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Metal Hydride Safety Testing

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[Editor's Note: The work described below was done in 1999 but the project was not completed. Unfortunately U.S. DOE funding was not made available for 2000. Planning and preparation for safety tests of $NaAlH_4$ were largely completed, but the actual tests, themselves, could not be carried out.]

Background

Work under IEA Task 12 (and elsewhere) has shown that catalyzed $NaAlH_4$ and related complexes have the potential for capacity-temperature properties heretofore never achieved with rechargeable hydrides. However, the air and water reactivities of alkali-metal-based complex hydrides such as $LiAlH_4$ and $NaAlH_4$ are well known and suggest detailed safety studies are necessary before moving catalyzed complex hydrides into public applications, e.g., public and private vehicles. Because of its past experience in the area of hydride safety (via the Denver Research Institute), Hydrogen Components, Inc. (HCI) was nominated for the safety studies.

Safety studies of rechargeable hydrides, conducted in the late 1970s at the University of Denver Research Institute (DRI), relied on some standard tests and some tests developed at DRI. Mil-Std-1751 assesses the sensitivity of materials to shock, impact and friction. The U.S. Bureau of Mines (now defunct) developed a method of measuring dust explosion hazards. Both sets of tests were conducted on rechargeable metal hydrides, including $LaNi_5$-hydride (including variants with additives) and FeTi-hydride [1,2]. In addition to these standard tests, DRI developed some qualitative tests to assess the fire hazards presented by spillage of rechargeable hydrides with subsequent ignition. Hydrides were also subjected to self-ignition tests by heating in an oxygen environment.

Work under the Project

HCI's limited 1999 work on $NaAlH_4$ safety was supported by DOE and performed under subcontract to the Sandia National Labs. It began by obtaining the latest version of Mil-Std-1751 and studying how the tests had changed during the last 20 years. The University of Denver is still involved in explosive studies and offered their assistance in performing the tests (e.g. 50 caliber gunfire). We also spoke with Applied Research Associates, specialists in ordinance testing, about the use of their firing range for the high explosive work called for in the Mil-Std. HCI fabricated some of the test apparatuses required to conduct the testing according to Mil-Std-1751.

The U.S. Bureau of Mines previously conducted the dust cloud tests using samples we prepared for them. Some of the people involved are now with NIOSH. Others went to MSHA after the Bureau was disbanded. The people involved in the earlier tests were found and consulted about options for dust cloud testing. NIOSH may be able to perform the tests if there are no commercial laboratories that offer this service. We did not begin the search for commercial labs in 1999, but we have some leads in this area.

HCI studied the accidental injection of water into a tank of $NaAlH_4$. HCI experience with hydrolysis of the analogous $LiAlH_4$ indicates that the heat of the hydrolysis reaction can drive thermal decomposition of the adjacent hydride. The hot (>100°C) hydrolysis reaction produces 2 moles of H_2 per mole of H_2O. Consequential thermal decomposition in adjacent hydride can increase the hydrogen yield by an order of magnitude, ~20 moles of H_2 per mole of H_2O injected.

Modern hydrogen connectors, e.g., Sherex (Canada) and Weh (Germany), cannot trap very much water when they are connected because of the way they are designed. Even if connected while submerged in water, such connectors could not trap and inject as much as 1 gram of water. The calculations were performed using 1 gram H_2O as an upper limit on credible accidental injection of water.

Automotive hydride containers will contain on the order of 100 kg of $NaAlH_4$, perhaps several times this much. The calculations were performed with 100 kg of hydride, packed to a powder density of 60% (40% void space). The worst-case H_2 pressure rise resulting from the injection of 1 gram of water into a 100 kg $NaAlH_4$ tank is just over 0.5 bar. This is not a significant fraction of the pressure rating of any credible container. Therefore, no significant hazard can arise from attaching a wet connector to a $NaAlH_4$ tank. Larger amounts of water can only be injected into a sealed (not broken) hydride container if common safety practices are ignored. Hydrogen pipes and hoses should be purged of all atmospheric contaminants, including water, before admitting hydrogen. Failure to follow accepted safety practices can cause a hazardous hydrolysis reaction, as well as a number of other safety problems that are outside the scope of the investigation.

The related issue of spilling large amounts of $NaAlH_4$ into water during an accident is more difficult to analyze. This is best approached through experimental simulation of credible accident scenarios. Likewise, pouring water into spilled $NaAlH_4$ is a likely result of an automobile accident. Analogous HCI experience with $LiAlH_4$ shows that there will be rapid evolution of hydrogen and heating to the ignition point.

We did not find a U.S. military standard for hydrolysis safety testing. There probably should be, given the contents of some modern batteries. IEA Task 12 participants were asked to provide information on whether any other country had a military standard that could be used as a guide us; however, we received no response.

Proposed Test Procedure

A test procedure was proposed that would have broad applicability to solid-state hydrogen storage media, not just $NaAlH_4$. The draft procedure is as follows:

Location: the test must be conducted in still air at 20±2°C in a well-ventilated location free of combustible materials and ignition sources. The test will be recorded on a video camera placed a minimum of 8 meters from the test specimen.

Test Procedure (and Rationales)

1. The size of various test specimens will be normalized for 100 standard liters of "deliverable" hydrogen capacity. (Rationale: "Deliverable" means the useable capacity in the intended application. For example, VH_2 holds 2 hydrogen atoms—only one is "deliverable" for room temperature applications.)

2. Prepare a first specimen by fully charging it with hydrogen and maintaining it in the charged condition at the typical use temperature until the start of the test. Prepare a second specimen by extracting its "deliverable" hydrogen capacity and maintaining it in the discharged condition at the typical use temperature until the start of the test. (Rationale: Reactivity of a depleted hydrogen storage medium, in general, is different from its reactivity in the charged condition. Both conditions are relevant to safe use. The material is most likely to be spilled when in use, e.g., on a motor vehicle. Temperature affects the reactivity of candidate hydrogen storage media with water, so the media should be exposed to water at the proposed use temperature).

3. The proposed container is only in the design stage. It should be designed to withstand the pressure of each candidate hydrogen storage medium in the fully charged condition. It must have a vent valve to relieve pressure prior to the start of a test and an internal stainless steel mesh cage to keep the material (typically powders) in place after the container is opened. The base of the cage will be weighted to cause submergence of the specimen. (Rationale: It would be very difficult to get repeatable test results by dropping powdered materials into water. Hydrolysis reactions, the buildup of heat within the specimen and the evolution of hydrogen will be affected by surface area. Jet trust from hydrogen evolution will affect how the specimens move in the water (perhaps out of the water). The goal is to eliminate as many random variables as possible from the test).

4. The water vessel (20±2°C) must have a large enough surface area so that the water consumed during the test does not reduce the level by 1%. The depth of the water will be set to submerge the specimen axially to the midpoint of the cage. The mass of water must be large enough to limit the average water temperature rise to less than 2°C. (Rationale: The objective of submerging the cage half way is to expose a portion of the specimen to a hydrogen fire, as might be the case in an accidental spill).

5. The cage will be lowered into the water at a controlled rate to minimize the unpredictable effects of splashing water. (Rationale: Splashing is another unpredictable variable that we want to eliminate).

6. If the specimen does not self-ignite, we will ignite the hydrogen cloud artificially. (Rationale: Ignition sources are abundant in motor vehicle accidents. We need to know what happens if ignition occurs naturally or by another source).

Analysis

The videotape will record the test for objective answers to the following questions:

- Was hydrogen evolved and if so, over what period of time?
- Did the specimen self ignite and if so, how long after the start of the test?
- Did the solid ignite and if so, is any smoke generated?

The videotape will also support subjective evaluations such as the following:

- Was the reaction sluggish, moderate or violent?
- How did the fire compare with a gasoline baseline (equal fuel energy)?

Additional consideration of a variant of the proposed test procedure should involve adding water to an excess of $NaAlH_4$. This is a credible result of a motor vehicle accident. If the hydride is spilled on the ground, water may be splashed or rained onto the pile.

Concluding Remarks

We are convinced that useful quantitative and qualitative safety tests can be performed on $NaAlH_4$, Na_3AlH_6 and other developmental hydrides using variants of basic test procedures developed under this project. It is unfortunate that the originally planned second year of funding did not materialize, to allow actual testing of $NaAlH_4$.

References

[1] C.E. Lundin, F.E. Lynch: "Solid-State Hydrogen Storage Materials for Applications to Energy Needs", First Annual Report for Contract AFOSR F44620-74-C-0020, University of Denver Research Institute, 1975.

[2] C.E. Lundin, F.E. Lynch: "The Safety Characteristics of FeTi Hydride", Proc. 10^{th} IECEC, (IEEE, New York, 1975), pp. 1386-1390.