

COMPLEX HYDRIDES AS SOLID STORAGE MATERIALS: FIRST SAFETY TESTS

Lohstroh, W.¹ (lohstroh@int.fzk.de), Fichtner, M.,¹ and Breitung, W.³

¹ Institute of Nanotechnology, Forschungszentrum Karlsruhe GmbH, Postfach 3640, 76021 Karlsruhe, Germany

²Institute for Nuclear and Energy Technologies, Forschungszentrum Karlsruhe GmbH, Postfach 3640, 76021 Karlsruhe, Germany

ABSTRACT

Hydrogen technology requires efficient and safe hydrogen storage systems. For this purpose, storage in solid materials, such as high capacity complex hydrides, is studied intensely. Independent from the actual material to be used eventually, any tank design will combine nanoscale powders of highly reactive material with pressurized hydrogen gas and so far, little is known about the behaviour of these mixtures in case of incidents. For a first evaluation of a complex hydride in case of a tank failure, NaAlH₄ (doped with Ti) was investigated in a small scale tank failure tests. 80-100 ml of the material were filled into a heat exchanger tube, and sealed under argon atmosphere with a burst disk. Subsequently, the NaAlH₄ was partially desorbed by heating. When the powder temperature reached 130 °C and the burst disk ruptured at 9 bar hydrogen overpressure the behaviour of the expelled powder was monitored using a high speed camera, an IR camera as well as sound level meters. Expulsion of the hydrogen storage material into (dry) ambient atmosphere yields a dust cloud of finely dispersed powder which does not ignite spontaneously. Similar experiments including an external source of ignition (spark / water reacting with NaAlH₄) yield a flame of reacting powder. The intensity will be compared to the reaction of an equivalent amount of pure hydrogen.

KEYWORDS:

solid state hydrogen tank, safety test, complex hydride, NaAlH₄

1.0 INTRODUCTION

Hydrogen storage in solid materials is considered a promising option for efficient energy carrier systems for fuel cell applications. However, classical hydrides such (e.g. LaNi₅H_x) [1,2] lack the required capacity since, for practical applications, a gravimetric and volumetric density of 0.048 kg H₂/ kg and 0.023 kg H₂/l [3] in the storage system are desired. After the discovery of Bogdanovic et al. [4] that NaAlH₄ doped with Ti can be loaded reversibly with hydrogen, the focus of attention has turned to complex hydrides as promising alternative. However, the details of the physical and chemical properties of hydrogen already discussed in detail in literature do not give insights into the potential hazards of solid state hydrogen storage, and additional factors have to be considered such as, e.g., the reactivity of the material, the contact surfaces for reactions, or altered dispersion behavior of hydrogen gas. Independent from the actual material to be used in the system, any tank design will combine nanoscale powders of highly reactive material with pressurized hydrogen gas. To our knowledge, there is only little work on the risk assessment for hydrogen storage systems based complex hydrides, so far. Therefore, it is mandatory to study the potential hazards and consequences of a tank failure to develop suitable tank designs and mitigate potential risks. In this paper we present some preliminary experiments dedicated to define the scope of requirements for future safety tests.

We chose Ti-doped NaAlH₄ for probing the behavior of such a complex hydride based storage system in a simulated tank failure. The sorption properties of NaAlH₄ doped with Ti have been investigated in numerous studies [5] and hence, its behavior is well known under normal operating conditions. Although NaAlH₄ falls short on the gravimetric requirements set by the automotive industry, it is

envisaged as storage material for other applications and the presented experiments scope its behaviour in a tank failure in order to define the conditions for more elaborate tests.

Composites of the complex hydride together with a suitable additive are prepared in order to enhance the kinetics of hydrogen uptake and release. The resulting powder is nano-crystalline with typical particle sizes of a few 10 nm [6]. The hydrogen release occurs in two steps



A third desorption step, the decomposition of NaH requires too high temperatures to be useful for applications. The dissociation pressure 1 bar H₂ are at 33 °C for NaAlH₄ (Eq. 1) and at 130 °C for Na₃AlH₆. From the above equations, it is obvious that, at any given time and hydrogen storage level, the tank will be filled with a mixture of highly reactive, nanoscale materials, e.g. Na₃AlH₆, NaH, or Al, possessing a large heat of reaction with oxygen and a large surface area, together with pressurized hydrogen gas (the gas pressure ranging from 1-10 bar during discharge and ≈ 100 bar during charging of the material). One of the potential reaction products, Al₂O₃, belongs to the most stable materials and assuming complete oxidation the energy content of the ~25 g powder of NaAlH₄ is in the order of 0.2 MJ. Similar conditions will be found for systems that make use of other complex hydrides (such as borohydrides or amides). In this paper, we present data on a simulated tank failure when the hydrogen / powder mixture is expelled into ambient, unconfined environment. The collected data on the powder ejection, flame speeds, heat loads etc. give useful insight in establishing a procedure for the safety assessment of solid storage hydrogen tanks.

2.0 EXPERIMENTAL SETUP

A sketch of the experimental setup and the reactor used is shown in Fig. 1 and 2. The active material was filled into a heat exchanger tube (~ 100 ml internal volume) equipped with a burst disk, having an opening pressure of 10 bar. Temperature and pressure inside the powder bed were monitored by means of a pressure gauge and a thermocouple while an external heater was used for temperature control (see Fig. 1). For each experiment ~25 g Ti-doped NaAlH₄ were used, filling the entire reactor with loosely compacted powder. All handling of the powder was done in a glove box in purified argon atmosphere (water and oxygen level below 0.1ppm). Heating the reactor to ~130 °C started the hydrogen release reaction and the pressure inside the tube increased until the limiting pressure of the burst disk was almost reached. At this point, an external H₂ pressure pulse was applied to rupture the disk. In this way, we had better control of the trigger of the monitoring equipment.

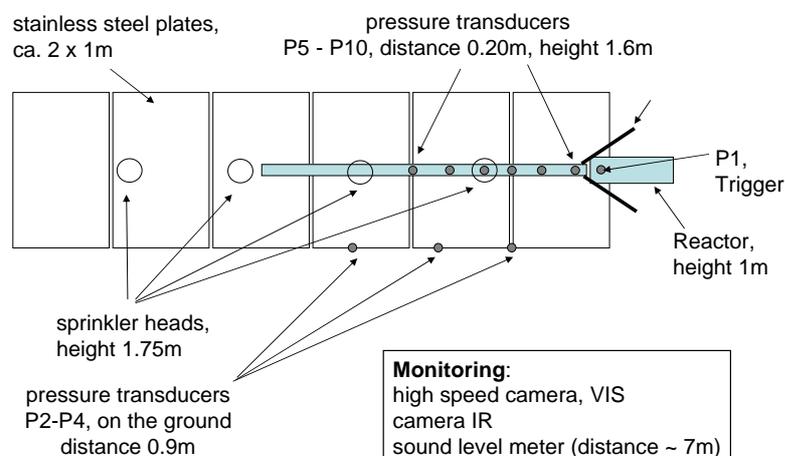


Figure 1: Schematic drawing of the used set – up (with dimensions)

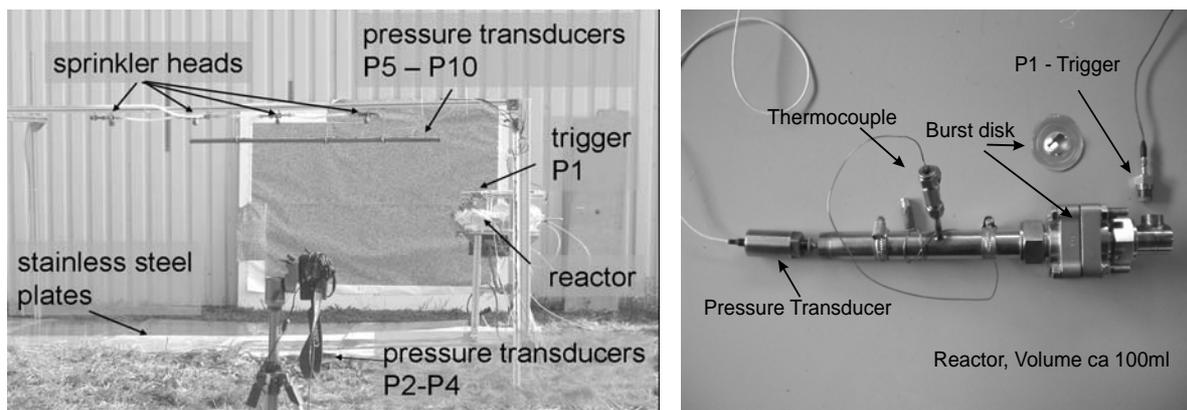


Figure 2: Photograph of the used set – up and reactor. The reactor was mounted on a test rig and the powder was expelled into ambient air. The picture shows the test stand with the reactor and the mounting construction for pressure transducers and water sprinkler heads. In the foreground, a photo-camera is visible.

The reactor was mounted on a test rig and the powder was discharged into ambient air. Above the test rig, an array of pressure transducers (with respective distance of 0.2 m) was mounted on a beam 1.60m above ground while a second set of fast pressure transducers was positioned on the ground. For intentional ignition of the H_2 / powder mixture a spark source was positioned directly in front of the opening of the reactor. For a second experiment, simulating a rain shower, four water sprinkler heads were mounted above the powder discharge area (see Fig.1 + 2). Experiments took place on a sunny day, temperature ~ 25 °C, and 40 – 45% relative humidity. The H_2 / powder ejection was additionally monitored using visible high speed video (1000 frames / s), infrared video, sound level meters (with probing frequency 10 μ s). This equipment was placed at a distance of ~ 7 m perpendicular to the jet axis of the expelled powder. Three different types of experiments were performed:

- (i) discharge of H_2 / powder mixture into ambient air
- (ii) discharge of H_2 / powder mixture into ambient air, ignition of the mixture by an external spark source
- (iii) discharge of H_2 / powder mixture into open, spray water environment

For reference purposes, experiment (ii) was repeated using pure hydrogen gas under similar conditions.

3.0 RESULTS

(i) The pressure burst of 10 bar led to powder ejection of 3- 4 meter and an angular spread of the powder cloud of 20-30 deg (see Fig. 3). Without external source of ignition the powder / hydrogen mixture did not ignite spontaneously. Consequently, the infrared video pictures confirm a continuously decreasing temperature of the cloud initially discharged at $T = 130$ °C. Remarkably, the ejected nanoscale powder was not finely dispersed in the turbulent flow field but agglomeration of the particles was observed. These larger chunks of material fell out of the powder jet while smaller particles propagated further. The material deposited on the ground was still active after ~ 10 min and able to react e.g. with water. Both sound level meter and the pressure transducer did not record any significant events due to the uneventful expulsion of the particle cloud.



Figure 3: Powder expulsion cloud without external source of ignition

(ii) In the second experiment the ejected powder was ignited intentionally immediately after rupture of the disk by an external electrical spark source. The solid material / gas mixture started to burn and a fireball was observed. The heat load of the reaction cloud exceeded 500 °C. Unfortunately, the high speed camera pictures were overexposed in this experiment hence reliable information on flame speeds could not be obtained. From the infrared camera data, it seems that an intense reaction takes place during the first ms after opening of the burst disk, the time frame for this initial reaction is estimated to be smaller than 80 ms. Afterwards, the reaction zone propagates mainly with the velocity of the expanding powder cloud. This is shown in Fig. 4 where we plotted the heat distribution at two different times after opening of the burst disk. In the figure, the reactor opening is at the right border and the jet of expelled powder (at a temperature >130 °C) is clearly visible. At $t_1 \approx 80$ ms, temperatures exceed 500 °C in a well confined reaction zone. As the cloud propagates further (at time $t_2 \approx 130$ ms), this reaction zone is taken along while, at the same time, it expands only slightly and cools down. Moreover, the consecutive powder also started to burn although with a much lower heat evolution. The pressure transducer readings show only a small signal at the rupturing of the burst disk but remain insignificant from a hazard point of view.

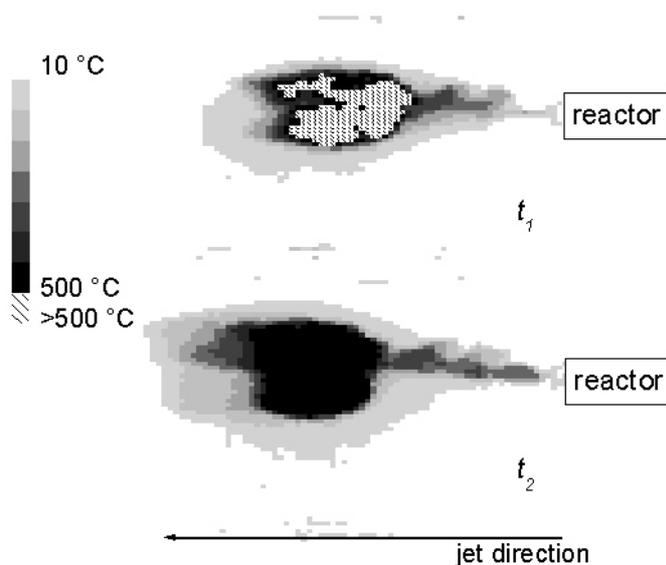


Figure 4: Heat distribution after expulsion of the powder and external spark ignition. The temperature is colour coded from white (10 °C) to black (500 °C). Temperatures above the saturation of the camera (> 500 °C) are indicated by pattern. Pictures are shown for times $t_1 \approx 80$ ms and $t_2 \approx 130$ ms after

opening of the burst disk. Once the cloud is ignited the main reaction zone travels mainly with the powder cloud, while the diameter increases only slowly.

(iii) Ejection of the powder / hydrogen mixture into a spray water environment (without igniter) led to ignition of the powder cloud. NaAlH_4 reacts exothermally with water under the emission of hydrogen gas to the stable products $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $\text{NaOH} \cdot y\text{H}_2\text{O}$. The released heat during these reactions is sufficient for the H_2 / powder cloud to burn. The reaction started at several points at the of the particle cloud/air boundary as can be seen in Fig. 5 and 6. These reaction zones show temperatures around 500°C and they increase in diameter. From the high speed camera pictures, the flame propagation velocity was estimated to be 2 -13 m /s. Remarkably, not all the powder was consumed in the reaction but again particle agglomerations fell out of the jet onto the ground where they reacted with water from the wet surface. The peak pressures measured remained below the detection limit of 3 mbar and thus, they are insignificant from a hazard point of view (for this experiment, the pressure transducers above the reactor, P5-P10, see Fig. 1 and 2, were removed).

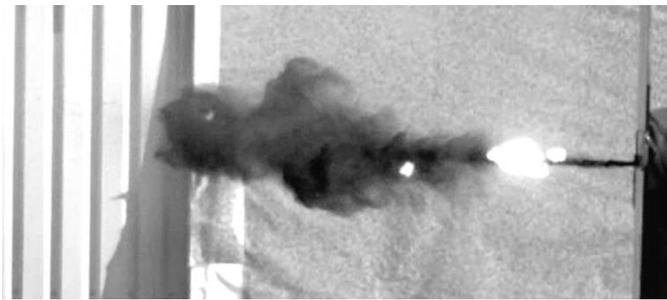


Figure 5: NaAlH_4 / H_2 in a spray water environment. The reaction starts at the border of the powder cloud.

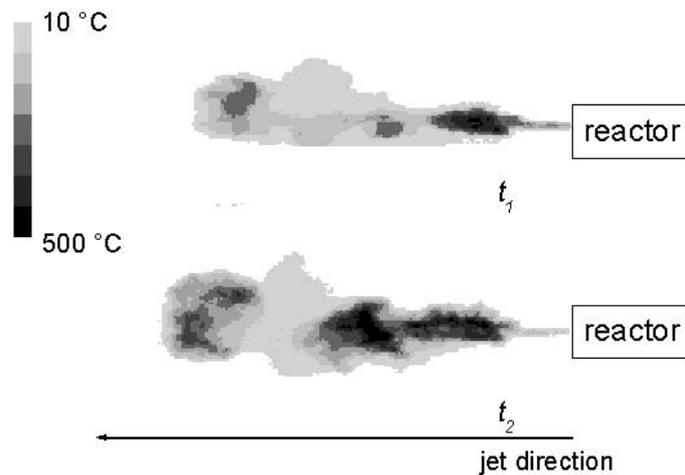


Figure 6: Heat distribution of the expelled powder in a spray water environment. The temperature is colour coded from white (10°C) to black (500°C). Pictures are shown for time $t_1 \approx 290$ ms and $t_2 \approx 370$ ms after opening of the burst disk. The reaction and corresponding heat evolution starts at several points at the borders of the powder cloud.

(iv) The reactor was filled with pure hydrogen and experiment (ii) was repeated. After opening of the burst disk, hydrogen was immediately ignited by electric sparks and deflagrated.

4.0 DISCUSSION

Three different cases of ejection of the complex hydride NaAlH_4 have been presented above. From the experiments, it becomes obvious that the behavior of the powder is comparably good natured despite its high reactivity, high reaction energy and small particle size. In ambient, unconfined conditions, the powder did not ignite spontaneously but the gas / powder mixture dispersed in air and eventually, the solid particles fell to ground. This result was quite unexpected. Especially, the non-ignition of the powder cloud when the material was expelled into ambient air (without external source of ignition) seems to be contradictory to the experience of laboratories working with complex hydrides (including ours): There are several reports on incidents that occurred during normal handling of Ti-catalyzed NaAlH_4 and even small traces of air or moisture are sufficient to initiate a rapid exothermic reaction and ignition of the released hydrogen [7]. The ignition energy is not known, but it appears to be quite small, e.g. as provided by scratching a metal spatula on some metal during handling. We can only speculate on the reasons of the unexpected outcome: A major difference between the setup used in the safety tests and the laboratory incidents is the dispersion of the powder: The effective surface area for heat exchange was increased considerably due to the fine distribution of the particles during expulsion and thus any heat generated in an exothermic reaction is efficiently removed. Moreover, the material was still reactive after it had fallen onto the ground, and a droplet of water was sufficient to ignite the small heaps of the powder on the stainless steel plate some 10 min after the expulsion into air. This indicates that a self-protection mechanism took place, probably by the formation of a thin surface oxide or hydroxide layer which mitigated or even blocked the reaction with oxygen and moisture from ambient air.

When an external source of ignition was provided (spark source or water spray environment), the powder / hydrogen cloud did ignite. However, the reaction zone is locally restricted along the jet axis and hence, in unconfined conditions, the effected area is determined mainly by the powder expulsion velocity and distance. The temperature loads in the center of the reaction zone amount roughly to 500 °C but again, it drops rapidly towards the border of the cloud. For all cases the pressure loads recorded at various distances (the closest at ~0.60 m directly above the reactor opening) were insignificant from a hazard point of view.

In experiment (ii), the initial spark results in a large heat evolution, however, subsequently, this reaction zone travels along the jet axis while it expands only slowly in diameter. Presumably, after consumption of the free, gaseous hydrogen, the reaction speed is limited by the solid reactant NaAlH_4 . This is consistent with the outcome of experiment (iii) where we observed only a relatively slow flame speed and much smaller heat loads compared to experiment (ii). By using water, we initiated an exothermal reaction with solid NaAlH_4 but it seems the free hydrogen gas initially present in the reactor was not taking part of the reaction. Presumably, the solid – water reaction only starts after the hydrogen gas has already been dispersed due to the unconfined conditions.

In Fig. 7, the sound level meter readings of the first milliseconds for the different types of experiments are plotted. In all cases, the very first event belongs to the opening of the burst disk. For the pure powder and the ignited powder ejection cases, the sound – level reaches ~85 dB, however, for the pure hydrogen deflagration, the readings are much higher fitting to the behavior of a turbulent deflagration of hydrogen gas. These results underline the findings that we obtained from the high speed camera pictures: although the total energy content of the pure H_2 experiments is lower than in the H_2 / powder mixture, the reaction speed and hence the intensity is much higher in the pure gas.

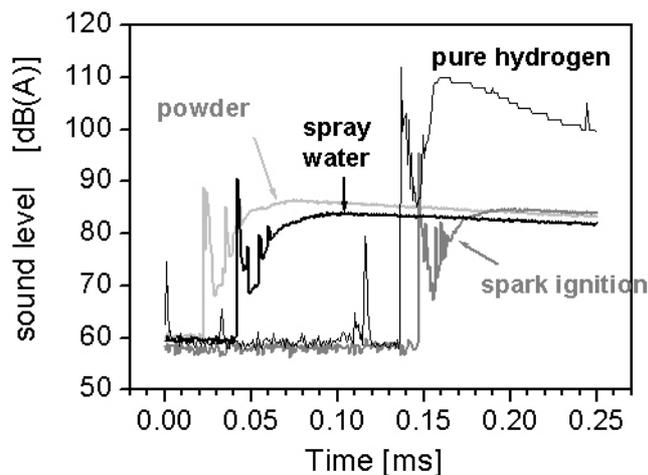


Figure 7: Sound level readings for the various tested scenarios.

5.0 CONCLUSIONS AND OUTLOOK

From the scoping experiments presented above, it seems that a major risk for mixtures of the complex hydride NaAlH_4 and hydrogen originates from the free hydrogen gas as demonstrated in experiment (ii) using a spark ignition. In comparison to the deflagration of pure hydrogen, the reaction speed in the powder – gas mixture is slower in all investigated cases. Also, the sound level meter readings point to relatively good natured reactions where the main hazard comes from thermal loads in the jet axis. Naturally, more sophisticated tests are needed. The apparent discrepancy of the laboratory experience and the reproducible outcome of our safety tests underline the necessity to investigate the safety behavior of potential hydrogen storage materials in more detail. The above experiments give a first introduction to the behaviour of complex hydrides in a tank failure in order to define better the conditions for more elaborate tests. It is mandatory to understand the conditions for self-ignition of the powder and how to mitigate the potential hazards. Further experiments will be performed in order to study the ejection of the hydrogen / powder mixture into liquid phases such as hot water and hot thermo-oil (as for instance used in heat exchangers). Moreover, larger amounts of material will be tested and compared to pure hydrogen events in order to study possible upscale effects and the experiments will be extended to include other complex hydrides such as borohydrides and amides.

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