FUNDAMENTAL SAFETY TESTING AND ANALYSIS OF SOLID STATE HYDROGEN STORAGE MATERIALS AND SYSTEMS

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Abstract

Hydrogen is seen as the future automobile energy storage media due to its inherent cleanliness upon oxidation and its ready utilization in fuel cell applications. Its physical storage in light weight, low volume systems is a key technical requirement. In searching for ever higher gravimetric and volumetric density hydrogen storage materials and systems, it is inevitable that higher energy density materials will be studied and used. To make safe and commercially acceptable systems, it is important to understand quantitatively, the risks involved in using and handling these materials and to develop appropriate risk mitigation strategies to handle unforeseen accidental events. To evaluate these materials and systems, an IPHE sanctioned program was initiated in 2006 partnering laboratories from Europe, North America and Japan. The objective of this international program is to understanding the physical risks involved in synthesis, handling and utilization of solid state hydrogen storage materials and to develop methods to mitigate these risks. This understanding will support ultimate acceptance of commercially high density hydrogen storage system designs. An overview of the approaches to be taken to achieve this objective will be given. Initial experimental results will be presented on environmental exposure of $NaAlH_4$, a candidate high density hydrogen storage compound. The tests to be shown are based on United Nations recommendations for the transport of hazardous materials and include air and water exposure of the hydride at three hydrogen charge levels in various physical configurations. Additional tests developed by the American Society for Testing and Materials were used to quantify the dust cloud ignition characteristics of this material which may result from accidental high energy impacts and system breach. Results of these tests are shown along with necessary risk mitigation techniques used in the synthesis and fabrication of a prototype hydrogen storage system.

1.0 INTRODUCTION

Hydrogen is seen as the future energy storage media due to its inherent cleanliness upon oxidation and its ready utilization in fuel cell applications. In searching for ever higher gravimetric and volumetric density hydrogen storage materials and systems, it is inevitable that higher energy materials will be studied and used. To make safe and commercially acceptable systems, it is important to understand, quantitatively, the risks involved in using and handling these materials and to develop appropriate safety systems to handle unforeseen accidental events.

The majority of research programs currently underway globally deal with the development of new solid-state hydrogen storage materials and their reversibility. There have been few programs concentrating on development of systems to utilize these materials and no program to date comprehensively dealing with their safety concerns. Meeting international standards for safety

will be required to commercially exploit these materials. Many of the materials currently being considered as solid state hydrogen storage media are sensitive to air, water and water vapor. The quantitative extent of their reactivity to these and other common environmental and processing materials are widely unknown. It will be particularly enlightening to determine the relative reactivity of the various compounds under study. By understanding the nature of the chemical reactivity of these materials, amelioration methods can be devised which will reduce the risks imposed in using them to acceptable levels. Through development of solid-state hydrogen storage safety systems globally, it is anticipated that international standards for testing and risk mitigation can be achieved.

This program seeks to understand the physical risks involved in synthesis, handling and utilization of these materials as hydrogen storage media as well as development of methods to mitigate these risks which would result in commercially acceptable high density hydrogen storage system designs. Through teaming a global network of laboratories expert in hydrogen storage: Savannah River National Laboratory, Sandia National Laboratory & United Technologies Corp. (USA), Forschungszentrum Karlsruhe (Germany), National Institute for Advanced Industrial Science and Technology (Japan) and Université du Québec à Trois-Rivières (Canada), a broad spectrum of expertise in solid sate hydrogen storage is produced and focused to fundamentally understand these phenomenon. This international collaboration will hasten the development and acceptance of these systems.

The objective of this study is to fundamentally understand the safety issues regarding solid state hydrogen storage materials through: (a) development of standard testing techniques to quantitatively evaluate both materials and systems, (b) understand the fundamental science of environmental reactivity of hydrides and physisorption materials, and (c) develop amelioration methods and systems to mitigate the risks to acceptable levels. These objectives will be met through (i) determination of the materials behavior under internationally recognized and standardized testing conditions, (ii) calculation of thermodynamic energy released due to anticipated environmental reactions and comparison to measurement of chemical kinetics and experimental evaluation of energy release rates, (iii) mitigation of observed risks through the development and testing of alleviation methods and solutions which will hinder or halt high energy release rate reactions through engineering solutions and (iv) prototype system testing of risk reduction strategies in subscale hydrogen storage components to validate mitigation strategy efficacy.

Standardized Materials Testing

A set of materials testing procedures, based on internationally accepted standards drawn from ASTM and United Nations testing procedures will be defined. These tests will include exposure to air, humidity, water, and proposed heat transfer fluids. The materials of interested are categorized as either reasonably well known, including: $NaAlH_4/2\%TiCl_3$, Mg_2NiH_4, $LaNi_5NH_6$ and $LiH+MgNH_2$, and relatively unknown compounds including: NH_3BH_3, AlH_3, activated carbon and $2LiBH_4+MgH_2$. All of these materials will be tested identically to quantitatively determine their reactivity under normally occurring environmental and operating conditions. The materials will be tested in the fully charged, partially discharged and fully discharged conditions in both packed and finely dispersed forms with and without an ignition source.

Thermodynamic Assessment and Chemical Kinetics Measurement

Independent studies will be performed to understand the chemical kinetics of these reactions with air, oxygen and water as both liquid and vapor as a function of temperature. Chemical reactivity with organic and inorganic solutions will also be studied to determine those fluids which are safe to use as heat transfer, processing and inhibitor liquids. Calorimetric studies will be performed to

investigate the time-dependent reaction rates of the materials. Time resolved x-ray diffraction facilities will be used to quantify chemical kinetics and reaction products. Depth-resolved surface analysis will be performed to investigate reaction progress and/or properties of inhibiting layers. Cycling studies will be performed to study the stability of the materials. Dynamic models will be developed to predict the behavior of leaking storage systems.

Risk Mitigation
Methods of mitigating the risk of exposure to air and humidity will be investigated. These mitigation methods may take the form of either materials modifications or system level methods which would lessen the probability or effects of environmental exposure. Proposed methods for inhibiting reactions include the application of thin film coatings or the use of liquid film inhibitors. Fluid dynamic simulations will be performed to study dispersion properties of leaks from sorption based storage systems.

Prototype System Testing
Subsystem evaluation tests will be defined in which prototype vessels of approximately one liter in volume will be filled with promising hydrogen storage materials and tested for vessel rupture, water ingestion, humid air ingestion etc. to determine the effect of larger contained amounts of hydride. These tests will be derived from internationally accepted standards for testing chemical and pressurized containers with the aim of setting standards for testing solid state hydrogen storage containment. Time will be allotted for interacting with standards setting agencies to guide development of these practices.

The standardized UN and ASTM tests have been completed for one candidate high hydrogen capacity media under consideration for storage system applications, catalyzed $NaAlH_4$. These experiments were conducted by the first two authors in preparation for demonstration of a prototype hydrogen storage device reported on previously [1]. While it is recognized that this material will not meet the stringent criteria required for commercial applications, it holds many of the characteristics that will be required including air and water sensitivity. In this regard, it is similar to other materials which do hold the promise of commercial application. Results of initial standardized tests on this active material will be given here to show the utility of the tests selected and to provide a base line by which other high hydrogen capacity materials can be compared.

2.0 EXPERIMENTAL PROCEDURE
Sodium aluminum tetra-hydride, $NaAlH_4$, was purchased from Albemarle Inc. in its commercial form. One kilogram of the as-received material was tumble ball milled with 2% (all compositions are given in mole % unless otherwise indicated) crystalline $TiCl_3$ for three hours under an inert nitrogen atmosphere. The material was divided into three parts with the first reserved as the ***Fully Charged*** material. The second portion was subjected to a thermal treatment of 100°C/24 hours under vacuum to achieve the ***Partially Discharged*** state which was composed of Na_3AlH_6 + 2Al. The final aliquot was heat treated at 150°C/24 hours under vacuum resulting in ***Fully Discharged*** material composed of NaH + Al.

These three compositions were tested for flammability, combustibility and water reactivity according to the United Nations recommendations for testing hazardous materials [2] as described in the following sub-sections.

2.1 Burning 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 250 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. The substance is classified as Packing Group II if burning time less than 45 seconds.

2.2 Spontaneous Combustion Test

The purpose of the spontaneous combustion test is to classify spontaneously combustible materials into two types: (i) Pyrophoric Substances, solid or liquid mixtures which, even in small quantities, ignite within 5 minutes of coming in contact with air, and (ii) Self-heating substances, substances which, in contact with air and without an energy supply, are liable to self-heating. These substances will ignite only when in large quantities (i.e. kilogram), and after a long period of time (i.e. hours or days).

The details of the test procedure followed UN-RTDG div. 4.2. The powder samples were loaded in 25x25x25 mm cubic baskets made of stainless steel screen with 0.05 mm openings and an uncovered top surface. A chromel-alumel thermocouple with 0.3 mm diameter was inserted in the center of the powdery sample to monitoring temperature. The baskets 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 cube is set in a hot air-circulating oven at ambient, 100, 120 and 140°C (±2°C) for at least 24 hours or until spontaneous ignition or hazardous self-heating was observed. The change of the temperature at the center of the cube was recorded for the duration of the test.

2.3 Pyrophoricity Test

The purpose of the pyrophoricity test is to verify the ability of a solid to ignite on contact with air and determine the time to ignition. The test procedure followed UN-RTDG part-3, test-N2. An aliquot of 1~2 ml of the sample was poured from approximately a one meter height onto a non-combustible surface. Observation was made as to whether the substance ignited during dropping or within 5 minutes of settling. This procedure was performed six times or until a positive result was obtained. The substance was classified as pyrophoric if ignition occurred during one of the free-dropping tests.

2.4 Water Reactivity Test

The purpose of the water reactivity test is to verify if the substance, when in contact with water, burns or emits flammable gases. The experimental details followed UN-RTDG part-3, test-N5 in which three separate tests were conducted. (i) A small quantity (approximately 2 mm diameter) of the test substance was dropped in a trough of distilled water at 20°C. (ii) A small quantity (approximately 2 mm diameter) of the test substance was placed on the center of a filter paper which is floated flat on the surface of distilled water at 20°C in a suitable vessel (i.e. a 100 mm diameter evaporating dish). The filter paper is to keep the substance in one place, under which condition the likelihood of spontaneous ignition of any gas is greatest. (iii) The test substance was formed into a small pile approximately 20 mm high and 30 mm diameter with a hollow in the top. A few drops of water are added to the hollow. If spontaneous ignition occurred at any stage, the substance is classified as a water reactive substance emitting flammable gases. No further testing is necessary.

2.5 Minimum Auto-Ignition Temperature Test

The purpose of the minimum auto-ignition temperature test is to determine the minimum temperature at which a dust cloud will automatically ignite in air. The experimental details followed ASTM Standard Test Method E1491-97. The sample was dispersed by a pulse of

compressed air into a heated chamber with a flap vent for generation of a fairly uniform dust cloud. The initial test concentration for most dust is 300-1000 g/m^3. The temperature of the chamber was increased from 50 to 100°C gradually until ignition of the dust occurred. A fast response thermocouple measured the temperature rise during ignition of the dust cloud in the chamber. A visual observation also monitored the flame out of the vent during ignition.

2.6 Minimum Ignition Energy Test

The purpose of the minimum ignition energy test is to determine the minimum energy for igniting a dust cloud in air. The details of the experimental plan followed ASTM Standard E2019-03. A pulse of compressed air blew a dust cloud of testing material into a discharge chamber. The energy stored in a capacitor is discharged into the dust-air mixture as a spark. The occurrence or nonoccurrence of a flame is recorded. Ignition was determined by visual observation of flame propagation away from the spark gap. The Minimum Ignition Energy, MIE, was determined by varying the spark discharge energy. In some cases, the MIE can be below the lower limit of the apparatus.

2.7 Minimum Explosive Concentration Test

The purpose of the Minimum Explosive Concentration (MEC) test is to determine the minimum concentration of a dust-air mixture that will propagate a deflagration. The experimental procedure followed ASTM Standard E1515-03a. An adequately uniform dust cloud was created as above in a closed combustion chamber at atmospheric pressure. The initial concentration was 100 g/m^3. If the initial concentration produced a deflagration, the concentration was decreased until no deflagration occurred or vise versa. The concentration increments were no greater than 25% of the MEC in the final determination. Ignition of the dust-air mixture via a spark from a capacitance discharge was performed. The pressure-time curves were recorded using a pressure transducer. At least five samples over a range of MEC were tested.

3.0 RESULTS & DISCUSSION

3.1 Burning Rate Test

The burn rates for the three materials Fully Charged, Partially Discharged and Fully Discharged were 51, 222, 27 mm/sec. respectively. The Partially Discharged material is significantly more active than either of the other two materials. These materials are thus all classified as Flammable Solids, Packing Group 2.

3.2 Spontaneous Combustion Test

3.2.1 Charged Material Self-Heating

The temperature vs. time plot for the fully charged material exposed to air at 100°C is given in Fig. 1 where the furnace temperature is given in red and the sample temperature in blue. The sample is seen to increase gradually in temperature to 100°C at which point it heats rapidly to ~175°C and stabilizes, above the 160°C limit to be classified as dangerously self heating. Heating again increases after roughly 300 seconds with thermocouple read out failure occurring at 300°C.

Neglecting water vapor reactions, the initial heating to above 100°C is attributed to the dehydrogenation reaction with subsequent oxidation of metal such as:

$$3NaAlH_4 + 3O_2 \rightarrow Na_3AlH_6 + 2Al_2O_3 + 3H_2 \quad (1)$$

This is reaction is the combination of the endothermic:

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (1a)$$

and the exothermic:

$$2Al + 3O_2 \rightarrow 2Al_2O_3 \quad (1b)$$

The endothermic dehydrogenation reaction is the likely cause of the temperature plateau. The second heating event is attributed to the second dehydrogenation reaction and metal oxidation such as:

$$Na_3AlH_6 + {}^3/_4O_2 \rightarrow 3NaH + {}^1/_2Al_2O_3 + {}^3/_2H_2 \quad (2)$$

This is again the combination of the endothermic:

$$Na_3AlH_6 \rightarrow 3NaH + Al + {}^3/_2H_2 \quad (2a)$$

and the exothermic:

$$Al + {}^3/_2O_2 \rightarrow {}^1/_2Al_2O_3 \quad (2b)$$

Again, the exothermic reaction yields the heating while the endothermic reaction results in the temperature plateau. The temperatures correspond to the dehydrogenation temperatures for these two reaction steps [3].

Examination of the sample after testing showed the stainless steel basket to have melted, requiring temperatures in excess of 1300ºC. The fire was observed to be white-hot to the eye, confirming a high temperature burn after the thermocouple data was lost. While the quantitative data was lost, it is qualitatively speculated that both a sodium and aluminum fire resulted after total dehydrogenation.

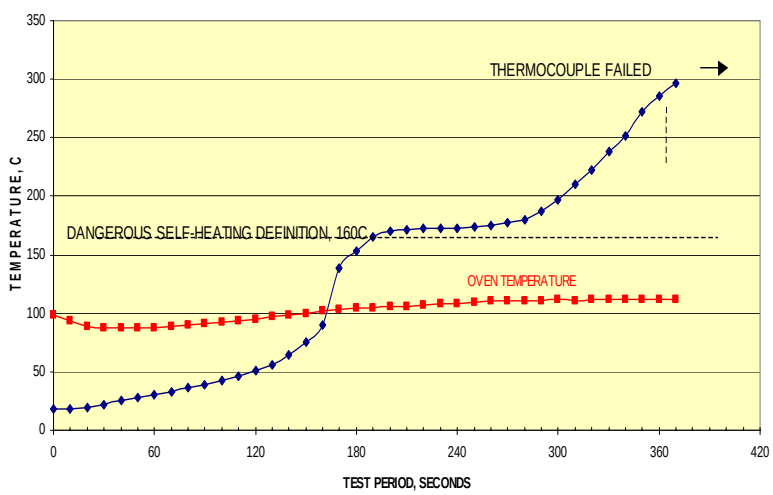

Figure 1 Self-heating and ignition of Fully Charged material in a 100ºC oven

3.2.2 Partially Hydrogenated Material Self-Heating

The temperature vs. time plot for the partially charged material exposed to air at 100°C is given in Fig. 2. Identically to the Fully Charged sample, it's temperature increased gradually to 100°C at which point it heated rapidly to ~175°C and stabilized. Heating again increased after roughly 100 seconds and stabilized at 850°C. After stabilizing again for approximately 100 sec. the temperature rose rapidly until thermocouple failure at 1300°C.

The Partially Dehydrogenated materials still contained some $NaAlH_4$, yielding the first temperature plateau as observed above. The second plateau observed at 850°C is the results of the endothermic dehydrogenation of NaH as:

$$NaH \rightarrow Na + {}^{1}/_{2}H_2 \quad (3)$$

Subsequent heating after this plateau is due to the exothermic:

$$Na + {}^{1}/_{2}O_2 \rightarrow Na_2O \quad (4)$$

Reaction (4) is highly exothermic, the burning of sodium, and would certainly result in the melting of the stainless steel mesh described for the fully charged material.

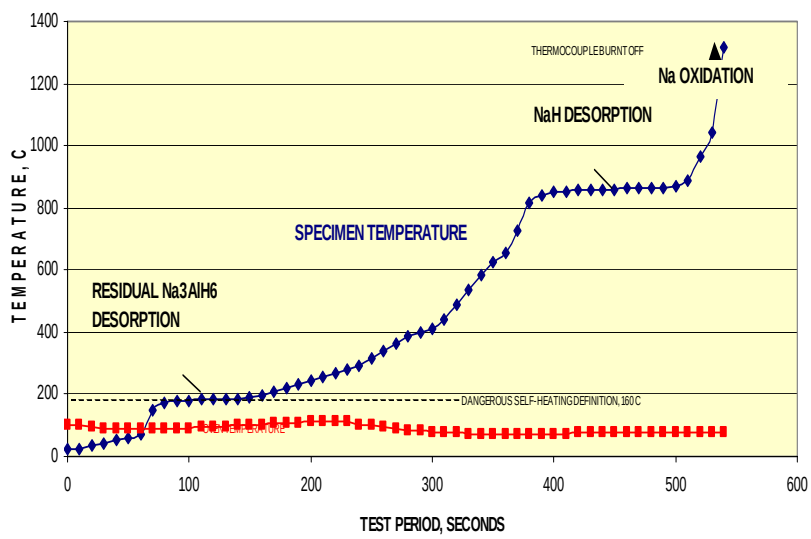

Figure 2. Self-heating and ignition of Partially Hydrogenated material at 100ºC

3.2.3 Fully Discharged Material Self-Heating

The Fully Discharged material did not exhibit dangerous self-heating in a 100ºC oven. Figure 3 starts out characteristically similar to Figures 1 & 2. The temperature only slightly surpasses that of the furnace to 134°C followed by settling to the furnace temperature. At no time did the sample exceed the 160°C maximum indicating dangerous self heating.

The partially Discharged material is significantly less susceptible to self-heating than either Fully Charged, $NaAlH_4$, or partially Discharged, Na_3AlH_6 + 2Al, particulate. Further tests to determine the products composition would need to be performed in order to confirm the suppositions made. These analyzes have not been performed to date.

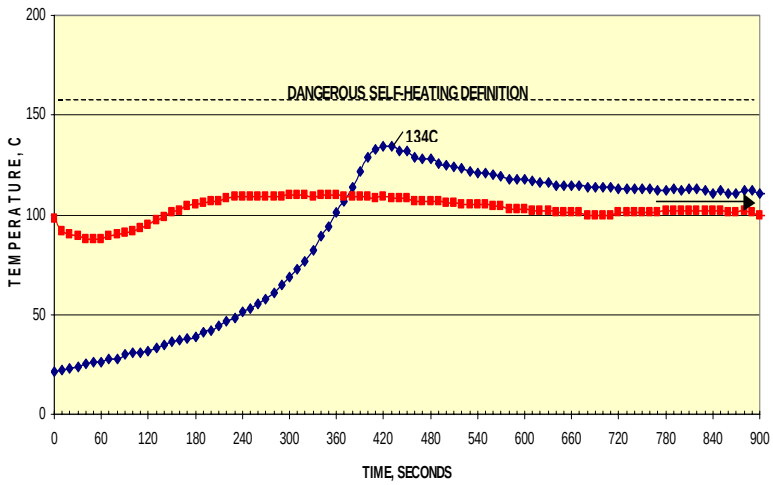

Figure 3. Mild self-heating of Fully Discharged material in a 100ºC oven

3.3 Pyrophoricity Test

Pyrophoricity tests were performed on all three materials with negative results at the standard starting temperature of 20°C. The tests were repeated 6 times with no incidence of spontaneous ignition. However, modifying the test procedure by heating the material to 80°C to represent the material in its state during storage system usage, the Partially Discharged material was found to be pyrophoric while the other two remained not. Incidental to cleaning up after the drop tests, the Fully Charged and Partially Discharged materials self-ignited a few minutes after being swept into a pile. This is not "pyrophoricity", according to the UN definition. It is "dangerous self-heating", discussed earlier in this report.

Table 1. Pyrophoricity Tests Results at Ambient and Operational Temperatures

	20°C *(Material transportation)*	**80°C** *(System application)*
Fully Charged	No	No
Partially Discharged	No	Yes
Fully Discharged	No	No

3.4 Water Reactivity Test

All three materials exhibited "Dangerous When Wet" characteristics, according to UN Manual 33.4.1.4.3. The Fully Charged and Partially Discharged materials ignited immediately when dropped into water while the Fully Discharged material did not. The test sequence calls for further testing of any material that fails to ignite when dropped into water. The next test requires dropping onto a filter paper floating on water. The Fully Discharged material ignited quickly during this test. All three materials show "a tendency for the gas produced to spontaneously ignite" (33.4.1.4.4.2) and therefore, are in Class 4.3, Packing Group I.

3.5 Dust Cloud Explosion Tests

The results of the three dust cloud explosion tests are given in Table 2. Only the fully charged and fully discharged materials could be handled and tested due to the very high reactivity of the partially discharged materials. The test results are given as: P_{max}, the maximum explosion pressure, R_{max}, maximum pressure rise, K_{st}, the maximum scaled rate of pressure rise, MEC, the minimum explosive concentration, MEI, the minimum spark ignition energy and T_c, the minimum dust cloud ignition temperature.

Table 2. Dust Cloud Explosion Test Results

	Test Materials		**Reference Materials**	
	$NaAlH_4$+ 2% $TiCl_3$	NaH+Al+ 2% $TiCl_3$	Pitt. Seam Coal Dust	Lycopodium Spores
P_{max} *bar-g*	11.9	8.9	7.3	7.4
R_{max} *bar/s*	3202	1200	426	511
K_{st} *bar-m/s*	869	326	124	139
Dust Class	St-3	St-3	St-1	St-1
MEC g/m^3	140	90	65	30
MIE *mJ*	<7	<7	110	17
T_c ^oC	137.5	137.5	584	430

As references, results for Pittsburgh Seam Coal Dust and Lycopodium Spores are also given. In all instances except for MEC, the Fully Charged material was more active than the Fully Discharged material. Similarly both of these materials were more active than either of the reference materials. The one exception is the Minimum Explosive Concentration, MEC, which is 30g/m^3 for Lycopodium Spores but 140 and 90 g/m^3 for the Fully Charged and Fully Discharged materials respectively. The low MIE is of particular note. The <7 mJ MIE noted is at the low limit of the testing system capability. Ignition energies below this may occur. This is indicative of a very sensitive material capable of dust cloud ignition from very small energy inputs.

4.0 CONCLUSIONS

A program has been outlined for determining the relative risks for an array of solid state hydrogen storage materials. A number of laboratories will be working closely to identify these risks and to determine risk mitigation strategies. It is important that these materials be compared to assess their relative risks not only against themselves, but also against other competing energy storage technologies. In efforts to continually find higher density energy storage methods, the risks associated with these methods will likely increase.

One material, catalyzed $NaAlH_4$ was tested using the aforementioned test outline. The materials ordered in rank of their reactivity are: Partially Discharged, Fully Charged and Fully Discharged. It is evident that the Na_3AlH_6 material is the most active species tested here. Free aluminum powder was available in copious quantities in the Fully Discharged case, but having the lowest reactivity, the aluminum powder can not be the source of the high reactivity. The material in all of its forms must be handled with care, taking special attention to avoid water contact. Systems designed with this material should use non-reactive heat transfer fluids to insure safe operation.

This test outline, with the inclusion of instrumented impact capacity, is sufficient to identify the risks associated in synthesizing handling and testing these materials. With the risks thus

identified, users of these materials, either in the laboratory or in prototype development, must take the proper safeguards to minimize the probability of the loss of property or personal injury.

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