50% yield) for the purpose of capturing the absorbance spectrum. And, in 1965, Kline and Cox reported preparation of PCA and mPCA in solution (88% and 56.5% yields respectively) for subsequent conversion to DL-glutamine by hydrogenation of the pyridazine product catalyzed by palladium on carbon.

Also described in the patent is a microbial process for decomposition of PCA and mPCA. The only substantiation to this claim is the previously mentioned 1979 article in which a single Pseudomonas species (PRL-F84) was found to degrade PCA by cleaving the N-N bond under controlled laboratory conditions (LaRue and Child). Conversely, increasing PCA concentration was found to have an inhibitory effect on PRL-F84 growth in the same study. Although mPCA was not specifically tested, the organism was not able to utilize any of the structurally similar hydrazine derivatives tested. No results for microbial degradation of mPCA are reported by NMHU in the patent or elsewhere in the literature.

Another questionable claim in the patent is the assumption that PCA and mPCA are non-toxic products. In the patent the author states that the MSDS for 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid (PCA) does not list any known acute toxicities and should thus be a non-hazardous waste. The toxicity of mPCA is not discussed. Despite the author’s assumptions, FDEP will not authorize discharge of the product stream into the sewage treatment plant until it
has been fully characterized including toxicity data. Treatment by AKGA is of little value over existing methods if the waste stream requires disposal as hazardous waste.

In addition, neither AKGA nor the EAA treatment candidates have been evaluated for applicability from a processing perspective. A thorough assessment of the effects of the proposed treatments on representative materials will be necessary before implementation is authorized by NASA for use on reusable flight hardware components and ground support equipment (GSE). Also, from a safety standpoint, lab studies will be required to confirm that the reaction does not present safety hazards to personnel during processing such as off-gassing of toxic vapors from the reaction solution.

**Research Objectives**

This dissertation specifically addresses processing concerns associated with implementation of this alternative hydrazine neutralization technology. The research was conducted in the NASA Component Refurbishment and Chemical Analysis (CRCA) facility at Kennedy Space Center at the request of Mr. William Gerstenmaier (NASA Associate Administrator for Space Operations). Wiltech Inc. has operated this facility since 1984 and is equipped with the infrastructure and expertise to evaluate these reactions for “real world” decontamination processing operations. The evaluation request was to explore potential cost and operational benefits to NASA for transition and retirement of the Space Shuttle Orbiters and other hardware decontamination and decommissioning, in addition to HZ and MMH waste treatment activities.
The objective of this dissertation is to assess the applicability of implementing either of the proposed alternative hydrazine neutralization reactions as a drop-in replacement for the existing technology. This includes (1) evaluation of efficacy of these reactions for the decontamination of hardware and soft goods, (2) characterization of the reaction and reaction products, and (3) development of processes and procedures for implementation as required for FDEP permitting requirements, precision cleaning specifications, and OSHA exposure regulations.

The first objective was accomplished by simulating “worst case scenarios” for decontamination processing of hardware and soft-goods. Historically problematic materials and components were contaminated with HZ or MMH then treated with EAA or AKGA solutions. The results were then compared to those typically obtained using the traditional glycolic acid solution. From these tests EAA was eliminated as a candidate for further consideration based on safety and non-volatile residue (NVR) concerns. Conversely, AKGA performed as well or in some cases better in terms of residual HZ or MMH after processing than the existing neutralizer solution. Thus, EAA was abandoned and AKGA was selected for further investigation.

Next, the reaction of AKGA with HZ and MMH in solution was characterized with emphasis on processing considerations such as reaction kinetics, solution viscosity, precipitate mitigation (in the case of reaction with HZ), and off-gassing of hydrazine vapors during the exothermic neutralization reaction. Initial pseudo-first order kinetic studies were performed by monitoring depletion of the MMH or HZ reactants in excess AKGA using an existing hydrazine derivatization / GC-NPD (gas chromatography–nitrogen phosphorus detector) method. This
approach was utilized because it was already in practice and because mPCA standards were not commercially available at the time. Once a standard for mPCA became available, another pseudo-first order kinetic study was conducted for comparison. This time the pyridazine products were monitored over time by UV-Vis spectrophotometry. This technique did not suffer the limitations associated with initial derivatization of HZ / MMH and longer analysis times and provided mass balance information. For confirmation of product structure, GC-MS spectra were obtained for AKGA, PCA, and mPCA. The mPCA spectrum was previously unpublished.

The third and final objective was developed based on the culmination of data and observations collected over the course of this research. The methods and procedures devised were developed for the seamless transition of AKGA as neutralizer with minimal modifications to existing infrastructure and standard operating procedures.
CHAPTER TWO: PROCESS TESTING FOR COMPONENT DECONTAMINATION USING ALTERNATIVE HYDRAZINE NEUTRALIZERS

Abstract

NASA Kennedy Space Center (KSC) conducted baseline characterization testing of two candidate reagents as potential alternatives to the current standard hydrazine family fuel neutralization techniques. Both reagents react with hydrazines to form stabilized cyclic compounds. The primary projected applications are for decontamination operations, waste stream treatment, and as drop-in replacements for the scrubber liquor currently used in KSC four-tower vapor scrubbers.

In all cases, these potential process changes may improve process safety and reduce or eliminate generation of hydrazine-laden waste streams. Additionally, the reaction products have potential commercial value that may offset the cost of implementation.

This paper addresses follow-up experiments designed to mimic historically encountered “worst case” decontamination scenarios. Lessons learned from these scaled down tests were used for procedure development directed towards decontamination of larger parts and components such as ground support equipment and flight hardware.

Baseline testing identified reagent, alpha-ketoglutaric acid (AKGA), as a viable prospect for further investigation. Another reagent, ethyl acetoacetate (EAA) was eliminated from
consideration. Practical procedures were tested, developed and executed on both contaminated hardware and soft goods. Although testing is ongoing, few additional mitigation measures are anticipated to maintain the current component cleaning standards while enhancing operational safety, and potentially eliminating the hydrazine waste stream.

Introduction

High volumes of hydrazine (HZ) and monomethylhydrazine (MMH) contaminated parts are processed for reuse or disposal under a NASA contract by Wiltech Inc. at Kennedy Space Center (KSC) Component Refurbishment and Chemical Analysis (CRCA) facility. These hydrazines are considered highly toxic and potentially carcinogenic (Choudhary, 1997; Schmidt, 2001). Consequently, contaminated parts undergo an intensive decontamination process to bring latent hydrazine (HZ and MMH) contamination down to acceptable safety limits. Currently, a glycolic acid (hydroxyacetic acid) based “neutralizer” containing antifoam and wetting agents is used. The action of this neutralizer is to reduce the vapor pressure, effectively immobilizing the hydrazine molecules in solution (Schmidt, 2001). They remain immobilized for as long as solution acidity at ambient temperature conditions are maintained. If the solution pH shifts to basic or temperature increases (such as in an accidental fire incident), the trapped fuel molecules are liberated, and will off-gas from the solution presenting a safety hazard to personnel.

Recently, New Mexico Highlands University (NMHU) patented (U.S. pat. #7,074,959, 2006) one chemical reagent, alpha-ketoglutaric acid (AKGA) for use in hydrazine spill remediation. They also identified ethyl acetoacetate (EAA) as a potential candidate reagent. Each of these chemicals reacts to convert (rather than immobilize) hydrazine molecules into stabilized cyclic products with potential market value as fertilizers and synthetic precursors. Wiltech Inc. was
tasked by NASA to conduct testing of these two candidate neutralizers for applicability in fuel decontamination processing operations. “Worst-case scenario” test procedures were developed drawing from Wiltech’s experience in processing a vast assortment of hydrazine compatible hardware and soft good materials at KSC. The goal of the following experiments was to determine if either of the candidate reactants could effectively function as a drop-in replacement for the current neutralizing solution used in decontamination processing operations with minimal overhaul of existing infrastructure and operating procedures while maintaining process safety standards.

The current decontamination processing procedure initially flushes contaminated “hot” parts with water, and then rinses with a glycolic acid based cleaning solution, followed by another water rinse. Next, the wet part is pH tested, and purged with hot gaseous nitrogen (GN₂). For decontamination confirmation, it is bagged or otherwise contained for one hour. After bagging, the air in the bag is “sniffed” using an Interscan® Series 4000 portable toxic vapor detector (TVD). If the TVD detects hydrazine vapor at or above the Acceptable Detection Limit (ADL) of 0.1 part per million (ppm), also known as the point source limit, the item is reprocessed as necessary until the required ADL is reached. The processing ADL is an order of magnitude higher and should not be mistaken for the occupational exposure limits set by Occupational Safety and Health Administration (OSHA). The entire decontamination operation takes place in a fume hood. Ambient air outside the fume hood is monitored by TVD. Throughout the process, technicians wear supplied air respirators for protection from hydrazine vapors.
Historically, soft goods such as Teflon and other hydrazine-compatible elastomers such as AF-E-332, are the most problematic for decontamination efforts. Off-gassing of soft goods occurs because these porous materials absorb, or swell with liquid HZ or MMH. The outermost regions of the swollen material can be decontaminated to meet acceptable detection limits in the short-term. However, the hydrazine within the component interior is not immediately removed. Over time, hydrazine molecules diffuse from the interior of the material to the surface and escape to the atmosphere. Therefore, a soft good that was ADL compliant after processing will ultimately emit HZ or MMH vapors at higher levels for days or weeks later. When possible, soft goods are removed and disposed of as hazardous waste. Throughout our test program, mitigation measures, such as application of heat and reduced pressure were implemented to accelerate HZ diffusion to the surface for subsequent neutralization.

Of the aforementioned candidate replacement neutralizers, EAA was eliminated from consideration early in the testing process. The flammable classification of this viscous organic liquid compounded existing safety concerns for use in proximity to hydrazine family fuels. In addition, EAA was found to trigger a false positive response on the Interscan® TVDs used throughout KSC. Operationally, the pyrazoline derivative product is a sticky, gummy, residue that proved difficult to remove from glass and metal surfaces. This is problematic for processing of flight hardware or ground support equipment (GSE) with strict particulate specifications.

AKGA, the other candidate reagent, also precipitates a solid product, 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid, (PCA) on reaction with HZ. Mitigation measures for this were explored in this testing. The MMH neutralization product, 1-methyl-6-oxo-4,5-
dihydro-pyridazine-3-carboxylic acid, (mPCA) is water soluble at room temperature and does not precipitate out of solution.

A key selling point for these candidate neutralizers is the potential irreversible conversion of hydrazine family fuels to stabilized derivatives. Presently, the hydrazine-laden processing waste stream must be treated as hazardous waste. The resulting waste stream is a substantial volume to contain and ship for disposal by incineration at considerable cost. Additionally, the potential for accidental exposure and environmental damage persists throughout transportation and incineration of the waste stream. From a cost standpoint, PCA and mPCA, have potential market value as fertilizers and synthetic precursors. Thus, if processing requirements can be met using existing infrastructure, and if environmental legislation allows for a non-hazardous classification, implementation of AKGA for decontamination processing could be a cost-effective, “green” means for enhancing operational safety at KSC.

This testing ranges from precipitate mitigation in a theoretical “hot” system to field scale decontamination processing of a flight-like fuel vessel. The fuel vessel decontamination represents the culmination of all lessons learned from laboratory testing. The spherical titanium tank contains a diaphragm made of AF-E-332 (an ethylene-propylene elastomer) and small stainless steel valves and fittings to span the range of historically problematic components.

**Experimental**

**Precipitate Mitigation**

Laboratory scale (1:2000 or 5.0 x 10^{-4}) neutralizations of a theoretical “hot” flight module were conducted to determine precipitate (ppt) formation boundaries. A “typical” flight-like
system was considered to bound the scope of this experiment. A notional total system volume of 50 gallons was assumed to still contain ~1 quart to 0.5 gallons (~0.5L to 2L) of residual liquid HZ throughout system fixtures. Complete conversion (100%) of HZ to PCA was assumed. This experimental set-up was devised to mimic in-situ neutralization of “hot” flight hardware. An aliquot of neat (anhydrous) HZ was added to glass beakers containing 100 mL AKGA solution of a given concentration at room temperature with constant stirring. The laboratory scale mock neutralization scenario was repeated using MMH to determine if higher concentrations would cause solid m-PCA to precipitate out of solution. Results are summarized in Tables 2 and 3.

**Off-gassing During Reaction**

In the previous experiment, off-gassing HZ vapors were detected by Interscan® TVD on addition of neat HZ to AKGA solution. Consequently, a study was conducted to monitor off gassing from AKGA solution. Addition of neat HZ to AKGA solution in controlled airspace was monitored using the TVD in conjunction with colorimetric personnel exposure dosimeter badges. These dosimeter badges are designed to estimate a time weighted average (TWA) of exposure for personnel working with hydrazines. For comparison to current technology, this experiment was repeated using 14% (w/w) citric acid (scrubber solution) and the glycolic acid based neutralizer. Results are summarized in Table 4.

**Stainless Steel Convoluted Flex Hose**

The convoluted flex hose is commonly encountered in processing and presents a “worst-case” scenario with respect to particulate formation and removal in ground support equipment. Tests were designed to mimic “trace” hydrazine contamination (i.e. hydrazine residue present)
and “direct” hydrazine contamination (i.e. aliquots of hydrazine trapped in fittings) to determine if and/or how ADL and particulate requirements could be met using AKGA for decontamination.

“Trace” Hydrazine Contamination

An approximately 2 foot (61 cm) long piece of ½” (1.3 cm) diameter clean convoluted stainless steel flex hose was capped off at one end and held upright open to the atmosphere. To contaminate, the hose volume (200 mL) was filled with 1.0 M (mole/L) aqueous HZ solution and allowed to sit for 45 minutes. The HZ solution was then poured off, and the hose was immediately re-filled to capacity with 2.0M AKGA (2:1 ratio) solution (see Figure 2). After 1 hour of reaction time, the product mixture was poured out, visually inspected for precipitate, and analyzed for free HZ via gas chromatography. Acetone was used as a solvent to form the stabilized azine for detection. A Perkin Elmer Autosystem XL equipped with a nitrogen phosphorus detector (NPD) was used. Separation occurred on a packed column with a 4% Carbowax 20M and 0.8% KOH on 60-80 Carbopack B stationary phase. The limit of quantitation of this method is 0.5 ppm (in solution). An Interscan® TVD was used to “sniff” the hose for residual HZ vapors after processing.
Figure 2: Stainless steel convoluted test hose experimental setup

“Direct” Hydrazine Contamination

The flex hose was capped off at one end and held upright as in the previous experiment. It was filled with a reaction mixture of 100 mL 1.0M aqueous HZ solution added directly to 100 mL of 2.0 M AKGA solution. After 24 hours reaction time, the product mixture was poured out of the hose and visually inspected for precipitate. The solution was analyzed via GC as before. The hose was placed in a sealed plastic bag along with a HZ dosimeter badge. After 1 hour of being sealed, the air in the bag air was “sniffed” using the Interscan® TVD. The bag was then re-sealed along with the dosimeter badge.
Hydrazine Compatible Elastomer AF-E-332

AF-E-332 Decontamination Treatment Duration (24, 48, and 96 hour immersion treatment)

Sample preparation began by immersing the ~0.25 in² (1.6 cm²) sample coupons in neat HZ. Sample size was dictated by the limited quantity of AF-E-332 available in-house for testing. All coupons were placed in the neat HZ simultaneously. They remained immersed for ≥ 48 hours. Samples were transferred from the neat fuel to glass jars containing 100 mL 4.0M AKGA solution for decontamination. The jar was sealed with a Teflon lined lid and the samples remained in the AKGA solution for 24, 48, 72, or 96 hour neutralization times. After treatment, the coupons were removed from the AKGA solution and placed directly into another clean 250 mL glass jar containing a hydrazine dosimeter badge (two coupons per 250 mL jar; see Figure 5). The colorimetric dosimeter badges were used for semi-quantitative detection of off-gassing HZ vapors within the jar. There was no rinsing or drying between transfers.

AF-E-332 Decontamination with Preliminary Water Rinse

Further testing was conducted to observe the effects of a preliminary water rinse on neutralization efficiency. Sample preparation began by simultaneously immersing all of the ~0.25 in² (1.6 cm²) AF-E-332 coupons in neat HZ. These samples were rinsed with water and patted dry with a lint free wipe between transfers. In previous tests, the samples were occasionally observed floating on top of the AKGA solution, and were shaken back down. To ensure treatment of the entire sample surface area, a stir bar was placed in the AKGA solution
and samples were stirred vigorously for the treatment duration. Sample sets were prepared to simulate processing with and without a preliminary water rinse.

For simulation of treatment following a preliminary water rinse, two contaminated samples (soaked in neat HZ for 48 hours) were rinsed, dried, and transferred to another jar for an 8-day water soak. After undergoing “water rinse”, these samples were rinsed, dried, and transferred to 100 mL 3.7 M AKGA solution for 9 days. After neutralization, they were rinsed, dried, and transferred to a clean jar containing a dosimeter badge for off gas monitoring.

To mimic immediate treatment without a preliminary water rinse, two contaminated samples (soaked in neat HZ for 31 days) were rinsed, dried and transferred to a clean jar containing 100 mL 3.7M AKGA solution and a stir bar for seven days. In post-treatment they were rinsed, dried, and transferred to a clean, sealed jar containing a dosimeter badge for off gas monitoring.

In addition, two control samples (soaked in neat HZ for 31 days) were rinsed, dried, and immersed in water for 7 days. For monitoring, they were rinsed, dried, and placed in clean, sealed jars with dosimeter badges. Two blank samples were immersed in water for 48 hours, rinsed, patted dry, and placed in clean, sealed jars with dosimeter badges for monitoring.

Dosimeter badges were visually monitored for 5 days. After 5 days in the confined 250 mL volume of the jar, the developed color was compared to the concentration estimator wheel. The TVD was used to sniff the air space immediately after removal of the lid.
AF-E-332 Decontamination Treatment Duration (1, 2, and 3 week immersion treatment)

The above described sample preparation process was repeated with a 7-day preliminary water soak and AKGA treatment durations ranging from 1 to 3 weeks for determination of neutralization efficiency. After two months post-treatment, the samples were placed in 250 mL jars with dosimeter badges for 8 hours to monitor potential off gassing.

AKGA and Hydrazine Uptake by AF-E-332

Teflon is able to absorb up to 2% of its weight of hydrazine. Published swelling determinations on AF-E-332 with hydrazine report uptake of 3% of its own weight within 48 hours (Schmidt, 2001). For comparison, an uptake by mass test was conducted on a small, representative sample of the AF-E-332 used throughout our experiments. A ~0.25 in² (1.6 cm²) sample was immersed in anhydrous HZ for a period of nine months. At regular intervals, the sample was removed from the hydrazine, rinsed with water, dried with a lint free wipe, and weighed

Another sample of similar size was soaked for a period of three months in 4.0M AKGA solution and monitored at regular intervals to determine the effects of the AKGA neutralizer on the sample.

Teflon

Teflon O-ring Decontamination

Initial testing sought to decontaminate Teflon o-rings of various sizes. These o-rings were immersed in neat hydrazine for several days. Then, they were transferred into 4.0M AKGA solution for a 4-day neutralization treatment. Another set of contaminated o-rings of similar
mass were contaminated and simultaneously soaked in the glycolic acid neutralizer. After 96 hours treatment by soaking, the o-rings were removed from the respective solutions and placed in separate sealed glass jars with dosimeter badges for HZ vapor monitoring. To accelerate diffusion from the interior of the o-rings, the jars were placed outside in the afternoon sun. Fresh dosimeter badges were placed in the jars each week. The air space was sampled by TVD when the jar was opened.

**Teflon Lined Flex Hose Decontamination**

Teflon lined flex hoses present a significant challenge in decontamination processing because the soft good cannot be removed and separately discarded as a hazardous waste. Two Teflon lined flex hoses were selected to simulate decontamination using AKGA. One hose was filled with MMH, the other was filled with HZ. Each hose had an inner volume of ~80mL. The hoses were filled with fuel and allowed to sit for 32 days. After contamination, the fuel was poured out and the hoses were each flushed with 1L water, collected into five 200mL fractions (R-1 to R-5). These fractions were analyzed for HZ to develop a rough estimate of the residual contamination in the hose. After rinsing with water, each hose was filled to capacity with 0.05M AKGA solution and allowed to sit for 18 days. After neutralization, they were sniffed using the TVD.

**Field Scale Decontamination of Flight Like Fuel Vessel**

Two hydrazine fuel vessels originating from a Boeing Inertial Upper Stage (IUS) space launch vehicle were obtained for field scale testing as shown in Figure 4. These spherical titanium diaphragm tanks contain an AF-E-332 membrane separating the liquid propellant
hemisphere from the gas pressurant compartment to ensure positive propellant expulsion. For maximum contamination, the liquid side of each vessel was filled with neat HZ and the gas sides were pressurized with ~95 psig (655 kPa) GN₂. Both vessels marinated outdoors this way for 50 days. Based on immersion data, back and forward diffusion of HZ across the diaphragm was assumed to be at equilibrium (net zero mass transfer) within this timeframe. The experimental vessel (Tank #1) was biased with respect to HZ contamination to test the limits of the AKGA neutralizer. The control (Tank #2) contained less raw fuel in the interest of personnel safety. After off-loading HZ, the liquid sides of each tank were loaded with a 4L water rinse. The ambient temperature during HZ offloading and the preliminary water rinse was ~40° F (4°C). Sample container size dictated fractional collection of the water rinsate. Four 1L fractions were drained from each fuel vessel and analyzed for free HZ via GC. This water rinsate had a < 30 minute dwell time in the liquid side of the fuel vessels.

After analysis of the preliminary rinse, the control tank (Tank #2) was again loaded with another 4 L water rinse. This second rinse on the control was allowed to sit for 2 weeks at 70±10°F (21±6°C) to ensure adequate mixing. This secondary water rinse was collected and analyzed as before to determine the residual pre-neutralization HZ concentration on the liquid side of the fuel vessels.

Contamination resulting from permeation through the AF-E-332 was expected in the GN₂ blankets on gas side of the fuel vessels. To quantify the HZ content, the GN₂ blankets were analyzed via a modified scrubber method. The gas sides were vented and purged through two glass impingers containing 14% citric acid solution (scrubber solution) connected in series as
shown in Figure 3. The volume of gas purged was measured via wet test meter. The citric acid was analyzed for HZ via GC-NPD and the gaseous hydrazine concentration was extrapolated from the solution concentration.

Figure 3. Fuel tank gas sampling schematic

After venting the gas side of the experimental tank, the AKGA solution was loaded for neutralization. Given that both sides of the diaphragm were contaminated, both sides required treatment. Therefore, to ensure complete neutralization, the entire 20 gallon (76 L) volume of
the tank was filled with 4.0 M AKGA solution. Based on the AKGA immersion data, any HZ still in the diaphragm would have to diffuse to the surface to react with the neutralizer. Additionally, air bubbles had to be avoided to ensure contact of the neutralizer solution with all contaminated surfaces.

The filling procedure utilized reduced pressure and heat to accelerate diffusion and avoid air bubble formation. To provide heat, the AKGA solution was maintained at 125° F (52°C) prior to loading. The tank was configured with the gas side oriented at the top of the vessel. To begin filling, a vacuum was applied to the gas side of the tank with the liquid side valve open to atmosphere to prevent tearing of the diaphragm. Next, 7 gallons (26.5L) of heated AKGA were loaded on the gas side. Subsequently, the gas side valve was closed and a vacuum was pulled on the liquid side of the tank. At reduced pressure, the liquid side was filled with slightly less than 13 gallons (49.2 L) of heated (125° F) AKGA solution. At this point, the gas side vent was opened and filling of the liquid side continued until AKGA solution emerged from the gas side valve. A 1L expansion volume was connected to the gas side valve to avoid complete liquid-lock and potential tank rupture due to ambient thermal effects. Finally, the valves on each side were closed. The neutralizer was allowed to sit in the vessel for 2 weeks. After 2 weeks treatment time, the neutralizer solution was drained and captured.

The gas sides of both tanks were monitored for HZ off gassing over time. Both were re-pressurized with GN₂ to 80±5 psig (~ 552 kPa) and valves closed. After 7 days, the gas was sampled as before. For secondary monitoring, both sides of Tank #1 were also “sniffed” via TVD.
Results and Discussion

Precipitate Mitigation

Precipitate mitigation is of utmost importance for applications with more stringent particulate requirements such as in Shuttle propellant management device screens within Orbital Maneuvering System (OMS) and Reaction Control System (RCS) tanks.

As expected, PCA precipitate formation was found to increase with increasing HZ concentration and decreasing AKGA concentration. Although particulate formation is undesirable, the dried PCA residue was easily removed by rinsing with water. And, precipitate formation can be avoided altogether by regulation of AKGA and HZ concentrations. Thus, procedural mitigation measures such as use of concentrated AKGA solution in conjunction with pre-neutralization dilution of residual HZ by initial water rinse will eliminate or minimize precipitate formation.

The MMH product (m-PCA) does not precipitate out of solution even as the MMH content exceeded that of AKGA.
Table 2. Mock in situ neutralization for determination of PCA ppt formation boundaries

<table>
<thead>
<tr>
<th>[AKGA], (mol/L)</th>
<th>Liquid HZ Remaining in Hot System (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5L</td>
</tr>
<tr>
<td></td>
<td>(250 µL)</td>
</tr>
<tr>
<td>0.5</td>
<td>No ppt</td>
</tr>
<tr>
<td>1.0</td>
<td>No ppt</td>
</tr>
<tr>
<td>2.0</td>
<td>No ppt</td>
</tr>
<tr>
<td>3.0</td>
<td>No ppt</td>
</tr>
</tbody>
</table>

*µL hydrazine added to 100 mL AKGA solution

Table 3. Mock in situ neutralization for determination of mPCA ppt formation boundaries

<table>
<thead>
<tr>
<th>[AKGA], (mol/L)</th>
<th>Liquid MMH Remaining in Hot System (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.2 gal</td>
</tr>
<tr>
<td></td>
<td>(2400 µL)</td>
</tr>
<tr>
<td>0.5</td>
<td>No ppt</td>
</tr>
<tr>
<td>1.0</td>
<td>No ppt</td>
</tr>
<tr>
<td>2.0</td>
<td>No ppt</td>
</tr>
</tbody>
</table>

*µL hydrazine added to 100 mL AKGA solution

Off-gassing During Reaction

On addition of HZ, the solution boiled momentarily at the site of entry, and a yellow cloud instantaneously formed over the solution. Also, the dosimeter badge began developing color and the TVD response measured 1 ppm. The boiling solution spattered droplets on the surface of the glass bell jar used for containment. These droplets may have contained unreacted HZ that subsequently triggered the TVD. Given that the reaction is exothermic, it is feasible that
on addition of neat hydrazine to AKGA solution, a high temperature “hot spot” occurs in the reaction mixture allowing hydrazine vapor to escape into the atmosphere. In contrast, hydrazine vapors were not detected when the same amount of HZ or MMH was added as an aqueous solution under the same conditions.

Table 4. Vapor emissions on addition of anhydrous HZ to neutralizer solutions as estimated by dosimeter badge

<table>
<thead>
<tr>
<th>Neutralizer, 100mL</th>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HZ, ppb - TWA</td>
<td>Duration, hrs</td>
</tr>
<tr>
<td>14% (wt/wt) Citric Acid</td>
<td>6.3</td>
<td>4</td>
</tr>
<tr>
<td>Glycolic Acid Neut.</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>4.0 M AKGA</td>
<td>1 (ppm)</td>
<td>1</td>
</tr>
</tbody>
</table>

The observed spattering and emission of hydrazine vapors from AKGA neutralizing solution on contact with anhydrous HZ or MMH introduces additional exposure risk for processing personnel. However, the observed “hot spot” formation and subsequent off gassing can be prevented by pre-neutralization dilution with water. The water serves as an insulating delivery vehicle by absorbing and dissipating the heat of reaction. Here again, dilution in the form of a preliminary water flush mitigates potential processing complications presented by the energetic AKGA neutralization reaction. This is especially important when processing contained systems (i.e. tanks) and components with small apertures (i.e. hoses).

Stainless Steel Convoluted Flex Hose

As for worst case scenario hardware processing, the decontaminated hoses exceeded ADL requirements with no HZ detected after neutralization by AKGA solution indicating
successful decontamination of the hardware. However, in the “direct” decontamination scenario solid PCA was observed within the hose and endcap (see Figure 4). It was allowed to dry over the weekend for maximum adherence. On return to the lab, the adhered PCA residue was easily removed with a water stream. A lighted boroscope was used for visual inspection. Particulate formation is problematic, but the ease of removal suggests that a procedural mitigation measure such as a final water rinse may be used to remove any particulate before moving on to the next step in the precision cleaning process.

![Figure 4. Reaction precipitate (PCA) collected in flex hose end cap](image)

**Hydrazine Compatible Elastomer AF-E-332**

AF-E-332 Decontamination Treatment Duration (24, 48, and 96 hour immersion treatment)

No off-gassing HZ vapors were detected within the jar airspace for seven consecutive days after removal from the AKGA solution. However, on return to the laboratory on day 10, a
pronounced color change was observed on the 24 and 96 hour AKGA treated samples. On day 11, the badges were compared to the badge concentration estimator wheel. The estimator indicated that the HZ vapor concentration within the confined 250 mL jars was < 10 ppb-TWA. A slight color change was also observed on the 48 hour treated sample. The 72 hour treated sample did not exhibit a color change. It should be noted this type of monitoring is beyond the quantitative limitations of these indicators. The badges are intended to monitor personnel exposure in ambient air through the course of a typical workday. The concentrations derived from their use as described here are rough estimates. These estimates are based on a visual comparison of the color developed on the indicator window to a concentration estimator wheel. Once opened and in use, they are subject to interference from UV light and humidity. The value of these results is in the qualitative detection of HZ and MMH vapors, as the badges are less susceptible to false positives from interferences than the Interscan® TVDs. The air in the jars containing the treated samples registered < 10 ppb HZ vapor via TVD, well beneath the 1.0 ppm ADL.

AF-E-332 Decontamination with Preliminary Water Rinse

The results of the preliminary water rinse are summarized in Table 5. There was no appreciable difference in the neutralization efficiency of samples undergoing a preliminary water rinse prior to treatment with AKGA. Thus, initial treatment with water does not facilitate neutralization of absorbed hydrazines in AF-E-332. The sample coupons, test vessels, and dosimeter badges are shown in Figure 5.
Table 5. Long term hydrazine vapor off-gassing of contaminated AF-E-332 samples after AKGA treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dosimeter badge estimate, TWA – 5 days, ppb</th>
<th>Concentration measured by TVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>9</td>
<td>&gt; 10 ppb</td>
</tr>
<tr>
<td>Preliminary water rinse</td>
<td>0.2</td>
<td>&lt; 10 ppb</td>
</tr>
<tr>
<td>Immediate AKGA treatment</td>
<td>0.2</td>
<td>&lt; 10 ppb</td>
</tr>
<tr>
<td>Blank</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

Figure 5. Sealed 250 mL jars containing AF-E-332 sample coupons and dosimeter badge

AF-E-332 Decontamination Treatment Duration (1, 2, and 3 week treatment times)

This study was conducted specifically for the Orion program to determine if extended AKGA treatment duration would result in complete decontamination of soft goods with no subsequent off-gassing over time. This would eliminate the need to remove soft-goods from the crew module. The results are presented in Table 6. Three weeks was considered the maximum
treatment time limit to avoid scheduling conflicts. Although below the ADL, the sample immersed in AKGA for the maximum treatment time did still off-gas hydrazine vapors two months after treatment. This was considered unacceptable for the target application of in situ decontamination of the Orion Crew Module in transit from California to Florida.

Table 6. Measured off-gassing of hydrazine vapors from AF-E-332 samples of varying AKGA treatment times

<table>
<thead>
<tr>
<th>AKGA Treatment Duration, weeks</th>
<th>HZ</th>
<th>MMH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dosimeter badge estimate, ppb</td>
<td>TVD, ppb</td>
</tr>
<tr>
<td></td>
<td>TWA – 8 hrs</td>
<td>TWA – 8 hrs</td>
</tr>
<tr>
<td>1</td>
<td>12.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

AKGA and Hydrazine Uptake by AF-E-332

The w/w% uptake by the sample soaking in hydrazine fluctuated from a minimum of 1.21% to a maximum of 2.17%. The results are presented graphically in Figure 6. The observed deviation is likely due to the small sample mass.
For the sample soaking in AKGA solution, no change in mass within +/- 0.0001g was observed indicating that the neutralizer was not absorbed by the sample. These results also suggest that the concentrated AKGA solution did not degrade AF-E-332 within a 3-month time span.

**Teflon**

**Teflon O-ring Decontamination**

Within 1 week of monitoring, the dosimeter badge monitoring the glycolic acid neutralized o-rings detected off gassing HZ vapor. In comparison, no HZ vapor was detected in the airspace surrounding the AKGA neutralized o-rings up to 4 months after treatment by AKGA.
For reproducibility, this study was repeated with duplicate samples of Teflon o-rings soaked in AKGA solution. The results of the second study are tabulated in Table 7. A larger mass of Teflon o-rings were used and the same size air space (250 mL) was monitored. In contrast to the previous trial, the dosimeter badges did detect HZ vapor in the jar air space within 24 hours. These jars were monitored for several weeks. The off gassing HZ vapors were ≤ 15 ppb-TWA. The difference in results is likely due to the increased mass (~10x) of Teflon used in the second trial. Accurate quantification of HZ vapors was limited by the capabilities of the available vapor detection technology.

Table 7. Long term monitoring of 250 mL airspace surrounding Teflon o-rings treated with AKGA solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>HZ, ppb – TWA (48 hrs. post treatment, 24 hr. monitoring)</th>
<th>HZ, ppb – TWA (7 days. post treatment, 8 hr. monitoring)</th>
<th>HZ, ppb – TWA (36 days post treatment, 8 hr. monitoring)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>2</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Duplicate</td>
<td>2</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

**Teflon Lined Flex Hose Decontamination**

The results of the water rinsate analysis are presented in Table 8. These measurements indicate low levels of hydrazine contamination present in the hose following the water rinse.
Table 8. Analysis of residual fuel in preliminary water rinse of contaminated Teflon flex hose

<table>
<thead>
<tr>
<th>Rinse Fraction</th>
<th>MMH hose, ppm</th>
<th>HZ hose, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-1</td>
<td>1,626</td>
<td>2,526</td>
</tr>
<tr>
<td>R-2</td>
<td>2.7</td>
<td>174</td>
</tr>
<tr>
<td>R-3</td>
<td>&lt; 1</td>
<td>85</td>
</tr>
<tr>
<td>R-4</td>
<td>&lt; 1</td>
<td>37</td>
</tr>
<tr>
<td>R-5</td>
<td>&lt; 1</td>
<td>25</td>
</tr>
</tbody>
</table>

The airspace in both hoses measured 0 ppm by TVD immediately after draining off neutralizer. The hoses were sealed and allowed to sit for 31 days. They were “sniffed” again immediately after opening and a short burst of ~10 ppb (0.01 ppm) was measured. Seconds later, the reading fell to < 10 ppb. The hoses were left open and placed in sealed plastic bags with dosimeter badges. The air in the bags was sniffed 1.25 hours later. No HZ or MMH was detected by TVD or dosimeter badge. The TVD sampling tube was pushed deep within the hose to measure any localized off gassing. The HZ hose measured 6 ppb (0.006 ppm) and the MMH hose measured 5 ppb (0.005 ppm). It should be noted that fluctuations in pressure and surrounding gas flow caused low level (< 10 ppb) fluttering on the TVDs. The narrow inner diameter of the hoses restricts flow to the detector relative to ambient air. This restriction may have been the source of these low level readings. To accelerate HZ diffusion within the Teflon, the hoses were sealed again and placed in a 100°C oven for ~ 1 hour. After heating, the hoses were sniffed again. The TVD measured an initial burst of ~ 10 ppb immediately after opening each hose. This reading lasted only a few seconds and then fell back to 0 ppb. For further
testing, the hoses were filled to capacity again with water and allowed to sit for 6 days to absorb any remaining HZ diffusing from the Teflon. The water rinses were analyzed via GC. No HZ or MMH was detected in the water rinses.

**Field Scale Decontamination of Flight-like Vessel**

GC analysis of the first post-hydrazine offload water rinse was intended to give an indication of the residual of HZ contamination in each tank. The expectation was that the HZ concentration in the water rinse would be consistent from the first fraction to the last. However, this was not what was observed.

**Table 9. Results of analysis of fuel vessel water rinse (pre-neutralization)**

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Rinse Fraction</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-1</td>
<td>R-2</td>
<td>R-3</td>
<td>R-4</td>
</tr>
<tr>
<td>Tank #1, ppm HZ</td>
<td>8,600</td>
<td>700</td>
<td>200</td>
<td>3,000</td>
</tr>
<tr>
<td>Tank #2, ppm HZ</td>
<td>8,452</td>
<td>960</td>
<td>530</td>
<td>6,500</td>
</tr>
</tbody>
</table>

The trend exhibited by both tanks is likely a result of stratification in the fuel vessel. The combined factors of low temperature, high pressure, and brief dwell time in the tank resulted in inadequate mixing. Consequently, the first and last fractions reflected a higher HZ content because these stratified layers were directly exposed to the surfaces of the diaphragm and the tank. It follows that the second and third layers were less concentrated because they were not in contact with the contaminated surfaces.
The second post-hydrazine offload water rinse of the control tank was analyzed to determine the level of hydrazine contamination on the liquid side of the flight vessels prior to neutralization. Results are tabulated below.

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Rinse Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-1</td>
</tr>
<tr>
<td>Tank #2, ppm HZ</td>
<td>5,881</td>
</tr>
</tbody>
</table>

The results of the measurement of permeated HZ content in the nitrogen blanket on the gas side of the fuel vessels after a 1 month dwell time are presented in Table 11.

<table>
<thead>
<tr>
<th>Impinger</th>
<th>Tank #1</th>
<th>Tank #2 (control)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GN₂ sparged, L</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>GN₂ Pressure, psig</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>HZ in scrubber solution, ppm (mg/L)</td>
<td>40,000</td>
</tr>
<tr>
<td></td>
<td>Calculated HZ in GN₂, ppm (µg/L)</td>
<td>10,000</td>
</tr>
</tbody>
</table>

Although both tanks were initially pressurized to 95±10 psig (~ 655 kPa) after HZ loading, the actual mass of GN₂ added to each was different due to significant difference in the HZ load volumes in each tank. The pressure on the gas side also fluctuated when loading and offloading.
the preliminary water rinse. The gas side pressure throughout these processes is summarized below.

**Table 12. Summary of hydrazine load and ullage fluctuations on both fuel vessels**

<table>
<thead>
<tr>
<th>Vessel Status</th>
<th>Tank #1</th>
<th>Tank #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrazine load, lbs (kg)</td>
<td>112 (50.8)</td>
<td>22 (10)</td>
</tr>
<tr>
<td>Calculated GN$_2$ ullage, lbs (kg)</td>
<td>0.354 (0.161)</td>
<td>1.284 (0.582)</td>
</tr>
<tr>
<td>Ullage volume ratio</td>
<td>0.295</td>
<td>0.887</td>
</tr>
<tr>
<td>Pre-offload GN$_2$, psia (kPa-abs)</td>
<td>92 (634)</td>
<td>102 (703)</td>
</tr>
<tr>
<td>Post-water rinse GN$_2$, psia (kPa-abs)</td>
<td>24.5 (169)</td>
<td>89 (614)</td>
</tr>
</tbody>
</table>

The GN$_2$ mass difference accounts for the apparent discrepancy in the concentration of permeated HZ between the two tanks. Although, the rate of diffusion should be the same through both diaphragms, there is a larger mass of GN$_2$ on the gas side of the control tank because the ullage volume at the time of loading was much smaller. The GN$_2$ acted as a diluent and resulted in a significantly lower HZ concentration in the control tank gas side.

After the two week treatment time, the neutralizer solution was drained and captured. The solution was analyzed via GC-NPD and HZ was not detected.

As for the gas side of the fuel vessel, the results of the 7 day post-treatment gas monitoring by venting through a scrubber solution are shown in Table 13. The secondary monitoring via TVD measured HZ vapors at a concentration of 0.03 ppm on both the gas and liquid sides of the fuel vessel. This discrepancy arises from the inherent limitations of hydrazine
vapor measurement technology. From a processing perspective the TVD measurement indicates successful decontamination as it is below the ADL.

**Table 13. Post-neutralization analysis of GN₂ on gas side of contaminated (control) and decontaminated fuel vessels**

<table>
<thead>
<tr>
<th>Impinger</th>
<th>Tank #1</th>
<th>Tank #2 (control)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GN₂ sparged, L</td>
<td>GN₂ Pressure, psig</td>
</tr>
<tr>
<td>1st</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>2nd</td>
<td>25</td>
<td>80</td>
</tr>
</tbody>
</table>

In the case of soft-good decontamination, the AKGA neutralizer solution did not present any advantages over that of the current glycolic acid solution with respect to long-term off-gassing concerns. Thus, complete decontamination of soft goods remains a challenge. Immersion test results indicate that although HZ is absorbed by Teflon and AF-E-332, AKGA molecules are not. Therefore, the rate of neutralization is entirely dependent on the rate of HZ diffusion through the material.

From a procedural development stance, mitigation measures such as application of reduced pressure and elevated temperature should be incorporated into the processing procedure to ensure maximum neutralization efficiency in cases where the soft goods cannot be removed and disposed of. Additionally, the current practice of sealing decontaminated hardware containing soft goods such as Teflon lined hoses should be revisited. Test results indicate that
the momentary “puff” of HZ or MMH vapor released when the hose is opened results from accumulation of very low-levels of off-gassing over time. If the item is left open to ambient air, the hydrazine vapor resulting from diffusion through the soft good is below detection limits and well below exposure limits. However, allowing such components to remain open would represent a paradigm shift in the current approach to post-treatment component handling.

In light of lessons learned from this test program, a processing procedure using AKGA solution and existing infrastructure can be recommended. The prescribed procedure begins with a preliminary water rinse to dilute any residual anhydrous hydrazine. This dilution is to prevent off-gassing from solution as well as precipitate formation. Just as in current processing, any disposable soft good should then be removed and contained in a 55-gallon drum containing neutralizer solution for an extended soaking/storage period prior to disposal. A flush with pre-heated concentrated AKGA solution will neutralize accessible hydrazine contamination. If the part being processed contains irremovable soft goods, a vacuum should be applied if possible followed by a hot gaseous GN₂ purge. The heat from the neutralizer solution and reduced pressure are intended to accelerate hydrazine diffusion to the surface for neutralization. Next, a secondary flush with heated neutralizer will treat hydrazine extracted from the soft good. A thorough water rinse and testing for confirmation of cleanliness complete the procedure. If the processed part does not meet ADL criteria, it should be reprocessed as needed.

Overall, concentrated AKGA solution appears to be a favorable replacement for the glycolic acid based neutralizer solution used in processing. This assessment is based on laboratory testing of real world worst case scenario processing scenarios from small-scale hoses.
and coupons up to functional flight-like fuel vessels. Hardware and soft good components neutralized by AKGA solution met (and in some cases exceeded) current cleanliness standards. Moreover, implementation of the developed procedure will require minimal modification of existing infrastructure. However, further characterization and a toxicological assessment of the reaction products will be required by FDEP for permitting consideration.

One limitation repeatedly encountered throughout the testing was in quantification of hydrazine vapors. Existing vapor detection systems were not in agreement. At times they differed by as much as an order of magnitude. A derivatization based hydrazine vapor detection method is recommended.
CHAPTER THREE: KINETIC EVALUATION OF THE NEUTRALIZATION OF HYDRAZINE FUELS BY REACTION WITH AKGA

Abstract

Preliminary testing has confirmed alpha-ketoglutaric acid (AKGA) as a potential alternative to the current standard hydrazine family fuel neutralization techniques in use at Kennedy Space Center (KSC). Thus far, the reagent shows promise for use in hardware decontamination operations, waste stream treatment, and as a drop-in replacement for the scrubber liquor currently used in KSC four tower vapor scrubbers. Implementation of AKGA as a neutralizer for hydrazine family fuels could cost-effectively improve process safety and reduce or eliminate costs and liabilities associated with generation, transport, and disposal of hydrazine-laden waste streams.

This chapter focuses on evaluation of the kinetics of the reactions of hydrazine (HZ) and monomethylhydrazine (MMH) with AKGA in solution to form 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) and 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA) respectively. Pseudo first order reaction rate constants with respect to both the reactants and the products were determined in the presence of excess AKGA. This data will be used to further assess the viability of these reactions as a “green” approach to hydrazine remediation for operations at KSC.
Introduction

The reaction of alpha-ketoglutaric acid (AKGA) with hydrazine ($N_2H_4$) to form a stabilized pyridazine derivative has long been documented, but not well characterized (Evans & Wiselogle, 1945; Kline and Cox, 1961). Recently, this reaction was patented for use in hydrazine remediation (U.S. Patent #7,074,959, 2006).

Currently, Kennedy Space Center (KSC) generates approximately fifteen thousand gallons of hydrazine-laden wastewater per year. This waste stream is shipped on public highways for disposal by incineration at a cost approaching $120K per year (Chuck Davis, personal communication, March 21, 2011). Hydrazine is considered highly toxic and potentially carcinogenic (Choudhary, 1997; Schmidt, 2001). Thus, the current practice presents a potentially catastrophic threat to personnel, the public, and the environment in the event of an accidental release. Consequently, neutralization of hydrazine family fuels by reaction with AKGA is being considered as an alternative chemical method for remediation of waste streams generated at KSC. Neutralization by reaction to form a stabilized product is a novel approach to the current practice of trapping hydrazine molecules in acidic solution for subsequent disposal by incineration. Projected applications for AKGA include waste treatment, use as a drop-in replacement for the current citric acid vapor scrubber liquor and use as an alternative to the glycolic acid cleaning solution in decontamination processing operations. Specific reactions of interest are those of hydrazine (HZ) and monomethylhydrazine (MMH) with AKGA to form the stabilized pyridazine products: 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) and 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA) respectively. If applicable, this chemical “neutralization” technique could minimize or eliminate the environmental and
workplace hazards and liabilities associated with the containment, transport, and disposal of such waste streams.

To satisfy permitting requirements and assess the viability of these reactions for use at KSC, these reactions must be extensively characterized. This chapter focuses on the kinetics of the reactions of AKGA with HZ and MMH for decontamination processing applications. Pseudo-first order reaction rates were obtained with respect to the reactants and products in the presence of excess AKGA. At the outset of testing the mPCA standard was not commercially available. Therefore, initial tests monitored the depletion of the hydrazine reactants over time by derivatization with acetone to form the corresponding azine and detection and quantification by gas chromatography with a nitrogen phosphorus detector (GC-NPD). Once the mPCA standard became available, product formation in solution was monitored via Ultraviolet-Visible (UV-Vis) absorption spectroscopy.

**Experimental**

**Chemicals**

For standards, hydrazine (HZ) sulfate (99+ %) was obtained from Acros Organics while monomethylhydrazine (MMH) sulfate (98%) and 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) were obtained from Alfa Aesar. The 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA) standard was provided by Enamine. Alpha-ketoglutaric acid was obtained from USB Corporation. HPLC grade acetone and glacial acetic acid were obtained from Fisher Scientific. The 2,6-ditert-butyl-4-methylphenol (≥ 99%) was obtained
from Sigma Aldrich. Neat hydrazine and monomethylhydrazine used in testing was obtained from Arch Chemicals.

**Reaction Rate Constants with Respect to HZ and MMH**

For determination of the pseudo first order reaction rate constant with respect to MMH ($k_{\text{MMH}}$) individual reaction mixtures were sampled and analyzed for MMH content over the course of the reaction. To initiate the reaction a 100 mL aliquot of 0.25M MMH was added to a beaker containing a stirring bar and 100 mL of 4.0M AKGA with vigorous stirring. Note that the initial MMH concentration ([MMH]₀) decreases by half (0.125M) in the reaction mixture as a result of the doubling in volume. The MMH reactant was added as an aqueous solution to prevent sample loss due to “hot spot” formation and resultant off-gassing of MMH vapors. An Interscan® Series 4000 portable toxic vapor detector (TVD) was used to monitor the airspace above the reaction mixture for off-gassing MMH vapors. A Drummond® fixed volume microdispenser displacement pipette was used to draw 1 mL samples from the reaction mixture for analysis. This reaction scenario was repeated two times with an initial MMH concentration of 0.25M and twice more with an initial MMH concentration of 0.50M.

For determination of the pseudo first order reaction rate constant with respect to HZ ($k_{\text{HZ}}$) individual reaction mixtures were again sampled and analyzed for HZ content as the reaction progressed. Again, the HZ was added as an aqueous solution with initial HZ concentrations of 0.25M, 0.35M, and 0.5M before reaction initiation. As before, a Drummond® fixed volume microdispenser displacement pipette was used to draw 1 mL samples from the reaction mixture for analysis and the airspace over the reaction was monitored by TVD. An acetone solution
containing 0.05 g 2,6-ditert-butyl-4-methylphenol, 100mL deionized water, and 5mL acetic acid per liter was used for derivatization and analysis of HZ and MMH in all samples and standards.

A Perkin Elmer Autosystem XL equipped with a nitrogen phosphorus detector (NPD) was used. Both the detector and injector temperatures were 250° C. The isothermal oven temperature was 180° C. The helium carrier flow was 25 mL/min. Separation occurred on a Supelco glass packed column with a 4% Carbowax 20M and 0.8% KOH on 60-80 Carbopack B stationary phase (2 m length x 2 mm ID). The sample volume was 1 μL. The gas flows on the nitrogen phosphorus detector equipped with a rubidium bead were optimized for nitrogen with a hydrogen flow of 2 mL/min and an air flow of 100 mL/min.

**Reaction Rate Constants with Respect to PCA and mPCA**

Pseudo first order reaction rate constants with respect to the products PCA and mPCA (k_PCA and k_mPCA) were obtained by monitoring product formation in the reaction mixture spectrophotometrically. A Perkin Elmer Lambda 900 spectrometer was used to measure the absorbance of the reaction mixture at 282 nm as both PCA and m-PCA were found to exhibit strong absorbances at this wavelength. Deionized water was used as the reference. Calibration curves were constructed in a matrix of excess AKGA to mimic the reaction environment. The total volume of each reaction mixture was 650 mL on initiation. As in previous experiments, the fuel was added as an aqueous mixture to prevent “hot spot” formation and off-gassing. Discrete 1 mL aliquots were transferred from the reaction vessel to a quartz cuvette using an adjustable pipette at approximately 20 second time intervals as the reaction progressed..
Results and Discussion

Reaction Rate Constants with Respect to HZ and MMH

The AKGA solution rapidly depleted the hydrazine fuels in solution. The reaction with MMH was most rapid with approximately 99% of the MMH converted in 15 minutes reaction time and a pseudo-first order rate constant of $k_{MMH} = 0.0053 \text{ sec}^{-1}$. In the same 15 minute reaction time frame approximately 80% of the initial HZ concentration was degraded with a pseudo-first order rate constant $k_{HZ} = 0.0011 \text{ sec}^{-1}$. Pseudo-first order kinetics plots of representative of each reaction trial are presented in Figures 7 and 8 and all results are summarized in Table 14.

![Figure 7. Pseudo-first order kinetics plot of MMH depletion in AKGA solution](image)

Figure 7. Pseudo-first order kinetics plot of MMH depletion in AKGA solution
Figure 8. Pseudo-first order kinetics plot of HZ depletion in excess AKGA

Table 14. Summary of results for reaction rate constant with respect to reactants depleted

<table>
<thead>
<tr>
<th>Commodity</th>
<th>Initial Concentration, M (mol/L)</th>
<th>Reaction rate constant, k (sec⁻¹)</th>
<th>Correlation coefficient, R²</th>
<th>Avg, k, (sec⁻¹)</th>
<th>Std dev..</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMH</td>
<td>0.25</td>
<td>0.0051</td>
<td>0.9670</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.0052</td>
<td>0.9862</td>
<td>0.0053</td>
<td>4.1 x 10⁻⁴</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.0050</td>
<td>0.9439</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.0059</td>
<td>0.9934</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZ</td>
<td>0.25</td>
<td>0.0009</td>
<td>0.8553</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0.0011</td>
<td>0.8723</td>
<td>0.0011</td>
<td>2.5 x 10⁻⁴</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.0014</td>
<td>0.9664</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Reaction Rate Constants with Respect to PCA and mPCA

There were several drawbacks associated with the GC-NPD analysis method employed to monitor reactant depletion. One was the necessity for derivatization of the reactive hydrazine molecule to form a stabilized azine prior to analysis. Another is the time required for compound separation on the analysis column. MMH was first to elute at 4.3 minutes followed by HZ at 19.2 minutes. These setbacks are particularly problematic in the case of kinetic analysis which is time dependent. In addition, the base deactivated column exhibited signs of breakdown such as increased retention times, decreased detector response, peak tailing, and the appearance of “ghost peaks”. This was likely the result of repeated exposure to the acidic AKGA solution. Also adversely affected was the rubidium bead used in the NPD. These beads required frequent power increases and replacement as a result of residue build-up. Both of these factors limited the number of replicates obtained.

Product formation observed spectrophotometrically, however was rapid with reaction rate constants of \( k_{mPCA} = 0.0064 \text{ sec}^{-1} \) and \( k_{PCA} = 0.0077 \text{ sec}^{-1} \). Pseudo-first order kinetic plots representative of each reaction are presented in Figures 9-10 and results are summarized in Table 15.
Figure 9. Pseudo-first order kinetics plot of mPCA formation in excess AKGA

Figure 10. Pseudo first-order kinetics plot of PCA formation in excess AKGA-Trial 2
Table 15. Summary of results for reaction rate constant with respect to product formation

<table>
<thead>
<tr>
<th>Commodity</th>
<th>AKGA Concentration, M (mol/L)</th>
<th>Initial hydrazine concentration, M (mol/L)</th>
<th>Reaction rate constant, k (sec⁻¹)</th>
<th>Correlation coefficient, R²</th>
<th>Avg. k., (sec⁻¹)</th>
<th>Std dev.</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>mPCA</td>
<td>6.00E-03</td>
<td>1.00E-03</td>
<td>0.0056</td>
<td>0.9984</td>
<td>0.0064</td>
<td>8.78E-04</td>
<td>13.72</td>
</tr>
<tr>
<td></td>
<td>6.00E-03</td>
<td>1.00E-03</td>
<td>0.0054</td>
<td>0.9764</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.00E-03</td>
<td>1.00E-03</td>
<td>0.0067</td>
<td>0.9839</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.00E-03</td>
<td>7.00E-04</td>
<td>0.0078</td>
<td>0.9957</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.00E-03</td>
<td>7.00E-04</td>
<td>0.0075</td>
<td>0.9732</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.00E-03</td>
<td>7.00E-04</td>
<td>0.0063</td>
<td>0.9946</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.00E-03</td>
<td>7.00E-04</td>
<td>0.0064</td>
<td>0.9844</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCA</td>
<td>8.00E-03</td>
<td>5.00E-04</td>
<td>0.0061</td>
<td>0.9936</td>
<td>0.0077</td>
<td>1.21E-03</td>
<td>15.71</td>
</tr>
<tr>
<td></td>
<td>8.00E-03</td>
<td>5.00E-04</td>
<td>0.0064</td>
<td>0.9948</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.00E-03</td>
<td>5.00E-04</td>
<td>0.008</td>
<td>0.9743</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.00E-03</td>
<td>5.00E-04</td>
<td>0.0087</td>
<td>0.9945</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.00E-03</td>
<td>1.00E-03</td>
<td>0.0065</td>
<td>0.9801</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.00E-03</td>
<td>1.00E-03</td>
<td>0.008</td>
<td>0.9817</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.00E-03</td>
<td>1.00E-03</td>
<td>0.0082</td>
<td>0.9775</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.00E-03</td>
<td>1.00E-03</td>
<td>0.0095</td>
<td>0.9626</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The spectrophotometric approach to monitoring product formation is advantageous over the GC-NPD method used to monitor reactant depletion for several reasons. For one, the pyridazine products (PCA and m-PCA) are more stable than their corresponding fuel reactants. Thus, no derivatization is required and values are not subject to sample loss and discrepancy due to reaction, degradation, or adsorption of the MMH and HZ reactant molecules. In addition,
analysis by UV-Vis takes is accomplished in seconds whereas the GC-NPD analysis requires several minutes for detection. In a reaction rate measurement scenario this analysis time can introduce significant error into the measurement. Moreover, there are opportunities for sample loss and degradation at the injector as well as decreased sensitivity arising from column degradation when using the GC method. Such systematic errors are circumvented by measuring the absorbance of the reaction mixture directly.

These reactions of HZ and MMH with AKGA are rapid when the latter is present in significant excess. If this “neutralization” technology is utilized for hydrazine remediation at KSC, these reaction rate constants will guide implementation and procedural development. Future work will include a toxicological assessment of the product mixtures and further characterization of these reactions with an emphasis on engineering and permitting considerations.
CHAPTER FOUR: CHARACTERIZATION OF ALPHA-KETOGLUTARIC ACID (AKGA) FOR USE AS AN ALTERNATIVE HYDRAZINE NEUTRALIZER

Abstract

Alpha-ketoglutaric acid reacts with hydrazine (HZ) and monomethylhydrazine (MMH) to form the stabilized pyridazine derivatives 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) and 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA) respectively. The viability of these reactions as an alternative method of hydrazine neutralization is under investigation by NASA for use at Kennedy Space Center (KSC). Specific applications of interest for AKGA include waste treatment, vapor scrubbing, and decontamination processing. If applicable, this reaction based approach to neutralization may eliminate the current need for containment and transport of large volumes of hydrazine-laden waste water for disposal by incineration. In turn, the hazards and liabilities associated with the handling and transport of this toxic waste stream on public highways would also be avoided.

This chapter focuses on characterization of these reactions and product mixtures with an emphasis on engineering and permitting considerations. Specific properties evaluated include reaction efficiency, product identification and characterization, surface tension and viscosity of AKGA solution, precipitate mitigation, and development of routine analytical methodology.
Introduction

Hydrazines, specifically hydrazine (HZ) and (MMH) are used extensively by NASA as propellants for rockets and spacecraft including the Space Shuttle. These strong reducing agents ignite spontaneously in the presence of strong oxidizers such as nitrogen tetroxide. This property of combustion in the absence of an external ignition source is termed hypergolicity. Hypergolic bipropellant combinations are especially useful in rocket engines that require frequent restarting. Also, unlike cryogenic propellants, these fuels can be stored at room temperature without boil-off losses. And, in terms of payload minimization, they are relatively lightweight. Hydrazines are also used as building blocks in polymer synthesis, as oxygen scavengers in boiler feed water, in metallurgical applications, as blowing agents in plastics processing, and as intermediates in pharmaceutical synthesis (Schmidt, 2001).

Hydrazines are considered highly toxic, and are classified as possible cancer-causing environmental contaminants (Choudhary, 1997). The current practice at KSC is to “neutralize” hydrazine contaminated wastewaster by addition of citric acid. This effectively immobilizes the hydrazine molecule in solution to prevent off-gassing of toxic hydrazine vapor (Schmidt, 2001). This entrapment is reversible and pH dependent. The resulting solution is contained and shipped on public highways for disposal by incineration. KSC produces roughly fifteen thousand gallons of hydrazine-laden wastewater for disposal at a cost approaching $120K per year (Chuck Davis, personal communication, March 21, 2011). This wastewater is transported for disposal on public highways presenting a potentially catastrophic scenario in the case of an accidental release.
The reaction of AKGA with hydrazine has previously been-documented, but not well characterized (Evans & Wiselogle, 1945; Kline and Cox, 1961). Reaction products of AKGA with HZ and MMH are the pyridazine derivatives 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) and 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA) respectively. Recently, New Mexico Highlands University (NMHU) patented this reaction for use in hydrazine remediation (U.S. Patent #7,074,959, 2006). The reaction of hydrazines with AKGA to form stabilized products is a novel approach to hydrazine remediation and may be of interest to NASA if it provides a cost effective means for lessened potential environmental impact and improved safety for personnel.

Extensive characterization is required to determine if these AKGA reactions are viable for processing operations at KSC and to guide implementation. This chapter focuses on characterization efforts with emphasis on engineering considerations, cost effectiveness, and permitting requirements. Specific concerns addressed include reaction efficiency under stoichiometric conditions, viscosity and surface tension properties of the AKGA solution at varying concentrations, product characterization, reaction of product mixtures to pH adjustment, and development of rapid routine analytical methods.

**Experimental**

**Chemicals**

For standards, hydrazine (HZ) sulfate (99+ %) was obtained from Acros Organics while monomethylhydrazine (MMH) sulfate (98%) and 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) were obtained from Alfa Aesar. The 1-methyl-6-oxo-4,5-dihydro-
pyridazine-3-carboxylic acid (mPCA) standard was provided by Enamine. Alpha-ketoglutaric acid was obtained from USB Corporation. HPLC grade acetone and glacial acetic acid were obtained from Fisher Scientific. The 2,6-ditert-butyl-4-methylphenol (≥ 99%) was obtained from Sigma Aldrich. High purity hydrazine and monomethylhydrazine used in testing was obtained from Arch Chemicals.

**Surface Tension**

Surface tensions of 0.5M and 4.0 M AKGA solutions were measured at 20.0°C using a Fisher Surface Tensiomat Model 21.

**Viscosity**

The viscosities of a range of AKGA solution concentrations were measured at typical operating temperatures (16, 22, and 30º C) using Cannon calibrated glass viscometers in a controlled temperature water bath.

**Adjustment of Product Mixture pH**

Reaction mixtures were prepared by addition of aqueous HZ or MMH solution to AKGA solution with stirring. A total of 5.0 mL neat HZ was added to 1 liter of 1.0M AKGA solution to form the PCA reaction mixture. A total of 6.0 mL neat MMH was added to 1 liter of 1.0M AKGA solution to form the mPCA reaction mixture.

The airspace over the reaction mixtures was monitored for off-gassing hydrazine vapor using an Interscan® Series 4000 portable toxic vapor detector (TVD).
After 24 hours reaction time pH measurements were taken and each solution was analyzed for residual HZ or MMH content using a Perkin Elmer Autosystem XL gas chromatograph equipped with a nitrogen phosphorus detector (NPD). Both the detector and injector temperatures were 250º C. The isothermal oven temperature was 180º C. The helium carrier flow was 25 mL/min. Separation occurred on a Supelco glass packed column with a 4% Carbowax 20M and 0.8% KOH on 60-80 Carbopack B stationary phase (2 m length x 2 mm ID). The sample volume was 1 μL. The gas flows on the nitrogen phosphorus detector equipped with a rubidium bead were optimized for nitrogen with a hydrogen flow of 2 mL/min and an air flow of 100 mL/min. An acetone solution containing 0.05 g 2,6-ditert-butyl-4-methylphenol, 100mL deionized water, and 5mL acetic acid per liter was used for pre-analysis derivatization of HZ and MMH in all samples and standards.

A sodium hydroxide solution was used to adjust the pH of the reaction mixtures to a pH of approximately 8.0 and again to a pH approaching 10.0. After each adjustment the resultant solutions were analyzed for residual hydrazine content by GC-NPD.

**Reaction Efficiency**

The percent conversion of reactants to products was determined by spectrophotometric analysis of product concentration in the mixture 24 hours after reaction initiation. AKGA was present in the reaction mixture at 1:1 and 2:1 ratios for each of the hydrazine fuel reactants (HZ and MMH). Reactions were conducted in triplicate. In each case the hydrazine reactant (HZ or MMH) was added to the AKGA solution as an aqueous solution to avoid sample loss due to “hot spot” formation and subsequent off-gassing. Constant stirring was applied. After reaction, the
product mixture was analyzed spectrophotometrically for the corresponding pyridazine derivative. A Perkin Elmer Lambda 900 spectrometer was used to measure the absorbance of the product mixtures at 286 nm as both PCA and m-PCA were found to exhibit strong absorbances at this wavelength in the target concentration range. Deionized water was used as the reference. Calibration curves were constructed in both deionized water and in 0.001M AKGA to mimic the two different target AKGA to product ratios. Samples were diluted by a factor of 10 for analysis in the linear dynamic range of the appropriate calibration curve.

**Product Characterization**

In the absence of standards, a saturated solution of AKGA, PCA, and mPCA in methylene chloride was analyzed by GC-MS using a Finnigan Incos 500 equipped with a DB-5MS capillary column (30m x 0.32mm x 0.25µm). The oven temperature was ramped from 80°C to 180 °C over 20 minutes. The injector temperature was 225 °C. The sample volume was 1µL. An electron impact source was used for ionization. The PCA was prepared by addition of neat HZ to an aqueous AKGA solution. After 24 hours reaction time, the remaining solution was boiled off. The mPCA was prepared by addition of MMH to another aqueous AKGA solution. Again, the mixture was allowed to react for 24 hours and the solution was boiled off. The resulting residues were subsequently dissolved in methylene chloride for analysis.

**Routine Method Development**

PCA and mPCA standards were used for development of a rapid routine method for analysis of PCA, mPCA, and AKGA content. Method parameters were adjusted for optimized separation and detector response. A Thermo Finnigan Trace GC/DSQ equipped with a Restek
Rxi-XLB capillary column (30m x 0.32mm x 0.5µm) was used. The oven temperature was ramped from 170ºC to 300ºC over 30 minutes. The injector temperature was 230ºC. A split flow of 74 mL/min was applied 0.10 minutes after injection. The MS transfer line temperature was 220 ºC. An electron impact source was used for ionization. The sample volume was 1µL.

**Results and Discussion**

**Surface Tension**

The 0.5M AKGA solution measured 68.74 dynes/cm and a 4.0M AKGA solution measured 57.17 dynes/cm. For reference, the surface tension of water at 20.0ºC is 72.75 dynes/cm.

**Viscosity**

Viscosity measurements are summarized in Table 16. Viscosity will be an important consideration for use of AKGA solution to decontaminate the Orbital Maneuvering System and Reaction Control System (OMS/RCS) propellant tank screens and flight pressure transducers where capillary effects due to dead-end tubing occur.

**Table 16. Summary of viscosity measurements of AKGA solution at varying concentrations**

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>0.5 M AKGA</th>
<th>2.0 M AKGA</th>
<th>4.0 M AKGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific gravity</td>
<td>Kinematic viscosity, cSt</td>
<td>Absolute viscosity, cp</td>
</tr>
<tr>
<td>16</td>
<td>16</td>
<td>1.036</td>
<td>1.3</td>
</tr>
<tr>
<td>22</td>
<td>22</td>
<td>1.030</td>
<td>1.1</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>1.028</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Adjustment of Product Mixture pH

No off-gassing hydrazine vapors were detected by TVD from over either reaction vessel before, during, or after pH adjustments were made.

The mPCA solution had an initial pH of 1.2. After 24 hours reaction time, no residual MMH was detected in solution. The pH was adjusted to 8.5 and again to 9.9. Residual MMH was not detected in solution after either adjustment.

The PCA solution had an initial pH of 1.3. After 24 hours reaction time, no residual HZ was detected in solution and a copious amount of crystalline PCA precipitated out of solution. The pH was adjusted to 8.5 and again to 10.7. Residual HZ was not detected in solution after either adjustment. Noteworthy is that the PCA precipitate dissolved back into solution when a pH of 10 was reached. This may provide a useful means for precipitate removal in cases where particulate formation could cause blockages such as in hardware lines, orifices, valves, and screens.

This experiment was designed to mimic the current practice of adjustment of non-hazardous waste to the required pH of 8.0 to 11.0 prior to discharge into the KSC Sewage Treatment Plant (STP). If these AKGA neutralization product streams were deemed safe for STP disposition, the acidic solution would require adjustment with sodium hydroxide. The results indicate the neutralization reaction is not reversed at increased pH.
**Reaction Efficiency**

**Table 17. Summary of percent conversion results for reaction efficiency study**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>1:1 (AKGA:reactant)</th>
<th>2:1 (AKGA:reactant)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration, M (mol/L)</td>
<td>% Conversion</td>
</tr>
<tr>
<td>mPCA (A)</td>
<td>5.16E-04</td>
<td>51.6</td>
</tr>
<tr>
<td>mPCA (B)</td>
<td>4.49E-04</td>
<td>44.8</td>
</tr>
<tr>
<td>mPCA (C )</td>
<td>4.58E-04</td>
<td>45.8</td>
</tr>
<tr>
<td>PCA (A)</td>
<td>8.03E-04</td>
<td>80.3</td>
</tr>
<tr>
<td>PCA (B)</td>
<td>8.41E-04</td>
<td>84.1</td>
</tr>
<tr>
<td>PCA (C )</td>
<td>8.42E-04</td>
<td>84.2</td>
</tr>
</tbody>
</table>

The NMHU patent claims that the reaction of AKGA with hydrazine provides “near quantitative” conversion of hydrazine to PCA. However, no data is reported by the authors regarding actual percent conversions of HZ to PCA or MMH to mPCA to support this claim. In the literature Kline and Cox reported an 88% yield of PCA and a 56.5% yield of mPCA under the same reaction conditions as in this experiment (1960). The 1:1 AKGA:HZ/MMH yields reported here (82.9% PCA; 47.4% mPCA) are slightly lower, but in relative agreement with those reported by Kline and Cox. As expected, these yields increased when the AKGA concentration was increased to 2:1 (63.9% mPCA; 106% PCA). Another patent (U.S. Patent #2,873,294) reported a 90% PCA yield under the same reaction conditions and a 34% yield of mPCA with 16N sodium hydroxide present in the reaction solution (1958). Similarly, Evans and Wiselogle reported a 50% yield of PCA in 3.8N sodium hydroxide reaction solution (1945).
Thus, increasing the pH of the reaction mixture by addition of sodium hydroxide appears to inhibit product formation.

Although a higher ratio of AKGA to hydrazine will drive the neutralization reaction equilibrium toward product formation, a 2:1 ratio of AKGA to hydrazine is likely the upper limit for this process to be cost effective in relation to current hydrazine disposal techniques. Ultimately the cost of AKGA will dictate how high this ratio can go. As for reaction time, 24 hours is the upper limit for practical implementation of this reaction in the field.

From a mass balance perspective, the yields reported here leave some MMH and HZ unaccounted for. Complete characterization of reaction products will be required for the Florida Department of Environmental Protection (FDEP) to consider authorization for disposition of the product stream into wastewater treatment facilities (e.g. the KSC STP), direct land disposal, or incineration.

**Product Characterization**

Each of the three components in the mixture was identified in the chromatogram. The total ion chromatogram (TIC) and mass spectra are presented in Figures 11 through 14.
Figure 11. Total ion chromatogram of AKGA, PCA, and mPCA mixture in methylene chloride
Figure 12. Mass spectrum of AKGA in methylene chloride
Figure 13. Mass spectrum of mPCA in methylene chloride
Figure 14. Mass spectrum of PCA in methylene chloride

As mentioned in the “Experimental” section of this paper, this was a qualitative analysis to determine if PCA, mPCA, and AKGA could be identified in the product mixture. The peak tailing observed in the TIC is likely due to column overload. Separation was achieved on the DB5-MS column with AKGA eluting first at ~9 minutes, followed by mPCA at ~12 minutes, and PCA detected at ~14 minutes.

The mass spectrum of AKGA is consistent with the spectrum published in the SciFinder spectral database with abundant ions at m/z 101, 73, 55, and 45. The molecular ion (m/z 146)
does not appear in the mass spectrum, but the base peak at m/z 101 (M – 45)$^+$ is consistent with the loss of a carboxylic acid group as is characteristic of straight chain carboxylic acids.

The molecular ion is present in the mPCA mass spectrum with abundant ions at m/z 156, 138, 83, 57, and 43. Spectral data for this compound was not found in the literature or in spectral databases. Although a commercial standard was not available at the time of analysis, this spectrum is consistent with that of the mPCA standard acquired later from a commercial source. Analysis of the standard is described in the “Experimental” section of this paper under “Routine Method Development”.

The PCA mass spectrum is also consistent with the corresponding mass spectrum as published in the SciFinder spectral database with abundant ions at m/z 43, 55, 69, 124, and the molecular ion at 142.

These spectra are in agreement with the expected products of the reaction of AKGA with HZ and MMH. Extraneous peaks indicating the presence of by-products in significant quantities do not appear in the chromatogram. However, it cannot be concluded that by-products are not present in the solution based on their absence in the chromatogram.

**Routine Method Development**

The total ion chromatogram resulting from analysis of a solution containing 400 ppm AKGA, mPCA, and PCA in methanol and the corresponding mass spectra are presented in Figures 15 through 18.
Figure 15. Total ion chromatogram of solution containing 400 ppm AKGA, PCA, and mPCA standards in methanol
Figure 16. Mass spectrum of AKGA in methanol
Figure 17. Mass spectrum of mPCA in methanol
If implemented, a rapid routine analytical method will be necessary for identification and quantification of solution components prior to sewage treatment plant (STP) disposition. Separation of AKGA, mPCA, and PCA was achieved in less than 5 minutes using this method. The detector response to AKGA was significantly weaker than the responses to mPCA and PCA. Therefore, GC-MS analysis may not be suitable for quantification for AKGA. However, this also suggests that the presence of unreacted AKGA in samples will not interfere with quantification of mPCA and PCA by this method.
Despite the weak detector response, the AKGA mass spectrum is in agreement with previously acquired data and published spectra. The mass spectra of the commercial mPCA and PCA standards are also consistent with those of the products formed in the laboratory by addition of HZ or MMH to AKGA solution during the previously mentioned product characterization studies.

The results reported here will be useful for procedural development and implementation of the AKGA neutralization methodology. However, further research will be necessary to satisfy FDEP permitting requirements. Specific concerns are the potential toxicity of the reaction products and by-products as well as the potential for biodegradation of these products.
CHAPTER FIVE: CONCLUSION

The alternative hydrazine neutralization methodology patented by NMHU has successfully neutralized HZ and MMH in solution and on contaminated hardware by reaction with AKGA (2-oxoglutaric acid; alpha-ketoglutaric acid) to form the stabilized pyridazine derivatives 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) and 1-methyl-6-oxo-4,5-dihydro-pyridazine-3-carboxylic acid (mPCA) respectively. These neutralization reactions were rapid as determined by monitoring both reactant depletion and product formation under pseudo-first order reaction conditions. The PCA and mPCA product structures were confirmed by GC-MS. The spectra acquired were compared to those of standards and in those scientific publications were found to be in agreement. In addition, the AKGA solution properties are suitable for use as a drop-in replacement for the existing neutralizer solutions which act to trap HZ and MMH for subsequent disposal by incineration. With permitting approval, implementation of this hydrazine neutralization methodology can proceed with minimal modification to existing infrastructure and standard operating procedures. Thus, hydrazine neutralization by AKGA solution has the potential to eliminate the substantial hydrazine-laden wastewater stream generated at KSC along with the associated expenses and liabilities.

The following recommendations for procedural development are based on data and observations collected during simulation of worst-case hardware and soft-good decontamination processing scenarios using AKGA solution. Preliminary studies suggesting complete
decontamination of soft-goods using AKGA were anomalous. Decontamination of hydrazine exposed soft-goods by AKGA solution is entirely dependent on diffusion of the absorbed hydrazine to the surface for reaction with the neutralizer. Thus, soft-good decontamination remains problematic due to long-term off-gassing of hydrazine vapors. Therefore, soft-goods should be removed and disposed of separately when possible. In addition, the current practice of “bagging” or otherwise closing soft-good containing equipment and hardware for storage after decontamination should be abandoned as this allows for concentration of hydrazine vapors diffusing from the soft-good to unacceptable levels over time. The result is the commonly encountered “puff” of hydrazine detected by TVD when equipment that has been successfully decontaminated to meet the ADL requirements is re-opened to the atmosphere. Instead, these components should remain open to atmospheric conditions after decontamination requirements are met.

Modification of the existing procedure by incorporation of a preliminary water rinse is also recommended. The purpose of the rinse is two-fold: (1) to prevent “hot spot” formation and subsequent off-gassing of toxic hydrazine vapors and (2) to circumvent PCA precipitation which presents complications in processing flight hardware and other components with stringent particulate specifications. After flushing, the water rinse can be treated externally by addition of AKGA as needed.

As for the neutralizer solution, a concentrated AKGA solution should be used for decontamination of hardware that has previously undergone a water rinse as prescribed. This solution can be re-circulated as is the practice with the current glycolic acid based neutralizer.
solution. Routine sampling and analysis for MMH and HZ in the solution should be conducted at a minimum of weekly. AKGA can be added to “sweeten” this solution as needed.

In all cases the neutralizer should be allowed the maximum reaction time. In cases of large scale decontamination efforts such as in fixed ground support equipment, the AKGA neutralizer solution should follow a preliminary water flush. After circulation, the water flush can be contained in a tanker and sampled for hydrazine content. The results of this analysis will dictate the concentration of AKGA to use for neutralization. The AKGA neutralizer solution should then be recirculated through the system undergoing contamination for a minimum of 24 hours. After neutralization, this solution should also be contained and analyzed for hydrazine content. If hydrazine is detected in the solution, AKGA should be added, allowed to react, and re-analyzed for hydrazine content. This should be repeated until hydrazine is undetected. After neutralization, the solution pH can be adjusted for final discharge to the STP.

From a regulatory perspective, the FDEP agreed that the reactions of HZ and MMH with AKGA can be considered chemical oxidation as defined by the technology code CHOXD under option (9) as described in 40 CFR §268.40:

Chemical or electrolytic oxidation utilizing the following oxidation reagents (or waste reagents) or combination of reagents: (1) Hypochlorite (e.g. bleach); (2) Chlorine; (3) Chlorine Dioxide; (4) ozone or UV (ultraviolet light) assisted ozone; (5) peroxides; (6) persulfates; (7) perchlorates; (8) permangnates; and/or (9) other oxidizing reagents of equivalent efficiency, performed in units operated such that a surrogate compound or indicator parameter has been substantially
reduced in concentration in the residuals (e.g., Total Organic Carbon can often be used as an indicator parameter for the oxidation of many organic constituents that cannot be directly analyzed in wastewater residues). Chemical oxidation specifically includes what is commonly referred to as alkaline chlorination.

Following a visit to the Wiltech decontamination facility at KSC to address a formal request for guidance, FDEP representatives advised that concerns to be addressed before permitting could be considered were (1) further characterization of reaction products (2) completeness of reaction, (3) biodegradation potential of reaction products, and (4) potential toxicity of reaction products.

PCA and mPCA product formation was confirmed by GC-MS. However, reaction efficiency studies left some HZ and MMH unaccounted for when the reaction proceeded under stoichiometric conditions. Reaction by-products were not detected by GC-MS or GC-NPD analysis. Hence, future research should include a full material balance including isolation and characterization of all reaction by-products to satisfy FDEP requirements for waste profiles.

Patent claims regarding microbial digestion of the pyridazine products are based on a single reference in which pseudomonas was found to utilize the PCA product as a nitrogen source in the laboratory by cleavage of the nitrogen-nitrogen bond (LaRue et al, 1979). This evidence is insufficient to conclude that the neutralization product stream is suitable for STP disposition. To address these concerns, simulated product streams were sent to Johnson Space Center to test their amenability to biological degradation in wastewater treatment plants. Given the limited toxicological data available with respect to PCA and mPCA, this approach sought to
test the toxicity of the product stream as a whole rather than isolating and testing products and by-products individually. Results are presented in Appendix B.

At this stage in the process development, several factors complicate accurate cost analysis. The most important being the fate of the AKGA neutralization product stream. The procurement cost of AKGA is significantly higher than that of the citric acid currently used. But, if the product stream were deemed non-hazardous and safe for STP disposition, the current costs associated with transport and disposal of the hazardous citric acid neutralizer stream would be eliminated. Furthermore, if the neutralization product streams were commercially viable, as is claimed in the patent, their sale could offset the substantial cost of AKGA procurement. Also, the cost of AKGA may be significantly less if purchased in bulk quantities. Consequently, at this stage in the process development, cost analysis can only be done with limited accuracy on a case by case basis. For example, a cost analysis was conducted to compare the costs of decontaminating one of the launch pads (LC-39B) using AKGA versus citric acid. It was assumed that the product stream would be discharged to the STP, and that a 1.5:1 stoichiometric ratio of AKGA to residual hydrazine would be sufficient to neutralize approximately 70 gallons of residual MMH. Under these assumptions, procurement of AKGA based on an estimated cost of $20/ lb was $72K. The cost of the citric acid equivalent was $3.6K. However, the citric acid waste processing costs were figured at $80K compared to $5K for AKGA. Therefore, the total cost of decontamination using AKGA was estimated at $77K versus $83.6K for decontamination with citric acid. Based on these numbers, decontamination of LC-39B by the alternative AKGA neutralization methodology was slightly less expensive with the advantages of lessened potential environmental impact.
With FDEP approval, the potential applications for this alternative hydrazine neutralization technology include decontamination of fixed systems such as the Launch Complex 39A, Orbiter Processing Facilities 1, 2, and 3, and the Hypergol Maintenance Area Facilities as well as decontamination the Space Shuttle Orbiters for museum preservation. Other projected applications are decontamination of portable equipment, parts, and empty containers, and replacement of citric acid scrubber liquor in vapor scrubbers. The most significant use for AKGA is for treatment of the large volume of consolidated “fuel soup” mixture which contains all of the spent scrubber liquor, off-specification HZ and MMH, and fuel rinsates leftover from processing operations.
APPENDIX A: FLIGHT-LIKE FUEL VESSEL NEUTRALIZATION PROCEDURE
TASK: Fuel Vessel Neutralization Test - VESSEL #1 (S/N 0050)

NOTE
Comply with all applicable safety requirements

INSPECTION
Inspect vessel exterior and end fittings for any anomalies. GAS and LIQUID side vessel valves should be closed. Per Eng. Direction, identify and label the GAS / LIQUID sides of the fuel vessels and external containers (stainless carboys) #1 and #2.

PROCESS
This procedure will be applied to the fuel vessel #1 (S/N 0050). Anticipated status is given for each vessel at the beginning of each section for reference.

1.0 PRE-NEUTRALIZATION GAS SAMPLING – Fuel Vessel #1

STATUS: See Prop. South Test Cond. Log sheet for offload operation of Fuel Vessels (02/06/09).

Vessel #1: liquid side - 0 lbs, water rinsed / gas side ~ 9.5 psi GN₂
GAS and LIQUID side VESSEL valves are closed.

WARNING: Diaphragm differential pressure cannot exceed 15 PSID.

1.1 Configure GSE valves and gauges as depicted in figures 1-4.
1.2 Verify that ALL valves are closed.
1.3 Connect tubing from GAS side GSE press/vent/liquid valve to the inlet of the scrubber apparatus provided by Wilttech (see figure 5).
1.4 Place dosimeter badge and TVD monitor in proximity of scrubber apparatus vent.
1.5 Open GAS side VESSEL valve.
1.6 Slowly open GAS side GSE press/vent/liquid valve to vent GAS side of fuel vessel through the scrubber apparatus. Use GSE press/vent/liquid valve to control vent flow.
1.7 Perform Toxic Vapor Detection (TVD) test at scrubber apparatus vent.
   Record: Gas side _______ ppb (ADL 100 ppb).
1.8 Continue venting until bubbling ceases (0 psig). Record vent time: _____ min.
1.9 Close GAS side GSE press/vent/liquid valve.
1.10 Connect facility GN₂ to liquid side of vessel. Pressurize LIQUID side to 15 psig.
    Record GAS side pressure; _________ psig.
TASK: Fuel Vessel Neutralization Test - VESSEL #1 (S/N 0050)

1.11 Collect scrubber fluid. Clean scrubber and reassemble for further testing.
1.12 Slowly open GAS side GSE press/vent/liquid valve to vent GAS side of fuel vessel through the scrubber apparatus. Use GSE press/vent/liquid valve to control vent flow.
1.13 Perform Toxic Vapor Detection (TVD) test at scrubber apparatus vent.
   Record: Gas side _____ ppb (ADL 100 ppb).
1.14 Continue venting until bubbling ceases (0 psig). Record vent time: __/He __0 min.
1.15 Close GAS side GSE press/vent/liquid valve.

2.0 Configure external containers for neutralization (ref. Figure 6)

2.1 Prepare AKGA solution per engineering instruction. Record weight of one gallon of AKGA/DM water solution; _____ 9.3 lbs.

2.2 Install drum heater on neutralizer containers per Eng. Direction.
2.3 Turn on drum heaters and heat neutralizer per Eng. Direction.
2.4 Verify scale is indicating zero pounds. Zero scale if necessary.
2.5 Record dry weight of external container # 1.
   _____ 7.96 __/min __55.72 __/min __ LBS

2.6 Record dry weight of external container # 2.
   _____ 79.08 __/min __ LBS

2.7 Fill external container #1 with ~ 7 gallons of AKGA solution.
   Record filled weight of external container #1 + drum heater.
   _____ 164.18 __/min __ LBS

2.8 Fill external container #2 with ~ 13 gallons of AKGA solution.
   Record filled weight of external container #2 + drum heater.
   _____ 168.82 __/min __ LBS

2.9 Attach outlet hose from external container #1 to GAS side GSE press/vent/liquid valve.

2.10 Record total weight of external container # 1 + drum heater + test hoses attached.
    _____ 18.58 __/min __ LBS
TASK: Fuel Vessel Neutralization Test - VESSEL #1 (S/N 0050)

3.0 Neutralization (see figures 1 – 4)

STATUS: GAS and LIQUID VESSEL valves open.
         GAS and LIQUID side GSE press/vent/liquid valves closed.
         #1: liquid side ~15lbs GN₂ / gas side - 0 psi

WARNING: Diaphragm differential pressure cannot exceed 15 PSID

NOTE: The next steps will establish a vacuum on each side of the test vessel. Warm AKGA solution will be added into the evacuated volume and remain static for ~2 weeks.
      Both the GAS and LIQUID sides of the vessel will be evacuated and filled with neutralizer solution.

3.1 GAS Side Evacuation

NOTE: Refer to Figure 1 for steps 3.1.1 - 3.1.7

3.1.3 Open LIQUID side GSE press/vent/liquid valve to vent. Valve to remain open for evacuation.

3.1.4 Open GAS side vacuum valve.

3.1.5 Evacuate GAS side of the fuel vessel to 1 (+/- 0.2) PSIA.

3.1.6 Close GAS side vacuum valve.

3.1.7 Close LIQUID side GSE press/vent/liquid valve

3.2 GAS Side Neutralizer Loading

NOTE: Refer to Figure 2 for steps 3.2.1 – 3.2.5

3.2.1 Pressurize external container #1 to 30 (+/- 5) PSIG.

3.2.2 Open GAS side GSE press/vent/liquid valve and load ~7 gallons of neutralizer from external container #1 into evacuated GAS side of vessel.

3.2.3 Close GAS side GSE press/vent/liquid valve.

3.2.4 Close LIQUID side GSE press/vent/liquid valve.
SPECIAL INSTRUCTION

TASK: Fuel Vessel Neutralization Test - VESSEL #1 (S/N 0050)

3.2.5 Record:

Neutralizer temperature 127 °F
External container #1 start weight 11,589 LBS
Target weight (less 7 gals.) 53,420 LBS
Actual weight (less 7 gals.) 55,118 LBS

3.3 LIQUID Side Evacuation

NOTE: Refer to Figure 3 for steps 3.3.1 – 3.3.3

3.3.1 Open LIQUID side vacuum valve. Verify GAS side GSE press/vent/liquid valve remains closed.

3.3.2 Evacuate LIQUID side of the fuel vessel to 1 (+/- 0.2) PSIA.

3.3.3 Close LIQUID side vacuum valve.

3.4 LIQUID Side Neutralizer Loading

NOTE: Refer to Figure 4 for steps 3.4.1 – 3.4.9 (LIQUID side neutralizer loading)

3.4.1 Attach outlet hose from external container #2 to LIQUID side GSE press/vent/liquid valve

3.4.2 Record total weight of external container #2 + drum heater + test hoses attached. 65,200 LBS

3.4.3 Pressurize external container #2 to 30 (+/- 5) PSIG.

3.4.4 Open LIQUID side GSE press/vent/liquid valve

3.4.5 Load ~ 13 gallons from external container #2 into LIQUID side of vessel with GAS side GSE press/vent/liquid valve closed.

3.4.6 Open GAS side GSE press/vent/liquid valve per Eng. direction to continue loading neutralizer until a steady stream of neutralizer emerges from GAS side GSE press/vent/liquid valve.
SPECIAL INSTRUCTION

TASK: Fuel Vessel Neutralization Test - VESSEL #1 (S/N 0050)

3.4.7 Record:

Neutralizer temperature 120 °F
External container #2 start weight 169.20 LBS
Target weight (less 13 gals.) 38.3 LBS
Actual weight (less 13 gals.) 51.2 LBS

3.4.8 Install expansion component on GAS side of fuel vessel. Verify GAS side vessel and GSE valves to expansion component remain open.

3.4.9 Allow neutralizer to remain static in fuel vessel for ~2 weeks.

4.0 Configure external containers for off-loading

4.1 Record empty weight of external container #1A 6.82 LBS.

4.2 Record total weight of dry external container #1A and test hoses 7.76 LBS.

4.3 Record empty weight of external container #2A 6.78 LBS.

4.4 Record total weight of dry external container #2A and test hoses 7.42 LBS.

5.0 Offload Neutralizer Rinse

STATUS: GAS side VESSEL and GSE valves open.
LIQUID side VESSEL and GSE press/vent/liquid valves closed.
External container #1A empty
External container #2A empty
#1: liquid side ~13 LBS AKGA solution / gas side ~7 LBS AKGA solution

WARNING: Diaphragm differential pressure cannot exceed 15 PSID

NOTE: In the next steps, neutralizer will drain from LIQUID side of fuel vessel into dry external container #2A. Next, the LIQUID side will be pressurized with GN2 to expel neutralizer from the GAS side of the fuel vessel back into dry external container #1A. Finally, the GAS side will be pressurized with GN2 to expel any neutralizer remaining in LIQUID side of fuel vessel after the initial draining. Toxic Vapor Detection (TVD) will be monitored at external container bung ports.
TASK: Fuel Vessel Neutralization Test - VESSEL #1 (S/N 0050)

5.1 Open LIQUID side GSE press/vent/liquid valve and allow neutralizer to drain from LIQUID side into external container #2A.

5.2 Open GAS side GSE press/vent/liquid valve (at to of expansion chamber). Pressurize to 5-10 psig per engineering direction.

5.3 Perform Toxic Vapor Detection (TVD) test at external container #2A bung vent. Record: Gas side $0\text{.}04$ ppm (ADL 0.1 ppm). Cal. Cont. #202/1621

5.4 Close LIQUID side GSE press/vent/liquid valve.

5.5 Record:

Neutralizer container #2A start weight $5.42$ LBS (from 4.3)

Target weight (plus 13 gals.) $125.32$ LBS

Actual weight (plus 13 gals.) $125.36$ LBS ($125.76$)

5.6 Disconnect external container #2A from LIQUID side GSE press/vent/liquid valve.

5.7 Connect GN2 line to LIQUID side GSE press/vent/liquid valve.

5.8 Open LIQUID side GSE valve and pressurize LIQUID side to 15 psi (to drive rinse neutralizer from gas side into neutralizer container #1A).

5.9 Perform Toxic Vapor Detection (TVD) test at external container #1A bung vent. Record: Gas side $0\text{.}01-0\text{.}04$ ppm (ADL 0.1 ppm). Cal. Cont. #202/1621

5.10 Maintain 15 psi blanket until rinse neutralizer is expelled from GAS side to (~ 7 gal).

5.11 Record:

Neutralizer container #1A start weight $5.46$ LBS (from 4.2)

Target weight (plus 7 gals.) $125.56$ LBS

Actual weight (plus 7 gals.) $125.88$ LBS ($126.61$ psi)

5.12 Disconnect neutralizer container #1A outlet hose from GAS side of fuel vessel

5.13 Connect GN2 line to GAS side of fuel vessel.

5.14 Re-connect neutralizer container #2A outlet line to LIQUID side of fuel vessel.
5.15 Record empty weight of neutralizer container #2A with outlet attached; 5.42 lbs.

5.16 Open LIQUID side valve and allow neutralizer to drain back into neutralizer container #2A. If possible, elevate fuel vessel in relation to external container #2A.

5.17 Open GAS side valve and pressurize to 15 psi. Maintain 15 psi blanket until rinse neutralizer is expelled from LIQUID side of fuel vessel into empty neutralizer container #2A (~13 gal). Record:

Neutralizer container #2A start weight 125.36 LBS
Final weight (plus 13 gals.) 125.36 LBS

5.18 Disconnect GN2 line from GAS side of fuel vessel.

5.19 Close GAS and LIQUID side VESSEL valves.

5.20 Disconnect neutralizer container #2A from LIQUID side GSE press/vent/liquid valve.

5.21 Record weight of empty fuel vessel 50.76 LBS

6.0 Sampling

6.1 Perform Toxic Vapor Detection (TVD) test at Gas and Liquid side ports.
Record: Gas side 0.3 ppm (ADL 0.1 ppm/100 ppb).
Record: Liquid side 0.3 ppm (ADL 0.1 ppm/100 ppb).

6.2 Liquid Side Evacuation - Refer to Figure 3

6.2.1 Open LIQUID side vacuum valve. Verify open GAS side GSE press/vent/liquid valve.

6.2.2 Evacuate LIQUID side of the fuel vessel to 1 (+/- 0.2) PSIA.

6.2.3 Close LIQUID side vacuum valve.

6.3 LIQUID SIDE WATER LOAD (ref. figure 1)

Note: This section will load the liquid side of the fuel vessel with 1 gal. of DM water. Gas side will be vented at this time.
STATUS: liquid side - evacuated / gas side ~ vented

6.3.1 Pressurize external container with DM to ~ 15 psig.
6.3.2 Open liquid side vessel valve. Gas side vessel valve and GSE valves to remain open during load.
6.3.3 Open GSE valve and load ~1 gal. (8.3 lbs) of DM water into liquid side of vessel.
6.3.4 Close all valves at completion of liquid side water load.

6.4 Gas Side Pressurization
6.4.1 Connect facility GN₂ to GAS side.
6.4.2 Open Gas side Vessel and GSE valves. Pressurize Gas side with GN₂ to ~ 80 psig.
6.4.3 Close all Vessel valves.
6.4.4 Allow Vessel to remain static for 1 week or per engineering direction.
6.4.5 Repeat section 6 per engineering direction.
7.0 Appendix

GAS side evacuation

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**FIGURE 1**

- Liquid side GSE valve open during evacuation
- Evacuate Gas Side to 1 (±0.2) PSIA
- GSE PRESS / VENT / WATER
- Supply Valve
- GSE VACUUM VALVE
- VESSEL VALVE
- DIAPHRAGM (15 PSID max)
GAS side loading

LOAD GAS SIDE with AKGA/DM WATER SOLUTION

Liquid side GSE vent valve open during load

Load Gas Side with ~7 gallons, 65.1 lbs of AKGA/DM Water Solution

FIGURE 2
LIQUID side evacuation

EVACUATE LIQUID SIDE
1 (+/-0.2) PSIA

Gas side GSE valves closed.

Gas Side Previously
Loaded with
7 gallons, 65.1 lbs of
AKGA/DM Water Solution

FIGURE 3
**TASK:** Fuel Vessel Neutralization Test - VESSEL #1 (S/N 0050)

**LIQUID side loading**

LOAD LIQUID SIDE WITH AKGA/DM WATER SOLUTION
~ 13 gal (120.9 lbs)

Gas side GSE valves closed initially

Gas Side Previously Loaded with ~7 gallons, 65.1 lbs of AKGA/DM Water Solution

Per Engineering Direction
Open Gas Side GSE Valve to Verify Steady Stream of Water

**FIGURE 4**
GAS SAMPLE THROUGH SCRUBBER

Liquid side water rinsed post Hz offload
Gas Side Pressurized to 9.5 psig GN2
Liquid side zero psig

Per Engineering Direction
Open Gas Side GSE
Valve to vent Gas side through scrubber

FIGURE 5
SPECIAL INSTRUCTION

TASK: Fuel Vessel Neutralization Test - VESSEL #2 (S/N 0041)

NOTE
Comply with all applicable safety requirements

INSPECTION
Inspect vessel exterior and end fittings for any anomalies. GAS and LIQUID side vessel valves should be closed. Per Eng. Direction, identify and label the GAS / LIQUID sides of the fuel vessel and external container #1B.

PROCESS
This procedure will be applied to the fuel vessel #2 (S/N 0041). Anticipated status is given for each vessel at the beginning of each section for reference.

1.0 CONFIGURE EXTERNAL CONTAINER FOR WATER LOAD – Fuel Vessel #2

STATUS: See Prop. South Test Cond. Log sheet for offload operation of Fuel Vessels, 02/06/09.

Vessel #2: liquid side - 0 lbs, water rinsed / gas side ~ 74 psi GN₂
GAS and LIQUID sides, VESSEL valves are closed.
GSE valves closed.

WARNING: Diaphragm differential pressure cannot exceed 15 PSID.

1.1 Configure GSE valves and gauges as depicted in figures 1-3.
1.2 Verify that ALL valves are closed.
1.3 Verify scale indicates zero lbs. Zero scale if necessary.
1.4 Record dry weight of external container #1B.

1.5 Fill external container #1B with ~ 5 gallons of DM water.
1.6 Attach outlet hose from external container #1B to liquid side GSE press/vent/liquid valve.
1.7 Pressurize external container #1B to 85 psig (~10 psig above gas side current pressure, ~74 psig).

LBS

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SPECIAL INSTRUCTION

TASK: Fuel Vessel Neutralization Test - VESSEL #2 (S/N 0041)

2.0 LIQUID SIDE LOAD (see figure 1)

Note: This section will load the liquid side of the fuel vessel with 1 gal. of DM water. Gas side will NOT be vented at this time. The vessel will remain static for ~2 weeks post water load.

STATUS: liquid side - 0 lbs, water rinsed / gas side ~ 80 psi GN₂
GAS and LIQUID sides, VESSEL valves are closed.
GSE valves closed.

2.1 Record start weight of external container #1B. 89.71 lbs.
2.2 Open liquid side vessel valve. Gas side vessel valve and GSE valves to remain closed.
2.3 Open GSE valve and load ~1 gal. (8.3 lbs) of DM water into liquid side of vessel.
2.4 Close all valves at completion of liquid side water load.
2.5 Allow water on liquid side and GN₂ on gas side to remain static in vessel for 2 weeks.

3.0 OFFLOAD WATER FROM LIQUID SIDE (see figure 2)

STATUS: GAS and LIQUID VESSEL valves CLOSED.
GAS and LIQUID side GSE press/vent/liquid valves closed.
liquid side ~1 gal. WATER / gas side ~ 80 psi GN₂

WARNING: Diaphragm differential pressure cannot exceed 15 PSID

NOTE: The next steps will offload the DM water from the liquid side of the vessel into an external container. Neutralizer will drain from LIQUID side of fuel vessel into a dry external container #2B.

3.1 Record empty weight of external container #2B; 7.0 lbs.
3.2 Open Liquid side Vessel valve.
3.3 Open LIQUID side GSE press/vent/liquid valve and allow DM water to drain from LIQUID side into external container #2B.
3.4 Close LIQUID side GSE press/vent/liquid valve.
3.5 Close Liquid side vessel valve.
3.6 Record final weight (+ 1 gal.) of external container #2B; 14.5 lbs.
SPECIAL INSTRUCTION

TASK: Fuel Vessel Neutralization Test - VESSEL #2 (S/N 0041)

4.0 TVD TEST

4.1 Perform Toxic Vapor Detection (TVD) test at Gas and Liquid side ports.
   Record: Gas side \text{See Sect. 5.3} \text{ ppm (ADL 0.1 ppm/100 ppb)}.
   Record: Liquid side \text{0.2} \text{ ppm (ADL 0.1 ppm/100 ppb)}.

5.0 PREPARE FOR GAS SAMPLING (see figures 1 & 3)

WARNING: Diaphragm differential pressure cannot exceed 15 PSID.

5.1 CONFIGURE EXTERNAL CONTAINER FOR WATER LOAD

5.1.1 Configure GSE valves and gauges as depicted in figures 1-3.
5.1.2 Verify that ALL valves are closed.
5.1.3 Verify scale indicates zero lbs. Zero scale if necessary.
5.1.4 Record dry weight of external container \# 1B. \text{48.0 LBS}

5.1.5 Fill external container \#1B with \sim 5 \text{ gallons of DM water.}
5.1.6 Attach outlet hose from external container \#1B to liquid side GSE press/vent/liquid valve.
5.1.7 Pressurize external container \#1B to 85 psig (\approx 10 \text{ psig above gas side current pressure, } \approx 74 \text{ psig}).

5.2 LIQUID SIDE LOAD (see figure 1)

Note: This section will load the liquid side of the fuel vessel with 1 gal. of DM water. Gas side will NOT be vented at this time.

STATUS: liquid side - 0 lbs, water rinsed / gas side \approx 74 \text{ psi GN}_2
GAS and LIQUID sides, VESSEL valves are closed.
GSE valves closed.

5.2.1 Record start weight of external container \#1B, \text{89.50 lbs.}
5.2.2 Open liquid side vessel valve. Gas side vessel valve and GSE valves to remain closed.
5.2.3 Open GSE valve and load \approx 1 \text{ gal. (8.3 lbs)} of DM water into liquid side of vessel.
5.2.4 Close all valves at completion of liquid side water load.
5.3 GAS SAMPLING (See figure 3)
5.3.1 Configure GSE valves and gauges as depicted in figure 3.
5.3.2 Verify that ALL valves are closed.
5.3.3 Connect tubing from GAS side GSE press/vent/liquid valve to the inlet of the scrubber apparatus provided by Wiltech (see figure 3).
5.3.4 Place dosimeter badge and TVD monitor in proximity of scrubber apparatus vent.
5.3.5 Open GAS side VESSEL valve.
5.3.6 Slowly open GAS side GSE press/vent/liquid valve to vent GAS side of fuel vessel through the scrubber apparatus. Use GSE press/vent/liquid valve to control vent flow.
5.3.7 Perform Toxic Vapor Detection (TVD) test at scrubber apparatus vent.
   Record: Gas side _____ ppb (ADL 100 ppb).
5.3.8 Continue venting per engineering direction. Record vent time: 45 min.
5.3.9 Close GAS side GSE press/vent/liquid valve.
5.3.10 Collect scrubber fluid. Clean scrubber and reassemble for further testing.
5.3.11 Record GAS side pressure 40 psig.
5.3.12 Connect facility GN2 to GAS side of vessel. Pressurize GAS side to ~80 psig.
5.3.13 Close Gas side Vessel valve.
5.3.14 Allow water on liquid side and GN2 on gas side to remain static in vessel for 1 week.

6.0 OFFLOAD WATER FROM LIQUID SIDE (see figure 2)
STATUS: GAS and LIQUID VESSEL valves CLOSED.
         GAS and LIQUID side GSE press/vent/liquid valves closed.
         liquid side ~1 gal. WATER / gas side ~ 80 psi GN2

WARNING: Diaphragm differential pressure cannot exceed 15 PSID

NOTE: The next steps will offload the DM water from the liquid side of the vessel into an external container. Neutralizer will drain from LIQUID side of fuel vessel into a dry external container #2B.

6.1 Record empty weight of external container #2B; ________ lbs.
6.2 Open Liquid side Vessel valve.
TASK: Fuel Vessel Neutralization Test - VESSEL #2 (S/N 0041)

6.3 Open LIQUID side GSE press/vent/liquid valve and allow DM water to drain from LIQUID side into external container #2B.

6.4 Close LIQUID side GSE press/vent/liquid valve.

6.5 Close Liquid side vessel valve.

6.6 Record final weight (+ 1 gal.) of external container #2B; _______________ lbs.

7.0 Repeat steps 5 and 6 as required per engineering direction.
8.0 Appendix

**FUEL VESSEL #2**

LOAD LIQUID SIDE with DM WATER

Load Liquid Side with ~1 gallon, 8.3 lbs of DM Water

---

**FIGURE 1**
SPECIAL INSTRUCTION

TASK: Fuel Vessel Neutralization Test - VESSEL #2 (S/N 0041)

FUEL VESSEL #2

OFFLOAD LIQUID SIDE

Offload DM Water from Liquid Side into Ext. Cont. #2B

FIGURE 2
TASK: Fuel Vessel Neutralization Test - VESSEL #2 (S/N 0041)

FUEL VESSEL #2

GAS SAMPLE THROUGH SCRUBBER
- Gas Side Pressurized to ~74 psig GN2
- Liquid side zero psig

Per Engineering Direction
Open Gas Side GSE Valve to vent Gas side through scrubber system

FIGURE 3
APPENDIX B: AQUATIC TOXICOLOGY REPORT
Section 1. Overview

The Space Toxicology office was asked to provide a toxicity assessment of 3 candidate chemicals AKGA (alpha-ketoglutaric acid), PCA (3-Pyridazinocarboxylic acid, 1,4,5,6-tetrahydro-1-methyl-6-oxo-), and MPCA (1-Methyl-6-oxo-1,4,5,6-tetrahydropyridazine-3-carboxylic acid). These chemicals are propellant reactants that will be used to decrease toxicity of hydrazine (HZ) and/or monomethylhydrazine (MMH). The subsequent byproducts will be disposed of as treated effluent (wastewater).

Acute toxicity testing was conducted on AKGA, AKGA+HZ and AKGA+MMH. The results from these tests are the focus of this report. The acute toxicity of PCA and MPCA is not available, since these samples have not been tested for toxicity.

A static renewal test was recommended since Static tests provide the most easily obtained measure of acute toxicity. Results of acute toxicity tests should usually be reported in terms of a median lethal concentration (LC50) or median effective concentration (EC50). In some situations, it might be necessary only to determine whether a specific concentration is acutely toxic to the test species or whether the LC50 or EC50 is above or below a specific concentration (ASTM E1192-97). Renewal tests refer to an assay where the test toxicant is replaced (or renewed) at defined intervals while the test species is maintained throughout the evaluation period. Four species of test species (2 freshwater and 2 saltwater) were used in the bioassays.

The four test species used in the bioassays are:
1. Ceriodaphnia dubia (common name: water flea – freshwater species),
2. Cyprinella ledezi (common name: Bannerfin Shiner – freshwater species),
3. Mysisopsis baalia (common name: Mysis Shrimp – saltwater species),
4. Menidia beryllina (common name: Silverside Minnow – saltwater species)

### Section 2. Results

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<th>Client Sample Description</th>
<th>% Sample</th>
<th>Test Species and Survival (%)</th>
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<tr>
<td></td>
<td></td>
<td><em>C. dubia</em></td>
<td><em>C. leeds</em></td>
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<tr>
<td>A, 1M alpha-ketoglutaric acid in water, adjusted with Sodium hydroxide to pH of 8, diluted to 0.002M with water</td>
<td>Control</td>
<td>100</td>
<td>100</td>
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<tr>
<td></td>
<td>6.25</td>
<td>100</td>
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<tr>
<td><strong>LC₅₀</strong></td>
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<td>66%</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>B, 1M alpha-ketoglutaric acid and 1M Hydrazine in water, adjusted with Sodium hydroxide to pH of 8, diluted to 0.002M with water</td>
<td>Control</td>
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</tr>
<tr>
<td></td>
<td>6.25</td>
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<tr>
<td><strong>LC₅₀</strong></td>
<td></td>
<td>71%</td>
<td>&gt;100%</td>
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<tr>
<td>C, 1M alpha-ketoglutaric acid and 1M Monomethyl hydrazine in water, adjusted with Sodium hydroxide to pH of 8, diluted to 0.002M with water</td>
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<td><strong>LC₅₀</strong></td>
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<td>71%</td>
<td>&gt;100%</td>
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*This test was originally conducted on 9/23/10 and repeated on 9/29/10*

Acute toxicity tests conducted by independent laboratory Hydrosphere Research laboratory specifically for NASA’s use through a Wyle Science & Engineering Group subcontract. See Appendix A for full report from Hydrosphere.
Section 3. Discussion

All 3 samples, AKGA, AKGA + HZ and AKGA + MMZ were tested for acute toxicity and show relatively low toxicity when diluted to at least 0.001M. These samples will henceforth be referred to as samples A, B & C.

Sample A (AKGA): 1M AKGA diluted to 0.002M with H₂O and adjusted to a pH of 8 with NaOH.

Sample B (AKGA + HZ) 1M AKGA + HZ diluted to 0.002M with H₂O and adjusted to a pH of 8 with NaOH.

Sample C (AKGA + MMZ) 1M AKGA + MMZ diluted to 0.002M with H₂O and adjusted to a pH of 8 with NaOH.

Freshwater Bioassay – C. dubia (Water flea)

The results of this assay showed the highest level of toxicity with LC 50 survival rates of 66% for Sample A, 71% for Sample B and 71% for sample C.

Sample A

- 0% survival rate at zero dilution or 100% strength of original delivered sample.
- 95% survival rate at 50% strength of original delivered sample.
- 100% survival rate at 25% strength of original delivered sample.
- 95% survival rate at 12.5% strength of original delivered sample.
- 100% survival rate at 6.25% strength of original delivered sample.

Sample A is highly toxic to C. dubia at 0.002M concentration (1M AKGA diluted to 0.002M concentration with H₂O and adjusted to a pH of 8 with NaOH). This concentration is NOT RECOMMENDED for effluent disposal due to its high acute toxicity in the C. dubia species.

Sample A shows very low acute toxicity to zero acute toxicity when diluted to at least 50% of its original concentration strength (0.001M). Sample A is safe for effluent disposal when diluted to at least 50% of the original sample concentration based upon acute toxicity results in C. dubia.

Sample B

- 0% survival rate at zero dilution or 100% strength of original delivered sample.
- 100% survival rate at 50% strength of original delivered sample.
- 100% survival rate at 25% strength of original delivered sample.
- 100% survival rate at 12.5% strength of original delivered sample.
- 100% survival rate at 6.25% strength of original delivered sample.
Sample B is highly toxic to *C. dubia* at 0.002M concentration (1M AKGA + HZ diluted to 0.002M concentration with H₂O and adjusted to a pH of 8 with NaOH). This concentration is NOT RECOMMENDED for effluent disposal due to its high acute toxicity in the *C. dubia* species.

Sample B demonstrates zero acute toxicity when diluted to at least 50% of its original concentration strength (0.001M). Sample B is safe for effluent disposal when diluted to at least 50% of the original sample concentration based upon acute toxicity results in *C. dubia*.

**Sample C**

- 0% survival rate at zero dilution or 100% strength of original delivered sample.
- 100% survival rate at 50% strength of original delivered sample.
- 100% survival rate at 25% strength of original delivered sample.
- 100% survival rate at 12.5% strength of original delivered sample.
- 100% survival rate at 6.25% strength of original delivered sample.

Sample C is highly toxic to *C. dubia* at 0.002M concentration (1M AKGA + MMZ diluted to 0.002M with H₂O and adjusted to a pH of 8 with NaOH). This concentration is NOT RECOMMENDED for effluent disposal due to its high acute toxicity in the *C. dubia* species.

Sample C demonstrates zero acute toxicity when diluted to at least 50% of its original concentration strength (0.001M). Sample C is safe for effluent disposal when diluted to at least 50% of the original sample concentration based upon acute toxicity results in *C. dubia*.

**Freshwater Bioassay – *C. leedsi* (Bannerfin Shiner)**

The results of this assay showed LC 50 survival rates of >100% for Sample A; >100% for Sample B and & >100% for sample C.

**Sample A**

- 90% survival rate at zero dilution or 100% strength of original delivered sample.
- 100% survival rate at 50% strength of original delivered sample.
- 100% survival rate at 25% strength of original delivered sample.
- 100% survival rate at 12.5% strength of original delivered sample.
- 100% survival rate at 6.25% strength of original delivered sample.

Sample A is shows very low acute toxicity to zero acute toxicity to *C. leedsi* at 0.002M concentration (1M AKGA diluted to 0.002M concentration with H₂O and adjusted to a pH of 8 with NaOH). Although this sample shows low toxicity in *C. leedsi*, this concentration is NOT RECOMMENDED for effluent disposal due to its high acute toxicity in the *C. dubia* species.
Sample A shows **very low acute toxicity to zero acute toxicity** when diluted to at least 50% of its original concentration strength (0.001M). Sample A is **safe for effluent disposal** when diluted to at least 50% of the original sample concentration based upon acute toxicity results in *C. leedsi*.

**Sample B**

- 100% survival rate at zero dilution or 100% strength of original delivered sample.
- 100% survival rate at 50% strength of original delivered sample.
- 100% survival rate at 25% strength of original delivered sample.
- 100% survival rate at 12.5% strength of original delivered sample.
- 100% survival rate at 6.25% strength of original delivered sample.

Sample B shows **zero acute toxicity** to *C. leedsi* at **0.002M concentration** (1M AKGA diluted to 0.002M concentration with H2O and adjusted to a pH of 8 with NaOH). **Although this sample shows no toxicity in C.leedsi, this concentration is NOT RECOMMENDED for effluent disposal due to its high acute toxicity in the *C.dubia* species.**

Sample B demonstrates **zero acute toxicity** when diluted to at least 50% of its original concentration strength(0.001M). Sample B is **safe for effluent disposal** when diluted to at least 50% of the original sample concentration based upon acute toxicity results in *C. leedsi*.

**Sample C**

- 100% survival rate at zero dilution or 100% strength of original delivered sample.
- 100% survival rate at 50% strength of original delivered sample.
- 100% survival rate at 25% strength of original delivered sample.
- 100% survival rate at 12.5% strength of original delivered sample.
- 100% survival rate at 6.25% strength of original delivered sample.

Sample C shows **zero acute toxicity** to *C. leedsi* at **0.002M concentration** (1M AKGA diluted to 0.002M concentration with H2O and adjusted to a pH of 8 with NaOH). **Although this sample shows no toxicity in C.leedsi, this concentration is NOT RECOMMENDED for effluent disposal due to its high acute toxicity in the *C.dubia* species.**

Sample C demonstrates **zero acute toxicity** when diluted to at least 50% of its original concentration strength (0.001M). Sample C is **safe for effluent disposal** when diluted to at least 50% of the original sample concentration based upon acute toxicity results in *C. leedsi*.

**Salwater Bioassay – Mysidopsi bahia (Mysid Shrimp)**

The results of this assay showed LC 50 survival rates of >100% for Sample A; >100% for Sample B and & >100% for sample C.
Sample A

- 90% survival rate at zero dilution or 100% strength of original delivered sample.
- 65% survival rate at 50% strength of original delivered sample.
- 90% survival rate at 25% strength of original delivered sample.
- 90% survival rate at 12.5% strength of original delivered sample.
- 95% survival rate at 6.25% strength of original delivered sample.

Sample A is shows very low acute toxicity to zero acute toxicity to *M. bahia* at 0.002M concentration (1M AKGA diluted to 0.002M concentration with H2O and adjusted to a pH of 8 with NaOH).

Although this sample shows low toxicity in *M. bahia*, this concentration is NOT RECOMMENDED for effluent disposal due to its high acute toxicity in the *C. dubia* species. Sample A demonstrated the highest level of toxicity at 50% strength (0.001M) showing a 65% survival rate. While these results do not reflect why lower toxicity was seen at full strength, they are still considered in the overall recommendation.

Sample A shows very low acute toxicity to zero acute toxicity when diluted to at least 25% of its original concentration strength (0.0005M).

Sample A is safe for effluent disposal at all dilution strengths tested in *M. Bahia*.

Sample B

- 80% survival rate at zero dilution or 100% strength of original delivered sample.
- 90% survival rate at 50% strength of original delivered sample.
- 100% survival rate at 25% strength of original delivered sample.
- 70% survival rate at 12.5% strength of original delivered sample.
- 85% survival rate at 6.25% strength of original delivered sample.

Sample B shows a range of toxicity that does not correspond with molar strength; the survival rate of 80% (zero dilution- 0.002M) as the dilution ratio increases to 25% (0.0005M) which showed 100% survival (no toxicity). However, the highest level of toxicity is seen at the next level of dilution of 12.5% strength (0.00025M) showing a 70% survival rate. 85% survival is seen at the highest dilution 6.25% (0.0001M).

Overall sample B shows mild toxicity to *M. bahia*. The weight of evidence in *M. bahia* and results in the freshwater *C. leedsii* demonstrate that Sample B is safe for effluent disposal when diluted to at least 25% of the original sample concentration.

Sample C

- 90% survival rate at zero dilution or 100% strength of original delivered sample.
• 95% survival rate at 50% strength of original delivered sample.
• **85% survival rate at 25% strength of original delivered sample.**
• 95% survival rate at 12.5% strength of original delivered sample.
• **85% survival rate at 6.25% strength of original delivered sample.**

Sample C shows **low toxicity** to *M. bahia* at **0.002M concentration** (1M AKGA diluted to 0.002M concentration with H₂O and adjusted to a pH of 8 with NaOH).

Sample C showed highest toxicity at 25% (0.0005M) & 6.25% (0.0001M) showing an 85% survival rate; this is still considered low toxicity.

Sample C is safe for effluent disposal at all dilution strengths tested in *M. Bahia*.

**Salwater Bioassay – *Menidia beryllina* (Silverside Minnow)**

The results of this assay showed LC 50 survival rates of >100% for Sample A; >100% for Sample B and >100% for sample C.

**Sample A**

• 95% survival rate at zero dilution or 100% strength of original delivered sample.
• 100% survival rate at 50% strength of original delivered sample.
• 100% survival rate at 25% strength of original delivered sample.
• 100% survival rate at 12.5% strength of original delivered sample.
• 100% survival rate at 6.25% strength of original delivered sample.

Sample A shows **very low acute toxicity** to *M. beryllina* at **0.002M concentration** (1M AKGA diluted to 0.002M concentration with H₂O and adjusted to a pH of 8 with NaOH).

Sample A demonstrates **zero acute toxicity** when diluted to at least 50% of its original concentration strength (0.001M). Sample A is safe for effluent disposal at all dilution strengths tested in *M. beryllina*.

**Sample B**

• 95% survival rate at zero dilution or 100% strength of original delivered sample.
• 100% survival rate at 50% strength of original delivered sample.
• 100% survival rate at 25% strength of original delivered sample.
• 100% survival rate at 12.5% strength of original delivered sample.
• 100% survival rate at 6.25% strength of original delivered sample.

Sample B shows **low acute toxicity** to *M. beryllina* at **0.002M concentration** (1M AKGA diluted to 0.002M concentration with H₂O and adjusted to a pH of 8 with NaOH).
Sample B demonstrates zero acute toxicity when diluted to at least 50% of its original concentration strength (0.001M). Sample B is safe for effluent disposal all dilution strengths tested in M. beryllina.

Sample C

- 100% survival rate at zero dilution or 100% strength of original delivered sample.
- 100% survival rate at 50% strength of original delivered sample.
- 95% survival rate at 25% strength of original delivered sample.
- 100% survival rate at 12.5% strength of original delivered sample.
- 95% survival rate at 6.25% strength of original delivered sample.

Sample C shows zero acute toxicity to M. beryllina at 0.002M concentration (1M AKGA diluted to 0.002M concentration with H2O and adjusted to a pH of 8 with NaOH). Sample C shows very low to no acute toxicity when diluted to at least 50% of its original concentration strength (0.001M). Sample C is safe for effluent disposal at all dilution strengths tested in M. beryllina.

Section 5. Conclusion

It is recommended that all solutions (A, B & C) be diluted to 0.001M concentration, or 50% of what was delivered at full strength for effluent disposal. This is based upon zero survival in the C. dubia species (water flea) when exposed to all samples at 0.002M concentration. All other dilutions show mild to no acute toxicity in all species tested. Raw test data is included in Hydrosphere report in Appendix A.

It is further recommended that chronic toxicity testing (7 day chronic static renewal) to determine the long term toxic effects.

We appreciate the opportunity to assist Kennedy Space Center in determining acute toxicity of candidate chemicals. If you have any further questions regarding this report and recommendations, please contact us.

Prepared & signed by:

Noreen Khan-Mayberry, Ph.D.
NASA Space Toxicologist
APPENDIX C: NEW MEXICO HIGHLANDS UNIVERSITY PATENT
“METHODS AND SYSTEMS FOR REMEDIATING HYDRAZINE-
CONTAMINATED EQUIPMENT AND/OR SURFACES”
Title: METHODS AND SYSTEMS FOR REMEDIATING HYDRAZINE-CONTAMINATED EQUIPMENT AND/OR SURFACES

Inventors: Merritt C. Helvenston, Las Vegas, NM (US); Raúl A. Martínez, Santa Fe, NM (US); José C. De Baca, Las Vegas, NM (US); John J. Juarez, Las Vegas, NM (US)

Assignee: New Mexico Highlands University, Las Vegas, NM (US)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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Filed: Aug. 1, 2002
Prior Publication Data

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Primary Examiner—Shailendra Kumar
(74) Attorney, Agent, or Firm—Luis M. Ortiz; Kermit D. Lopez; Ortiz & Lopez, PLLC

ABSTRACT
Methods of and systems for remediating hydrazine spills, solutions and hydrazine-contaminated objects including areas thereof. Initially, an aqueous solution comprising a dicarbonyl-compound can be prepared. The aqueous solution can then be provided for application to an object contaminated with a hydrazine-group compound. The hydrazine group compounds are converted to a stable organic compound as a result of a reaction with the dicarbonyl-compound and hydrazine group compound. Conversion assists in the remediation of the hydrazine group compound from the object. The stable organic compound produced as a result of the reaction between the dicarbonyl-compound and hydrazine group compound can then be treated with a metal catalyst and hydrogen to produce glutamine or a derivative thereof. Both the stable organic compound and glutamine can undergo microbiological degradation without further remedial intervention.

20 Claims, 4 Drawing Sheets
Fig. 1

Fig. 2
Fig. 3

Fig. 4
**Fig. 5**

1. PREPARE SOLUTION
2. SOLUTION INCLUDES A DICARBONYL COMPOUND
3. AQUEOUS SOLUTION APPLIED TO HYDRAZINE-CONTAMINATED OBJECT OR SPILL
4. REACTION OF HYDRAZINE AND DICARBONYL COMPOUND
5. CONVERSION OF HYDRAZINE TO A STABLE ORGANIC MOLECULE

**Fig. 6**

1. INITIATE TREATMENT OF STABLE ORGANIC COMPOUND
2. ISOLATE SOLID MATERIAL OR STABLE ORGANIC COMPOUND
3. REACTION OF METAL CATALYST AND HYDROGEN WITH STABLE ORGANIC COMPOUND
4. PRODUCTION OF GLUTAMINE OR GLUTAMINE DERIVATIVE
5. COMPLETE DIGESTION WITH SOIL MICROBES
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**HEAT OF Rxn: 2KG & HZ**

\[
y = 1.5881x - 0.1951 \]

\[
R^2 = 0.9913
\]

*Fig. 7*
METHODS AND SYSTEMS FOR REMEDIATING HYDRAZINE-CONTAMINATED EQUIPMENT AND/OR SURFACES

TECHNICAL FIELD

The present invention is generally related to decontamination and remediation methods and systems. The present invention is also related to hydrazine (H₂) and hydrazine-based compounds, such as monomethylhydrazine (MMH) or 1,1-dimethylhydrazine (UDMH). The present invention additionally relates to methods and systems for remediating hydrazine from hydrazine-contaminated objects, including hydrazine-contaminated areas (hereof). The present invention is also related to dicarbonyl compounds, including dialdehydes, diketones, aldehyde-ketones, aldehyde-acids, aldehyde-esters, keto-acids and keto-esters. The present invention is specifically related to the involvement of the following compounds in remediation of hydrazine: 2-keto-glutaric acid (2KGA), 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCAc), and glutamine.

BACKGROUND OF THE INVENTION

An environmentally conscious remediation process for the emergency treatment/disposal of hydrazine fuels spills is needed. The highly toxic hydrazine family of fuels is utilized as rocket propellants in virtually all U.S. space programs including both launch vehicles and satellite propulsion systems. Since large volumes of these fuels are annually shipped all over the United States, accidental major spills of these propellants could potentially occur near populated communities during transport over the nation’s highways. In addition, smaller spills could also occur during launch operations and storage at the user facilities.

An inadvertent release of hydrazine to the environment can be extremely hazardous due to the mutagenic nature of such chemical compounds, which can induce tumor growth in human beings years following even a low level exposure. Hydrazine compounds are classified as suspected human carcinogens and their permissible levels of exposure have been reduced to 10 parts per billion (ppb). A hydrazine spill remediation process, to be developed, should not only destroy the propellant fuel but also should not generate other hazardous materials. An in-situ processing method involving direct application of the treatment reagent or process to the spill is preferred.

Currently, a small hydrazine spill, occurring at launch facilities, is washed down with water. The diluted water is treated with an oxidizing agent such as sodium hypochlorite or alternatively, the hydrazine containing water is transported to a hazardous waste facility for incineration. The former treatment method with UDMH is unsatisfactory in that a strong carcinogen, n-Nitrosodimethylamine, is generated. In addition, the hypochlorite oxidation of both UDMH and MMH yields volatile halogenated hydrocarbons, which are priority pollutants. In the case of a spill on soil, the contaminated material is transported for disposal at an incineration facility.

An accident involving a transport trailer may spill four to five thousand gallons of the hydrazine fuel, whereas a catastrophic failure of a fuel storage vessel at a launch facility may release twenty thousand gallons or more of the propellant. A rail car derailment resulting in a hydrazine (i.e., commercial use) release occurred in Southern California several years ago.

A major spill of a hydrazine transport trailer could potentially result in legal action amounting to millions of dollars. Additionally, minor hydrazine spills resulting from leaks or other causes are not unusual during space launch operations. These spills, which can result in evacuations and expensive launch delays, are washed down into the waste fuel tank for later disposal. A greater concern is a major accidental spill of a hydrazine transport trailer, occurring off-site during shipment of the propellant over the public highways. Although such an incident has not occurred to date, a treatment/disposal process should be developed and be available when needed. An environmentally conscious, inexpensive method for the complete conversion of the spilled hydrazine into innocuous materials is needed. This treatment process may entail chemical reactions, bioremediation, or other methods such as pyrolysis, photolysis, or catalysis.

Hydrazine group compounds, including hydrazine, monomethylhydrazine (MMH), and 1,1-dimethylhydrazine (UDMH), are widely used as fuels (e.g., in rocket propulsion systems and fighter jets), corrosion inhibitors (e.g., in nuclear industry), catalysts, emulsifiers, or dyes. Hydrazine is typically utilized as a monopropellant in rocket propulsion applications because it can readily ignite when placed in contact with noble metal catalysts. Hydrazine is particularly popular with satellite companies because hydrazine, when used as a monopropellant, saves space, complexity and weight. Hydrazine and hydrazine-based compounds can also function as a precursors in the synthesis of a number of drugs, polymers, plasticizers and pesticides. As indicated above, however, hydrazine is also extremely toxic and dangerous. Note that as utilized herein, the term “hydrazine” is generally analogous to the chemical formula N₂H₄, while the term monomethylhydrazine (MMH) is generally analogous to the chemical formula CH₃N₂H₄. Additionally, the term dimethylhydrazine (UDMH) can be referred to by the chemical formula (CH₃)₂NNH₂.

The U.S. Occupational Safety and Health Administration (OSHA), for example, requires the prevention of exposure to hydrazine and its derivatives at concentrations greater than one part per million (1.3 mg/m³). Hydrazine and hydrazine derivatives are readily combustible reducing agents that react violently with oxidizing agents and thus present a serious safety hazard. Hydrazine and hydrazine derivatives are well known components of liquid rocket fuels in conjunction with an oxidizing agent such as dinitrogen tetroxide. Thus, at facilities where liquid-fueled rockets are prepared for flight, there is a particular need to provide reliable and sensitive methods and systems for decontaminating objects, such as fighter jets and maintenance equipment thereof, and exposed environments which can become contaminated with hydrazine. Ideally, such hydrazine remediation methods and systems should also have a limited, if negligible effect on the environment.

Many reactions of hydrazine with dicarbonyl compounds are known. For example, Gerd Kaupp and Jens Schmeyers have investigated hydrazine reactivity, as reported in “Solid-State Reactivity of the Hydrazine-Hydroquinone Complex,” J. Phys. Org. Chem. 2000, 13: pp. 388–394, which is incorporated herein by reference. Kaupp and Schmeyers investigated the solid-state reactivities of the hydrazine-hydroquinone 1:1 complex and of hydrazine hydrochloride with solid aldehydes, ketones, carboxylic acids, thiocyanate, and 4-nitrophenyl isothiocyanate. Kaupp and Schmeyers reported that only the hydrazine complex provides quantitative additions, condensations, ring openings and ring closures. The solid-state mechanisms were investigated...
by atomic force microscopy (AFM) and far-reaching anisotropic molecular movements were correlated with the crystal packing, both on the hydrazine complex surface and on the surface of two benzaldehydes. Based on this research Knapp and Schmeyers concluded that the hydrazine can move into the aldehyde crystals for chemical reaction without melting. Knapp and Schmeyers also reported that characteristic surface features could be created by common phase rebuilding and phase transformation on both the hydrazine-donating and -accepting crystals.

The present inventors have examined compounds that will react with hydrazine rapidly and quantitatively. The present inventors have investigated several compound classes in order to tailor these derivatives of hydrazine for facile detection (i.e., to required levels) by current analytical methods.

Decontamination methods and systems can be separated into three major categories: physical removal, chemical inactivation, or a combination of both physical and chemical means. Wiping, sweeping, scraping, blowing, vacuuming, rinsing with water, and steam cleaning are all examples of physical methods for the removal of contaminants. In many cases, physical removal of gross contamination is an initial step in decontamination and remediation thereof. Physical removal of gross contamination usually is not sufficient to reduce contaminant concentrations to background levels. In most cases, physical removal is followed by a wash and rinse process using cleaning solutions. These cleaning solutions often dissolve contaminants and keep them in a solution until they can be rinsed away. Rinsing removes contaminants from an affected object or area through the dual process of dilution and solubilization. Multiple rinses with clean water can remove more contaminants than a single rinse.

Despite use of present cleaning solutions and rinsing procedures, contaminants generally still persist after remediation, although in a diluted form, and can be relocated to areas surrounding the object or area targeted for decontamination. Such is the case where hydrazine is diluted and allowed to run off along a surface (e.g., earth or pavement) away from the decontamination zone, or worse is absorbed into the earth and into water aquifers.

More effective methods and systems are needed for remediation of hydrazine from contaminated objects, solutions, and areas. The present inventors recognize this need and have invented method of and systems for hydrazine remediation.

BRIEF SUMMARY OF THE INVENTION

The following summary of the invention is provided to facilitate an understanding of some of the innovative features unique to the present invention, and is not intended to be a full description. A full appreciation of the various aspects of the invention can be gained by taking the entire specification, claims, drawings, and abstract as a whole.

It is therefore one aspect of the present invention to provide improved remediation methods and systems.

It is therefore another aspect of the present invention to provide methods and systems for remediating hydrazine from hydrazine contaminated objects and areas thereof.

It is yet another aspect of the present invention to provide an aqueous solution prepared from a dicarbonyl compound.

It is yet another aspect of the present invention to provide a cleaning solution that includes a dicarbonyl compound for converting hydrazine to a stable organic compound.

It is still an additional aspect of the present invention to treat a stable organic compound produced as a result of a reaction between a dicarbonyl compound and a hydrazine with a metal catalyst and hydrogen to produce glutamine or a derivative thereof.

The above and other aspects of the invention can be achieved as will now be described. Methods and systems for remediating hydrazine from hydrazine-contaminated objects (including areas) are disclosed herein. Initially, an aqueous solution comprising a dicarbonyl compound can be prepared. Such a dicarbonyl compound can be, for example, 2-ketoglutaric acid. (Note that the term “dicarbonyl compound” as utilized herein generally refers to a dicarbonyl diketone, aldehyde, diketone, aldehyde-ketone, aldehyde-acid, aldehyde-ester, keto-acid and/or a keto-ester.) The aqueous solution can then be applied to an object contaminated with a hydrazine group compound, such that the hydrazine group compound is converted to a stable organic compound as a result of a reaction of the dicarbonyl compound and hydrazine group compound in order to remediate the hydrazine group compound from the object. Such a hydrazine group compound can be, for example, hydrazine (H₂N), monoaminedihydrazide (MMH), or 1,1 diamethylenehydrazine (UDMH).

The solution, which may be aqueous, can be applied to the object contaminated with the hydrazine group compound following an initial attempt at a physical removal (e.g., wiping, sweeping, scraping, blowing, vacuuming, rinsing with water, steam cleaning, etc.) of the hydrazine group compound from the area, object or solution. Alternatively, the aqueous solution can be applied directly to the object, thereby skipping this physical removal step. The solution can be prepared in the form of a cleaning solution. Application of such an aqueous or cleaning solution to the object can occur by rinsing the object with the solution. Finally, the stable organic compound produced as a result of the reaction between the dicarbonyl compound and hydrazine group compound can then be treated by microbiological degradation or with a metal catalyst and hydrogen to produce glutamine or a derivative thereof. Glutamine can then be permitted to undergo microbiological degradation thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying figures, in which like reference numerals refer to identical or functionally-similar elements throughout the separate views and which are incorporated in and form part of the specification, further illustrate the present invention and, together with the detailed description of the invention, serve to explain the principles of the present invention.

FIG. 1 illustrates a schematic diagram depicting a reaction between a dicarbonyl compound and a complex of hydrazine;

FIG. 2 depicts a schematic diagram illustrating a production of glutamine;

FIG. 3 illustrates a schematic diagram depicting a reaction of 2-ketoglutaric acid, which provides a near quantitative conversion of hydrazine to a 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid, in accordance with a preferred embodiment of the present invention;

FIG. 4 depicts a schematic diagram illustrating the reaction of MMH and UDMH with 2-ketoglutaric acid followed
by hydrogenation, in accordance with a preferred embodiment of the present invention;

FIG. 5 illustrates a high-level flow chart of operations illustrating logical operational steps, which can be implemented in accordance with a preferred embodiment of the present invention;

FIG. 6 depicts a high-level flow chart of operations illustrating logical operational steps, which can be implemented in accordance with a preferred embodiment of the present invention; and

FIG. 7 illustrates a plot of experimental data, which can be collected in accordance with an alternative embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The particular values and configurations discussed in these non-limiting examples can be varied and are cited merely to illustrate an embodiment of the present invention and are not intended to limit the scope of the invention.

FIG. 1 illustrates a schematic diagram 100 depicting a reaction between a dicarbonyl-compound and a complex of hydrazine. Two cases 102 and 104 are illustrated in FIG. 1. In each case, the solid compounds were ball milled at room temperature in a ratio of 2:1 (dicarbonyl-compound to hydrazine complex) and a near quantititative yield was obtained. The 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonylic acid formed from the reaction of 2-ketoglutaric acid and the hydrazine complex comprises a high melting solid (i.e., melting point within a range of approximately 106°C - 198°C).

FIG. 2 depicts a schematic diagram 200 depicting the treatment of hydrazine waste to glutamine or a derivative thereof, in accordance with a preferred embodiment of the present invention. The hydrogenization of pyridazine using 5% Pd/C can provide glutamine in a 45% yield. Although this pyridazine is not easily biodegraded, the present inventors believe that glutamine can be utilized as a plant nutrient or that it is easily biodegradable. Glutamine can be specifically utilized as a source of energy and for nucleotide synthesis by all rapidly dividing cells. Thus, rather than acting as an environmental hazard, glutamine or a derivative can actually benefit plants exposed to it during a hydrazine remediation process, as described herein.

FIG. 3 illustrates a schematic diagram 300 depicting a reaction of 2-ketoglutaric acid, which provides a near quantitative conversion of hydrazine to a 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid, a preferred embodiment of the present invention. In general, the chemical transformation depicted in schematic diagram 300 of FIG. 3 allows for the removal of hydrazine from aqueous solutions generated by the decontamination processes described herein. The reaction with concentrated hydrazine also can provide the desired product with some evolution of heat. The solubility of the compound in water allows for the separation of most of this adduct by a simple filtration.

The MSDoS for 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid does not list any known acute toxicities and thus it should be a nonhazardous waste. However the ideal situation would be to find a method for the safe destruction or remediation of the 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid. The use of microbes (e.g., a pseudomonas species found in the soil) as a method for the metabolism of a nitrogen-nitrogen bond can thus be implemented, in accordance with the methods and systems described herein. After about ten minutes thereafter, a white precipitate can be formed, which is generally characterized by Nuclear Magnetic Resonance to be the expected product, 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carbonic acid. The reaction generally appears to be a quantitative reaction with the aqueous hydrazine.

FIG. 4 depicts a schematic diagram 400 illustrating the reaction of MMH and UDMH with 2-ketoglutaric aid followed by hydrogenation, in accordance with a preferred embodiment of the present invention. The schematic diagram 400 depicted in FIG. 4 can be implemented by adding a sample of the hydrazine derivative to a slight excess of an aqueous solution of 2-ketoglutaric acid. Note that the solution described herein (i.e., which includes a dicarbonyl compound) can be prepared as aqueous solution or a non-aqueous solution, depending on particular desired applications. Thus, the use of an aqueous solution is not considered a limiting feature of the present invention. Rather the use of an aqueous solution represents merely one possible embodiment of the present invention. Non-aqueous solutions represent another possible embodiment of the present invention.

FIG. 5 illustrates a high-level flow chart 500 of operational steps, which can be implemented in accordance with a preferred embodiment of the present invention. As illustrated at block 502, a solution can be prepared that includes, as indicated at next at block 504, a dicarbonyl-compound.

Each solution can be prepared in the form of a cleaning solution. The solution can be an aqueous solution or a non-aqueous solution. An example of a dicarbonyl-compound that can be utilized in accordance with the methods and systems of the present invention is a keto-acid, such as a 2-ketogluartic acid. Once the solution has been prepared, it can be provided for utilization in hydrazine remediation.

As indicated next at block 506, the solution as provided via processing of the operations described at blocks 502 and 504 can be applied to an object contaminated with a hydrazine group compound. Application can occur, for example, through a rinsing of the hydrazine contaminated object with the solution that includes the dicarbonyl-compound. Examples of hydrazine group compounds that may contaminate an object or area thereof can include simply hydrazine, MMH, or UDMH.

It can be appreciated by those skilled in the art that the application of the dicarbonyl compound solution to the hydrazine contaminated object and/or area (e.g., a hydrazine spill) thereof can take place following an initial attempt at a physical removal of the hydrazine group compound from the object or area thereof. As indicated previously, wiping, sweeping, scraping, blowing, vacuuming, rinsing with water, and steam cleaning are all examples of physical methods for the removal of contaminant. Such physical removal techniques can thus occur in tandem with the application of the dicarbonyl-compound solution described herein.

A reaction can then occur, as illustrated at block 508 between the hydrazine group compound and the dicarbonyl-compound. As a result of this reaction, the hydrazine group compound is converted to a stable organic compound, as indicated at block 510, in order to remediate the hydrazine group compound from the object. Thus, based on the foregoing it can be appreciated that the present invention allows for the use of a solution of a dicarbonyl-compound (e.g., 2-ketoglutaric acid) for the treatment of hydrazine waste. Prior art solutions for the treatment of hydrazine generally involve solubilization and dilution processes. The hydrazine remediation methods and systems described herein do not only involve solubilization and dilution. Rather, the present invention involves a conversion of hydrazine to a stable organic compound. Such a conversion can occur after application of the dicarbonyl-compound solution through the use of solubilization and dilution processes, among others. Note that the step of treating a stable organic compound with a
metal catalyst and hydrogen to produce glutamine, can also includes the step of producing a derivative of glutamine, rather than simply glutamine.

FIG. 6 depicts a high-level flow chart 600 of operations illustrating logical operational steps, which can be implemented in accordance with a preferred embodiment of the present invention. Once the stable organic compound has been created as a result of the reaction between hydrazine and the dicarbonyl compound, the stable organic compound can be treated with a metal catalyst and hydrogen to produce glutamine and/or a derivative thereof.

Thus, as indicated at block 602, treatment of the stable organic compound can be initiated. The compound (or solid material formed thereof) can be isolated as indicated at block 603. A decision can be made, as indicated at block 604, to determine whether or not the stable organic, should be treated at another location, or treated directly, as indicated by processes described at blocks 606 to 610. If it is determined to isolate the stable organic compound for treatment at another location, then the operation indicated at block 610 can be processed elsewhere. As indicated at block 610, any remaining material (i.e., the stable organic compound) can simply be digested via soil microbes.

If necessary, however, the stable organic compound can be treated with a metal catalyst and hydrogen as illustrated at block 606, which follows decision block 604. As depicted at block 606, a reaction can occur between the metal catalyst and hydrogen and the stable organic compound. As a result of this reaction, glutamine or a glutamine derivative can be produced, as depicted at block 608. Finally, as illustrated at block 610 complete digestion with soil microbes can occur. For example, the reaction of hydrazine with a 2-ketoglutaric acid, followed by hydrogenation, can yield glutamic acid, a compound which has been utilized to enhance fertilizer use.

A system for remediating hydrazine in accordance with the present invention thus generally includes a solution that can be formed from a dicarbonyl compound, and an application mechanism for applying the solution to an object or area (e.g., a spill) contaminated with a hydrazine group compound. A dicarbonyl compound can be implemented as a solution (e.g., an aqueous solution), which can then be applied to an object or area contaminated with a hydrazine group compound. Such a hydrazine group compound can include at least one of the following: hydrazine (H₂N), monomethylhydrazine (MMH), and 1,1-dimethylhydrazine (UDMH). The application mechanism itself can be implemented as a rinsing mechanism for rinsing the object contaminated with the hydrazine group compound with the solution. Such a rinsing mechanism can be, for example, a hose or other fluid delivery device and/or system. The application mechanism can also be implemented in the form of objects or devices such as sponges, pads, spray bottles, and so forth. A metal catalyst and hydrogen can thus be applied to the contaminated objects with the application mechanism to produce glutamine thereof.

FIG. 7 illustrates a plot 700 of experimental data, which can be collected in accordance with an alternative embodiment of the present invention. Note that a graph 704 is associated with chart 702, which depicts such experimental data. Note that the experimental techniques utilized to collect the data depicted in FIG. 7 represent merely one possible embodiment of the present invention. Those skilled in the art can appreciate that many other embodiments can be implemented. An insulated reaction vessel can be utilized to ensure that heat evolution will not be underestimated. A 1-cup Styrofoam™ cup equipped with stir bar and thermometer, 75 ml of 2-ketoglutaric acid solution can be added and stirred a few minutes before the addition of a 1.1 eq of hydrazine monohydrate. The temperature can be monitored at 30 sec to 1-minute intervals for 15 minutes. After about 45 seconds, seed crystals of 6-oxo-1,4,5,6-tetrahydropridazin-3-carboxylic acid can be added to the solution; otherwise two exotherms can be observed (i.e., one large temperature rise immediately and second smaller one after about 10 minutes associated with the heat of crystallization). Initial temperatures can be about 18°C, and the highest final temperature can be approximately 84°C, although the same boiling occurred in the mixing zone as the hydrazine can be added to the 41.5% 2-ketoglutaric acid solution.

Hydrazine monohydrate (98%), deuterium oxide and dimethylsulfoxide-d₆ can be utilized, along with 6-oxo-1,4,5,6-tetrahydropridazin-3-carboxylic acid (97%) and 2-ketoglutaric acid (98%) to results. The reaction of solid 2-ketoglutaric acid with hydrazine monohydrate can generally be produced as follows: A 2-ketoglutarate (450 mg) can be combined with hydrazine monohydrate (70 μL), which produces heat immediately. Extraction of the reaction residue with water may only partially dissolved the solid, and the solution provided an NMR spectrum consistent with the expected product. The remaining solid can be dissolved in a mixture of MeOH, chloroform and DMSO, and can possess NMR spectra consistent with the expected product.

Note that a product from one of the aforementioned reactions can be derived with N,N-bis(trimethylsilyl)trifluoroacetamide at room temperature and analyzed by both EI and CI mass spectrometry. In the EI spectrum, several chromatographic peaks can be observed with the largest corresponding to the 6-oxo-1,4,5,6-tetrahydropridazin-3-carboxylic acid. One peak can be viewed for in a CI chromatogram with a mass spectrum dominated by 287 m/z (M+1). The mass balance of the product can be high and the melting point low, presumably owing to inclusion of the hydrazinium salt of the product. Addition of a 10% equivalent of 2-ketoglutaric acid to consume excess hydrazine, and recrystallization from hot water can afford a material with the same melting point as the standard material, 194-196°C. NMR chemical shifts can vary with concentration and pH, and are generally identical to the standard material: 1H (δ, D₂O, MeOH ref. 3.30 ppm, 300 MHz) 2.56 (2H, t, J = 8.9 Hz), and 2.85 (2H, t, 8.9 Hz) ppm; 13C (δ, D₂O, MeOH set to 49.0 ppm, 75 MHz) 20.6, 24.9, 146.0, 166.1, and 170.9 ppm.

The present invention offers a number of advantages. The removal of hydrazine according to the methods and systems described herein will allow for the remediation of hydrazine to useful by-products or biodegradable forms, which not only provide environmental benefits, but also reduces the cost of hydrazine waste disposal. The methods and systems described here can be utilized at airports, military facilities, and rocket launches and space vehicle-launching pads (e.g., the Space Shuttle). In particular, the present invention can also find use in orbiting facilities such as the International Space Station in which hydrazine exposure can be problematic. The present invention has particularly useful applications to wash water cleanup and spill abatement.

The embodiments and examples set forth herein are presented to best explain the present invention and its practical application and to thereby enable those skilled in the art to make and utilize the invention. Those skilled in the art, however, will recognize that the foregoing description and examples have been presented for the purpose of illustration and example only. Other variations and modifications of the present invention will be apparent to those of skill in the art, and it is the intent of the appended claims that
such variations and modifications be covered. The description as set forth is not intended to be exhaustive or to limit the scope of the invention. Many modifications and variations are possible in light of the above teaching without departing from the spirit and scope of the following claims.

It is contemplated that the use of the present invention can involve components having different characteristics. It is intended that the scope of the present invention be defined by the claims appended hereto, giving full cognizance to equivalents in all respects.

The invention claimed is:

1. A method for neutralizing harmful effects of hydrazine contamination, said method comprising the steps of:
   providing an aqueous solution comprising a 2-ketoglu- 
   taric acid, said solution adapted for application to
   hydrazine contaminated equipment and/or ground sur-
   faces; and
   applying said solution to equipment and/or ground sur-
   faces contaminated with a hydrazine group compound,
   wherein said hydrazine group compound is converted
to a stable organic compound as a result of a reaction
between said solution comprising said 2-ketoglutaric acid
and said hydrazine group compound.

2. The method of claim 1 wherein the step of applying
   said solution to an equipment and/or ground surfaces con-
   taminated with a hydrazine group compound, further
   comprises the step of:
   applying said aqueous solution to said object contami-
   nated with said hydrazine group compound following
   physical removal of debris also contaminated with said
   hydrazine group compound from said equipment and/or
   ground surfaces.

3. The method of claim 1 wherein the step of applying
   said aqueous solution to an equipment and/or ground sur-
   faces contaminated with a hydrazine group compound, fur-
   ther comprises the step of:
   using an application mechanism to rinse said equipment
   and/or ground surfaces contaminated with said hydra-
   zine group compound with said aqueous solution.

4. The method of claim 1 further comprising the step of:
   treating said stable organic compound with a metal cata-
   lyst and hydrogen to produce glutamine thereof,
   wherein said hydrazine group compound is converted
to a stable organic compound as a result of a reaction
of said 2-ketoglutaric acid and hydrazine group com-
 pound.

5. The method of claim 1 wherein said hydrazine group
   compound comprises monomethylhydrazine (MMH).

6. The method of claim 1 wherein said hydrazine group
   compound comprises 1,1 dimethylhydrazine (UDMH).

7. The method of claim 1 wherein said aqueous solution
   is a cleaning solution.

8. A method for treating hydrazine contaminated equip-
   ment and/or ground surfaces comprising the steps of:
   providing a cleaning solution that includes 2-ketoglutaric
   acid; and
   rinsing at least one of equipment or ground surfaces con-
   taminated by a hydrazine group compound with said cleaning solution.

9. A method using a dicarboxyl-compound for decontami-
   nating equipment and/or ground surfaces accidentally con-
   taminated in an operational environment or during an oper-
   tional activity with a hydrazine group compound, said
   method comprising the steps of:
   providing an application mechanism adapted to manage
   use of an aqueous cleaning solution said aqueous
   cleaning solution comprising 2-ketoglutaric acid; and
   applying said aqueous cleaning solution to equipment
   and/or ground surfaces contaminated with a hydrazine
   group compound, wherein said hydrazine group com-
   pound is converted to a stable organic compound as a
   result of a chemical reaction between said aqueous
   solution and said hydrazine group compound.

10. A system for treating hydrazine-contaminated equip-
    ment or ground surfaces, said system comprising:
    an aqueous solution comprising a 2-ketoglutaric acid; and
    an application mechanism for enabling a user to manage
    the application of said aqueous solution to equipment
    or ground surfaces accidentally contaminated with a
    hydrazine group compound, wherein said hydrazine
    group compound is converted to a stable organic
    compound as a result of a reaction between said aqueous
    solution comprising said dicarboxyl-compound and
    said hydrazine group compound.

11. The system of claim 10 wherein said hydrazine group
    compound comprises at least one of the following:
    hydrazine (H2), monomethylhydrazine (MMH), and 1,1 dim-
    ethylhydrazine (UDMH).

12. The system of claim 10 wherein said application mechanism
    further comprises:
    a rinsing mechanism for rinsing said object contaminat-
    ed with said hydrazine group compound with said aqueous
    solution.

13. The system of claim 10, further comprising a metal
catalyst and hydrogen, said metal catalyst and hydrogen
    is applied to said contaminated objects with said application
    mechanism to produce glutamine thereof.

14. The system of claim 13 wherein said hydrazine group
    compound comprises at least one of the following: hydra-
    zine (H2), monomethylhydrazine (MMH), and 1,1 dimethyl-
    hydrazine (UDMH).

15. The system of claim 10 wherein said hydrazine group
    compound comprises hydrazine.

16. The system of claim 1 wherein said hydrazine group
    compound comprises monomethylhydrazine (MMH).

17. The system of claim 10 wherein said hydrazine group
    compound comprises 1,1 dimethylhydrazine (UDMH).

18. The system of claim 10 wherein said aqueous solution
    comprises a cleaning solution.

19. A system for remediating equipment and/or ground
    surfaces contaminated with hydrazine, said system compris-
    ing:
    a cleaning solution comprising a 2-ketoglutaric acid;
    a metal catalyst and hydrogen; and
    a rinsing mechanism for rinsing said equipment and/or
    ground surfaces contaminated with a hydrazine group
    compound with said cleaning solution, said metal cata-
    lyst and said hydrogen.

20. A system for decontaminating equipment and/or
    ground surfaces contaminated with a hydrazine group
    compound, said system comprising:
    an aqueous solution managed by an application mecha-
    nism and comprising 2-ketoglutaric acid; and
    an application mechanism for enabling a user in the
    application of said aqueous solution to equipment and/or
    ground surfaces accidentally contaminated with a
    hydrazine group compound, wherein said hydrazine
    group compound is converted to a stable organic
    compound as a result of a reaction between said aqueous
    solution comprising said 2-ketoglutaric acid and said
    hydrazine group compound.

* * * * *

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APPENDIX D: INDIVIDUAL KINETIC PLOTS FOR DETERMINATION OF PSEUDO FIRST ORDER REACTION RATE CONSTANTS
Individual MMH Degradation Plots

Pseudo 1st Order Degradation Plot of MMH in Excess AKGA-Trial 1

\[ y = -0.0041x + 8.747 \]
\[ R^2 = 0.967 \]

Reaction time, sec

\( \ln([\text{MMH}]) \)
**Pseudo 1st Order Degradation Plot of MMH in Excess AKGA-Trial 2**

\[ y = -0.0051x + 8.4345 \]

\[ R^2 = 0.9862 \]

**Pseudo 1st Order Degradation Plot of MMH in Excess AKGA-Trial 3**

\[ y = -0.0059x + 9.1512 \]

\[ R^2 = 0.9439 \]
**Individual HZ Degradation Plots**

**Pseudo 1st Order Degradation Plot of MMH in Excess AKGA-Trial 4**

\[ y = -0.0052x + 9.1232 \]

\[ R^2 = 0.9934 \]

**Pseudo 1st Order Degradation Plot of HZ in Excess AKGA-Trial 1**

\[ y = -0.0009x + 8.4449 \]

\[ R^2 = 0.8553 \]
Pseudo 1st Order Degradation Plot of HZ in Excess AKGA-Trial 2

\[ y = -0.0011x + 8.5201 \]
\[ R^2 = 0.8723 \]

Pseudo 1st Order Degradation Plot of HZ in Excess AKGA-Trial 3

\[ y = -0.0014x + 8.862 \]
\[ R^2 = 0.9664 \]
Individual mPCA Formation Plots

Pseudo 1st Order Formation Plot of mPCA in Excess AKGA- Trial 1

\[ y = 0.0056x - 12.918 \]
\[ R^2 = 0.9984 \]

Pseudo 1st Order Formation Plot of mPCA in Excess AKGA- Trial 2

\[ y = 0.0054x - 12.637 \]
\[ R^2 = 0.9764 \]
Pseudo 1st Order Formation Plot of mPCA in Excess AKGA- Trial 3

\[ y = 0.0057x - 12.829 \]
\[ R^2 = 0.9969 \]

Pseudo 1st Order Formation Plot of mPCA in Excess AKGA-Trial 4

\[ y = 0.0067x - 13.144 \]
\[ R^2 = 0.9839 \]
Pseudo 1st Order Formation Plot of mPCA in Excess AKGA- Trial 5

\[ y = 0.0078x - 13.596 \]
\[ R^2 = 0.9957 \]

Pseudo 1st Order Formation Plot of mPCA in Excess AKGA- Trial 6

\[ y = 0.0075x - 13.663 \]
\[ R^2 = 0.9732 \]
Pseudo 1st Order Formation Plot of mPCA in Excess AKGA- Trial 7

\[ y = 0.0063x - 13.274 \]
\[ R^2 = 0.9946 \]

Pseudo 1st Order Formation Plot of mPCA in Excess AKGA- Trial 8

\[ y = 0.0064x - 13.509 \]
\[ R^2 = 0.9844 \]
Individual PCA Formation Plots

Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 1

\[ y = 0.0061x - 11.905 \]
\[ R^2 = 0.9936 \]

Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 2

\[ y = 0.0064x - 11.89 \]
\[ R^2 = 0.9948 \]
Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 3

\[ y = 0.008x - 12.194 \]
\[ R^2 = 0.9743 \]

Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 4

\[ y = 0.0087x - 12.788 \]
\[ R^2 = 0.9945 \]
Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 5

y = 0.0065x - 11.279
R^2 = 0.9801

Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 6

y = 0.008x - 11.488
R^2 = 0.9817
Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 7

$y = 0.0082x - 11.56$
$R^2 = 0.9775$

Pseudo 1st Order Formation Plot of PCA in Excess AKGA-Trial 8

$y = 0.0095x - 12.002$
$R^2 = 0.9626$
REFERENCES


