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6. AUTHOR(S)
Paul Sarkisian

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rocky Research
1598 Foothill Drive
Boulder City, NV 89005

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Report developed under SBIR contract for topic A02-056. Under this project, specifications necessary for the selection of the ammoniated complex best suited to this application were obtained. These included delivery pressure, heat available for operation, ammonia discharge rate required, the desired number of missions and the ambient temperature range for operation. Suitable ammoniated complex compounds were then identified that would provide operation under these conditions. Design software suitable to the evaluation of the complex compounds for this particular application was developed that would determine the size and weight of the complex compound sorber to be used for ammonia storage.

In constructing the first prototype storage device, the technology for low mass sorber design for ammonia storage at reduced vapor pressures was advanced using Rocky Research's complex compound technology in a low mass and volume manner. In this first attempt at ammonia storage for the 72 hr, 518 gram NH3 discharge application suitable to the Palm Power 3-day mission application, the resulting sorber weight was 3.06 lbm when discharged. The sorber was capable of providing up to 530 g of ammonia using heat input at temperatures associated with the ammonia decomposition reactor and the fuel cell exhaust.

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Ammonia Storage as Complex Compounds for a Safe and Compact Hydrogen Storage

PHASE I FINAL REPORT

Prepared by:

Paul Sarkisian
Kaveh Khalili
Lance Kirol
James Langeliers
Dr. Uwe Rockenfeller

Rocky Research
1598 Foothill Drive
Boulder City, NV 89005

For:

U.S. Army Robert Morris Acquisition Center
Research Triangle Park Contracting Division
P.O. Box 12211
Research Triangle Park, NC 27709-2211

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Phase I Research and Development Objectives

The U.S. Army has an ever-increasing need for portable electrical power for individual soldiers. As one facet of their strategy to develop practical portable power systems, they are hosting development projects for backpack mounted fuel cells. Various hydrogen sources to provide fuel to cell are being pursued. One of the most promising and novel hydrogen sources is ammonia, which can be decomposed to deliver hydrogen.

This project is directed toward developing a system for storing and releasing ammonia as feed for a decomposition reactor which provides hydrogen to the fuel cell. The storage system must be compact and lightweight, and provide safe storage of ammonia at pressures below that of liquid ammonia. Orientation and acceleration insensitivity are also desired, to avoid restrictions on soldier movement when using the fuel cell.

Phase I had three primary objectives:

1. Define requirements for the H2 storage system, including requirements specific to the ammonia decomposition reactor and fuel cell
2. Identify and characterize suitable absorption media—specifically ammoniated complex compounds— and select the most promising candidate(s).
3. Design and demonstrate a working sorber for storing the required mass of ammonia

These objectives were met during Phase I of the project.

Summary of Phase I Research

Under Phase I of the project, specifications necessary for the selection of the ammoniated complex best suited to this application were obtained. These included delivery pressure, heat available for operation, ammonia discharge rate required, the desired number of missions and the ambient temperature range for operation.

Next, suitable ammoniated complex compounds were identified that would provide operation under these conditions. To this end, laboratory testing of some complex compounds in the microbalance was required to obtain information on ammonia uptake a function of temperature. Design software suitable to the evaluation of the complex compounds for this particular application was developed that would determine the size and weight of the complex compound sorber to be used for ammonia storage.

Finally, a first prototype complex compound sorber, suitable to this application, was constructed. In this development, disks of suitable material were impregnated with complex compound and encased in a lightweight pressure vessel. An outer CPVC shell was added with a passage to allow for products from the fuel cell and ammonia decomposition reactor to flow and to be used to provide heat for liberation of the ammonia from the complex compound sorbent.

Successful tests were conducted on this sorber which showed that 530 grams of ammonia could be liberated from the sorber, which is more than the 518 grams required for a 3 day continuous 20 Watt mission.

Background on Complex Compound Technology

Complex Compound Chemistry and Kinetics

A coordination complex compound is a compound formed by an inorganic salt that bonds to several small molecules acting as complexing agents, better known as ligands. The complex compounds proposed for ammonia storage as a hydrogen source consist of solid simple inorganic salts that serve as absorbents and ammonia as the ligand. Such complexes are examples of the chemistry studied by Alfred Werner 100 years ago. The absorbent salts complex the ammonia vapor directly from the gas phase, and this reaction is accompanied by release of heat. The reaction is reversible, where with the input of heat the ammonia can be made to desorb or release from the absorbent. Coordination complex compounds have two intrinsic features that make them superior media for ammonia storage; monovariance and high refrigerant holding capacity.

Monovariance: Monovariance refers to the independence of vapor pressure and absorbed ammonia concentration. The complexes are crystalline both as absorbed and as desorbed compounds, and only certain definite well-defined lattice structures occur. Thus as the salt absorbs ammonia, one solid crystalline phase with a small amount of ammonia converts microcrystal by microcrystal to another crystalline phase which contains a higher fixed amount of refrigerant. As a consequence of the presence of the two solid phases, and the Gibbs Phase Rule, "plateau" behavior of the pressure results, in which the refrigerant is held at one vapor pressure up to a certain absorbed concentration. Then, the pressure increases in nearly a step function to a higher vapor-pressure plateau with a new set of two solid absorbent phases. These phases are the relatively more absorbed crystal lattice from the former step, and a new crystal lattice, one that incorporates an even higher number of ligands.

Monovariance is important for the application of a sorbent for ammonia storage because the pressure and temperature remain fixed during the desorption process. All ammonia can be released without the requirement of constantly increasing temperature.

High refrigerant holding capacity: Refrigerant holding capacity of complex compounds is very high, often as high as 70% of the absorbent dry weight. Several moles of refrigerant can be bonded to a single mole of salt. This allows the amount of refrigerant mass which can be bound by complex compounds to be four to five times greater than the mass found for either other absorbent systems or from adsorption including zeolite, activated carbon, and liquid-vapor media such as aqua-ammonia. Figure 1 shows relative refrigerant holding capacity for several complex compounds contrasted to other sorption media such as liquid solutions and zeolite or activated carbon.

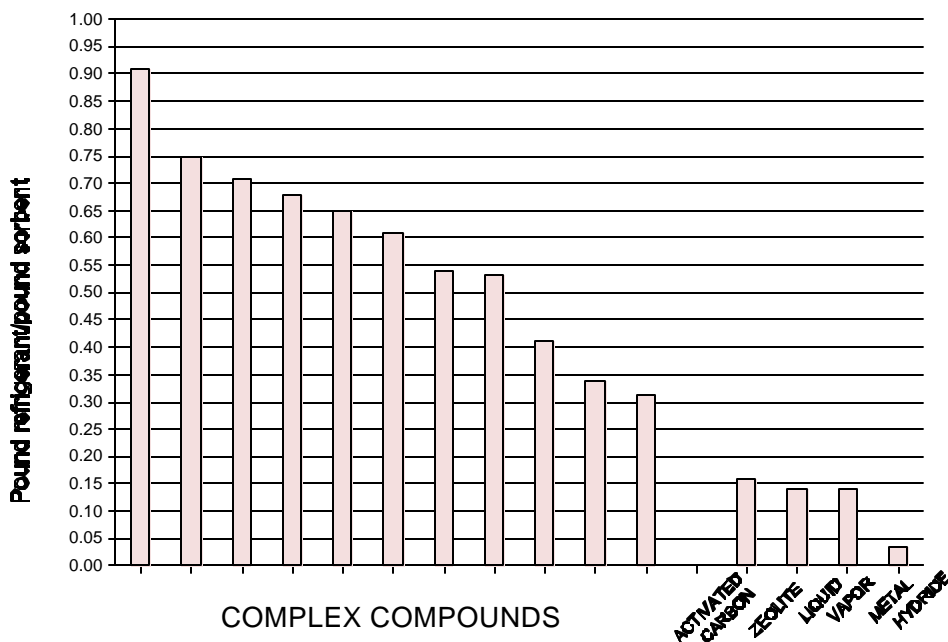## COMPARISON OF REFRIGERANT HOLDING CAPACITY

Figure 1. Ammonia storage density of complex compounds.

It is common to refer to each absorption step as a coordination sphere. Each ligand molecule in a given coordination sphere is bonded with the same energy, and a partially filled sphere has the same vapor pressure as a completely filled coordination sphere[1,2]. Typical coordination spheres are illustrated by $SrCl_2$ which has a step from 0 to 1 moles of ammonia per mole of salt, and second step from 1 to 8. Seven moles of ammonia can be absorbed or desorbed in the second step without changes in pressure. On a mass basis, 119 grams of ammonia are adsorbed per 175 grams (1 mole $SrCl_2$ plus one mole of ammonia in the first step) of $SrCl_2 \bullet 1NH_3$, or a refrigerant density of 68%. This is much higher than is attainable with any other sorption media.

Thousands of complex compounds exist, and almost any desired vapor pressure temperature relationship is available. Nernst[3] developed a general vapor pressure relationship for complex compounds, given by:

$$\log p = \frac{Qo}{2.303 \, R \, T} + 1.75 \log T - a \, T + C \qquad (1)$$

Qo represents the heat evolution, R is the universal gas constant, p is pressure, T is absolute temperature, a is a function of the coordination step and C is a constant for the ligand. C values for various ligands range from 0.6 to 3.5, with water and ammonia being 3.3 and 3.6, respectively. The a value has been approximated with a formula by Biltz and Huettig. They derived a direct linear function between a and the coordination number[2],

$$a = 1.4286 \times 10\text{-}4 \times n + 1.5381 \times 10\text{-}3 \qquad (2)$$

with n being the coordination number of the ammonia complex. This approximation is a simple tool to predict the heat evolution with an accuracy of approximately ±7%. The equations are only valid for pressures well below the critical pressure of the ligand.

Rocky Research has measured vapor pressure of many complex compounds to obtain data much more accurate than provided by the Nernst approximation formula. The Nernst formula is useful for screening compounds to determine those for which measured data are desired.

Vapor pressure of ten ammoniated complex compounds is plotted against temperature in Figure 2. This plot includes compounds with measured pressure and some from the Nernst formula. Each curve represents a different ammoniated complex compound. Names are not given as some compounds plotted are proprietary to Rocky Research.

The lower plot in Figure 2 is log of vapor pressure versus the inverse of absolute temperature. As is apparent from the form of the Nernst formula, data plotted in this domain is nearly linear.

Figure 2 illustrates that many ammoniated complex compounds are available with vapor pressure in the general range needed for ammonia storage. Specific compounds studied will not be limited to those illustrated.

Summarizing, complex compounds exhibit inherent characteristics which make them ideal adsorbents for ammonia storage as a hydrogen
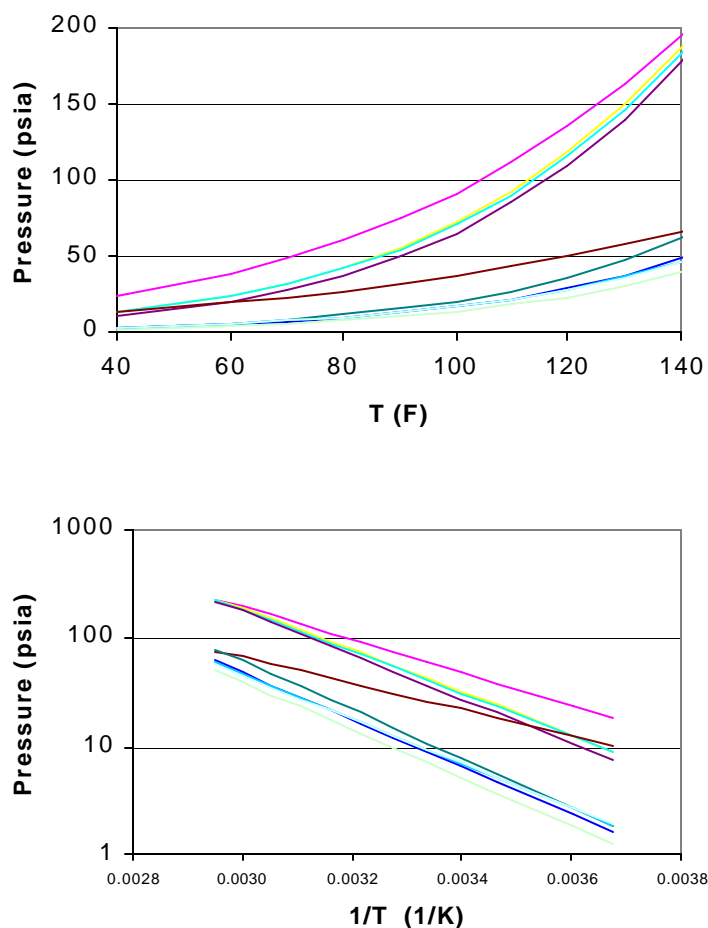
Figure 2. Vapor pressure curves for 10 ammoniated complex compounds.

source for fuel cells.

1. High usable refrigerant mass per unit mass of adsorbent.
2. Monovariance: Heat flows occur at constant temperature.
3. Many compounds are available permitting selection of near-ideal absorbents.

Reaction Kinetics & Sorbent Stabilization

Proprietary solid-vapor reactor hardware has been developed to enable reaction rates over an order-of-magnitude greater than those obtained by conventional means. Per conventional means, reactions are normally conducted with solid reactant poured in powder form on a heat exchange surface, and exposed to refrigerant vapor on the upper surface. Comparison of rates obtained with the conventional method and

with the Rocky Research Heat Exchange Hardware (RRHEH) are provided on our web site[3]. Peak reaction rates of less than 4 moles of ammonia per mole of salt per hour (mol/mol-hr) were obtained with conventional methodology, while rates above 17 mol/mol-hr were obtained with the RRHEH.

This ammonia storage application does not require rapid absorption and desorption of ammonia, so reaction kinetics would seem to be less important. However, designs that enable high reaction rates also promote absorption and desorption at low approach temperatures and pressure. Heat input need be only a few degrees above equilibrium temperature to release ammonia to the fuel processor and fuel cell. The approach used in sorber design by Rocky Research also fully stabilizes the salt against movement during absorption and desorption and against mechanical vibration and shock.

Results of Phase I Research and Development

A breakdown of the efforts under Phase I of the project on a task-by-task basis follows.

Task 1 – Select and Screen Candidate Sorbents

In order to select the complex compound with the most promising thermodynamic characteristics suitable for use in the ammonia storage device, specifications for operating conditions as well as the duty were established. Operating (delivery) pressure and the temperature of the available heat source is of critical importance in the selection of a candidate complex compound, since the vapor pressure of the ammonia complexed will represent the delivery pressure of the ammonia to the ammonia decomposition reactor.

Based on a conversation with the contacting officer's technical monitor, Dr. Richard Paur, we were directed to contact Meso Systems, the developer of the ammonia decomposition reactor. Conversations were held with M.R. Powell of Meso, who provided us with information on the requirements for the two candidate ammonia decompostioin reactors. One of these reactors includes a membrane to assist in ammonia scrubbing and one does not. The device with membrane requires considerably higher pressure ammonia. We were provided with more information about the non-membrane system. Meso informed us that each system has its merits and detriments. We agreed that the system ultimately chosen may be partially based on the ammonia storage device, since the total weight and volume for the entire system is critical to minimize.

The following are the operating specifications for the ammonia storage device as per the information provided:

General Specifications:

Mission Duration:	3 days
Required Ammonia Delivered:	518.4 g
Average Ammonia Delivery Rate:	0.12 g/min
Temporary Duty (for seconds):	0.36 g/min
Temporary Duty (for minutes):	0.24 g/min
Desired Number of Missions:	50 (can be a single mission if much lighter)
Ambient Temperature Range:	-40°F to 140 °F

Ammonia Decomposition Reactor Related Specifications:

	Non - Membrane System	Membrane System
Operating Pressure (psig)	2	35 to 40
Butane Exhaust Temperature (°C)	60	
Butane Flow Rate (stdcc/min)	50	
Combustion Air Flow Rate (l/min)	1.3	
Output Products Temperature (°C)	60 to 70	
Output Flow Rate (stdcc/min)	730	

Based on these specifications, candidate complex compounds were screened using information from Rocky Research's database, which is likely the most extensive database worldwide for ammoniated complex compounds. After detailed investigation of Rocky Research's database, six complex compounds were identified. These compounds are formed from five different salts, and are shown on Figure 3. For one salt, two coordinative complex compounds (CC714-1330 and CC470-1330) can be formed, each with it own characteristic monovariant behavior. It should be noted that the plot shows two horizontal lines, one of which (system A) represents the operating pressure required for the low pressure fuel cell and the other (system B) is the operating pressure for the higher pressure fuel cell. As the figure shows, different levels of vapor pressure suppression (vs. the ammonia ligand) are possible, with three of the complex compounds having greater suppression and the other less. The three complex compounds which offer lower vapor pressure suppression (CC714-1330, CC053-1030 and CC030-0535) have vapor pressures high enough that under many practical situations would allow the fuel cell to start before heat was being generated in the ammonia decomposition reactor and the fuel cell for feedback to the storage unit. The other three complex

compounds (CC480-1110, CC180-1580 and CC670-1330) would require heat input previous to usage. These do, however have some advantage in allowing for a possibly lighter pressure vessel design.

Vapor Pressure as a Function of Temperature
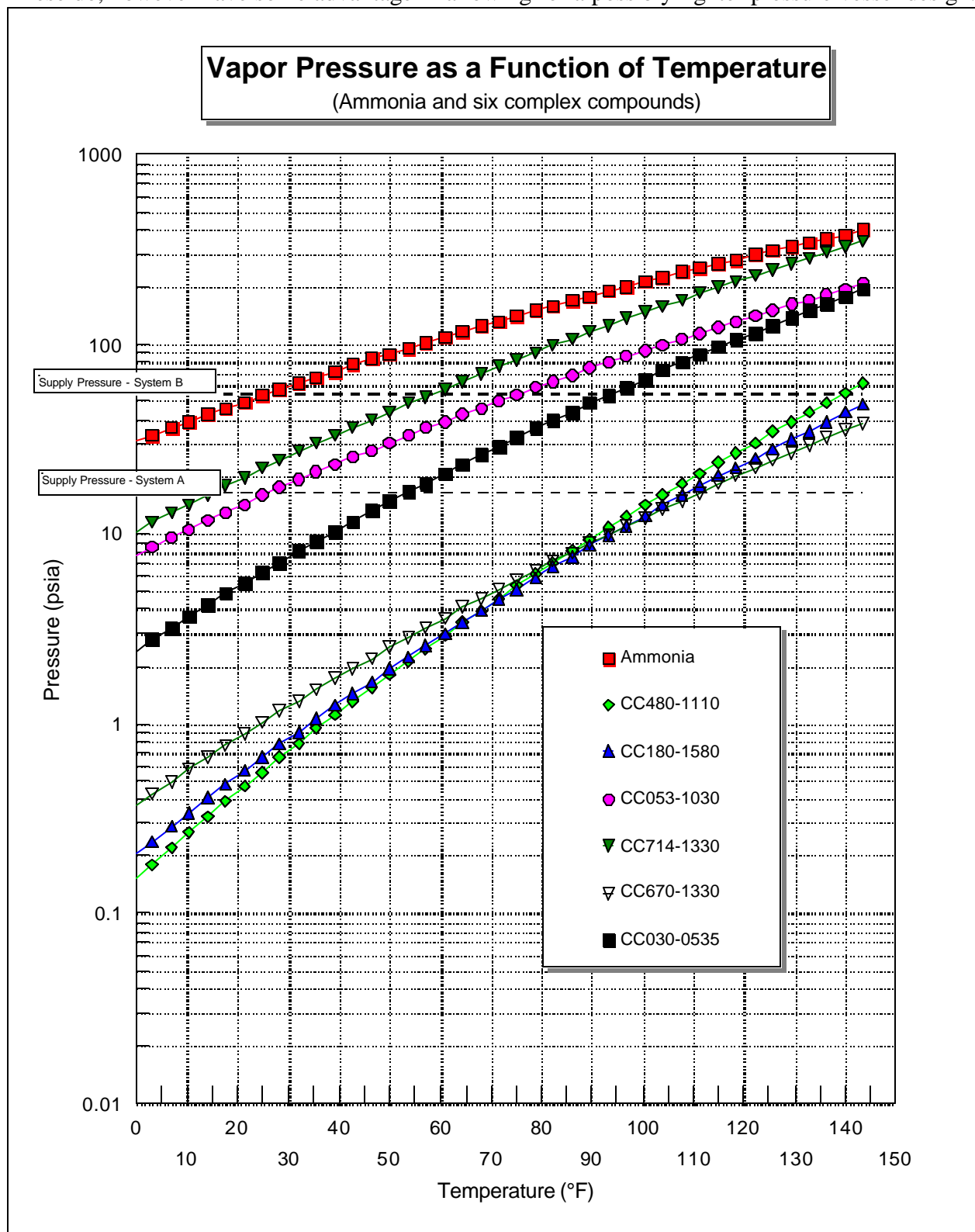### (Ammonia and six complex compounds)

Figure 3. Vapor Pressure Characteristics of Six Candidate Complex Compounds
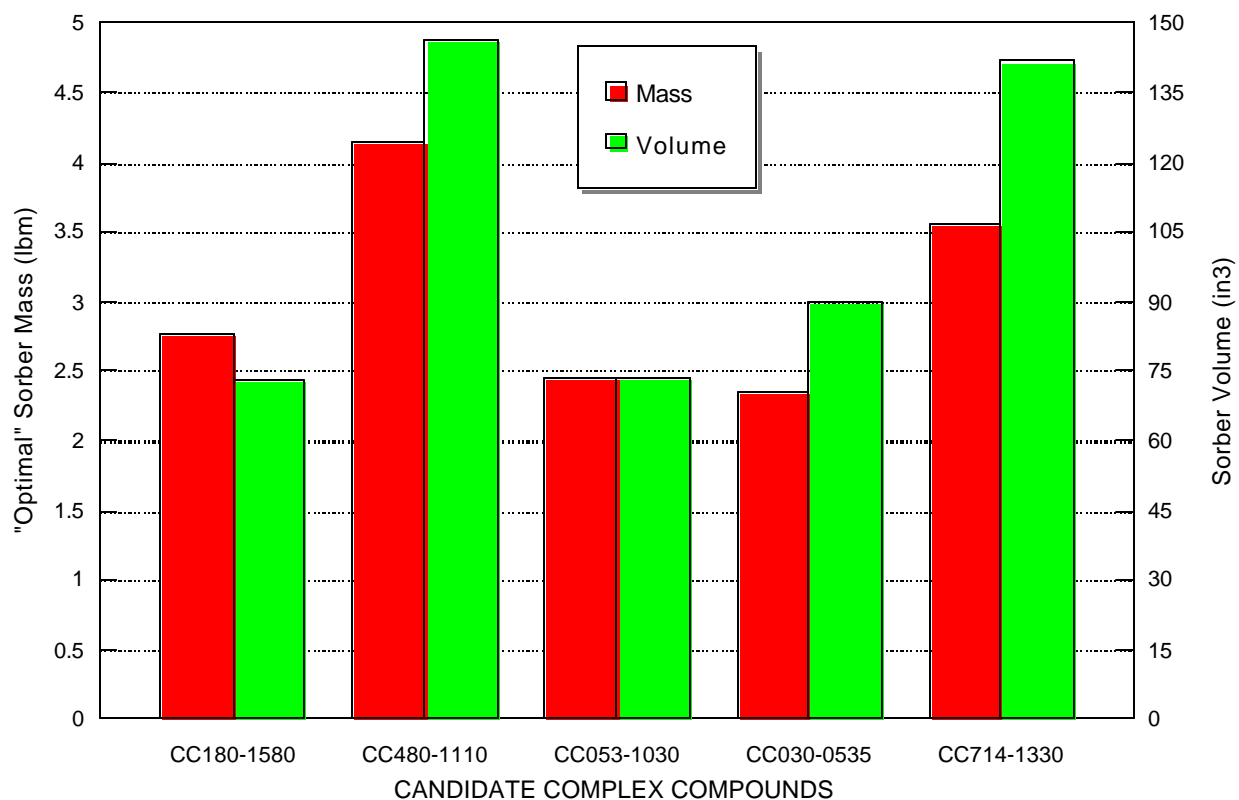
Based on these results, the complex compound CC670-1330 was deemed to be not useful. This complex compound is a lower ammonia coordination step of the same salt as CC714-1330. It was believed that upon additional heating of the CC714-1330 complex compound, more ammonia could be liberated in the CC670-1330 step. This is true, but to heat nearly 100°F higher temperature implies two different types of heating means for the sorber, (for example heating from ambient air then followed by heating via exhaust or combustion). This is likely to be impractical.

For the remaining five complex compounds, a spreadsheet was written and an analysis done to determine the anticipated sorber mass and volume for the 518.4 g of ammonia delivery over the 72 hour period. This analytical work was done using theoretical coordination characteristics for the complex compounds as well as assuming that the sorber shell has zero mass. The zero mass sorber shell was assumed to eliminate the need for a detailed sorber design, and its corresponding weight, at this point.

Figure 4 shows the results of this analysis. Three candidate complex compounds, CC180-1580, CC053-1030 and CC030-0535 showed the best promise in terms of mass and volume required. It should be noted that CC180-1580 is a higher vapor suppression complex compound, of which Rocky Research has extensive knowledge of in terms usage in small appliances. CC053-1030 and CC030-0535 are lower vapor suppression complex compounds which are much more experimental in nature.

Of some importance to this application is the heat input required for operation. As Figure 5 shows, there is not a great difference in the heat input requirements for the three leading candidate complex compounds. Each requires 4.3 to 4.7 W for operation. However, there are significant differences in the temperature levels required for these at 17 psia operation. This pressure level corresponds to 2.3 psig, which is the approximately the operating pressure required for the low pressure fuel cell. Figure 5 also shows this comparison. For the three best candidates, the CC180-1580, CC053-1030 and CC030-0535, the corresponding temperatures required are 110°F, 28°F and 54°F, respectively.

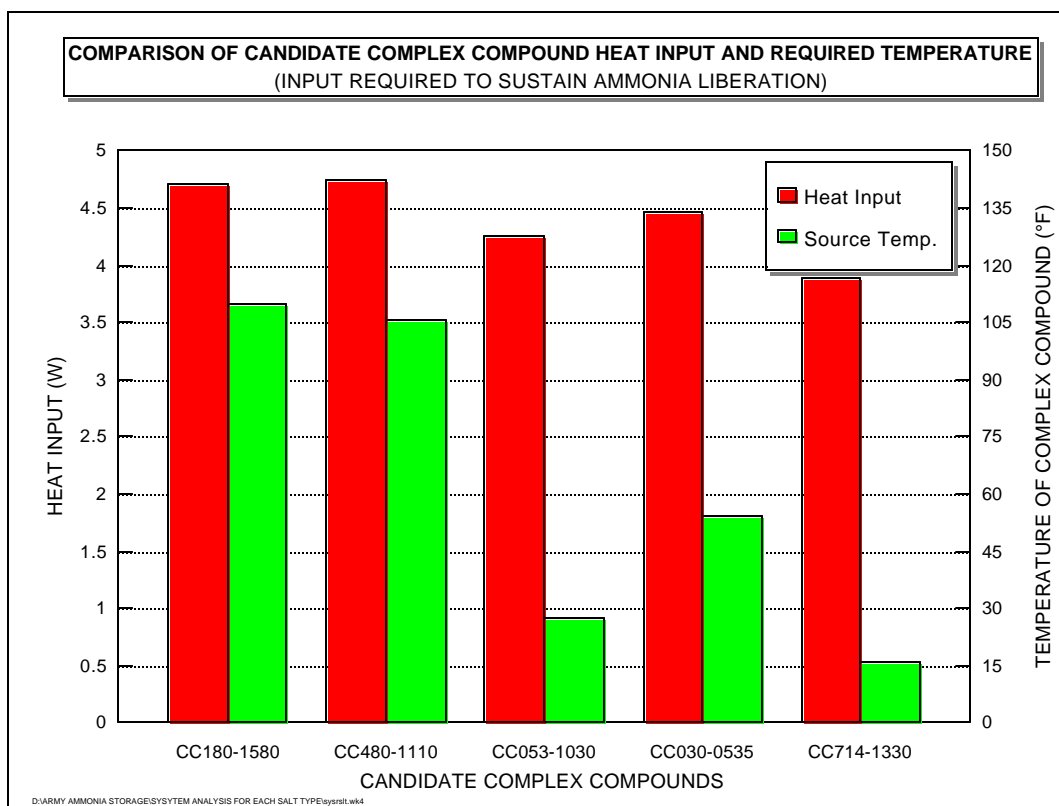Figure 4. Comparison of Mass and Volume Requirements for Five Candidate Complex Compounds

Figure 5. Heat Input and Temperature Required for Candidate Complex Compounds

Task 2 – Absorbent Characterization

Characterization of some of the complex compounds chosen was done using the Thermogravimetric analyzer. Thermogravimetric analysis (TGA) is used to characterize the ammonia uptake and reaction kinetics of ammoniated salts. TGA experiments are done with a Cahn C1100 pressure microbalance modified for dual flowing gas experiments. This apparatus directly measures sample weight as function of temperature and pressure in inert and ammonia atmospheres from ambient pressure to 20 bar and ambient temperature to 300°C. The balance is configured for samples up to 100 mg and a resolution of 0.01 mg. A schematic of the TGA dual flowing gas configuration is shown in Figure 6 and a picture of the actual apparatus is shown as Figure 7. Helium flows directly into the balance mechanism housing and ammonia flows upward in the hangdown tube; the two gas streams mix and exit below the balance mechanism but well above the sample. In this manner, corrosive ammonia vapor is kept away from the balance mechanism while the sample remains in an ammonia atmosphere. A three-way valve allows the sample to be purged with helium as well.

Typical TGA analysis is done as follows. A small sample of anhydrous salt with a target value of 6 - 7 mg NH_3 at 1:1 stoichiometry (20 - 80 mg salt, depending on molecular weight) is loaded into the balance. Residual hydration is removed by heating under helium purge until weight loss ceases. Unammoniated sample weight is recorded at ambient temperature and pressure, then NH_3 pressure is applied. After the weight stabilizes, indicating maximum NH_3 uptake, weight and temperature are recorded as the sample is heated and cooled through desorption and absorption transitions. These measurements yield isobaric tension curves, from which stoichiometry, vapor pressure vs. temperature, and heat of reaction are derived.

An assay of some CC030-0535 we had on hand was done and showed a purity of 90%, the balance presumably being absorbed water, as this salt is known to be hygroscopic. While attempting to dehydrate a sample by heating under a helium atmosphere in the microbalance, the sample weight decreased to 81% of the original weight. The weight loss began at 125 - 150°C and was still occurring when heating was terminated at 195°C. This was due to sublimation at elevated temperature. After cooling to room temperature, the atmosphere was switched to ammonia and the pressure was slowly increased. Ammonia absorption commenced at about 4.3 bar, and at 6 bar the sample absorbed 3.2 moles of ammonia per mole of salt, or 51% by weight ammonia. TGA heating and cooling curves at 6 bar following this absorption are shown in Figure 8. The regions labeled "liquid or solid solution" are evidence of bivariance, i.e. the concentration is a smooth function of temperature. Complex compounds normally exhibit monovariance, which is also seen here in the vertical portion of the curves, where the concentration is a stepwise function of temperature. When this sample was unloaded it was obvious that some melting had occurred. It was not clear whether this was due to the high temperature exposure or ammoniation.

New CC030-0535 salt with 99.5% minimum purity was purchased and assayed, and again showed 90% purity. The problem was traced to titrant that had been standardized improperly. After restandardization, the assay showed 100%. When this salt was dehydrated at a lower temperature, 60°C, the weight decreased less than 0.5% and stabilized. This salt was ammoniated at 5 bar and absorbed 2.7 mol/mol, or 46% by weight ammonia, consistent with the bivariance noted above. When the atmosphere was switched to helium and the pressure reduced to ambient, the sample weight and temperature readings became highly erratic. The sample was unloaded and had completely melted, flowing through the fine wire mesh support in the sample holder and touching the temperature probe. Because ammoniated CC030-0535 melts at room temperature, it is not suitable for use with conventional solid-vapor hardware. However, it may be suitable to a new type of sorber design which employs capillary action to maintain internal integrity.
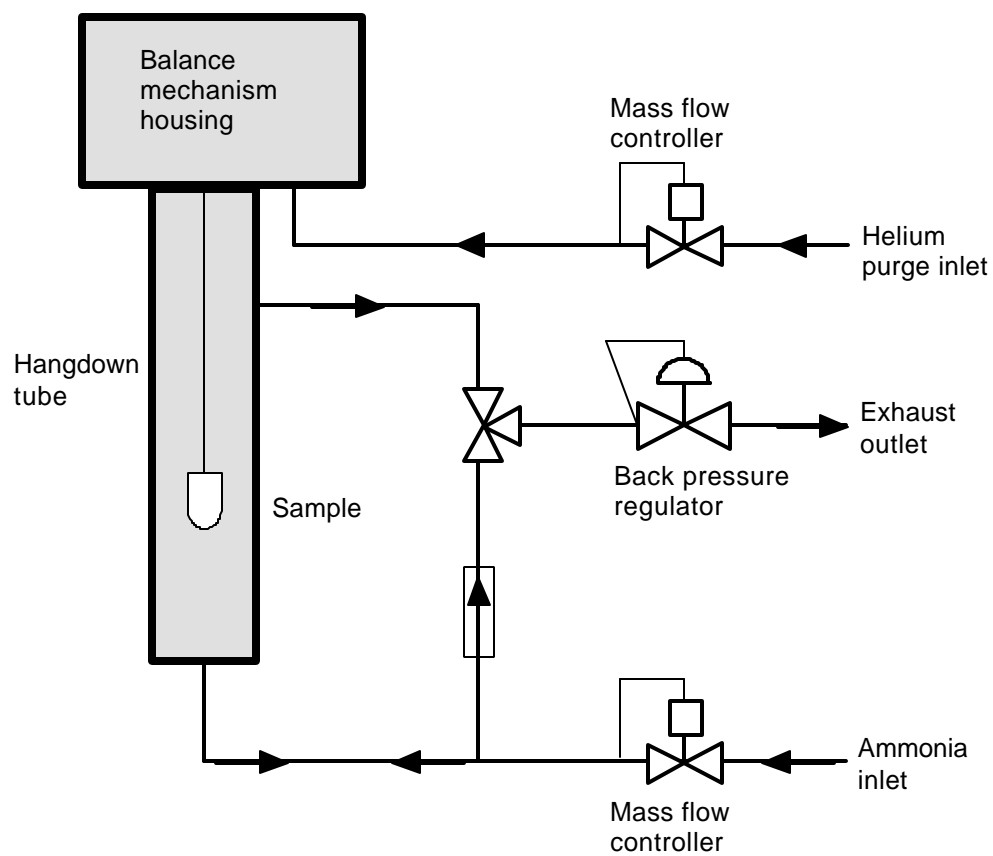
Figure 6. Schematic of Thermogravimetric Analyzer

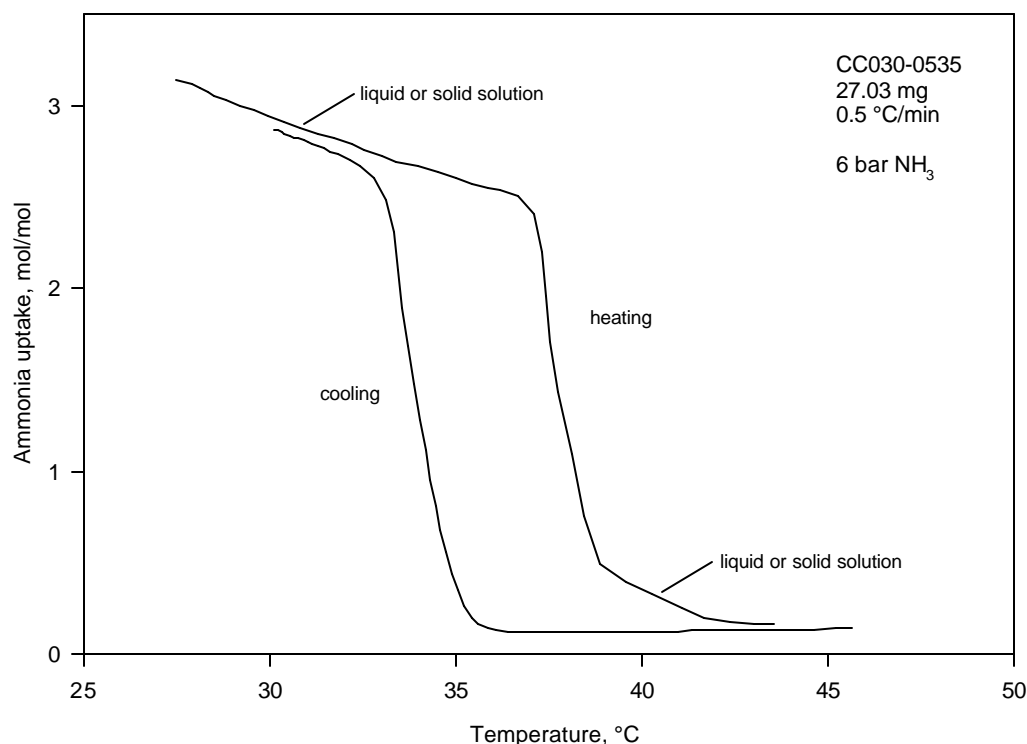Figure 7. Photo of the Thermogravimetric Analyzer

Figure 8. TGA scan for CC030-0535

CC053-1030 salt with 99% minimum specified purity (lot analysis showed 99.5%) was also purchased for TGA testing. This salt did not absorb at room temperature when 4 bar ammonia pressure was applied. At room temperature and 5 bar ammonia pressure, the salt absorbed 4.9 moles of ammonia per mole of salt, or 45 percent by weight. TGA heating and cooling scans for CC053-1030 at 5 bar ammonia pressure are shown in Figure 9. As seen with the CC030-0535 salt last month, there is bivariance evident in the non-stepwise regions of the scans. The area of the heating scan labeled with a question mark shows a transient *decrease* in temperature. The reason for this is unclear. One possible explanation is that the salt melted and some dripped on the tip of the temperature probe where it desorbed rapidly and cooled. Not much salt could have been lost here because the cooling scan shows absorption nearly equal to the original ammonia uptake.

Following the scans shown in Figure 9, the sample was left under a slow helium purge overnight and desorbed completely as expected. When 5 bar ammonia pressure was applied at room temperature, the sample weight suddenly decreased markedly about midway through the absorption, indicating probable melting. The sample was unloaded and almost nothing remained in the sample holder. Stains and residue showed that the salt had melted, run down the skirt area of the sample holder and dripped off.
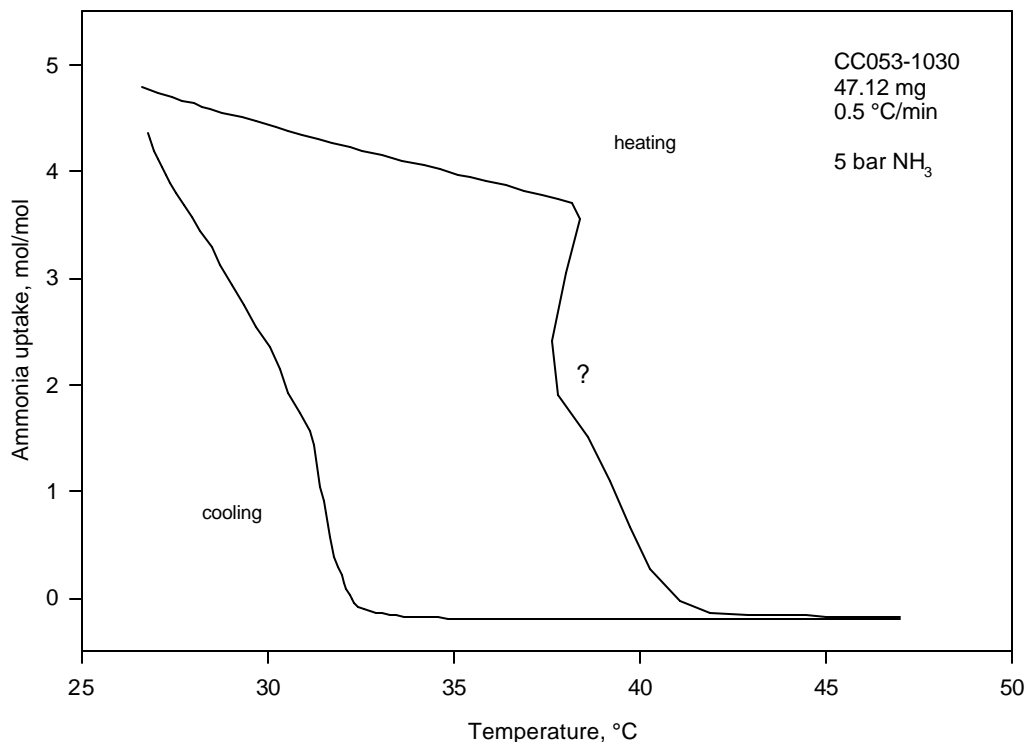
Figure 1. TGA scan for CC053-1030 at 5 bar ammonia pressure

Figure 9. TGA Scan for CC053-1030 at 5 bar Ammonia Pressure

Because ammoniated CC053-1030 melts at room temperature, as does CC030-0535 which was tested last month, it is not suitable for use with more conventional impregnates in solid-vapor hardware. However, it may be suitable to a new type of sorber design that employs impregnates with capillary action to maintain internal integrity, especially since the life expectancy is a maximum 50 missions. This effort would be pursued under a Phase II of the project while this ongoing Phase I effort will focus on the development of a first prototype using CC180-1580.

Tests with CC180-1580 have been done with a subscale prototype rather than with the thermogravimetric analyzer. This is because this complex compound has been used for other applications and its thermogravimetric analysis has bees completed and more information on its performance in actual sorber designs is known. Performance in an actual prototype sorber may sometimes be lower than that in the microbalance because of inactive or only partially active portions of the sorber limiting heat and mass transfer.

Tests on a subscale prototype CC180-1580 were done on the cycling sorber test stand depicted in Figure 10. In this apparatus, a subscale sorber (such as those shown on the table) is installed in the location where the yellow fiberglass insulation is shown. The sorbers are connected to the ammonia ligand column (see tall vertical column in the figure) and either cooler water is run through the sorber heat exchanger tube for absorption of ammonia into the complex compound or hot water is run to the sorber for desorption of the ammonia back into the column. In this apparatus, this can be done automatically, and some sorbers in the past have been run over 70,000 cycles.

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Figure 10. Cycling Sorber Test Stand

Results of a subscale sorber test stand test of this complex compound are shown in Figure 11. The figure shows both the reaction rate in moles NH3/mole salt hr as well as the total desorbed amount in moles NH3/mole salt. As the figure shows, this desorption test was only run for 100 minutes and the total desorbed amount was 5.8 moles NH3/mole salt. The test was begun with the complex compound in the fully absorbed state, as it would be when delivered to the soldier in the field. The test gives credence to the early estimate that 6 moles NH3/mole salt are possible. This value was used in the estimates of performance for the units. It should be noted that the reaction rates shown on the plot are far higher than would be required by the sorber. In fact, the minimum shown is approximately 40 times greater since the system for the soldier only requires a reaction rate of only 0.083 moles NH3/mole salt hr. This test sorber was made with a higher capability heat transfer core than is required for the ammonia/hydrogen storage

device. Because of the high reaction rates shown in this test, the heat transfer surface can be reduced dramatically and the volume required for it can be eliminated.
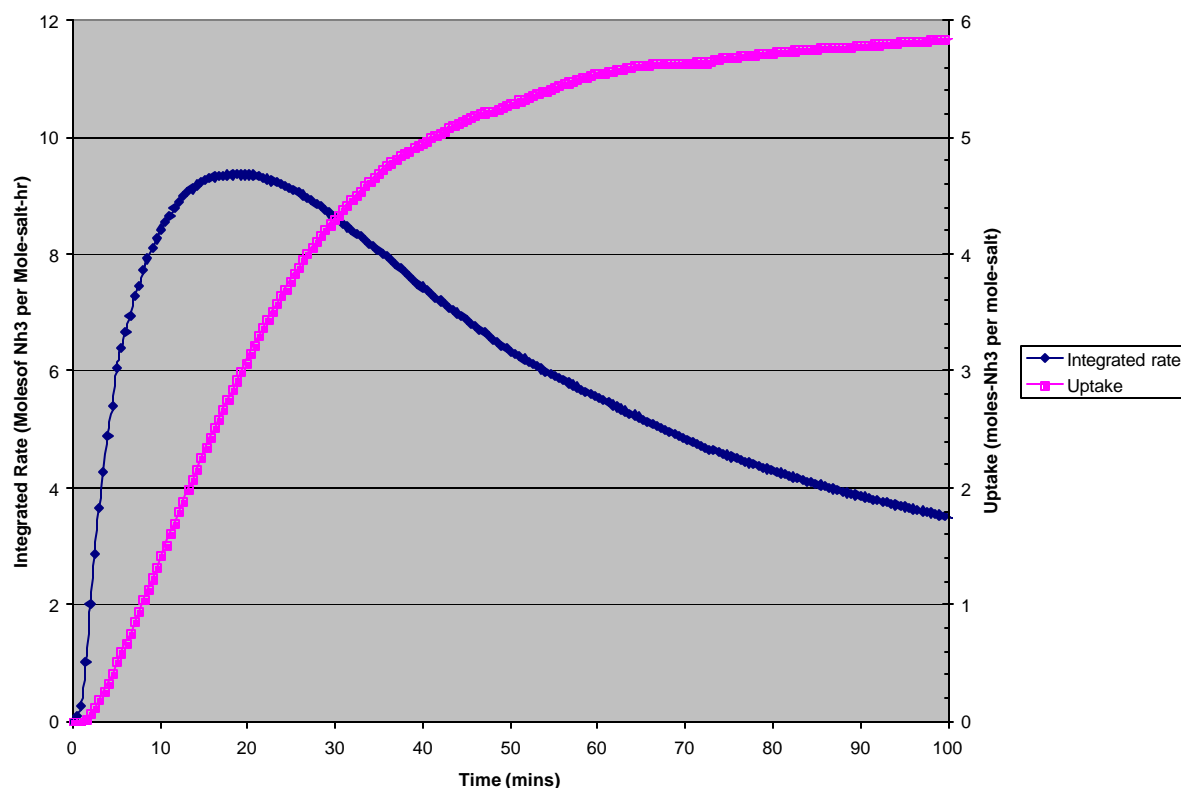

Figure 11. Reaction rate and uptake information for a CC180-1580 sorber

Task 3 – Preliminary Design and Total Mass Estimation

The preliminary design specifications for the sorber continue to be based on an assumption of an ammonia capability of 6 moles NH3/mole salt. This is due to the fact that the aforementioned test results showed that 5.8 moles NH3/mole salt are easily possible, even for much shorter than the desired 72 hr time period for the unit. The estimate for the sorber size is 95.8 in3. However, this assumed a vessel volume utilization for the complex compound of 80%. The anticipated weight of the sorber including the fixed ammonia mass and the ammonia mass to be discharged, but not including the shell weight is shown on Figure 12. The resulting unit has a weight of 3.03 lbm with a specific storage density of 1003 Wh/kg.

To proceed with the design, this high vessel volume utilization assumption needed to be proved and this required the impregnation of a new class of salt retaining material. Since this impregnation is actually the beginning of the fabrication of the sorber, the description of this work is included under Task 4.

MASS DISTRIBUTION FOR STORAGE
(WEIGHT AND SPECIFIC STORAGE AS INDICATED)

3.30
1002.8

0.00 (0.0%)
1.14 (34.7%)
1.77 (53.8%)
0.38 (11.6%)
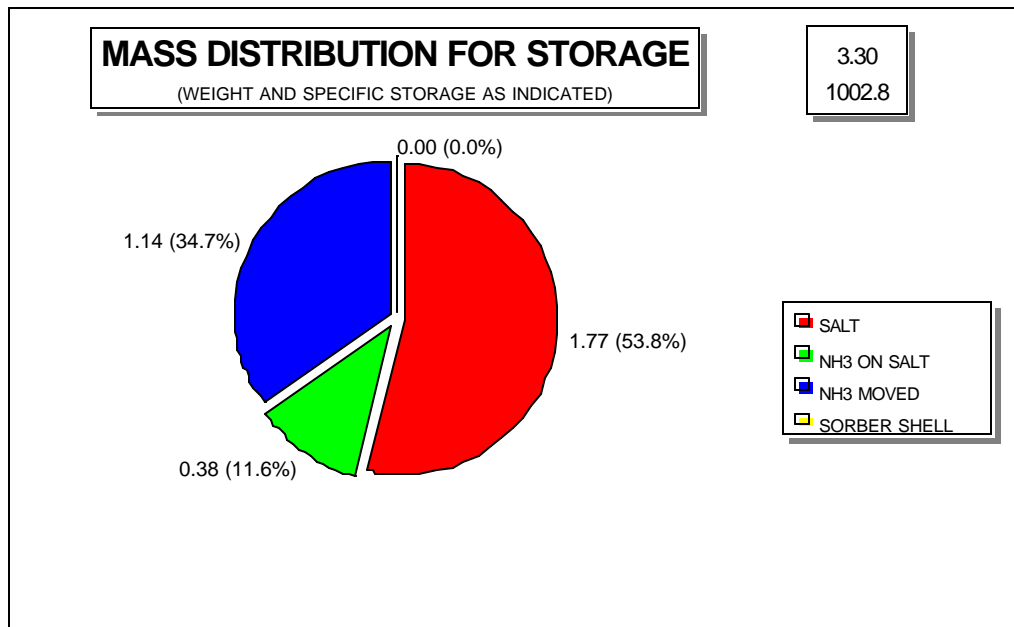
- SALT
- NH3 ON SALT
- NH3 MOVED
- SORBER SHELL

Figure 12. Mass Distribution for Storage Device

Task 4 – Build One Demonstration Ammonia Storage Vessel

The complex compound CC180-1580, has slightly less ammonia storage density than CC053-1030 and CC030-0535, but does remain a solid at room temperature when fully ammoniated. Because of this, CC180-1580 will be the focus of the efforts to develop the first prototype storage device. This complex compound does hold the ammonia at a much lower pressure at ambient temperatures, which leads to improved safety and lighter vessel shell thickness versus the other two. Also, higher temperature elevation is required to promote ammonia flow to the fuel cell portion of the system but the system is capable of providing the necessary heat feedback for this during operation.

Fabrication of an extremely high density impregnate with CC180-1580 was accomplished. As per the previously existing Rocky Research technology, the complex compound was immobilized in an impregnated mesh. This helps to inhibit the growth of the complex compound upon ammoniation and allows cycling (multiple charges and discharges in the case of this product) without damage to the sorber. Since the expected life of this unit is only 50 missions, the first impregnate was made with a very open carbon fiber mesh, which had the promise of not taking up too much valuable space in the sorber, improving its compactness.

The resulting impregnate with this mesh is shown on Figure 13. As the figure depicts, the salt has been immobilized into the carbon structure. Measurements have shown that the volume of the impregnated material shown is 87% salt, which is higher than has been achieved in earlier efforts.
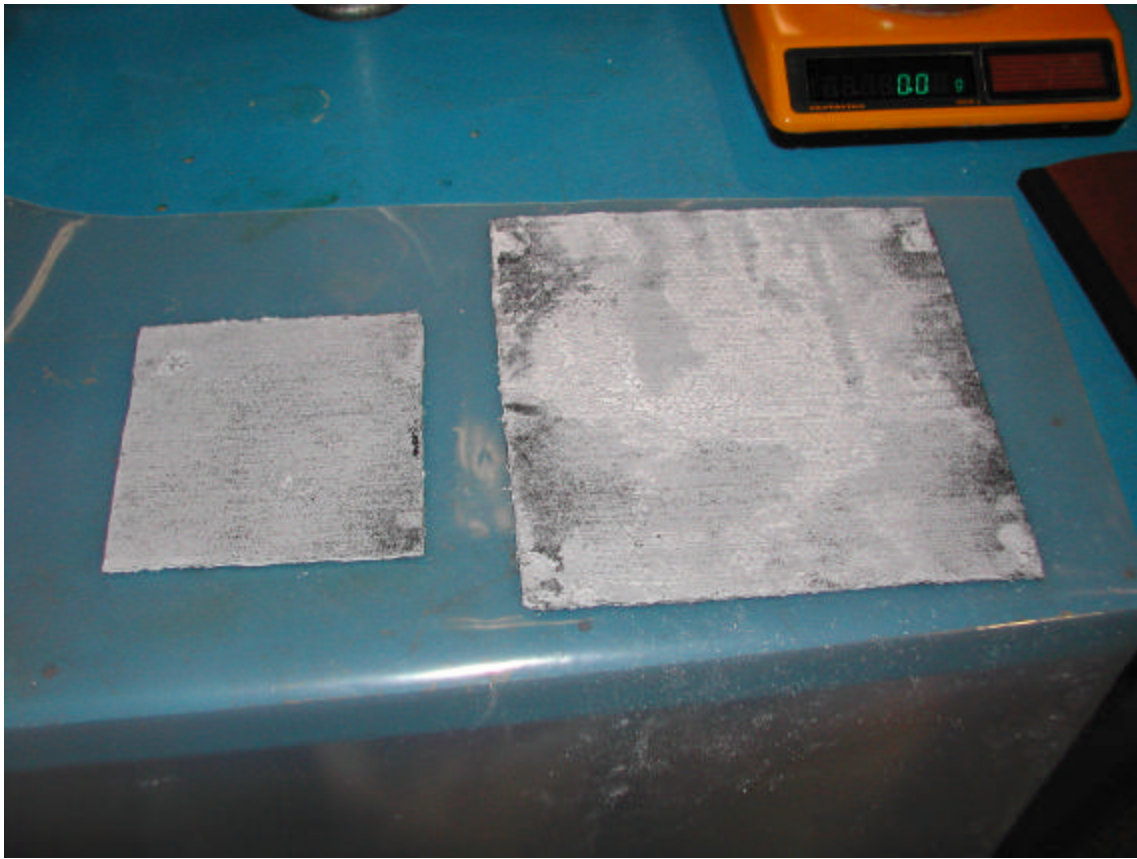
Figure 13. Carbon Fiber Impregnate with CC180-1580

The resulting impregnate with this mesh as stamped is shown on Figure 14. The demonstration ammonia storage sorber design has heat transfer to and from the outer shell, with no heat transfer tubes or structures inside the pressure boundary. This design, together with high volume fraction of salt in the impregnate, resulted in overall vessel volume utilization greater than the 80% target.
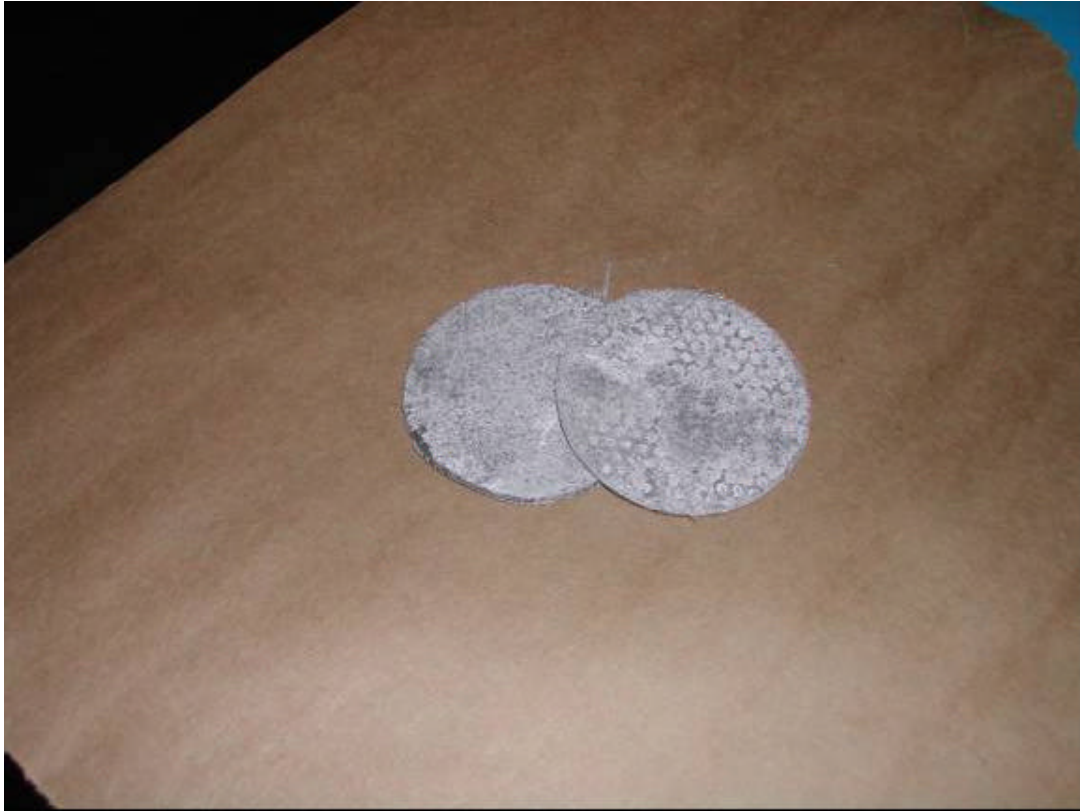
Figure 14. Impregnated Complex Compound Disks

After it was proven that salt could be impregnated into the open carbon mesh at the required density, fabrication of components for the demonstration sorber was performed. The sorber is primarily comprised of disks of carbon mesh impregnated with CC180-1580, and a containment shell. On the outside of the shell is a wire that is wound spirally and joined to the surface. Over this wire is a thin CPVC housing. The gap formed by the spiral wire in between the housing and the shell is a passage for the heated products from the ammonia cracker and the fuel cell to pass. This serves as the heat addition point for the sorber. This heat addition is the driving force for the liberation of the ammonia from the complex compound sorber. A photograph of the sorber, prior to being covered by the CPVC housing is shown as Figure 15.
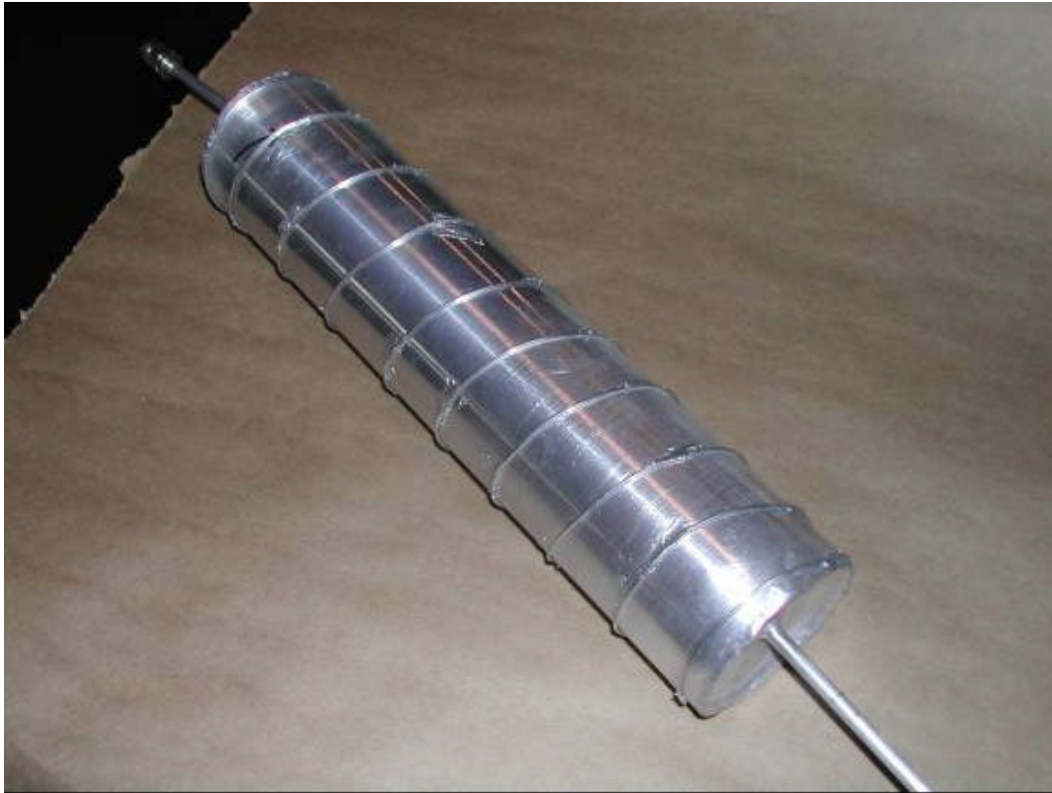
Figure 15. Ammonia Storage Sorber Without CPVC Housing

The sorber is 3 inch diameter and 13.5 inches long for a volume of 95 in3. After assembly, the demonstration sorber was ammoniated for the first time. The unammoniated weight of the sorber was 1210 g (2.67 lbm). The sorber was able to absorb 709 g (1.56 lbm) of ammonia. Based on the chemistry of the complex compound and Rocky Research's experience with the subscale unit, it was expected that this will be capable of providing 532 g (1.17 lbm) of ammonia for fuel cell usage. This is slightly greater than required for this development. Storage of 1.17 pounds in a total weight of 4.23 pounds is a mass ratio of 3.6 pounds of total mass per pound of stored ammonia. It is believed that with a lighter weight composite material of more exotic metal in addition to a possibly less dense substrate that the total sorber weight could be reduced even further.

The apparatus used for the first ammoniation of the sorber was modified to allow for desorption also. A small blower was added along with a heater and thermocouples to measure heated air temperature. Data acquisition via a PC was utilized.   A photograph of this test apparatus is shown on Figure 16. The sorber is the grey cylinder near the center of the photograph. Other equipment in the photograph includes instrumentation to measure process conditions such as temperature and pressure, and utilities to heat and cool the sorber for absorption and desorption. Ammonia flow is measured by a flow meter. Total ammonia uptake is determined volumetrically using a graduated glass column, shown toward the far right of the photograph. This column contains liquid ammonia and precise height markings; the change in liquid height during ammonia or deammoniation provides accurate measurement of ammonia moved. Temperature and pressure of the liquid ammonia in the column are constantly measured and controlled, so density can be accurately determined.

Figure 16. Test Apparatus for Absorption/Desorption of Complex Compound Sorber (grey cylinder)

The simulated warm exhaust flow needed for ammonia desorption was simulated using an air blower and an electrical heater in the air stream, which is shown in Figure 17. The ammonia flow and pressure were measured and were logged on a PC. The ammonia desorbing from the sorber was at atmospheric pressure conditions at Boulder City, NV, which is at 2500 ft. altitude (13.54 psia).

The first desorption test was done at 62°C air inlet temperature. Results are shown in Figures 18 and 19. In Figure 18 ammonia mass flow and air inlet temperature are shown over only a few hours of the total operating period. Figure 19 shows the integrated ammonia mass over the same period. The flow rates shown are higher than needed for the fuel cell. The goal is total of 518 grams of ammonia over 72 hour period or a rate of 7.2 grams-NH3 per hour. A total of 530 grams of ammonia was desorbed during this test over a 40 hour period, or 13.25 grams-NH3 per hour. At the time of this test we could not run the test stand continuously and unattended due to safety reasons. For this reason, the second portion of the data is not depicted in the plot. The test stand was enhanced later for continuous runs as shown in next figures.

Figures 20 and 21 show the results for the second desorption test of the sorber, which was at 55°C air inlet temperature. The figures show desorption over the first 52 hours. The mass flow rates are close, but only slightly lower than the goal, but the air inlet temperature, at 55°C is lower than the available 60°C source from the fuel cell and ammonia decomposition reactor. It should be noted that the desorption rate is

relatively constant for a long period. This is an important aspect of complex compounds. Due to monovariance (a fixed pressure for a given temperature regardless of the concentration), relatively constant flow can be obtained from the device with only control of the sorber temperature being required.
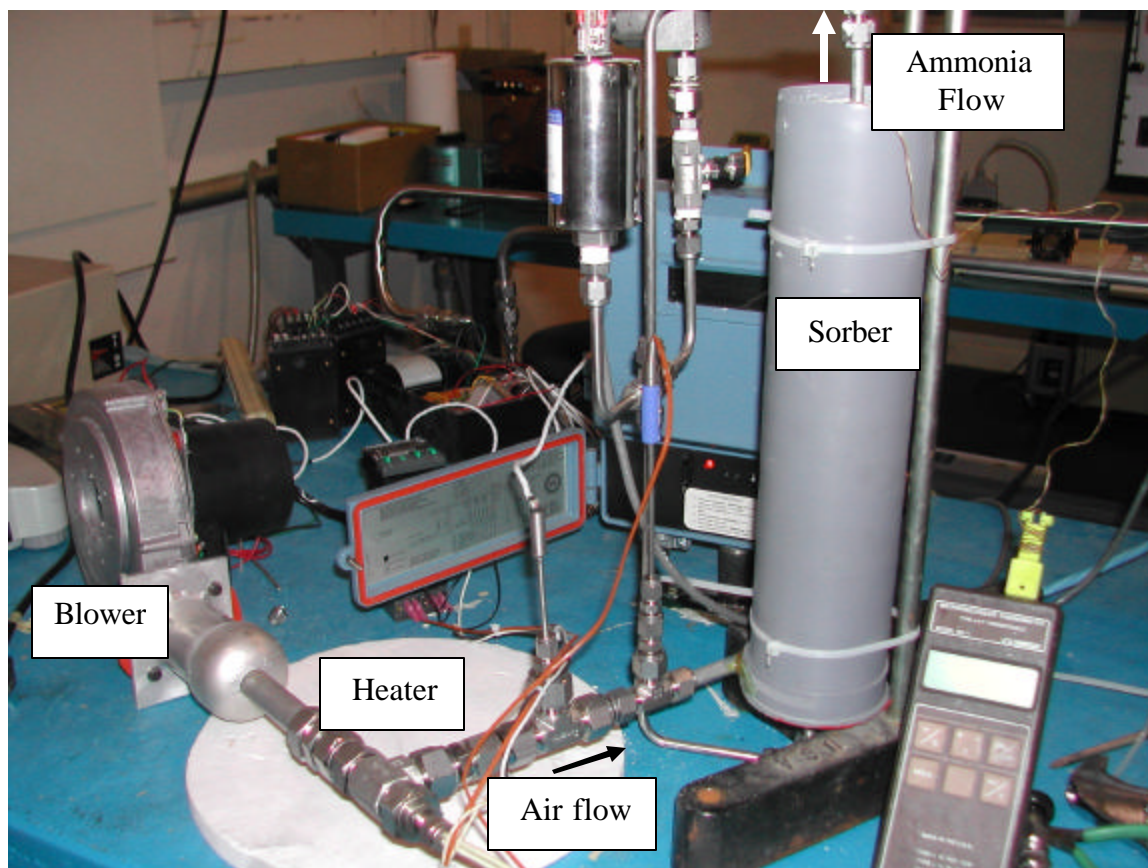

Figure 17. Test Apparatus Showing Desorption Blower and Heater

At the end of the 72 hour test period, a total of 495 grams of ammonia was desorbed, as shown on Figure 22 of the data. Thus the prototype is very close to the desired performance of 518 g of ammonia output, even at this low heat input temperature.

The current sorber was built with the goal of mass savings, and hence the heat transfer area was reduced to a minimum. This heat transfer capability could be enhanced and can also allow for much lower heat source temperatures with a very low weight penalty by the addition of more surface inside the sorber.

In Rocky Research's experience, the sorber as built represents excellent performance for a first attempt at low mass, slow reaction rate sorber design using this complex compound. The desorption performance in terms of ammonia flow is nearly identical to that desired for the fuel cell application.
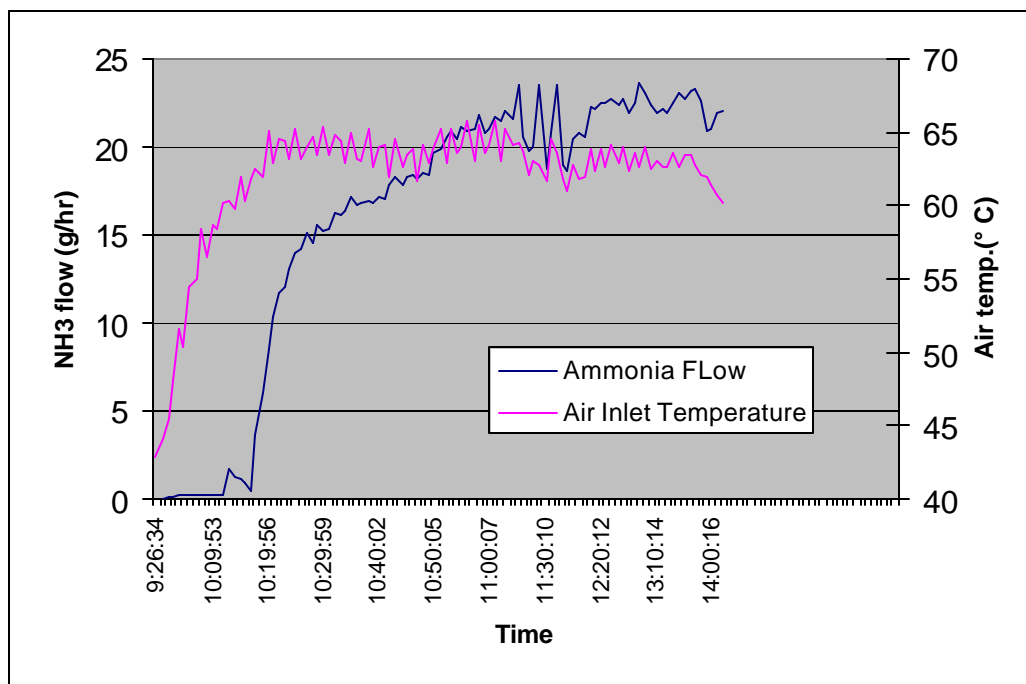
Figure 18. Test results at 62°C, Flow Rate and Air Temp. as a Function of Desorption Time
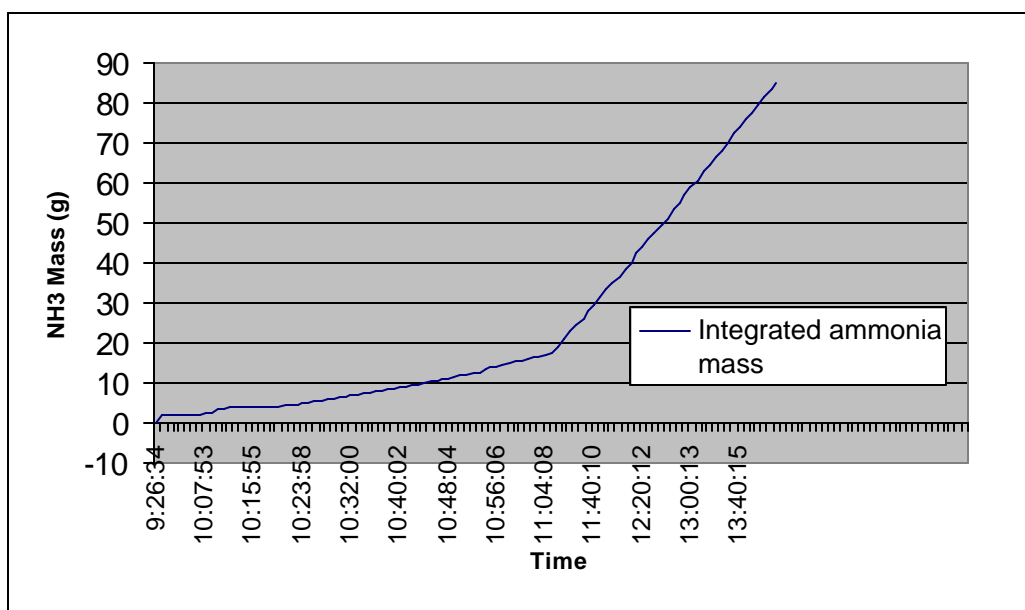

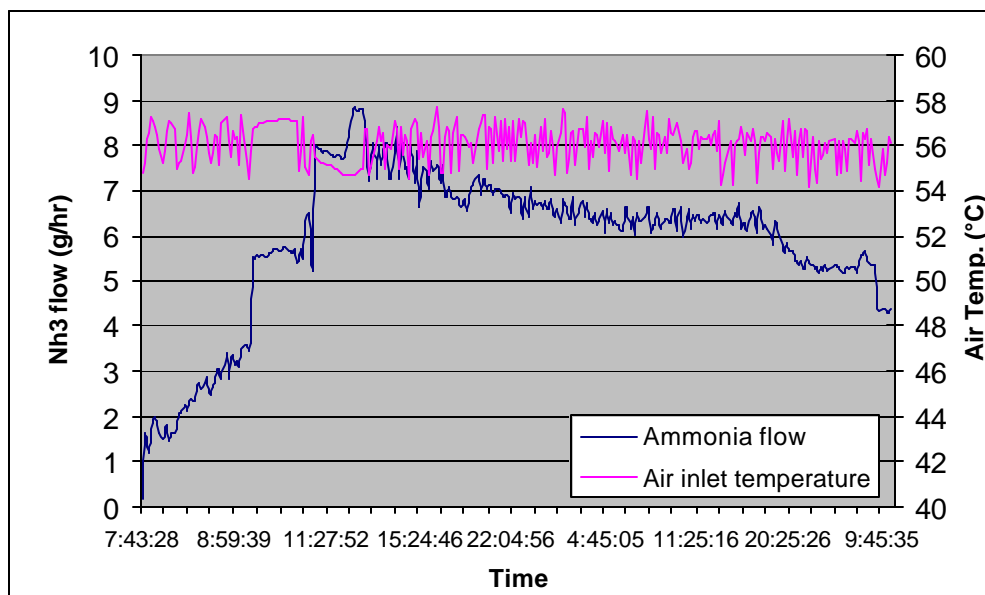Figure 19. Test results at 62°C, Ammonia Desorbed as a Function of Time, Initial Part of Desorption

Figure 20. Test results at 55°C, Flow Rate and Air Temp. as a Function of Desorption Time
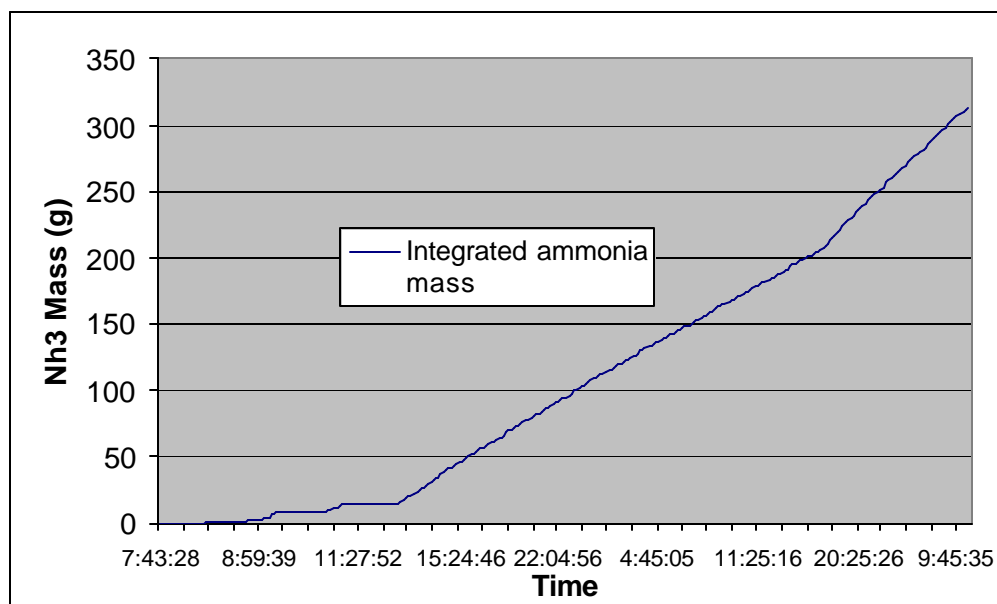

Figure 21. Test results at 55°C Ammonia Desorbed as a Function of Time, Initial Part of Desorption
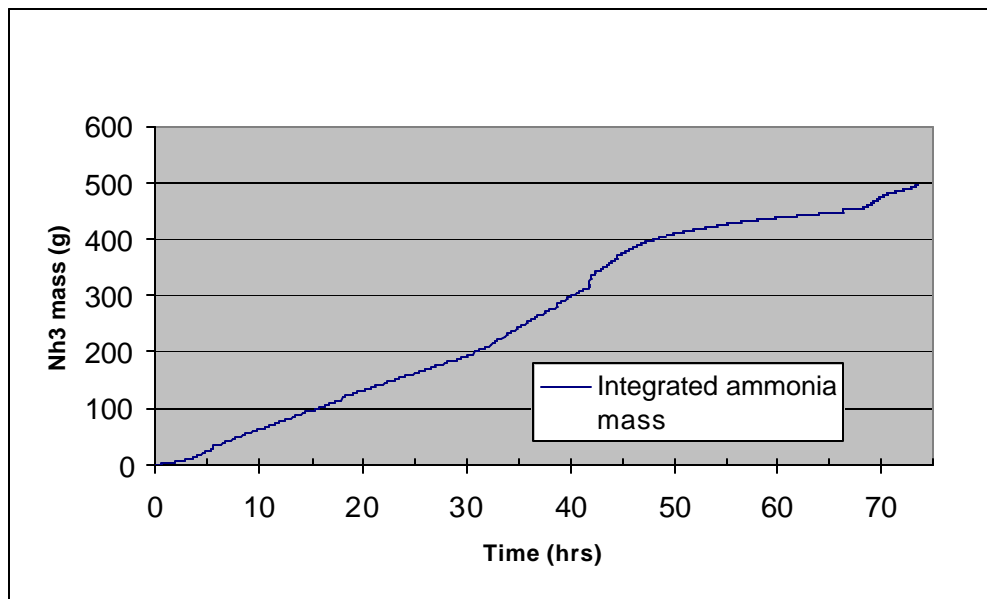
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Figure 22. Test results at 55°C Ammonia Desorbed as a Function of Time

Task 5 – Reporting

During the course of the project, six monthly reports were provided. This final report represents the completion of the reporting requirement for the project.

Future Work

In Phase II of the project, it is expected that the heat transfer capability of the sorber will be enhanced slightly to allow lower temperature desorption for more robust operation. The use of lightweight materials and an integrated structure shell design including the heating air stream passages may reduce the unit charged weight by approximately 10%. Also, efforts directed towards other complex compounds with not only solid/vapor ammonia storage, but with additional melting capability to enhance the ammonia desorption per unit mass of storage, should have an even more significant impact on weight and volume. It is expected that these could reduce the weight of the unit an additional 10% to 20%.

Conclusions

Under this project, the technology for low mass sorber design for ammonia storage at reduced vapor pressures was advanced using Rocky Research's complex compound technology in a low mass and volume manner. In this first attempt at ammonia storage for the 72 hr, 518 gram NH3 dishcarge application suitable to the Palm Power 3-day mission application, the resulting sorber weight was 3.06 lbm when discharged in a 95 in3 sorber shell size. The sorber was capable of providing up to 530 g of ammonia using heat input at temperatures associated with the ammonia decomposition reactor and the fuel cell exhaust.

It is believed that the goal of attaining an energy density of 2000 Whr/kg is an extremely difficult one for any true vapor pressure suppression technology, assuming a 20 W, 72 hr load. This is because the ammonia itself (518 g) to be utilized results in an energy density of 2782 Whr/kg, not including any containment vessel.   For the complex compound sorbent utilized in this effort, just the ammonia and the complex compound impregnated core itself resulted in an energy density of 897 Whr/kg. With the shells included, this was reduced to 750 Whr/kg.   Since complex compounds represent the highest absorption mass per unit mass sorbent of any solid/vapor sorbent/ammonia technology known by a factor of 4 or 5, it is doubtful that any significant vapor pressure suppression technology would provide the necessary energy density desired.   This does not mean that improvements in the complex compound energy density realized in this project cannot be improved. It is expected that with an integrated (a structural shape with pressure retention as well as air passages) design shell of high tech material and a complex compound that takes advantage of some melting capability that up to an approximate 30% reduction in weight is possible, to a potential energy density of as high as 1100 Whr/kg.

Bibliography

1. W. Nernst, The New Heat Theorem, New York: Dover Publications, Inc., 1969.

2. W. Blitz, G. F. Huettig, "Ueber Ammoniakverbindungen der Haloginide", Zeitschrift f. anorg. Chemie, 109, S. 89, 1919.

3. http://www.rockyresearch.com