

REACTIVITY CHARACTERIZATION TESTS OF SELECTED SOLID-STATE HYDROGEN STORAGE MATERIALS

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ABSTRACT

Solid-state hydrogen storage materials such as complex metal hydrides, chemical hydrides, and adsorbents are promising alternatives to the use of compressed hydrogen gas or liquefied hydrogen for on-board vehicular applications. However, acceptance by the general public to the use of hydrogen, in any of its on-board storage forms, as an energy carrier in the transportation sector requires assurance that this application is safe and poses no additional risks above the current risk acceptance criteria associated with use of gasoline/diesel in the transportation sector.

This research discusses the results of an experimental program covering materials reactivity tests, dust cloud combustion characterization tests, mechanical impact sensitivity tests, and material/hot surface contact tests. These tests were performed to identify safety-critical characteristics of selected solid-state hydrogen storage materials. Based upon the results of those tests, risk mitigation methods were proposed to eliminate or mitigate the identified risks. The effectiveness of the proposed risk mitigation methods was also examined. The insights gained from the experimental program could be useful to ongoing research efforts aimed at identifying the best hydrogen storage materials from a safety standpoint as well as supporting current and future risk-informed hydrogen safety standards such as NFPA-2, ISO, and IEC.

INTRODUCTION

One of the most significant issues affecting consumers' acceptance and adoption of hydrogen-fueled vehicles is safety. Through DoE efforts to understand general public opinions, people have indicated that when selecting a fuel type for their vehicles, safety is the most important factor that drives their decision.

The DoE hydrogen storage technical target for safety has been specified generally as "meets or exceeds applicable standards" but for solid-state hydrogen storage, no such standards currently exist. Furthermore, such standards would be high level with limited detail, being primarily focused on systems certification and would not provide guidance to assist the developers of new storage media in understanding the safety significance of their materials.

Under the U.S. Department of Energy (DoE) contract award DE-FC36-07 [1], UTRC developed a formal qualitative and quantitative risk analysis framework [1,3] as well as a comprehensive experimental program [2,4] to identify the safety-critical characteristics of candidate on-board solid-state hydrogen storage media of interest to the DoE safety program.

Research Objective and Impact

Safety Codes and Standards (C&S) is one of the technical barriers described in the Hydrogen Storage Section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [2]. To address this technical target, this research aims at examining the safety aspects of candidate hydrogen storage materials under development in the DoE Hydrogen Program. This paper summarizes the results of the UTRC experimental hydrogen safety program for the following hydrogen storage media: complex metal hydrides (NaAlH_4 and $3\text{Mg}(\text{NH}_2)_2 \cdot 8\text{LiH}$), chemical hydrides (NH_3BH_3 and AlH_3), and adsorbents (Maxsorb AX-21).

As a result of this effort [1], the general DoE safety target will be given useful meaning by establishing a link between the characteristics of new storage materials and the satisfaction of safety criteria. This will be accomplished through the development and application of formal risk analysis methods, standardized materials testing, chemical reactivity characterization, novel risk mitigation methods and subscale/prototype system demonstration [3-6].

EXPERIMENTAL PROGRAM

To accomplish the objective of this research, an experimental program (outlined in Table 1) has been designed and executed to better understand and characterize potential safety-critical aspects associated with the use of solid-state hydrogen storage materials being considered by the DoE Hydrogen Safety Program.

*Table 1
UTRC Hydrogen Safety Experimental Program*

TEST TYPE	STORAGE MATERIAL	COMMENTS
Dust cloud combustion characterization.	Materials tested: see footnote 1.	Powder (particle size $\leq 75 \mu\text{m}$).
Materials reactivity.	Materials tested: see footnote 2.	Powder and powder

TEST TYPE	STORAGE MATERIAL	COMMENTS
		compact (wafers)
Mechanical impact sensitivity.	Materials tested: see footnote 2.	Powder compact (wafers)
Material/hot surface contact.	Materials tested: see footnote 3.	Powder and powder compact (wafers)
Risk mitigation.	NaAlH ₄ mixed with various flame-retardant additives.	Powder and powder compact (wafers)

Footnotes:

(1) Charged and discharged AlH₃, 2LiBH₄+MgH₂, charged NaAlH₄, NH₃BH₃, and Maxsorb AX-21.

(2) NaAlH₄, 3Mg(NH₂)₂.8LiH, and NH₃BH₃.

(3) Charged NaAlH₄, charged 3Mg(NH₂)₂.8LiH, and NH₃BH₃.

Dust Cloud Combustion Characterizations

Under DoE Contract [1], UTRC conducted a series of combustion characterization tests for selected hydride storage materials as shown in Table 1. The tests were conducted per ASTM standards listed in Table 2. Furthermore, ASTM E11-04 recommends that the explosibility and ignition studies of dusts be conducted on a sample that passes through a No. 200 sieve screen ($d < 74 \mu\text{m}$).

Table 2
ASTM Standards for Dust Cloud Combustion Characterizations

Test	Test Method
<ul style="list-style-type: none"> Maximum explosion pressure (P_{MAX}). Maximum rate of pressure rise (ΔR_{MAX}). K_{ST} explosion severity index. 	ASTM E-1226
Minimum explosible concentration (MEC) of combustible dust.	ASTM E-1515
Minimum ignition energy (MIE) of a dust cloud in air.	ASTM E-2019
Minimum ignition temperature (TC) of dust clouds.	ASTM E-1491

With respect to the classification of combustible dusts, a Class-II combustible dust is defined by NFPA-499 "Recommended Practice for the Classification of Combustible Dusts and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas."

Where Class-II combustible dusts are used, the requirements in 29 CFR 1910.307 "Hazardous (classified) locations" and NFPA 70 National

Electrical Code, Article 500 applies. A dust is classified Class-II if either its Explosion Severity (ES) per Equation (1) or Ignition Sensitivity (IS) per Equation (2) exceed certain thresholds. Most dusts can be definitively classified by ES criteria alone. In cases where the classification by ES is indeterminate, it is necessary to evaluate the IS criteria. The cost to determine the ES of a dust is less than determining its IS . As such, determination of IS is usually conducted only when the classification of a dust by ES is indeterminate, that is, when $0.4 < ES < 0.5$. This procedure is intended to meet the requirements of OSHA Directive No. CPL 03-00-06 (*Combustible Dust National Emphasis Program*, October 18, 2007) Annex E, Section 7.

$$ES = \frac{(P_{MAX} \cdot R_{MAX})_{sample_dust}}{(P_{MAX} \cdot R_{MAX})_{ref_dust}} \dots \dots (1)$$

P_{MAX} = maximum explosive pressure.

R_{MAX} = maximum rate of pressure rise, $(dP/dt)_{MAX}$, bar/s.

$$(P_{MAX} \cdot R_{MAX})_{ref_dust} = 3,110 \text{ (bar)}^2/\text{s.}$$

$$IS = \frac{(T_C \cdot MIE \cdot MEC)_{ref_dust}}{(T_C \cdot MIE \cdot MEC)_{sample_dust}} \dots \dots (2)$$

$$(T_C \cdot MIE \cdot MEC)_{ref_dust} = 4,182,750 \text{ }^\circ\text{C} \cdot \text{mJ} \cdot \text{g}/\text{m}^3$$

Table (3) shows the interpretation of explosion severity (IS) test results.

Table 3
Interpretation of Explosion Severity Test Results

Test Results	Dust Classification
$ES > 0.5$	Class-II combustible.
$ES < 0.4$	Combustible but not Class-II.
$0.4 < ES < 0.5$	Indeterminate. Combustible but not Class-II based on ES criterion alone.*
$P_{MAX} < 1 \text{ bar}$	Not combustible.

*For $0.4 < ES < 0.5$, OSHA recommends determination of the ignition sensitivity (IS) to definitively determine whether a dust is Class-II or not.

The K_{ST} index, defined by Equation (3), is an internationally recognized index used for classifying the explosion severity of combustible dust clouds in air. It is computed on the basis of the "Cube Law" (derived from formal mathematical analysis of deflagration development in closed

spherical vessels) that normalizes the effect of vessel volume on the observed value of R_{MAX} . As such, the K_{ST} Index allows comparisons to be made between the test material and other well-defined combustible substances.

$$K_{ST} = R_{MAX} \cdot V^{1/3} \quad \dots \dots (3)$$

V = volume (20 liters) of the Kuhner spherical explosion apparatus.

The results of the dust characterization tests are discussed in the “Results and Discussion” Section.

Materials Reactivity Tests

A series of tests were performed to evaluate the reactivity of selected complex metal hydrides, NaAlH_4 and $3\text{Mg}(\text{NH}_2)_2 \cdot 8\text{LiH}$, and chemical hydride, NH_3BH_3 , under environmental conditions that may exist during a postulated vehicular accident. In the immersion tests, loose powders as well as powder compact (wafers) were immersed in different liquids at room temperature. The liquids used in the immersion tests were water, windshield-washing fluid, thermo-oil typically as a heat transfer medium, engine coolant (antifreeze), engine oil, and 1-molar NaCl solution (brine), respectively. The immersion tests were then repeated using powder compact (wafers) instead of loose powder. In the droplet tests, each of these liquids was dropped on a 1-gram pile of the hydride loose powders. The tests were then repeated using powder compact (wafers) instead of loose powder.

Mechanical Impact Sensitivity Tests

A series of tests were performed for complex metal hydrides (partially charged NaAlH_4 and charged $3\text{Mg}(\text{NH}_2)_2 \cdot 8\text{LiH}$) and chemical hydride (NH_3BH_3). Figure 1 shows the test rig. The test involves the free fall of a 10-kg weight from a 0.5m distance (or 1 meter) above the powder compact (wafer). The energy released upon a single impact can be calculated as follows:

$$\begin{aligned} \text{Free-fall mechanical impact energy} \\ &= m \cdot g \cdot h = (10 \text{ kg}) \cdot (9.8 \text{ m/s}^2) \cdot (0.5 \text{ m}) \\ &= 49 \text{ Joules OR } 98 \text{ Joules (if } h = 1 \text{ m)} \end{aligned}$$

Where: the force (in Newtons) = mass (in kg) x acceleration (in m/s^2). The energy in Joules equals the force (in Newtons) x distance (in meters).

The results of the mechanical impact sensitivity tests are discussed in the “Results and Discussion” Section.

Material/Hot Surface Contact Tests

In the risk analysis performed by the author of this work [4,6], some of the postulated accident scenarios assume hydride storage vessel breach

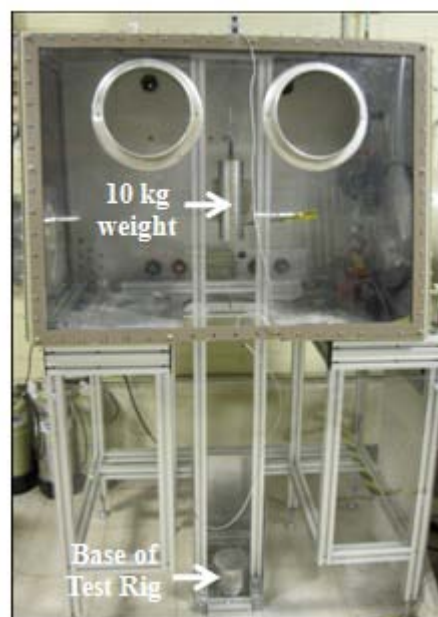


Figure 1: Mechanical impact test rig

followed by contact of the spewed chunks of the stored hydride material with hot metal surfaces in the presence of air. To investigate the consequences of this postulated accident scenario, a NaAlH_4 wafer placed in a glass beaker was brought into direct contact with an electrically heated metal surface. The temperatures of the wafer as well as the metal surface were measured as a function of time during the heating process.

Risk Mitigation Tests

Several flame-retardant chemical additives were experimentally examined to demonstrate their effectiveness in eliminating the sensitivity of sodium alanate (NaAlH_4) powder compact to mechanical impact. The examined flame-retardant chemical additives included sodium tetraborate, melamine borate, graphite, and a mixture of melamine and boric acid. The test samples were prepared by mixing 1-gram sodium alanate powder with 10 wt% graphite powder, 10 wt% melamine borate, and 20 wt% melamine borate, respectively, and ball milled for 15 minutes. The scope of flame-retardant chemical additives was later expanded to include (10 wt% and 20 wt%, respectively) aluminium oxide (Al_2O_3), aluminium hydroxide ($\text{Al}(\text{OH})_3$), and magnesium hydroxide ($\text{Mg}(\text{OH})_2$).

Following the mixture ball milling step, the powder samples were then compacted in the form of wafers and subjected to the mechanical impact test. Another series of tests were performed to examine the effectiveness of each of these chemical additives in suppressing the known pyrophoricity of sodium alanate powder when exposed to air. For the pyrophoricity tests, samples were prepared by mixing 1-gram sodium alanate powder with 10 wt%

graphite, 10 wt% melamine borate, 20 wt% melamine borate, and a mixture of 10 wt% boric acid and 10 wt% melamine, respectively.

The results of risk mitigation tests are presented under the “Results and Discussion” Section.

RESULTS AND DISCUSSION

This Section contains the results and discussion for each of the tests outlined in Table 1.

Results of the Dust Cloud Combustion Characterization Tests

Table 4 shows the results of the dust cloud combustion characterization tests. The two important insights that can be derived from Table 4 are:

- Discharged alane powder is more reactive than the charged alane when dispersed in air as shown by the maximum pressure rise (P_{MAX}) and the maximum rate of pressure rise $(dP/dt)_{MAX}$. This could be due to the rapid oxidation of the aluminium powder in the discharged alane.
- Dispersed ammonia borane (NH_3BH_3) dust cloud in air is very reactive with the maximum pressure rise (P_{MAX}) about 2.5 times greater than (P_{MAX}) of the ASTM reference material (Pittsburgh Seam Coal).

Results of the Materials Reactivity Tests

The results of these tests demonstrated that powder compaction has a potential for reducing reactivity risks by suppressing the hydride/liquid reaction and, thus, preventing consequential ignition of the evolved reaction gases. This could be due to the fact that powder compaction reduces the available surface area that contacts the liquid. Figure 2 shows the reactivity of $NaAlH_4$ (loose powder and powder compact) when it comes in contact with windshield washing fluid. In Figure 2 (A), the windshield washing fluid was dropped on a pile (0.25-gram) of the hydride Powder. Vigorous reaction with flame production was observed. In Figure 2 (B), the hydride wafer (1-gram) dropped in 25-ml windshield washing fluid. In this case, a mild reaction without flame production was observed.

Results of Mechanical Impact Sensitivity Tests

Figure 3 shows the $NaAlH_4$ mechanical impact test results. The wafer ignited upon first impact. The $3Mg(NH_2)_2 \cdot 8LiH$ powder compact was also found to be sensitive to mechanical impact where the test sample ignited upon first impact. The NH_3BH_3 powder compact, however, did not ignite during the impact tests.

Results of the Material/Hot Surface Contact Tests

The consequences of contacting powder compacts with hot surfaces in the presence of air were

investigated; a condition that could be encountered during postulated accident scenarios [4].

Figure 4 shows the $NaAlH_4$ wafer placed on an electrically heated metal surface. Thermocouples were used to measure the wafer’s temperature. When the temperature of the wafer reached $\approx 85^\circ C$, it ignited and the evolved gases burned but the wafer did not disintegrate. Based on the insights gained from this test, the author of this work is developing additional risk mitigation methods (in addition to powder compaction) to prevent/suppress the observed hydride fires. Figure 4 shows snapshots taken during the hot surface contact test. When the ammonia borane (NH_3BH_3) wafer was subjected to the same test, the material gradually swelled and foamed but did not ignite.

Results of the Risk Mitigation Tests

Overall, the risk mitigation testing results showed that none of selected flame-retardant chemical additives was successful in suppressing the mechanical impact sensitivity and subsequent ignition of the $NaAlH_4$ test samples.

The samples containing 10 wt% graphite and 10 wt% melamine borate immediately ignited upon contact with air and, hence, failed the pyrophoricity test. The samples containing 20% melamine borate and a mixture of 10 wt% boric acid + 10 wt% melamine did not ignite and, hence, passed the pyrophoricity test. However, these samples ignited when water was poured on the powders.

CONCLUSIONS

The main conclusions that can be derived from the results of this experimental program are as follows:

- Powder compaction was effective in reducing the risks associated with reactivity of the examined hydride materials. However, this risk mitigation method failed to suppress sensitivity of the examined hydrides to mechanical impact and hot surface contact.
- Solid ammonia borane (NH_3BH_3) is highly reactive when dispersed in air as a dust cloud.
- Some complex metal hydrides such as $3Mg(NH_2)_2 \cdot 8LiH$ and chemical hydrides such as AlH_3 are more reactive in the discharged phase compared to the charged phase.
- Some of the complex metal hydrides such as charged $NaAlH_4$ and charged $3Mg(NH_2)_2 \cdot 8LiH$ powder compacts are sensitive to mechanical impact. The effectiveness of selected flame-retardant chemical additives was examined as a means for mitigating this risk. The author of this work continues to examine other flame-retardant additives that could effectively eliminate or mitigate this risk.

Table 4
Dust Cloud Combustion Characterizations of Solid-State Hydrogen Storage Materials

Dust Cloud Combustion Characterization Parameter	Solid-State Hydrogen Storage Materials (Complex Metal Hydrides, Chemical Hydrides, and Adsorbents)						Pittsburgh Seam Coal ⁽¹⁾	H ₂ Gas ⁽²⁾
	Maxsorb (AX-21)	Charged AlH ₃	Discharged AlH ₃	2LiBH ₄ + MgH ₂	Charged NaAlH ₄	NH ₃ BH ₃		
P _{MAX} , bar-g	8.0	3.7	10.3	9.9	11.9	18.4	7.3	7.9 ⁽³⁾
(dP/dt) _{MAX} = R _{MAX} , bar/s	449	370	4,082	1,225	3,202	2,840	426	5,435 ⁽³⁾
MIE ⁽⁴⁾ mJ	Range 500 - 1,000	< 10	< 10	< 9.2	< 7.0	< 8.9	110	0.02
MEC ⁽⁵⁾ g/m ³	80	30	125-250	30	140	< 20	65	4 vol% H ₂ in air
T _C ⁽⁶⁾ , °C	760	200	710	230	137.5	n/a	585	n/a
Hazard Class	St-1	St-1	St-3	St-3	St-3	St-3	St-1	
Explosion Severity (ES)	1.16	0.44	13.5	3.9	12.3	16.54	1.0	13.8
K _{ST} ⁽⁸⁾ bar-m/s	122	101	1,100	333	869	771	116	1,477
Dust Classification	Class-II	Footnote (7)	Class-II	Class-II	Class-II	Class-II	Class-II	n/q

(1) ASTM reference material for dust cloud characterization.

(2) Added for comparison only.

(3) At 29 vol% H₂ in air.

(4) MIE = minimum ignition energy.

(5) MEC = minimum explosive concentration.

(6) TC = minimum ignition temperature of dust cloud.

(7) Dust is combustible but not Class-II based on ES criterion only.

(8) K_{ST} = volume normalized maximum rate of pressure rise of the dust cloud.

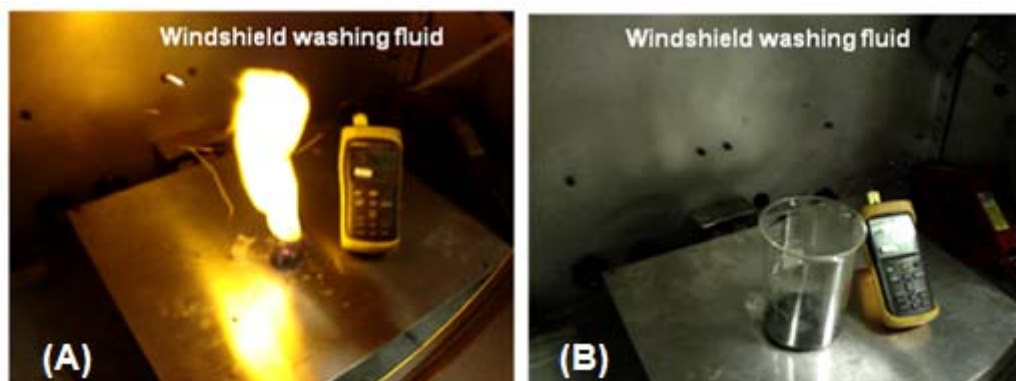


Figure 2: NaAlH₄ reactivity: loose powder (A) vs. powder compact (B)



Figure 3: A 4-gram NaAlH₄ wafer ignited upon first impact (free fall height = 1 m)

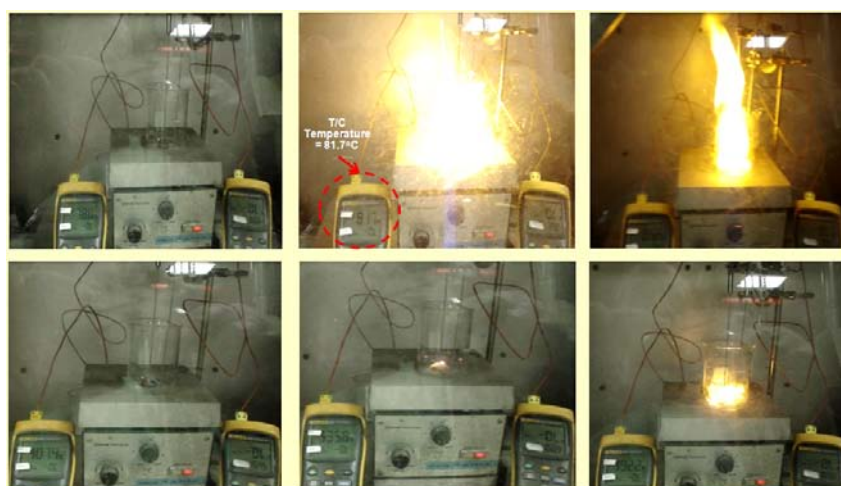


Figure 4: Contact of NaAlH₄ powder compact with a hot metal surface

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