

INCORPORATION OF α -KETOGLUTARIC ACID AS A FIXED BED SCRUBBER MEDIA FOR THE NEUTRALIZATION OF HYDRAZINE FAMILY HYPERGOLIC FUELS

R. W. DeVor
ASRC Aerospace
Kennedy Space Center

E. Santiago-Maldonado and J. K. Parkerson
National Aeronautics and Space Administrations
Kennedy Space Center

ABSTRACT

A candidate scrubber media, alpha-ketoglutaric acid (α KGA) adsorbed onto a silica-based substrate was examined as a potential alternative to the hydrazine-family hypergolic fuel neutralization techniques currently utilized at NASA/Kennedy Space Center (KSC). Helvenson *et. al.* has indicated that α KGA will react with hydrazines to produce non-hazardous, possibly biodegradable products. Furthermore, the authors have previously tested and demonstrated the use of α KGA aqueous solutions as a replacement neutralizing agent for citric acid, which is currently used as a scrubbing agent in liquid scrubbers at KSC. Specific properties examined include reaction efficiency, the loading capacity of α KGA onto various silica substrates, and the comparison of α KGA media performance to that of the citric acid vapor scrubber systems at KSC and a commercial vapor scrubber media. Preliminary investigations showed hydrophobic aerogel particles to be an ideal substrate for the deposition of the α KGA. Current studies have shown that the laboratory produced α KGA-Aerogel absorbent media are more efficient and cost effective than a commercially available fixed bed scrubber media, although much less cost effective than liquid-based citric acid scrubbers (although possibly safer and less labor intensive). A comparison of all three alternative scrubber technologies (liquid α KGA, solid-phase α KGA, and commercially available sorbent materials) is given considering both hypergolic neutralization capabilities and relative costs (as compared to the current citric acid scrubbing technology in use at NASA/KSC).

INTRODUCTION

In early 1940, German "rocketeers" made an immensely important discovery in the realm of rocket propulsion media - that certain fuels (aniline and turpentine being the first discovered) ignited spontaneously upon contact with an oxidizer such as nitric acid. The spontaneous igniters were classified as "hypergols".

The discovery of hypergolicity was of major importance. The operation of a rocket motor is relatively easy, but shutting it down without a catastrophic failure can be much more difficult. Starting it up multiple times without disaster can be a real problem as well, but if the propulsion mixture is hypergolic, it is possible to avoid the dangers inherent in the use of ignition sources and devices and allow the chemistry to do the work. The process becomes much simpler and more reliable.¹ Other characteristics of hypergols also make them advantageous for space flight propulsion. Given proper handling, hypergolic propellants may be safely stored and are stable at ambient conditions. They also have a high specific impulse when used for propulsion, are stable to impact as long as no ignition source is present, can withstand the extremes of hot and cold which are present in the vacuum of space, and can be frozen and then thawed without detrimental effects to the chemical properties or storage vessels due to their ability to contract when frozen.¹¹ While extremely useful for space propulsion, hypergolic fuels are toxic to almost all living organisms (including humans), and extreme care must be taken when handling these chemicals.

Hydrazine (Hz) and Monomethylhydrazine (MMH) commodities are widely utilized in combination with Dinitrogen Tetroxide (NTO) as fuels for spacecraft hypergolic propulsion systems; therefore, the Kennedy Space Center (KSC) must be prepared to process future spacecraft utilizing these commodities. As with any toxic commodity, how to safely and efficiently handle the commodity waste created during

hardware processing is a challenge. During nominal and off-nominal operational conditions at KSC, Hz/MMH liquid and vapor commodity must be "neutralized", and the resulting "neutralized" waste must be properly disposed of. The KSC Hz/MMH waste stream has been estimated to be the largest hazardous waste stream at KSC. Legacy (Apollo/Shuttle) ground support equipment (GSE) for Hz/MMH neutralization has utilized liquid absorption systems with citric acid as the neutralizing agent.

An inherently simpler and safer alternative to the liquid absorption system used at NASA/KSC for hydrazine scrubbing is to transition to a fixed bed toxic vapor scrubber system. As described above, the citric acid scrubbers at NASA/KSC require recirculation pumps that are prone to failure and require a great deal of preventative maintenance, plumbing that has the potential to leak, valves that can fail, electricity, control system data and communication, and a large volume of hazardous scrubber liquor. A fixed bed scrubber minimizes and, in some cases, completely eliminates these problematic and overly complex features inherent to a liquid absorption scrubber.

A fixed bed scrubber can be as simple as a pipe or other container of geometric choosing that is filled with a solid material (substrate) containing a chemical component that interacts and neutralizes an array of, or specific hazardous component in a vapor flow. This system has the benefit of not requiring complicated pumps or hazardous scrubber liquor solution - only a container and the neutralization media to fill it with. In some cases, a fan may be utilized to assist in drawing the gas flow through the bed, but in some cases, this is not even needed. Because of the fixed bed scrubber's design, there is no "on" or "off" mode. The fixed bed scrubber can be connected to a vent/drain system downstream of the liquid separator, and it is always online, ready to neutralize any hazardous vapors that pass through the media.

The reduction in complexity gained by the transition to a fixed bed scrubber system also suggests that the operation and maintenance costs of such a system would be much less than that of the liquid absorption systems currently utilized at NASA/KSC. This is merely a qualitative observation, and future investigation into the savings incurred in terms of operation and maintenance costs will need to be investigated and fully quantified.

Regardless of cost savings, it is an undeniable fact that fixed bed systems are inherently simpler to operate and maintain than liquid based systems, and can minimize or eliminate the opportunity for personnel, hardware, and environmental exposure to hazardous situations involving liquid hazardous waste spills. The saving incurred as a result of the inherently safer design in terms of safety to personnel, hardware and the environment are extremely difficult to quantify.



Figure 1. NASA/KSC Mobile Hydrazine Fuel Toxic Vapor Scrubber

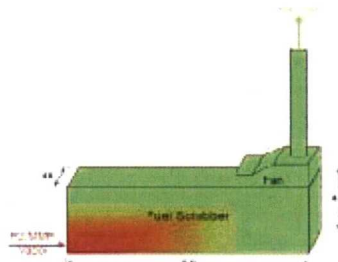
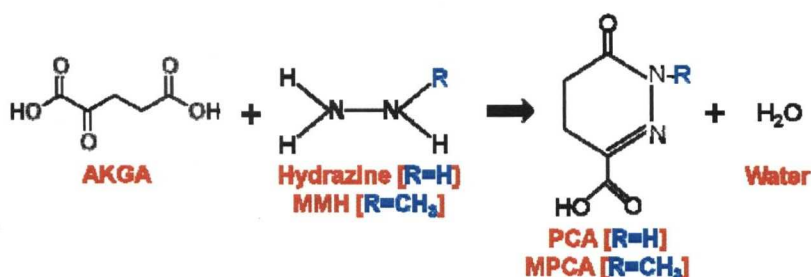


Figure 2. Basic Conceptual Design of Fixed Bed Toxic Vapor Scrubber

In 2006, Helvenson, *et al*, of New Mexico Highlands University suggested (in US Patent Number 7,074,949 B2) that α KGA may be used as a method for remediating hydrazine contaminated equipment and surfaces. Helvenson, *et al*, proposed that α KGA reacted with hydrazine-family fuels to form a stable, non-hazardous, possibly biodegradable, pyridazine product.¹¹¹ In response to this concept, NASA/KSC has primarily investigated the use of an α KGA solution as a decontamination agent for Space Shuttle MMH system decontamination and preparation for safe storage in museums. There has also been some interest in replacing the 14% citric acid solution in the current NASA/KSC hydrazine toxic vapor scrubbers with a solution of α KGA. More recently, NASA/KSC has investigated the deployment of α KGA in a fixed bed scrubber system in an attempt to gain the advantages of such a system as discussed above.

α KGA is a dicarbonyl organic molecule that reacts with hydrazines to form a pyridazine product. α KGA is a vital player in the Krebs Cycle (cellular energy production) as an amino acid precursor, and it is commonly used as a dietary supplement.

Pyridazines are heterocyclic compounds containing an N-N bond in their ring structure. They rarely occur in nature, but are often intermediates of synthetic chemical processes generating more complex molecules. The pyridazine products formed in the reaction of hydrazine and α KGA is 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (PCA) and in the reaction of MMH and α KGA, the pyridazine product is 1-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (MPCA). While PCA and MPCA are both carboxylic acids, the reaction with the basic components Hz and MMH is not of the reversible acid-base type as with citric acid. Instead, the reaction with α KGA chemically neutralizes the Hz/MMH by converting the hazardous commodity to the non-hazardous pyridazine product. The reaction seen below illustrates the reaction proposed by Helvenson, *et al.*ⁱⁱⁱ



Two methods of interfacing α KGA with the hydrazine waste have been studied at NASA/KSC: in an aqueous solution for use in the current liquid absorption scrubbers and in a solid media deposited onto/into a silica substrate for use in a fixed bed scrubber system.

RESEARCH AND DISCUSSION

MATERIALS AND METHODS

α -ketoglutaric acid was obtained from Fluka. Absolute ethanol was obtained from Pharmco-AAPER. Purafil SP, the commercial media, was obtained from Purafil, Inc. Nanogel Translucent Aerogel Grade TLD302 silica granules were obtained from Cabot, Inc. Silica Gel (Type II, 3.5 mm beads) was obtained from Sigma-Aldrich).

A vacuum rotational evaporator (Buchi Rotavapor EL 131 w/ 461 Water Bath) and a HAAKE G chiller unit were used to produce the solid-phase α KGA-Aerogel particles at various loadings (weight %). A Kin-tek Model 361 Precision Vapor Generator was used to produce the low level Hz (~114ppm) vapor stream used in the solid phase α KGA-Aerogel testing. An Interscan Model 4000 was used as a monitoring device during the testing process.

NEUTRALIZATION OF HYDRAZINE FUELS VIA α KGA IN AN AQUEOUS SOLUTION

The Applied Chemistry Laboratory at NASA/KSC performed laboratory scale testing of an aqueous α KGA solution as a replacement for the citric acid currently used as the neutralization agent in the scrubbers at NASA/KSC. A laboratory scale absorption unit was constructed to duplicate the operating parameters of the NASA/KSC hydrazine scrubbers, and the system was used to gather data concerning the performance of aqueous α KGA solutions as a hydrazine neutralization agent.

The laboratory scrubber was a 1/10th scale version of the packed scrubber column used at KSC during hypergolic fuel operations. A gas delivery system capable of delivering concentrations of Hz and

MMH up to 10,000ppm and 20,000ppm, respectively, was used to provide a quantifiable, steady flow of Hz and MMH to the scrubber. Once powered up, sufficient time was allowed for the gas generation system to reach equilibrium before an analysis of the scrubber inlet concentration was performed using constant current coulometry. During scrubber column testing, the scrubber outlet vapor concentration was monitored using an Interscan hydrazine detector, and the vapor and inlet concentration of the scrubber was measured periodically using constant current coulometry.

During initial testing with a 0.73M α KGA solution in the scrubber, a reaction precipitate was formed, and accumulated throughout the scrubber column (structured packing, fittings, tubing, etc.). Precipitate formation is not desirable when operating a scrubber column; hence, efforts were directed to determine the concentration of α KGA in solution where the precipitation of the PCA/MPCA product could be avoided. Precipitation testing was performed with 0.73M, 0.44M, and 0.2M α KGA using an impinger filled with the solution in place of the laboratory scale scrubber.^{IV} The results of the precipitation study are given in Table 1 below.

Table 1: Precipitation Study Results

Fuel	α KGA Scrubber Solution	Reaction Product Concentration [wt%]	Precipitate?
Hz	0.73M	5.0%	Yes
Hz	0.44M	3.8%	Yes
Hz	0.2M	2.8%	No
MMH	0.2M	2.8%	No
MMH	0.73M	7.7%	No

The precipitation study suggested that the solubility of the PCA resulting from the reaction of α KGA and Hz has a solubility limit in an aqueous solution somewhere between 2.8% and 3.8% PCA by weight. No solubility limit was found for the MPCA product, and it is assumed to be much higher than the PCA product.

Following the precipitation study, the high concentration Hz study was completed using a 0.2M α KGA solution, followed by the testing of a 0.73M α KGA solution for MMH neutralization. A 0.73M solution of citric acid was also tested as a baseline. The results of the high concentration testing are given in Table 2, below.

Table 2: High Concentration Results of Lab Scale Testing

Fuel	Scrubber Solution	Inlet Concentration	Outlet Concentration
Hz	0.73M Citric Acid	10,192 ppm	nd
Hz	0.20M α KGA	7,287 ppm	nd
Hz	0.73M α KGA	5,334 ppm	nd
MMH	0.73M α KGA	16,669 ppm	nd

The 0.2M solution of α KGA successfully neutralized a 7,000+ ppm Hz flow without the formation of precipitates, and produced an outlet concentration below the ability of detection (~ 10 ppb). A 0.73M solution of α KGA successfully neutralized 16,000+ ppm MMH flow without the formation of precipitates, and produced an outlet concentration below the ability of detection. In both cases, the α KGA solution reduced the concentration sufficiently below the OSHA-PEL Hz/MMH concentration limits required by law.^{V,VI}

These studies demonstrated that aqueous solutions of α KGA may be used as a drop-in replacement of the citric acid solution currently used by NASA/KSC. For use as a MMH neutralization agent, no particulate formation was found; however, when neutralizing Hz, only the use of a 0.2M solution of α KGA yielded no formation of precipitates. As the scrubber units at NASA/KSC must neutralize both Hz and MMH, this limits a drop-in replacement for citric acid to a 0.2M ($\sim 2.8\%$ by weight) solution of α KGA to ensure that no precipitates are formed.

Because such a low concentration of α KGA is required to avoid precipitates in solution, the scrubbers currently used at NASA/KSC would lose up to 93% of their current capacity if the 14% citric acid solution was replaced by a 2.8% α KGA solution. This is a substantial loss of capacity, and as a result, would require more frequent solution replacements, increasing the cost of operation and maintenance. This limits the advantages of the liquid α KGA as a replacement scrubbing technology.

Another disadvantage to the delivery of α KGA in an aqueous solution is that water can act as a weak acid and form the same Hz/MMH salts that are present in the citric acid solution. While this theory has not been tested in the aqueous solution of α KGA, if correct, the α KGA scrubber solution would also need to be disposed of as hazardous waste; therefore, defeating the purpose of replacing the citric acid. Given the issues associated with utilizing aqueous α KGA in the current scrubbers at KSC, an effort has been made to search for other methods of delivery.

In addition to the low and high concentration testing of α KGA, and the precipitation study, the PCA product suggested by the NMHU patent was verified to indeed be PCA via proton nuclear magnetic resonance spectroscopy (H-NMR) and carbon nuclear magnetic resonance spectroscopy (C-NMR) analysis. These NMR spectra, seen in Figure 3, below, were analyzed and compared to predicted NMR spectra using chemical analysis software.

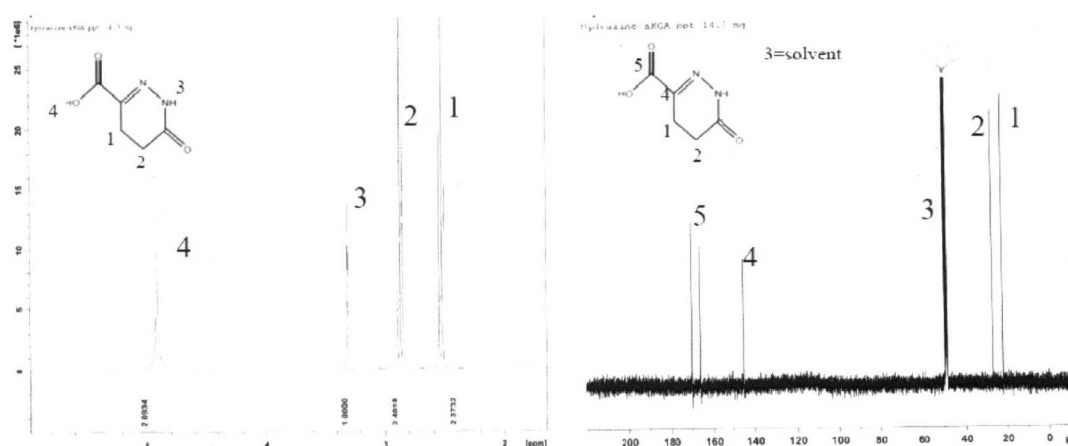


Figure 3: H-NMR and C-NMR Analysis of α KGA and Hz PCA Reaction Product

NEUTRALIZATION OF HYDRAZINE FUELS VIA α KGA AS A FIXED BED SCRUBBER MEDIA

In the search for an alternative α KGA method of delivery, the notion of depositing α KGA onto a silica bead substrate was initially considered. To prepare the solid α KGA-silica material, a method that would allow for the uniform dispersal of the solute was needed. To accomplish this, rotary evaporation

was used. While initial testing proved it was possible to successfully deposit the material onto the silica substrate, the product was dusty (α KGA powder). Problems were also encountered where the deposition solution became extremely viscous and difficult to evaporate at higher α KGA concentrations (greater than 15% by weight compared to the silica beads). It was suggested that a Silica Aerogel substrate be used instead. Aerogels have many properties that make them ideal solute delivery substrates, but have not been widely used for this purpose as a result of their price. As demand for Aerogels has begun to increase, the cost is now trending downward, making them available and affordable solutions for more applications. For this reason, Aerogels have been considered for a substrate to facilitate the delivery of α KGA in a fixed bed scrubber.

Aerogels are the world's lightest solid materials, composed of up to 99.98% air by volume, and have many other properties unlike any other material known. Essentially, an aerogel is the dry, low-density, porous, solid framework of a gel (the part of the gel that gives the gel its solid-like cohesiveness) isolated in-tact from the gel's liquid component (the part that makes up most of the volume of the gel). Aerogels are open-porous, that is, the gas in the aerogel is not trapped inside solid pockets, allowing its use as a gas phase scrubber substrate. With an extremely high internal and external surface area, these materials perform much better as solute delivery substrates than the non-porous silica beads originally considered as a method of α KGA delivery. As little as five grams of the material can have a surface area equivalent to one (or more) football field(s).^{VII} Silica based aerogels are non-hazardous, non-toxic, and pose no risk (other than small particle inhalation hazards) for personnel, the environment, or hardware as the material is essentially an amorphous structure of sand.

The α KGA-Silica Aerogel Fixed Bed media was produced and tested in the Applied Chemistry Laboratory at NASA/KSC. To produce the media, an ethanol solution containing α KGA was produced and an appropriate amount added to Cabot Aerogel TLD302 particles such that a one to one ratio by weight of α KGA to silica aerogel was achieved. A batch of media was also produced with five times the amount of α KGA as silica aerogel without issue. This mixture was added to a round bottom flask, and the ethanol was evaporated off in a rotational vacuum evaporating (rotavap) unit to ensure even distribution of the α KGA throughout the pore space of the silica aerogel media. The rotavap process reverses the aerogel production process to a degree, resulting in a decrease in the volume of silica aerogel (creating a xerogel in the process). By using supercritical carbon dioxide to displace the ethanol, the ~70% reduction in volume incurred during the rotavap process could be eliminated, and if this method is developed further at NASA/KSC, a study into the feasibility of large scale supercritical carbon dioxide extraction of ethanol from the silica aerogel media will be required. Figure 4, seen below, depicts the α KGA-Silica Aerogel media produced for fixed bed testing.

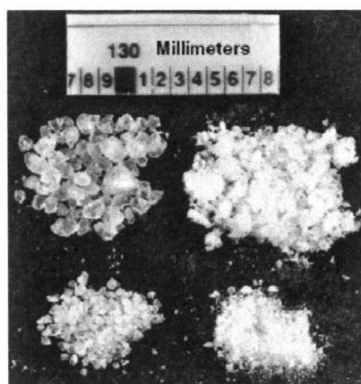


Figure 4: Final α KGA-Aerogel Product

In Figure 4, above, the top-left image is an α KGA-Silica Aerogel media containing five times the amount of α KGA than Silica Aerogel by weight. The material was also not completely dried in the rotavap

unit. The top-right sample in the image above is the result of crushing the media. It is clearly visible that the α KGA powder is well contained within the porous structure of the media. The lower-left and right samples in the image above represent the product tested in the Applied Chemistry Laboratory. The silica aerogel media tested contained α KGA in a one to one ratio (by weight) with the aerogel. Notice the reduction in particle size incurred by fully drying the media by mere heat.

For initial low concentration hydrazine exposure tests for the media that was developed, a laboratory scale fixed bed scrubber system was constructed. Standard operations for the generation and coulometric quantification of Hz/MMH gas were utilized. Figure 5, seen below, illustrates the test setup.

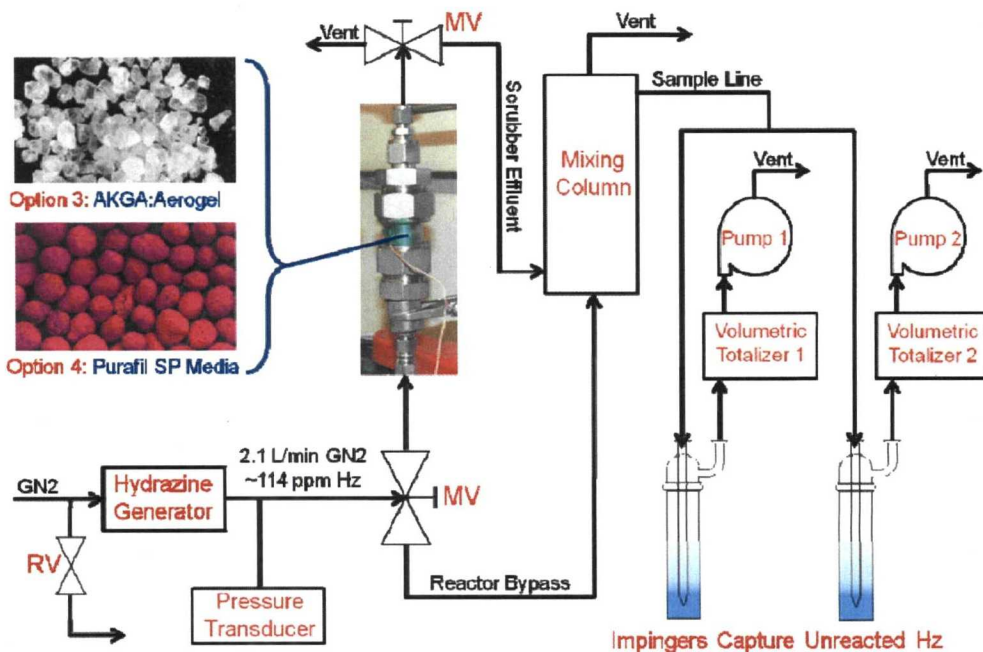


Figure 5: Laboratory Scale Test Setup for Fixed Bed Media Testing

The system utilized a Kintek Hz/MMH Model 361 Vapor generation unit to provide a 2.1 L/min flow of gaseous nitrogen containing an average Hz concentration of 114ppm. The gas flow could either be diverted to the mixing column (bypassing the fixed bed scrubber column) to quantify the inlet concentration using constant current coulometry, or the gas flow could be passed through the 27cm³ fixed bed scrubber containing the media being tested. The scrubber effluent was routed to a mixing column, and a known volume of reactor effluent was passed through a 0.1M solution of sulfuric acid to capture any residual hydrazine not captured by the media. The sulfuric acid complexes with any remaining hydrazine to form hydrazine sulfate. The quantity of hydrazine sulfate captured was then quantified using constant current coulometry. With the inlet and outlet concentration of the scrubber bed known, the performance of the media can be analyzed.

Breakthrough plots are often used to describe the performance of fixed bed scrubber media. In such a plot, the percent of hazardous vapor not removed by the media is plotted against the duration of exposure to the hazardous vapor flow. After a period of exposure, the performance of the bed will usually begin to rapidly decrease, and a spike in the percentage of hazardous vapor not removed by the scrubber media will occur. The point at which a loss of performance in the fixed bed media begins to occur is known as the breakpoint. This is commonly defined as the point at which the exit concentration of hazardous vapor is sufficient in quantity to constitute five percent of the scrubber inlet concentration of

hazardous vapor. Being on the more conservative side at NASA/KSC, it was decided to to classify breakthrough as the point at which the scrubber outlet concentration of hydrazine was equal to one percent of the scrubber inlet concentration of hydrazine. Figure 6, seen below, depicts the breakthrough plot for the α KGA-Silica Aerogel media developed and tested at the NASA/KSC Applied Chemistry Laboratory.

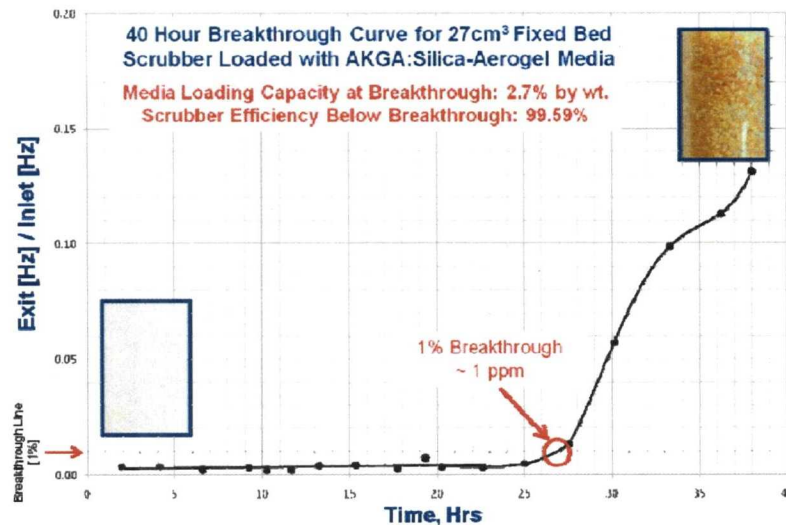


Figure 6: α KGA:Silica Aerogel Fixed Bed Media Breakthrough Plot

Analyzing the plot above, it is clear that the one percent breakthrough point for the α KGA-Silica Aerogel media occurred at approximately twenty seven hours. The average media performance calculated prior to the breakthrough point is approximately 99.59%. The bed capacity at breakthrough may be calculated by integrating the percent hydrazine removed over the duration of time until breakthrough. This is represented mathematically as:

$$\text{Media Loading Capacity at Breakthrough} = \int_{t_0}^{t_b} \left(1 - \frac{\text{exit Hz concentration}}{\text{inlet Hz concentration}} \right) dt$$

For the α KGA-Silica Aerogel media tested, the breakthrough time, t_b , was 27 hours, and the integral may be calculated to be 0.027 lbs of Hz captured per lb of α KGA/Aerogel media used, or a loading capacity (neutralization factor) of 2.7% by weight.

The plot above also depicts the color change of the media observed as a result of the formation of the PCA product. The color change would allow for visual indication of the depletion of the fixed scrubber bed, and allow for only the portion of the bed depleted to be replaced versus the entire scrubber bed.

As an experimental control, blank TLD 302 Aerogel (no α KGA present) was tested, in the same manner as the α KGA-Aerogel media discussed above, to confirm that the neutralization was in fact due to the α KGA and not to the Aerogel particles. An identical volume of media was used, and the one percent breakthrough point occurred between the two and four hours of exposure to Hz vapors. This indicates

that a small amount of the absorption may be due to the Aerogel, but that majority of the neutralization is taking place between the α KGA and the Hz.

Preliminary higher concentration Hz exposure tests were also conducted to determine the effectiveness of the α KGA-Aerogel media in neutralizing vapor streams in excess of 5,000ppm. The test setup shown in Figure 5 was altered slightly (not shown) to allow for this higher concentration testing. Instead of a Kin-tek Model 361 Precision Vapor Generator, the headspace of permeation device was directly sampled (bypassing the permeation tubing) at a flow rate of 2.0 LPM. The concentration of the Hz vapor was determined by setting the oven controlling the temperature of the permeation device and further controlled by varying the flow rates used to dilute the gas flows in the testing system. The permeation device was weighed both before and after testing, and gas was only passed through the permeation device during exposure to the fixed bed reactor. This, coupled with monitoring of the total exposure time, total flow rates of gas, and total loss of mass of hydrazine allow for the calculation of the concentration of the vapor stream. The gas flow was passed through a fixed bed reactor containing the α KGA-Aerogel media being tested. A calibrated Interscan electrochemical detector was used to monitor the output of the fixed bed reactor in real-time and determine the effectiveness of the α KGA-Aerogel media in neutralizing the Hz vapor streams. For the purposes of the high concentration tests, breakthrough was defined as an Interscan reading of 2 ppm at which point the testing was terminated and the permeation device removed from the testing setup (to prevent additional mass loss of hydrazine). A 0.5:1 α KGA-Aerogel media and a 1:1 α KGA-Aerogel media was tested at ~5,000 and 10,000 ppm concentration of Hz, and the results are given below in Table 3.

Table 3. Results of High Concentration α KGA:Aerogel Hz Testing

	0.5x AKGA		1x AKGA
	Test 1	Test 2	Test 3
ppm Hz	4239	5046	10572
Breakthrough (hrs)	7.33	2.36	1.77
% Loading (wt%)	13.97%	9.94%	14.62%

The average loading capacity of from these initial experiments was ~12.8% at the defined breakthrough point of 2ppm Hz. This loading capacity is higher than initially observed for the lower concentration tests due to the difference in defined breakthrough points, although the observed data trend is the same (α KGA-Aerogel has a higher loading capacity than Purafil SP at comparable Hz vapor concentrations). The breakthrough time varied due to different masses of α KGA-Aerogel media used in the different test runs, as well as some unreacted media left in the fixed reactor bed upon breakthrough (noticed upon replacement of the media). The unreacted media was most likely due to small channels forming in the α KGA-Aerogel. Further tests will need to be conducted for more accurate loading capacities at higher concentration vapor streams.

NEUTRALIZATION OF HYDRAZINE FUEL VIA PURAFIL® COMMERCIAL MEDIA

A commercial provider of a product to neutralize hydrazine in a fixed bed system is Purafil, Inc. and their product has been used in the aerospace industry to neutralize Hz/MMH vapors. This material was chosen for investigation to allow for a baseline comparison to a functional hypergolic fuel fixed bed scrubber media. The active ingredient in Purafil's Purafil SP media seems to be sodium permanganate; however, the MSDS^{VIII} list an additional proprietary ingredient. The permanganate oxidizes the Hz or MMH; therefore, it neutralizes the hazardous portion of the vent flow. The proprietary ingredient in the Purafil formulation is unknown, and the reaction that occurs between the Hz/MMH and the Purafil SP media is not well understood, and it is believed that the products of the reaction may still need to be handled as hazardous waste. The reaction, as currently understood by NASA/KSC is represented by

Figure 7, seen below. Figure 8, given below, depicts the composition of the Purafil SP media recently evaluated by NASA/KSC in the Applied Chemistry Laboratory.^{viii}

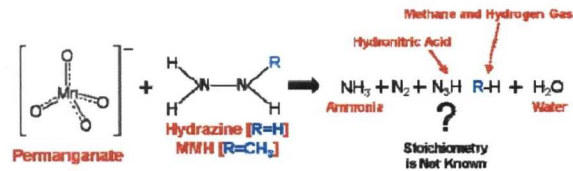


Figure 7: Purafil SP Reaction with Hz/MMH

Constituent	Weight Percent
Aluminum Oxide Substrate	35-60%
Water	10-35%
Proprietary Ingredient	10-20%
Sodium Permanganate	10-16%

Figure 8: Purafil SP Media Composition

The Purafil SP media was tested using the laboratory scale system described above, and the same analysis concerning the media performance that was performed on the αKGA-Silica Aerogel media was performed on the Purafil SP media (for both the low and high concentration tests). The breakthrough plot for the low concentration testing of the Purafil SP media is given in Figure 9, seen below.

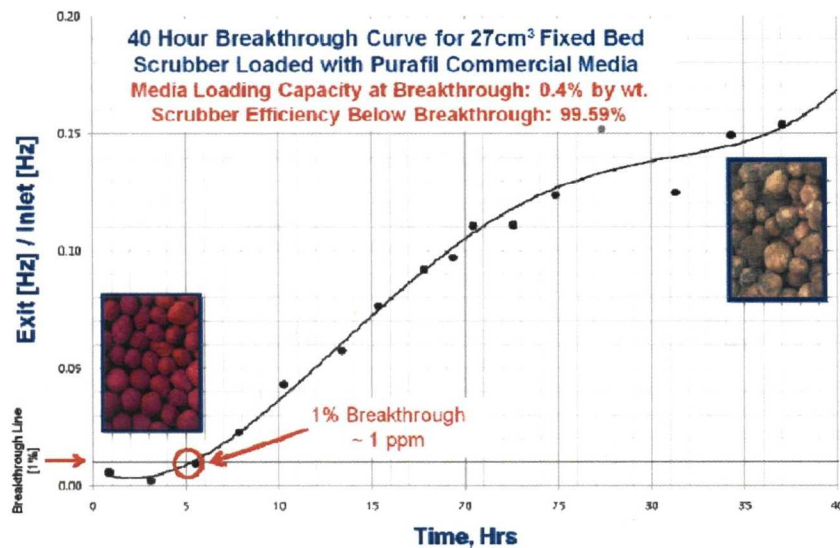


Figure 9: Purafil SP Fixed Bed Media Breakthrough Plot

Analyzing the plot above, it is clear that the one percent breakthrough point for the Purafil SP media occurred at approximately five hours. The average media performance calculated prior to the breakthrough point is approximately 99.59%. The bed capacity at breakthrough may be calculated by integrating the percent hydrazine removed over the duration of time until breakthrough. This is represented mathematically as:

$$\text{Media Loading Capacity at Breakthrough} = \int_{t_0}^{t_b} \left(1 - \frac{\text{exit Hz concentration}}{\text{inlet Hz concentration}} \right) dt$$

For the Purafil SP media tested, the breakthrough time, t_b , was 5 hours, and the integral may be calculated to be 0.004 lbs of Hz captured per lb of Purafil SP media used, or a loading capacity (neutralization factor) of 0.4% by weight.

The plot above also depicts the color change of the media observed as a result of the depletion of the purple colored permanganate constituent of the Purafil SP media. The color change would allow for visual indication of the depletion of the fixed scrubber bed, and allow for only the portion of the bed depleted to be replaced versus the entire scrubber bed.

High concentration Hz vapor tests were conducted for the Purafil SP media using the same test setup as described in the previous section of this report, and the results are located in Table 4.

Table 4. Results of High Concentration Purafil SP Hz Testing

	Purafil		
	Test 1	Test 2	Test 3
ppm Hz	4416	4130	4847
Breakthrough (hrs)	1.97	2.425	2.43
% Loading (wt%)	2.85%	3.34%	4.19%

The average loading capacity for the high concentration Hz vapor test on the Purafil SP media was ~3.5%, which mirrored the trend seen at the lower concentration vapor tests (lower absorption capacity than α KGA-Aerogel). Again, some unreacted media was seen upon unloading of the reactor bed.

COMPARISON OF HYDRAZINE VAPOR NEUTRALIZATION METHODS INVESTIGATED

Three aforementioned options have been proposed as alternative methods for hydrazine fuel toxic vapor neutralization at NASA/KSC. The first proposed alternative method considered involves the replacement of the 14% citric acid solution in the current scrubbers with a 2.8% α KGA solution. The second proposed method involves the use of an α KGA-Silica Aerogel fixed bed media developed at NASA/KSC, and the third proposed method involves the use of a commercial media, Purafil SP, in a fixed bed design. Here the advantages and disadvantages of each proposed method will be discussed.

To summarize the findings of the material found in the previous sections of this report, the neutralization factor found for each of the proposed methods of Hz/MMH vapor neutralization is given in Figure 10, seen below (for the low concentration tests, the more conservative of the results).

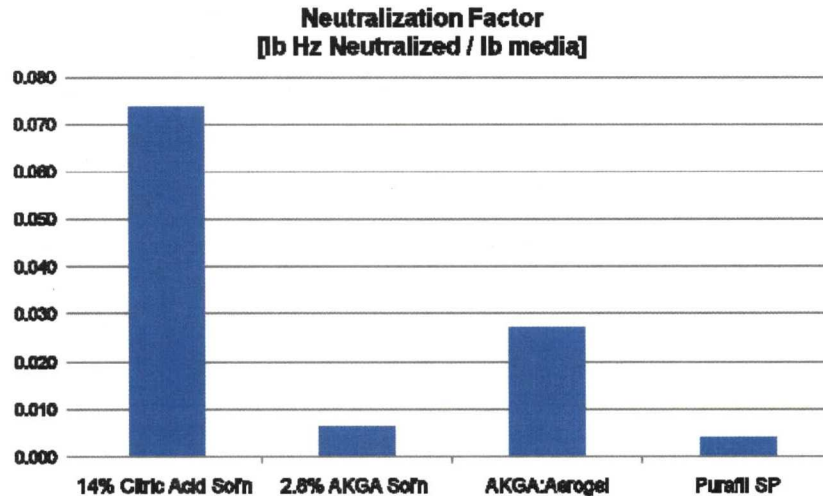


Figure 10: Neutralization Factor for Options Investigated (lower concentration testing)

The current method of Hz/MMH at NASA/KSC, the 14% citric acid scrubbers, has the highest neutralization factor of the methods considered. The neutralization factor for these scrubbers is approximately 7.4% by weight, indicating that 0.074 lbs of Hz/MMH may be neutralized per lb of scrubber solution used. The 2.8% αKGA solution has a neutralization factor of only 0.6%, significantly less than that of the citric acid. For this reason, using the αKGA solution as a drop-in replacement for the citric acid solution would result in up to a 93% loss in the Hz/MMH neutralization capacity of the current scrubbers. This is complicated by the possibility of precipitation byproducts formed during the course of the neutralization reactions (which is not observed during the current citric acid scrubbing technology).

The 1:1 αKGA-Aerogel media developed at NASA/KSC has an un-optimized neutralization factor of approximately 2.7% by weight. It is believed that through further product development and optimization, absorption capacity could be increased through increased loading of αKGA within the Aerogel particle (the preliminary testing only utilized a 1:1 αKGA-Aerogel loading, although a 5:1 αKGA-Aerogel loading was achieved with minimal effort). The Purafil SP commercial media was found to have a neutralization factor of approximately 0.4% by weight, the lowest of all the options considered.

An investigation into the relative costs of Hz/MMH incurred from media purchasing and waste disposal was also conducted for each method considered (as compared to the currently used citric acid scrubbing method). These costs comparisons have been investigated based upon the results from the lower concentration testing. The waste management organization at NASA/KSC was consulted for insight into the cost of hazardous Hz/MMH waste in addition to the cost of solid Hz/MMH waste disposal. The cost of dumping large quantities of liquid to the NASA/KSC sewage system was also evaluated. Cost for the media were calculated based on the cost of purchasing the raw materials needed to produce the media and the technical limits possessed by the media.

The 14% citric acid solution is the cheapest method considered and was used as the baseline for comparison, but does not have the advantage of being as environmentally friendly as the αKGA-based methods. Also, while the cost of the media and disposal is not as expensive as the alternative options considered, the cost of operations and maintenance of the liquid scrubbers should be significantly higher than that of the fixed bed design, but the cost of operations and maintenance on these units has not been fully investigated.

The 2.8% solution of αKGA costs ~4.7x per pound of Hz/MMH neutralized (compared to 14% citric acid), but once again would be just as costly to operate and maintain as the current system. It should actually cost more due to the increase in operations required to replace the scrubber solution that is the result of a significantly lower neutralization factor for the αKGA solution when compared the citric

acid solution. It is also possible that the α KGA solution may still be considered hazardous waste as the water in solution may complex with Hz/MMH to form hazardous products.

The α KGA-Aerogel media developed at NASA/KSC currently has a cost of ~23.3x per pound of Hz/MMH neutralized (as compared to 14% citric acid). While this is significantly higher than both of the liquid options, it is much cheaper than a commercial fixed bed scrubber media. In addition, the cost of the media may come down as further development and optimization of the media is completed. Several other factors may also contribute to the decrease of the α KGA-Aerogel media. For one, the cost of operations and maintenance on a fixed bed scrubber should be significantly less than that of the current scrubber systems utilized at NASA/KSC. Also, the PCA/MPCA product formed has value and may be sold/traded under a NASA Space Act Agreement to mitigate the cost of the media itself. The silica aerogel media that currently represents approximately 34% of the media cost has also begun to decrease as the demand for aerogel increases.

The Purafil SP commercial media has an extremely low neutralization factor; therefore, it requires a very large quantity of media to neutralize even miniscule amounts of Hz/MMH. For this reason, even though the Purafil SP media by weight is not very expensive, the total cost of neutralizing Hz/MMH is expensive due to the large quantity required. Given the data obtained from testing at NASA/KSC, the cost of the Purafil SP method is estimated to be at ~93.3x greater per pound of Hz/MMH neutralized (as compared to 14% citric acid).

SUMMARY AND CONCLUSIONS

Based on the investigation, for which the results have been presented in this report, two conclusions have been reached.

The first conclusion, concerning liquid absorption scrubbers at NASA/KSC, finds that the exchange of the 14% citric acid solution for a 2.8% solution of α KGA would result in up to a 93% reduction in scrubber capacity, and is not advised. This is a very large decrease in capacity, and would result in an increase of operations and maintenance cost for the scrubbers. In addition, the α KGA solution may still be considered hazardous waste, in which case nothing is gained by the exchange of scrubber solutions.

The second conclusion, concerning the fixed bed media considered, finds that the α KGA-Silica Aerogel media developed at NASA/KSC is far better than a commercial Hz/MMH fixed bed scrubber media, and that with sufficient development and optimization, the media may not cost significantly more than the scrubber systems currently used at NASA/KSC.

While more expensive, a fixed bed scrubber design is inherently simpler and safer than liquid scrubber designs. As the products of the α KGA-Silica Aerogel media are non-hazardous, the risk of personnel, wildlife, environment, and hardware exposure to hazardous solutions of Hz/MMH scrubber liquor could be eliminated, and if for this reason alone, the media should be developed further.

References

- I. Clark, John D. *Ignition! An Informal History of Liquid Rocket Propellants*. New Brunswick, N.J.: Rutgers UP, 1972. Print.
- II. Nufer, Brian M. *A Summary of NASA and USAF Hypergolic Propellant Related Spills and Fires*. Tech. no. NASA/TP-2009-214769. Kennedy Space Center, Fl, 2009. Print.
- III. Helvenson, M., R. A. Martinez, J. C. de Baca, and J. J. Juarez. U.S Patent 7,074,959 B2 "Methods and Systems for Remediating Hydrazine-Contaminated Equipment and/or Surfaces" (2006)
- IV. Santiago-Maldonado, E., B. J. Meneghelli, C. Davis, and C. Berger. "Preliminary Characterization of Alternative Hydrazine and Monomethyl Hydrazine Vapor Scrubber." *JANNEF*. Print.

- V. *Hydrazine Anhydrous*; Material Safety Data Sheet No. 11040; Fisher Scientific: Fair Lawn, NJ, (July 1999), <http://fscimage.fishersci.com/msds/11040.htm> (accessed November 2010).
- VI. *Methyldiazine*; Material Safety Data Sheet No. 39720; Acros Organics: Fair Lawn, NJ (August 1998), <https://fscimage.fishersci.com/msds/39720.htm> (accessed November 2010).
- VII. *Aspen Aerogel: Aerogel Morphology*. <http://www.aerogel.com/features/morphology.html> (accessed November 2010).
- VIII. *Purafil SP*; Material Safety Data Sheet; Purafil, Inc: Doraville, GA, (July 2008) http://www.purafil.com/PDFs/MSDS/msds_purafil_sp_EU.pdf (accessed November 2010)