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Environmental Reactivity of Solid-State Hydrogen Systems: Fundamental Testing and Evaluation

Charles W. James Jr., Jose A. Cortés-Concepción, David A. Tamburello, and Donald L. Anton*

Savannah River National Laboratory
Aiken, SC, 29808 USA,

* Corresponding Author: Tel: +1 803-507-8551, Fax: +1 803-652-8137
Email: *donald.anton@srnl.doe.gov*

Abstract

In order to enable the commercial acceptance of solid state hydrogen storage materials and systems it is important to understand the risks associated with the environmental exposure of various materials. In some instances, these materials are sensitive to the environment surrounding the material and the behavior is unique and independent to each material. The development of testing procedures to evaluate a material's behavior with different environmental exposures is a critical need. In some cases material modifications may be needed in order to reduce the risk of environmental exposure. We have redesigned two standardized UN tests for clarity and exactness; the burn rate and self-heating tests. The results of these and other UN tests are shown for ammonia borane, NH_3BH_3, and alane, AlH_3. The burn rate test showed a strong dependence on the preparation method of aluminum hydride as the particle size and trace amounts of solvent greatly influence the test results. The self-heating test for ammonia borane showed a failed test as low as 70°C in a modified cylindrical form. Finally, gas phase calorimetry was performed and resulted in an exothermic behavior within an air and 30%RH environment.

Keywords: Environmental Reactivity, Metal Hydride, Chemical Hydride, Hydrogen Storage, Calorimetry

1.0 Introduction

As hydrogen is still explored as an alternative automotive fuel, there is continued focus on developing new and improved hydrogen storage systems outside of compressed hydrogen gas. These systems include but are not limited to metal hydrides, chemical hydrides, or adsorbent systems. While there is extensive information related to each system's hydrogen storage capabilities, little information is available involving the hazards and risks associated with using and handling these types of materials. Therefore, appropriate risk mitigation strategies need to be developed to account for the potential of reaction events to occur such as a breach-in-tank scenario. This scenario involves the hydrogen storage media being dispersed from the tank and the reaction with air and/or water and the potential for a vigorous reaction to take place. The key aspect in risk identification is the development of rigorous testing standards and procedures related to the environmental reactivity of the hydrogen storage media in air or water exposure.

The United Nations (U.N.) developed a testing protocol for the transportation of dangerous goods [1], but this test protocol while useful as a starting point is not wholly sufficient to describe the risks of exposure of metal hydrides, chemical hydrides, or adsorbent materials. Therefore, modifying the testing approach is necessary in order to evaluate these condensed phase storage materials. The modified U.N. procedures categorize materials as "pyrophoric" in two categories: flammability and water reactivity. Flammability tests involve the introduction of heat to the sample through various scenarios including self-heating, burn rate, and pyrophoricity. The water reactivity tests involve water exposure to the sample in different capacities, i.e. – water drop, water immersion, surface contact.

This paper will discuss the UN testing, focusing on burn rate and self heating tests, for ammonia borane (NH_3BH_3) and aluminum hydride, i.e.- alane (AlH_3) [2]. Additionally, time resolved calorimetry data will be reported, which allows for the enthalpy of reaction to be

measured at temperature. This information supports a computational modeling effort to elucidate the hazards associated with a breach-of-tank scenario [3-5]. These experiments are also used to validate the computational efforts, which will allow insight into the risks associated with environmental exposure scenarios and, ultimately, will help reduce the number of experiments needed to explain the environmental reactivity behavior of different solid-state hydrogen storage materials.

2.0 Experimental

2.1 Material Preparation

Hydrogen storage grade ammonia borane (97% pure) was purchased from Sigma Aldrich and used as-received. Two grades of alane were used in this study, one procured commercially and a second made internally for this study. Aluminum hydride was synthesized following the procedure provided in Brower et al [6] with no additional modification. The crystallite size was calculated to be 40 nm using the Scherrer method. Commercially obtained aluminum hydride was purchased from ATK with a grain size determined by SEM analysis of between 4 and 32 microns and used in the as-received condition.

2.2 U.N. Testing

A set of materials testing procedures was developed based on internationally accepted standards drawn from United Nations testing procedures [1]. These tests include exposure to air, humidity, and water. Generally, the U.N. test procedures were modified by the addition of thermocouples to monitor the temperature within the hydrogen storage material, or in near proximity to the material, as appropriate. All tests were video recorded. The burn rate and self heating tests were modified to use smaller quantities of material with the results verified against standard tests.

2.2.1 Burn Rate Test

The purposes of the burn rate test are the classification of rapidly combustible solids, differentiation of ignitable, rapidly burning and dangerous burning substances and assessment of the relative hazard of rapidly combustible solids. The test procedure details followed UN-RTDG part-3, test-N1[1]. The powdery hydrogen storage material was deposited as a strip on a platform to measure the burning rate. The powder strip with 100 mm of length and a 100 mm^2 cross-section was ignited from one end and burning propagation time measured for 100 mm after an initial stabilization period. A series of 6 thermocouples was fitted along the axis of burn rate propagation at regular intervals, so that the temperature at a point ~5 mm into the pile could be monitored as a function of time. These tests were video recorded to provide quantitative and qualitative data acquisition.

2.2.2 Self Heating Test

The details of the test procedure followed UN-RTDG div. 4.2 [1]. The powder samples were loaded in 1 in^3 cylindrical basket made of stainless steel screen with 0.05 mm openings and an uncovered top surface. 2 chromel-alumel thermocouples, with 0.3 mm diameter were inserted into the cylindrical sample container and positioned at the top and center of the powdery sample to monitor temperature. The basket was housed in a cubic container cover made from a stainless steel net with a mesh opening of 0.60 mm, and slightly larger than the sample container. The cylinder is set in a hot circulating air oven at a set temperature of 40, 70, 150, or 250°C for at least 1 hour or until a spontaneous ignition was observed. It was observed that a ~10°C overshoot of the measured internal oven temperature occurred. A furnace temperature of 70 and 150°C was chosen to be close to dehydrogenation steps of ammonia borane.[7] The sample temperature was recorded at the center and top of the cylinder during the duration of the test. The oven temperature was also recorded by a thermocouple located near the sample. The self-heating test

is deemed a failed test if the sample temperature reaches a temperature above 60°C of the oven set temperature. The time of onset is defined as the time it takes for the sample temperature to start to increase from room temperature once the furnace temperature is set.

2.3 Calorimetry

To quantify the heat released through contact with dry and humidified air, i.e.- oxidation and hydrolysis studies, were performed in a Seteram C-80 Calvet calorimeter. The heat flow (mW) was normalized with respect to hydride and plotted versus time. Controlled dry or humidified air reaction measurements were conducted at a relative humidity of 30% RH and a temperature of 40°C.. In addition, the calorimeter had an air flow rate of 20 ml/min with 5-10 mg of solid sample.

3.0 Results and Discussion

Previous results have captured the environmental reactivity of such complex hydride materials as $2LiBH_4$:MgH_2 [3, 4, 8], $NaAlH_4$ [9, 10], and 8LiH:3Mg$(NH_2)_2$ [11]. Each material displayed a unique behavior when it is put through the various exposures tests with respect to their thermal and water contact behavior. Table 1 provides a summary for the UN testing performed on two materials of interest in this study, ammonia borane and alane. The ammonia borane material displayed a fairly benign environmental behavior with respect to the addition of heat and water. The alane material was stable in air due to the formation of stable oxides, but highly reactive when exposed to water. This reactive behavior is due to the aluminum metal left from the synthesis and not the aluminum hydride. This was evident in the surface contact and water immersion test where intense sparking occurred, which was due to the reaction of water with the aluminum metal. [12].

Table 1. Summary of U.N. Testing results for ammonia borane and alane.

Material\ UN Test	Pyrophoricity	Self-Heat*	Burn Rate^	Water Drop	Surface Contact	Water Immersion
NH_3BH_3	No ignition event Observed. Hygroscopic material appeared to absorb H_2O from air	Self-Heated near 300°C within 10 minutes at a T_{oven}=150°C	Flame propagated at a rate of 33 mm/sec	No reactivity detected	No ignition detected. Gas evolved for nearly 5 minutes.	No reactivity detected
AlH_3#	No ignition detected.	Test not complete	Flame propagated at a rate of 250 mm/sec.	Material ignition observed upon contact with water	Material sparked upon contact with wet surface	Material sparked upon contact. Gas evolved for 15 minutes

* cubic self-heating at $T_{furnace}$= 150°C, ^100 mm length burn rate, # Synthesized by ref 6 at SRNL

3.1 Modified Burn Rate Test

Overall, the reactivity rank beginning with the most reactive would be $8LiH:3Mg(NH_2)_2$ followed by $NaAlH_4$ (w/4 mol % $TiCl_3$), AlH_3, $2LiBH_4:MgH_2$, and NH_3BH_3 [12]. For example, $8LiH:3Mg(NH_2)_2$ and $NaAlH_4$, has shown to react instantaneously upon contact with water and exposure to heat.[12] However, the reactivity of AlH_3 and $2LiBH_4:MgH_2$ was sensitive to the specific test being conducted as in the case of the water immersion test where an ignition event was not observed for either material and the other tests were. For NH_3BH_3, no ignition or reactivity event was detected for water exposure (water drop, surface contact, or water immersion) or pyrophoricity test. Only the self-heating test of ammonia borane failed because the sample reached close to 300°C, which exceeds the 60°C difference at a furnace set point temperature of 150°C. The burn rate test results of the other materials seem to correlate well with the overall reactivity ranking except alane. This is due to the preparation method of the alane material used for the test.. There are many factors that can impact the reactivity of the material including processing conditions, addition of catalysts, or the use of solvents. This will be become evident in our comparison of aluminum hydride prepared by different methods. In addition, the amount of material needed for each of these reactivity tests can require significant amounts of material as in the case of the self-heating and burn rate tests. Not all materials are

commercially available and synthesizing or milling large quantities can become tedious therefore, modifications to these reactivity tests, i.e.-burn rate test, will allow less material to be use while obtaining the same information in return. In Figure 1, a modified burn rate is shown for ammonia borane (Figure 1(a)) and alane (Figure 1(b)).

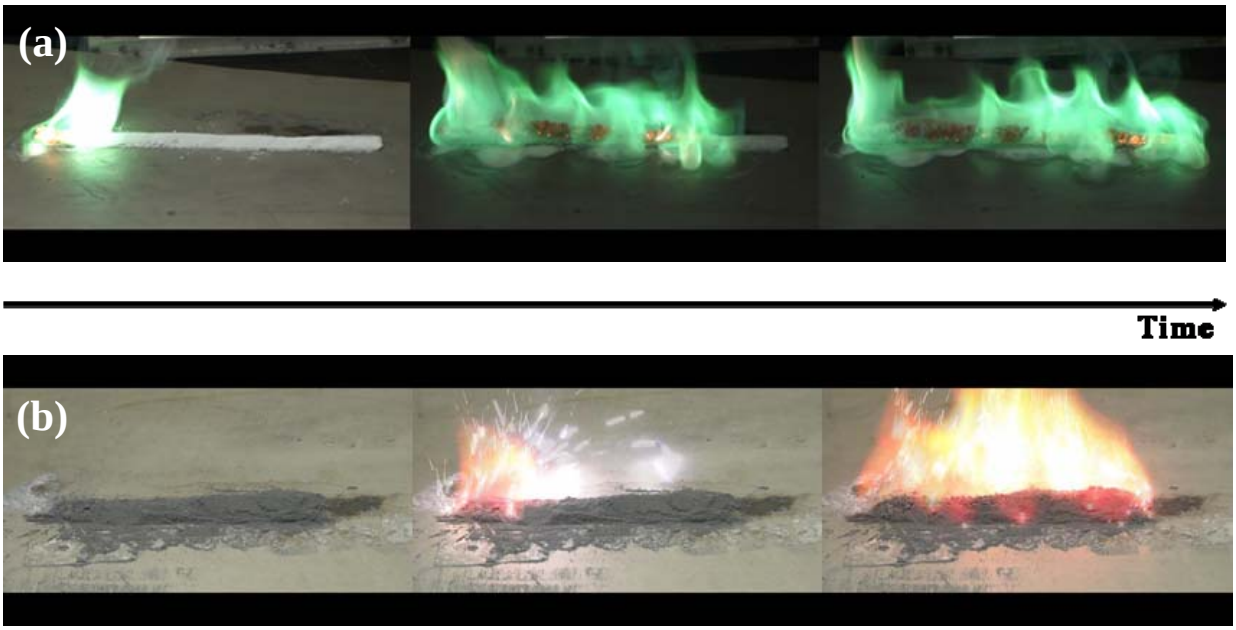

Figure 1. Modified burn rate test for (a) as-received ammonia borane and (b) chemically synthesized alane.

The modified burn rate test (20mm x 100mm x 10mm) has been validated by being compared to the full scale burn rate test (20mm x 250mm x 10mm) for ammonia borane. The average burn rate on the modified scale was 33 mm/sec, which was performed three times and found to be within $\pm$ 3% of the full scale burn rate test. For the case of ammonia borane, Figure 1a, a green flame appeared immediately upon the introduction of a heat source (propane torch) and proceeds to propagate to the endpoint of the material. The green flame is associated with the burning of borane and well known.

For alane the initial flame burned cleared due the presence of aluminum metal. The color then changed to a red and orange color due to the trace levels of solvent used within the synthesis

process, i.e – diethyl ether. The results from the burn rate test indicated the formation of aluminum oxides (α-Al_2O_3, γ-Al_2O_3) using x-ray diffraction. It is important to note that for both ammonia borane and alane, the intensity (height) of the flame increased once the material is fully ignited due to the localization of heat. This test has been shown to be sensitive to the preparation method of the material as seen in Table 2. The burn rate for ammonia borane was calculated to have a flame propagation rate of 33 mm/sec. This is a fairly slow burn rate compared to previously materials as $2LiBH_4$:MgH_2, $NaAlH_4$ (4 mol% $TiCl_3$), and 8LiH:3$Mg(NH_2)_2$, which can range from 51 to 453 mm/sec. Aluminum hydride chemically synthesized within our laboratory had a calculated burn rate of 250 mm/sec compared to a commercially available aluminum hydride from ATK, Inc which burned at a rate of 8 mm/sec. This is important information even though aluminum hydride does not have pyrophoric-type behavior; it does give information on how the material will react when in contact with a localized heat source. This also allows for the appropriate risk mitigation strategies to be developed.

Table 2. Comparison of the burn rate test results for various complex metal hydrides.

Material	**Burn Rate (mm/sec)**
Ammonia borane (Aldrich)	33
Aluminum hydride (SRNL)	250
Aluminum hydride (ATK)	8

3.2 Cylindrical Self-Heating Testing

The geometry used in the self-heating test was modified from a 1 in^3 cube to a cylinder with dimensions consisting of a 1 in diameter and 1 in height. This change was made in support of the computational simulations to be reported elsewhere. Figure 2(a) shows the typical temperature profile at within the ammonia borane sample. Thermocouples were located at the top surface and center of the sample. There was an additional thermocouple near but not in contact with the sample to measure the furnace temperature. The furnace achieved the set-point of 70°C within the first 3 minutes of the experiment. Once the furnace temperature was set, the

sample temperature began to increase. At 150 and 250°C, the sample temperature began to increase before the oven-temperature was reached, but is negligible. The sample reached the furnace set-point temperature of 70°C within 30 minutes of exposure to heat. The sample temperature continued to increase for an additional 26 minutes at which time, a spike in temperature was observed. The maximum temperature reached approximately 236°C at the center of the sample. The thermocouple located at the top of the sample only reached 200°C. In both cases, the temperatures observed would cause this ammonia borane sample to fail the self-heating test because the temperature difference between the furnace set-point and sample was greater than 60°C. Figure 2(b) visually shows the result of the sample after the experiment. The self-heating event that was observed correlated to a significant hydrogen release and possibly an ignition event. The furnace set-point temperature of 70°C is important, as it is close to the initial dehydrogenation step of ammonia borane, which is 77°C [7]. In this case with our set-point temperature of 70°C, the increase in the sample temperature through self-heating could have caused other dehydrogenation steps to take place and the sample temperature reached 325°C. In addition, an ignition event could have occurred, but was not observed as the experiment took place inside a closed furnace.

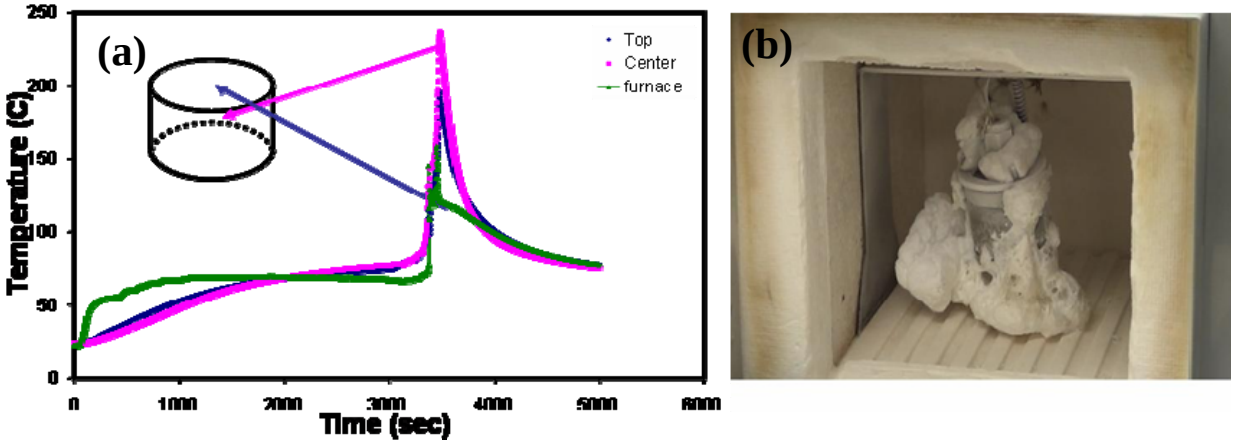

Figure 2. Modified self-heating results at 70°C for ammonia borane. (a) represents the temperature profile at various positions within the oven (top and center of ammonia borane and furnace temperature) (b) photograph of ammonia borane after self-heating at 70°C.

The self-heating test has shown to be dependent on the set temperature of the furnace. Table 3 shows the results of the maximum sample temperature observed and the onset of the temperature rise at various furnace temperatures. At an initial furnace temperature of 40°C, the sample only reached 51°C, which was held for longer than 1 hour. This time is well within the scope of the test for a passed test. However, the sample reaches 70°C, the material begins to self-heat within 1 hour of the test and reach a maximum sample temperature of 236°C. This is a difference in temperature of 166°C, which constitutes a failed test as per the UN definition. As the set-point temperature is increased to 150°C and 250°C, the time for the sample temperature to start to rise decreases from 13 to 7 minutes respectively. The maximum sample temperature at a furnace set-point temperature of 250°C is lower compared to a furnace temperature of 150°C due to the amount of hydrogen available for discharge. At 150°C, three dehydrogenation steps have occurred accounting for the release of 12 wt% H_2.[13] This release could account for the large difference in temperature of 175°C between the furnace and maximum sample temperature. At 250°C, the difference in the furnace and sample temperature is only 73°C due to the lack of

hydrogen available for reaction and a dehydrogenation occurred during the ramping of the furnace.

Table 3. Experimental test results of ammonia borane self-heating in a cylindrical geometry.

Furnace Temperature Set point (°C)	**Maximum Sample Temperature (°C)**	**Time for onset (min)**
40	51	Not observed
70	236	56
150	325	13
250	313	7

3.3 Calorimetry

Figure 3 shows the thermal response of ammonia borane with exposure to dry air and air with 30% RH exposure at 40°C. In the case of dry air, a slight endothermic behavior is observed with a calculated enthalpy of 5.9 kJ/mol NH_3BH_3. However, the introduction of 30% water vapor to the system initiates an exotherm of -15.2 kJ/mol NH_3BH_3. The XRD pattern of the as-received ammonia borane was distinctly crystalline; while, that of the reacted materials appeared to be a foam-like material. This is shown in Figure 2(b). The addition of water vapor to the system accelerates the dehydrogenation of ammonia borane. The actual reactions based on air and water vapor exposure are not well understood, as the decomposition product is difficult to characterize using XRD due to foaming of the ammonia borane.

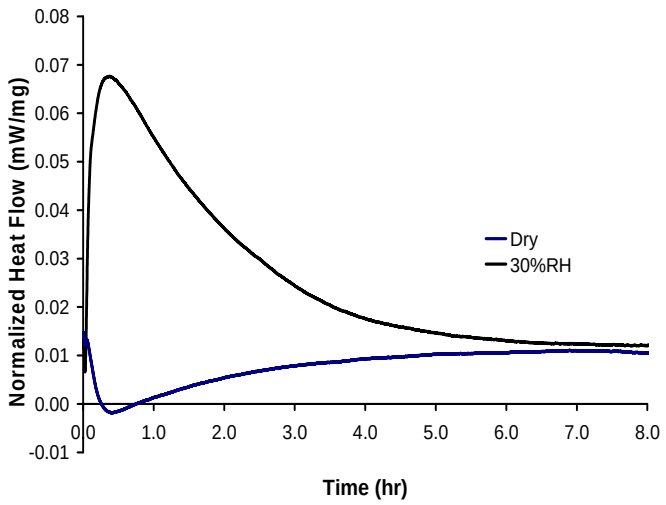

Figure 3. Gas phase calorimetry of ammonia borane

4.0 Conclusions

The risks associated with air and water vapor exposure have been elucidated for both ammonia borane and alane. In comparison to other hydrides studied such as $8LiH:3Mg(NH_2)_2$, $NaAlH_4$, AlH_3 and $2LiBH_4:MgH_2$, ammonia borane is the least reactive hydride and is not pyrophoric with regards to air or water exposure. For alane, exposure to dry air provides the least reactive situation due to the formation of stable oxides, which prevented a possible ignition event from occurring while the addition of water caused an ignition event to occur, i.e.- water drop test.

The development of testing procedures to evaluate the behavior to different environmental exposures has been critical to understand a specific material. In some cases modifications were needed, which reduced the amount of material needed and to still conform to a more realistic exposure scenario. We redesigned the burn rate and self-heating tests and validated them with respect to the original test results. The preparation method of aluminum hydride showed a strong dependence on preparation method as the burn rate can range from 250 to 8 mm/sec for internally synthesized and commercial forms of alane. In addition, ammonia

borane had failed self-heating tests above a furnace set-point of 70°C and a decrease in the onset time of the increase in the sample temperature. Finally, gas phase calorimetry showed a slight endothermic behavior, almost non-existence, in dry air conditions. The addition of 30%RH resulted in an exothermic behavior.

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