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Down Select Report of Chemical Hydrogen Storage Materials, Catalysts, and Spent Fuel Regeneration Processes

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August 2008



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Down Select Report of Chemical Hydrogen Storage Materials, Catalysts, and Spent Fuel Regeneration Processes

**Chemical Hydrogen Storage Center of Excellence
FY2008 Second Quarter Milestone Report**

**Submitted by:
The Chemical Hydrogen Storage Center of Excellence
Coordinating Council**

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Executive Summary

The Chemical Hydrogen Storage Center of Excellence (CHSCoE) partners have studied more than 60 materials since the Center's inception in early calendar year 2005. This report contains the outcome of the Center's storage material down select process and the status of these materials in moving forward to Phase II R&D conducted by the Center's partners.

During the first three years of the Center's research, several concepts for the storage of hydrogen in chemical hydrogen storage materials have been developed and tested. The key classes of materials investigated include endothermic release materials (such as organocarbenes, imidazolines, magnesium alkoxides, and silicon nanoparticles and clathrates), exothermic release materials (such as ammonia borane (AB) and mixtures with ionic liquids or scaffolds containing ammonia borane, metal amidoboranes, and amine boranes), and polyhedral boranes (such as alkali metal salts of decaborane, undecaborane, and dodecaborane anions). To release hydrogen from these classes of materials, approaches including thermolysis, hydrolysis, and catalysis have been or are being developed. All three of these approaches are yielding promising hydrogen storage capacities or rates of hydrogen release or both in some cases. Other concepts (e.g. coupled endothermic/exothermic reactions, nanoparticle hydrides, and polyhedral borane hydrolysis) have also been tested but have not resulted in hydrogen release rates or capacities that have the potential to meet DOE targets for 2010, and these systems have been discontinued for further study.

Of the more than 60 materials the CHSCoE investigated, approximately 50% of the materials have been discontinued. They include endothermic imidazolines, nanoparticles and silicon clathrates, magnesium alkoxides, and polyhedral boranes. Certain release concepts of other materials have also been discontinued, such as the use of Bronsted acid catalysis of hydrogen release from ammonia borane, substoichiometric LiH/ammonia borane mixtures, and methylamine borane. Studies of these materials or release concepts are discontinued for reasons of either low capacity, poor release kinetics, high release temperatures, or the spent fuel products require regeneration of borates (regeneration of borates was discontinued as a part of DOE's sodium borohydride go/no go decision at the end of fiscal year 2007).

About 30% of the materials show promising capacities and/or rates of release, but require near-term answers or solutions to potential problems such as long-term stability or problematic low temperature or solubility properties. If solutions are not found, these materials may not remain a priority for the Center's Phase II activities, and may be discontinued in the near term.

The balance of the materials, approximately 20%, show high potential (high capacities with high rates of release) to meet or exceed DOE's 2010 technical targets. These material classes include AB and many related mixtures or scaffolds containing AB, metal amidoboranes, and alkylamineboranes and remain a high priority in the Center's ongoing research and development efforts.

To develop the rationale for down selecting the most promising materials and processes from the Center's portfolio for focused development in Phase II R&D activities, a Center-wide meeting

was held in November 2007. Down selection criteria (Table 2) were developed and derived from key DOE hydrogen storage targets most relevant to chemical hydrogen storage materials. A decision tree (Fig. 2) was also developed with decision criteria placed in a logical flow to identify and select the storage materials of interest for further development. The Center has also been building a database (Appendix 1) in the past few years collecting key parameters of interest of all of the materials being investigated. The data collected for each material were run through the decision tree and the outcome from that process (Appendix 2) formed the basis of this report. This report documents the outcome of the Center's storage material down select process regarding: 1) storage materials or material classes for continued focus and priority for additional research and development as the Center moves into Phase II activities; 2) materials that showed some promise and worthy of some level of investigation before making the final decision of whether to proceed or discontinue; and 3) materials to be discontinued.

The Center has also been working on the regeneration of the most promising material, ammonia borane, from spent fuel. From a myriad of possible chemical pathways and permutations of pathways to regenerate ammonia borane, the Center has focused on three processes that show potential to achieve the DOE's goals of greater than 60% "well to tank" energy efficiency. Currently, each of the Center's three AB regeneration processes consists of four key steps that include digestion of spent fuel BNH_x followed by addition of hydride by a reducing agent to form BH_3 units, and addition of ammonia to complete the formation of AB. In addition, the reducing agent also needs to be recycled from MX to MH to complete the AB regeneration cycle. The three processes under investigation by the Center differ mainly in their approaches to the digestion step of the AB regeneration process. Much progress has been made on the AB regeneration efforts. For the regeneration processes, criteria considered are: 1) the overall thermodynamic efficiency of the regeneration processes demonstrated to date, 2) the chemical yields at each step, and 3) the overall chemical yield of the spent fuel to fuel conversion processes that have been demonstrated. A near-daily activity of the regeneration R&D is to select and reject potential chemical reaction pathways or reagents for regeneration. Much of this early input to this type of down selection involves the use of theory for the computation of reaction pathway energetics.

The three AB regeneration processes investigated to date currently have a wide range of overall thermodynamic efficiencies (ranging from 45 to 81%) and chemical efficiencies (involving individual steps with yields ranging from 30% to 100%). The Center is learning that there are significant synergies among these three routes that are yielding ideas to enable steady improvements in the chemistry of regeneration. Based on this observation, the Center will continue on with these three processes during Phase II of the Center work at which time a total energy assessment may be made that can distinguish among these options.

Background

The DOE Hydrogen Storage Program is focused on identifying and developing viable hydrogen storage systems for onboard vehicular applications. The program funds applied research and development directed at identifying new materials and concepts for storage of hydrogen having high gravimetric and volumetric capacities and acceptable rates of hydrogen release, among other criteria that will be described in more detail below. The major categories of approaches currently being examined are reversible metal hydride storage materials, reversible hydrogen

sorption systems, and chemical hydrogen storage systems. The latter approach concerns materials that release hydrogen in endothermic or exothermic chemical bond-breaking processes. To regenerate the spent fuels arising from hydrogen release from such materials, chemical processes must be employed. These chemical regeneration processes are envisioned to occur off board the vehicle.

The DOE established three Hydrogen Storage Centers of Excellence in 2005 to foster collaboration among researchers on applied R&D, enabling accelerated advancement and providing a focal point for the technical management for each of the three distinct material classes for hydrogen storage. DOE also funds independent hydrogen storage projects on promising approaches to meet near and long-term targets. To focus resources on the most promising systems that have the potential to achieve DOE technical targets, the DOE has encouraged each Center to develop criteria to down select materials that hold promise and discontinue work on materials and processes that are less promising or that do not meet set criteria.

This report details the down selection processes that the CHSCoE has implemented to meet the second Quarter FY2008 Milestone for down selection of chemical hydrogen storage materials and accompanying regeneration processes.

Technical Barriers and Targets

There are many technical challenges on the path to developing viable onboard hydrogen storage systems to achieve more than 300 mile range across different vehicle platforms without compromising performance or space on-board the vehicle. Of particular importance to the research and development of storage materials are the considerations of overall system weight and volume. The gravimetric hydrogen capacity and the volumetric hydrogen capacity of the material are key contributors to overall system capacity, and as such are primary parameters for our selection criteria. The rate and energetics of hydrogen release from the storage material are also crucial criteria, as slow release or a release at temperatures outside the range of vehicular application is of little interest for onboard vehicular storage where transient response is vital to system operability. Stability of the fuel is another challenge, as there should be no release of hydrogen from the material under typical ambient conditions found in automotive applications. Of course, once the hydrogen is released from the material, an important criterion is the demonstration of a chemically and energetically efficient method for regeneration of spent fuel. The physical form of the fuel and spent fuel is also a parameter of note, as off boarding spent fuel and reloading of fuel will be impacted by whether the material is a liquid, a solid, or slurry. Cost and durability of the storage material become important criteria as the materials discovery phase transitions into the development phase.

To address these technical challenges, DOE has set targets to focus technical efforts and drive technology development forward. The technical targets may be found within DOE's Multi Year Program Plan for hydrogen storage at <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/>. The document describes the evolution of targets and tasks with time, and gives the targets for 2007, 2010, and 2015. Many of the materials-driven parameters that are most important in the materials discovery phase are summarized in Table 1 for 2007, 2010 and 2015. The MYPP should be consulted for the complete and detailed table of technical targets for onboard hydrogen

storage systems that address the criteria that are increasingly more important as the materials move beyond the discovery phase into the development phase.

Storage Parameter	Units	2007	2010 (current focus)	2015
System Gravimetric Capacity	Wt. % H ₂	4.5%	6%	9%
System Volumetric Capacity	g H ₂ /cc	.036	.045	.081
Operability (Operating ambient T)	°C	-20/50	-30/50	-40/60
Operability (Min/max delivery T)	°C	-30/85	-40/85	-40/85
Discharge Rate (min full flow rate)	g H ₂ /sec/kW	.02	.02	.02
Hydrogen Purity	% H ₂	99.99	99.99	99.99
Storage System Cost (&fuel cost)	\$/kWh net	6	4	2
	(\$/kg H ₂)	(200)	(133)	(67)
	\$/gge at pump		2-3	2-3

Table 1. Summary of Selected Materials-Related Parameters

Note: In addition, hydrogen storage systems must be energy efficient in delivering hydrogen to the vehicle power plant. For on-board reversible systems, greater than 90% energy efficiency for the energy delivered to the power plant from the on-board storage system is required. For systems regenerated off-board, the overall efficiency is also important. In this case, the energy content of the hydrogen delivered to the automotive power plant should be greater than 60% of the total energy input to the process, including the input energy of hydrogen and any other fuel streams for generating process heat and electrical energy.

Tasks

Among the tasks that must be accomplished along the way to developing a viable storage system are to

- Identify families of chemical hydrogen storage materials capable of meeting mass and volume targets
- Characterize the hydrogen release reaction chemistries, kinetics and thermodynamics of the most promising candidates
- Rank viable candidates based on potential to meet technical targets

- Identify and develop improved processes, chemistry, catalysts, etc. for the complete fuel cycle (release and regeneration of spent fuel)
- Identify and investigate new materials and concepts that have the potential to meet or exceed DOE targets

It is these tasks that the CHSCoE has been most involved with, as the Center has progressed towards the Down selection Milestone. The remainder of this document describes the Center's deliberations surrounding the down selection process and the outcomes of the process. The Center will use these results of the down selection process to focus Center resources on the most promising systems capable of achieving DOE 2010 and 2015 technical targets.

Approach to Development of Down Selection Criteria

Selection of chemical hydrogen storage materials must be based on some criteria that are different than those for reversible systems. As an example, a majority of the CHSCoE materials release hydrogen exothermically and will require off-board regeneration. For such exothermic systems, considerations such as release temperature or heats of reaction are not as critical to the on-board efficiency as for endothermic hydrogen release systems, because exothermic hydrogen release reactions may be engineered to sustain release with negligible on-board energy input; this is a key consideration in our materials development efforts.

In building a decision process for the CHSCoE, we had some experience garnered from the sodium borohydride (SBH) go-no go decision process that took place in September 2007. The process used for the SBH decision, and its outcome, have given us useful guidance in the development of the current Center-wide philosophy and processes for down selection of systems for future R&D. First and foremost was the notion that liquid-to-solid phase changes in the fueling system are almost impossible to accommodate on-board. Systems with a liquid product are the most desirable, while systems that process solids will require innovation to enable practical fueling and refueling. Difficulty abounds when liquid fuels have the potential to solidify or gel in the fueling system. At best, this complicates off boarding of spent fuel, and at worst could result in clogging and disabling of the fuel system.

Secondly, on-board system considerations and off-board regeneration were considered equally during the development of our down selection decision process. Lastly, we have made an effort to use SBH hydrolysis as a baseline for comparison of other chemical hydrogen materials. Millennium Cell (MCEL) reported a design that has the potential to meet 4.5 wt % system based on a 7.6 wt% fuel (described within the document found at <http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/42220.pdf>). If we assume that system hardware mass is independent of material wt%, we can use the following equation to relate material wt% to system wt% for chemical hydrides:

Equation 1.

$$\text{System Wt\%} = \frac{\text{Hydrogen Mass}}{\text{Hardware Mass} + \frac{\text{Hydrogen Mass}}{\text{Material Wt\%}}}$$

MCEL used a system size of 10.8 kg of H₂ in their estimate with a hardware mass of 71.8 kg. Figure 1 shows an extrapolated curve (in red) for system gravimetric density based on the design estimate from MCEL. Hardware mass changes of +10, -10, and -33% were used to obtain the other curves. The $\pm 10\%$ curves indicate the sensitivity of material mass requirements on changes in system mass. The curve describing the removal of 33 wt.% of the system hardware relates to consideration of the MCEL design for SBH versus a potential design for another chemical hydride.

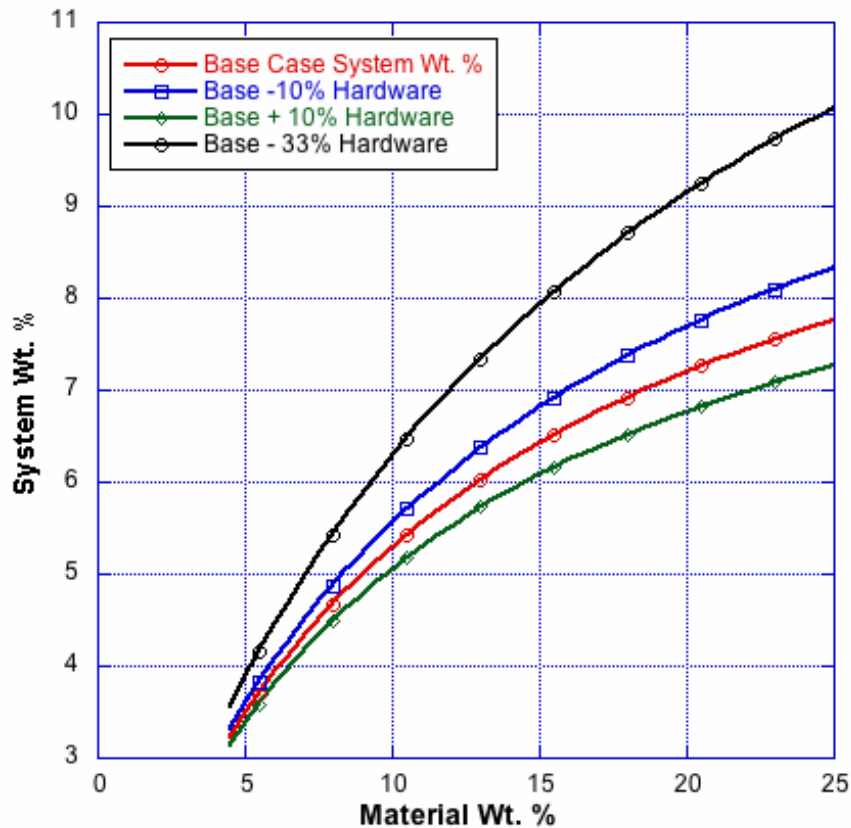
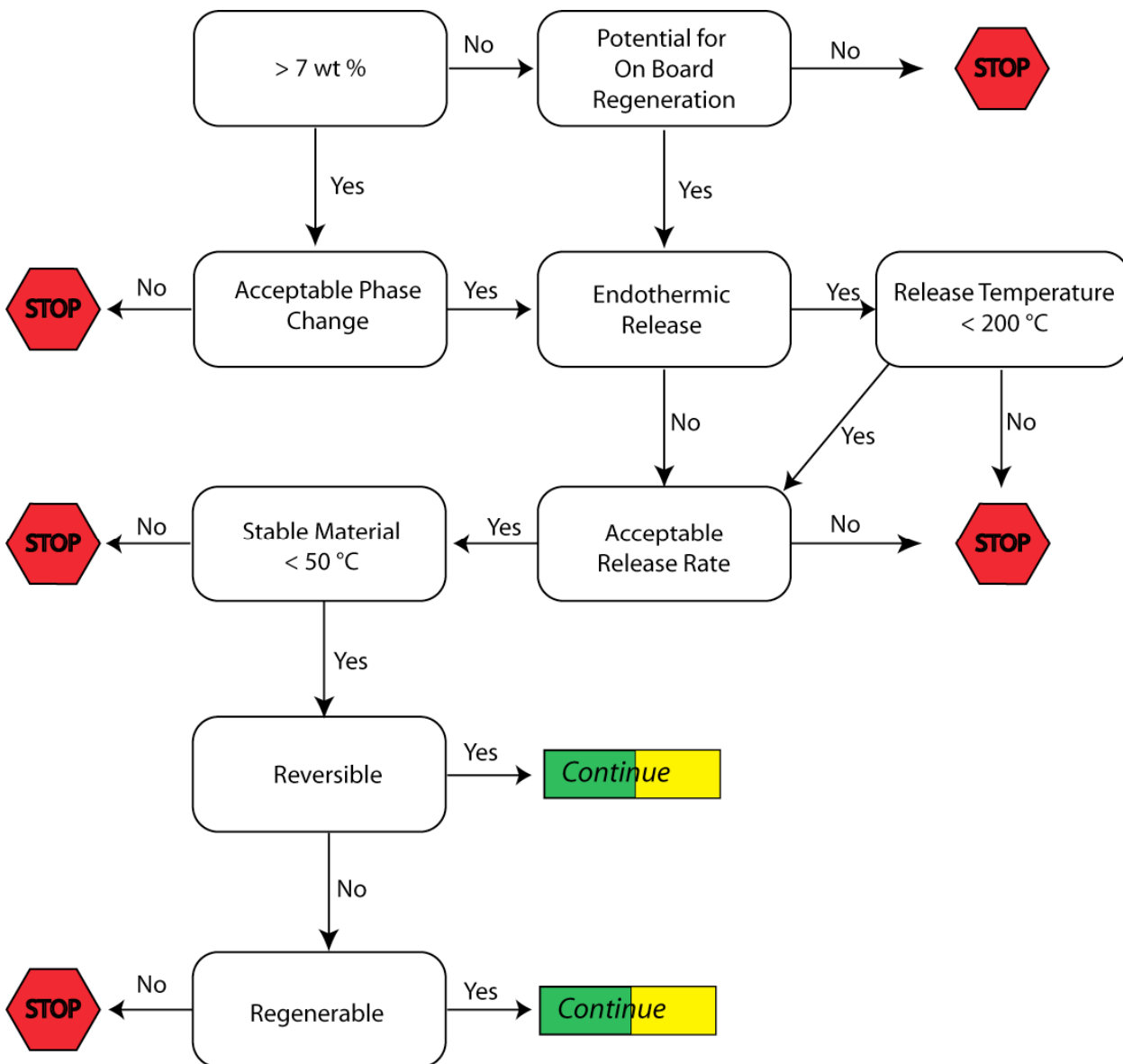


Figure 1. System Weight % vs. Material Wt. % extrapolated from the MCEL design using Equation 1.

The MCEL design includes a gas-liquid separations component at 23.7 kg. In an alternative system this component may not be needed, and hardware mass could be reduced by around 33%. So in a best-case scenario a 9 wt% material can potentially meet the 2010 DOE target of a system gravimetric density of 6 wt %. This led us to a primary down-selection metric of 7 wt.% (with future potential to meet or exceed 9 wt. %). From this metric we developed a decision tree to consider all materials under investigation within the CHSCoE. The decision tree is shown in Figure 2 and includes additional criteria based on rates of release, phase changes, fuel stability, reversibility or

Figure 2. Decision Tree for the CHSCoE Materials Down-Selection Process



regenerability, among others. More details on the specifics of the decision tree metrics appear in the criteria definitions, below. The decision tree contains many off ramps for materials, and materials that are worthy of further investigation must meet all of these criteria. In some stages,

there is a ‘yes/maybe’ decision, with the caveat being that the data is not yet available, or that there is still some uncertainty in the data for that material. In these cases, we will continue but with the requirement that necessary data for a down-select be obtained immediately. Also, those materials that are perhaps borderline cases may remain ‘yellow’ and are considered of lower priority for future research.

Down-Selection Criteria

In the Center’s consideration of materials and processes to move forward into the next phase of research and development, we focused on the following set of criteria listed in Table 2 that are most relevant to the materials discovery phase of the Center’s activities.

Criterion	Description	Metric
Gravimetric Capacity	Maximum calculated hydrogen weight fraction	> 7 wt. % H ₂
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/maybe
Regenerable	Ability to chemically reprocess spent fuel off board	yes/no/maybe
Acceptable Phase Change	Problematic liquid to solid phase change, or volatile byproducts	yes/no/maybe
Acceptable Release Rate	Maximum rate of hydrogen release, T < 125 °C	> .02g H ₂ /s/kg material
Material Stability	Stable in fuel tank < 50 °C	yes/no/maybe
Endothermic Release	Hydrogen release occurs endothermically	yes/no/maybe
Low Temperature	For endothermic reactions, temperature of release < 200 °C (with potential for lower T, i.e., 80 °C, release)	Temperature

Table 2. Down Selection Criteria for Chemical Hydrogen Storage Materials

Gravimetric Capacity: This is a primary criterion for any practical hydrogen storage material. This Center’s decision is to use 7 wt. % as the cutoff point. While the preceding analysis indicates that it is likely necessary to develop materials that exceed 9 wt. % to achieve the 2010 target, we did not wish to exclude materials of slightly less capacity that might be directly rehydrogenated on-board. We have not placed much focus on volumetric capacity as the densities of these storage materials are relatively high (compared to, for example, sorbents) and are not well measured at this point in time. Only estimates of volumetric capacity are known for a few of materials under study by the Center, and this parameter is a strong function of the materials engineering of the storage compound, e.g. pellet density, the presence of additives to broaden the liquid range, etc. It is in general true that the theoretical densities (where they are known) of the materials we are examining result in volumetric capacities that can meet DOE targets.

Potential to regenerate on-board: The Center is investigating new materials that have chemical properties that offer the possibility of direct rehydrogenation of the spent fuel. Directly regenerable spent fuel materials could offer on-board regeneration potential, a desirable outcome. This decision tree parameter anticipates these systems.

Regenerable: If spent fuel material cannot be rehydrogenated, then there must be a chemical processing scheme to regenerate the fuel off-board. If there is no obvious path forward to chemical reprocessing of spent fuel, then this is a clear off ramp for a storage material. Also of primary interest in the regeneration of a spent fuels is the energy efficiency of the overall process, which must eventually be greater than 60% with a near –term goal of 40% overall efficiency from primary energy. The overall chemical yield must also be exceedingly high to avoid losses and energy intensive recycle of byproducts.

Acceptable phase change: The SBH go/no-go decision process taught us that any on-board storage system that undergoes a liquid-to-solid phase change on dehydrogenation presents an extremely difficult engineering problem. The precipitation of borate from the spent SBH fuel was a major contributor to the no-go decision for aqueous SBH. Liquid-to-liquid processes are highly desired, with solid-to-liquid and solid-to-solid processes requiring innovation for onboard engineering solutions. Clearly, any phase change to volatile products other than hydrogen is to be avoided because of the potential for volatile byproducts to impact fuel cell performance, but also to avoid loss of spent fuel materials from the process.

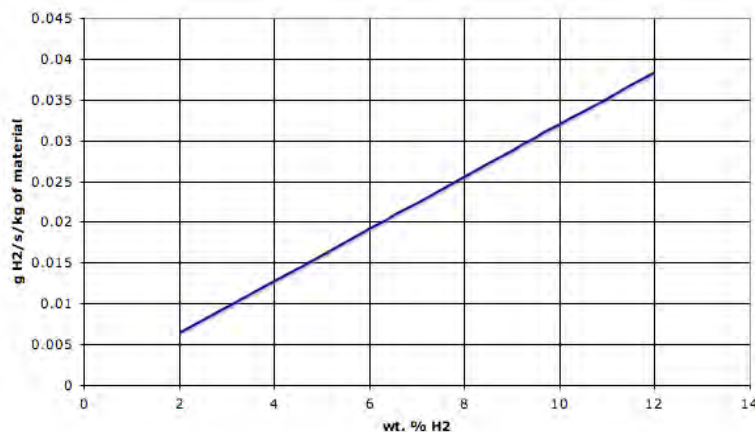
Acceptable H₂ release rate: If a storage material does not release hydrogen at a rate that allows for the intended operability of the propulsion system at a reasonable system temperature, it is of little practical interest. This criterion is based upon the rate of hydrogen release needed to meet the anticipated power demand of an automotive propulsion system. The release rate technical target is in units of mass of hydrogen per second per unit power of the propulsion system. Power is not a variable in our laboratory experiment, rather we measure the hydrogen release rate for a given mass of material. To relate the rate of release for a given mass back to the release rate required for a given power requirement, we perform the following calculation based on the following inputs: power = 80kW; rate = .02g/s/kW; mass of H₂ required for 300 mile range = 5 kg.

Rate of release/kg [g H₂/s/kg of material] = 80kW x .02g/s/kW]/5kg H₂ x mass fraction H₂ in material.

For example, for a 7 wt. % H₂ material, the required rate of release per kg of material is:

$$80\text{kW} \times .02\text{g/s/kW}] / 5\text{kg} \times .07 = .022 \text{ g H}_2/\text{s/kg of material}.$$

Note that the rate of release required for the system is a function of the weight % H₂ in the material. For a 10 wt. % H₂ material, the rate of release to achieve the technical target is .032 g H₂/s/kg of material. The relationship between the required minimum rate of release/kg of



material and the weight % H₂ in the material is shown in the plot above.

Stable Material < 50 °C: The storage material must be stable to premature hydrogen release under ambient conditions. The 2010 target for the upper end of ambient temperature for automotive applications is 50 °C; any material that releases hydrogen (or other contaminants/by-products) below this temperature does not have sufficient stability.

Endothermic release, and temperature of release: These two criteria are related. Endothermic release materials are of little interest if the hydrogen is released at too high a temperature. While a release temperature of 80-120 °C is desirable for fuel cell applications, the Center has chosen 200 °C as the upper limit of endothermic release to be of continued interest at this preliminary stage of R&D. While this temperature is higher than currently desired, if a system shows promise for catalyzed endothermic release, these criteria are intended to maintain those candidates within the pool of potentially useful storage materials for more careful consideration.

Hydrogen Purity: The purity of hydrogen delivered to the fuel cell must be adequate to avoid poisoning electrode catalysts, membranes, or other fuel cell components and causing decay in fuel cell performance or lifetime. We choose at this time to not use hydrogen purity as a metric for materials down selection, as we find that we are able to mitigate impurities from a chemical hydrogen storage compound by choice of conditions or processes to release the hydrogen, and that some impurities may be readily removed from the hydrogen stream. Because we feel that there are opportunities to deal with impurities at the process and materials design level, we don't wish to deselect materials based upon impurity release at this time. In the future, impurity levels may become more crucial in down select decisions not only because of hydrogen purity issues, but also from the aspect that loss of fuel materials from the system must be readily recovered for the regeneration to be overall chemically efficient.

Down-Selection Process

Since the inception of the CHSCoE, the second Quarter 2008 Materials Down select Milestone has provided a focal point for many of the Center's planning activities.

The Center collects materials storage performance data on a frequent basis to track progress and aid in the planning of future work. The database was updated in late October of 2007 prior to the Center's November meeting in Denver, Colorado. The intent of that Center meeting was to discuss progress, agree on down select criteria, perform a first-cut down select as a team and gain consensus of the researchers. We also used the opportunity to plan future work as the Center moves toward the initiation of Phase II research and development.

The data sheet used to collect information for the database is shown in Appendix 1. With this information collected from the Center partners, and assisted with a preliminary set of selection criteria, the Center meeting was held, and a Center-wide consensus was developed of the down selection criteria to be used to develop the down selection. The Center's Coordinating Council met immediately after the conclusion of the meeting to discuss the outcome of the meeting and begin to develop material down select, and for the path forward to Phase II research and development.

This report contains the results of the down select regarding which materials should be off-ramped to inactive status, which materials need additional work to determine whether to move forward or to off ramp, and which materials are of high priority for continued R&D.

The Coordinating Council also considered fuel regeneration processes. Criteria considered for fuel regeneration are the overall thermodynamic efficiency of the regeneration processes demonstrated to date, the chemical yields at each step, and the overall chemical yield of the spent fuel to fuel conversion processes that have been demonstrated. It must be noted that a key near-daily activity of the regeneration R&D is to select and reject potential chemical reaction pathways or reagents for regeneration. Much of this early input to this type of down selection involves the use of theory for the computation of reaction pathway energetics.

The down selection data and results of the process are given below.

Down-Selection Summary

The summary is broken down into sections to simplify the discussion. We have divided up the Center's materials portfolio into:

I) Endothermic Chemical Hydrides

II) Endothermic Chemical Hydrides:

- 1) Metal-Boron-Nitrogen Materials,
- 2) Ammonia Borane-based Materials,
- 3) Polyhedral Boranes; Rh-catalyzed Aqueous Hydrolysis.

The decision tree process resulted in down selection to identify the most promising candidates within each class. A summary of the background and current status for each material within these classes is provided below. A synopsis of the outcome from the down select process for each class of materials is also included in the summary. The data is summarized in Appendix 2.

I) Endothermic Chemical Hydrides

Background

For the most part the general class of endothermic chemical hydrides has been avoided by the Center to avoid duplication of the independent DOE project at Air Products & Chemicals, Inc. Their scope of study covers the larger C-N-H space, making our efforts in this area quite limited. The few areas where we have had some effort are in coupled endothermic-exothermic reactions, silicon nano-structured materials, heterocyclic imidazoline systems that eliminate hydrogen exothermically and exergonically, and heterocyclic and oligomeric carbene systems that eliminate hydrogen under mildly endo/exothermic conditions.

The coupled chemistries focused on the release of hydrogen from $\text{Mg(OMe)}_2/\text{H}_2\text{O}$. This system involves on-board conversion of magnesium methoxide and *in situ* CO_2 capture with the products being H_2 and magnesium carbonate. In this scheme it was hoped that the exothermicity of the CO_2 capture step would at least partially balance the endothermicity of methoxide decomposition and that the CO_2 capture would be kinetically coupled to the primary hydrogen release step, accelerating release. Neither of these situations prevailed.

The silicon nanomaterials involved two classes of materials studied at UC Davis: silicon nanoparticles¹ and silicon-based clathrate² materials. In both cases these materials store hydrogen in a chemisorbed form. In the nanoparticles the hydrogen is stored as a surface species on the outside of the particle, and in the clathrates hydrogen is stored in interstices within a clathrate material formed at moderate (atmospheric) pressure.

For the C-N polymer systems and carbenes there were two approaches considered. The University of Alabama developed C-N oligomer and carbene-based reversible systems based on thermal release of hydrogen, while LANL examined the reaction of imidazolines with acids to eliminate hydrogen catalytically.

Current Status

The coupled reaction scheme did show promise in reducing the endothermicity of methanol reforming by capture of the carbon dioxide as magnesium carbonate, but results showed a limited reduction in the release temperature. Secondly, the CO₂ capture internally to the system was only about half as much as expected indicating that at the current development levels this approach is not CO₂ neutral. Hydrogen was released at appreciable rates only above 200 °C.

The silicon nanoparticle materials were demonstrated to store hydrogen, but the release temperatures are considerably higher than that of the existing reversible metal hydride systems with comparable storage densities. The clathrate materials represent a new class of materials discovered in this project, but the storage densities do not offer sufficient incentive to continue including them in an applied research program.

The catalytic approach for release of hydrogen from imidazoline precursor materials via reaction with weak acids was successful in initial demonstrations. Hydrogen was released at low temperature and showed good rates with the use of a heterogeneous catalyst. The imidazolines were designed to have favorable thermodynamics of hydrogen release by 1,2- elimination dehydrogenation. This was demonstrated by both experiment and theory³. The molecules used had large substituents on the imidazolines, which limited the gravimetric storage density to about 1 wt%.

Work on C-N monomeric and polymeric carbene systems has suggested that these materials reversibly adsorb/desorb hydrogen at temperatures ranging from room temperature to 50 °C and at moderate pressures (one to five atmospheres.) Results to date have been on monomeric materials with storage densities on the order of 1wt%, at ambient conditions but the release of free H₂ is inferred from secondary hydrogen transfer reactions, not from volumetric measurements of hydrogen gas.

Down Select Results

Coupled reactions: Work on the H₂O/Mg(OMe)₂ system was discontinued early on because of insufficient coupling of reactions leading to too high a release temperature and insufficient CO₂ capture. Coupled reactions as a general concept are still valid as a Center approach moving ahead.

Silicon-based nanomaterials: Discontinue investigations as storage materials due to high release temperatures > 300 °C and low storage density < 4.5 wt%. These materials may have a role as hydride transfer materials for chemical regeneration of other systems such as ammonia borane.

Imidazolines: Work on these materials was discontinued during the early phases of the Center's research because of gravimetric capacities < 2 wt%. Efforts to reduce the size of the R groups to enable larger storage density were unsuccessful, and even if they had been successful, this route releases only one hydrogen per element, limiting the ultimate hydrogen storage potential to below 7 wt%.

Reversible C-N carbene oligomers: Results showing near room temperature reversibility at moderate pressure is of interest. Work in the short term must demonstrate that the 1 wt% storage density measured on monomer systems can be translated to the proposed polymers having potentially up to 7 wt % hydrogen at rates or release that achieve the DOE target. This project must demonstrate > 3 wt% hydrogen release from the polymer material by July 2008 using a PCT system or shall be off-ramped from the Center portfolio.

II) Exothermic Chemical Hydrides

1) Metal-Boron-Nitrogen Materials

Background

Early work in this area was initiated by one of the Center partners, Professor Sneddon at the University of Pennsylvania. His group researched the release of hydrogen from sub-stoichiometric mixtures of ammonia borane, (AB) and LiH or LiNH₂ and AB using a 'proton sponge' (a non-nucleophilic organic base) to initiate the dehydrogenation of AB.

As part of the International Partnership for Hydrogen Economy (IPHE) efforts coordinated with the Center's activities, PNNL and LANL are collaborating with researchers from New Zealand's Industrial Research Lab, (IRL), the National University of Singapore, the Universities of Oxford, Birmingham, and the UK's neutron scattering center ISIS at Rutherford Appleton Laboratory on ammonia borane derivatives formed from reaction of AB with endothermic metal hydrides. This has resulted in the development of a new class of metal-nitrogen-boron systems exhibiting hydrogen release reactions of lower exothermicity relative to the parent compound AB. The Center is currently investigating whether or not the energetics and kinetics can be tailored such that a directly reversible system may be achievable.

Current Status

Sneddon *et al* found that release of hydrogen from LiH/AB or LiNH₂/AB mixtures exceeded the amount of hydrogen expected from consideration of the separate components. Up to around 10 wt % hydrogen was observed but with rather low rates of release at 85 °C. From this work they proposed a new anionic dehydroligomerization mechanism for hydrogen release from AB.

Sneddon's group has also shown that the addition of an organic base 'proton sponge' also results in initiation of a dehydroligomerization of AB to release hydrogen. This was notable, in that this latter pathway avoided the generation of ammonia and LiBH₄ that was observed in the LiH- and LiNH₂-promoted reactions.

Within the IPHE efforts, there are two principal results that have now shown B-N chemistry can be modified substantially via reaction of AB with metal hydrides. There are two seminal papers from this work just published in peer-recognized journals at the end of 2007. The first is on Ca(NH₂BH₃)₂⁴. The second regards LiNH₂BH₃ and NaNH₂BH₃ materials⁵. In both cases the release temperature is lower and the rate of the second equivalent of hydrogen release is

substantially greater relative to the parent compound AB. Other metal substitutions have been made and the resulting compounds are being investigated currently. Initial results on Al, Ti, and Li/Zn substitution appear promising.

There are also new routes to AB-F compounds, but these results are just beginning to be assessed, and so this report does not address the down select result for this new class of compounds.

Down Select Results – Continue this work as one of a high priority. This work started just under a year ago with recognition by IPHE to pursue this project. Initial results are promising with materials having been demonstrated with > 7 wt. % hydrogen released at lower temperatures than AB, but reversibility has not been attempted. The main questions remaining involve the degree to which such systems might be chemically regenerated and the mechanism(s) that drive and control hydrogen release. It is too early to down-select in this area as new results are beginning to shed light on how B-N chemistry may be modified through reactions with metal hydrides. The new fluorine-containing AB-F class of materials has provided some interesting preliminary results, and should be followed up to assess whether they have the properties deemed useful for continued investigation.

2) Ammonia Borane-based Materials

Background

The Center has focused a good deal of effort on developing pathways for release of hydrogen from ammonia borane (AB). AB has a high hydrogen content (19.6 wt.%), one of the highest material capacities among systems currently under investigation. The Center has developed four main approaches to hydrogen release: 1) thermolysis from the solid state material, 2) thermolysis from nanoporous composites^{6, 7}, 3) thermolysis in ionic liquids⁸ and chemical additives to promote dehydrogenation of AB, and 4) catalytic dehydrogenation of solutions of AB. Center partners published early results from acid⁹-, precious metal¹⁰-, and base-metal catalyzed dehydrogenation of AB¹¹ and have recently reviewed the topic of catalyzed release of hydrogen from AB¹².

As the Center has dedicated a good deal of its effort toward developing AB as a hydrogen storage system, there is more data available for the down selection of this material.

Current Status

The Center partners' work on ammonia borane has led to a good understanding of the mechanisms of hydrogen release, intermediates along the dehydrogenation pathways, spent fuel characteristics, stability, and kinetics of release. The work has also resulted in the identification of several promising routes to dehydrogenate this material.

1) Thermolysis of solids. Solid AB dehydrogenates thermally with somewhat low rates at 85 °C, but with rates that can exceed the DOE target rate by a factor of approximately five at 130 °C, where AB releases 9 wt.% hydrogen with an average rate of 0.1 gH₂/s/kg AB. Solid AB has a volumetric capacity of around 0.12 g H₂/cc derived from the amount of hydrogen that can be liberated at 150 °C (17 wt %), which shows potential to meet/exceed the DOE system target of .045 g/cc. Work at PNNL has shown that for a solid fuel system, a densely packed bed (<30%

voids) of AB pellets can still have the potential to achieve DOE 2010 system targets, even with only 2.5 out of 3 possible equivalents of hydrogen being liberated per mole of AB.

There are several significant issues with solid AB that the Center is working to address. Much progress has been made in all areas. One is the increase in volume that the solid undergoes upon liberation of hydrogen. A second issue is that the dehydrogenation of AB is exothermic and so thermal management of the process is crucial to the success of this approach. A third is the stability of AB at temperatures up to 50 °C which is primarily a function of impurities that destabilize AB. Another is that a fuels handling system for solids will require novel solutions to materials engineering and systems engineering. Working through these multiple problems is crucial to developing a solid fuel system that has appropriate properties for vehicular applications. Given the progress being made in addressing these issues and the significant gravimetric and volumetric capacity of AB, solid AB remains of interest to the Center.

As part of the Center's studies on AB thermolysis, results from known intermediates along the hydrogen release pathway from AB have also been incorporated into the summary database in Appendix 2. Solid AB interconverts to a structural isomer, the diammoniate of diborane, DADB, and then dehydrogenates to polyaminoborane (a mixture of BH_2NH_2 oligomers we call PAB) or under certain catalytic release conditions to a cyclic oligomer that we refer to as 'the pentamer', cyclo- $(\text{BH}_2\text{NH}_2)_5$, and subsequently on to cyclotriborazine $(\text{BHNH})_6$. The hydrogen release properties of these compounds have also been measured. Work at PNNL has recently indicated that ammonium borohydride may be somewhat more stable than what is reported in the literature, and may be interesting if its low temperature stability can be improved or managed. Each of these materials has capacity, rate, or stability issues, and may prove to be impractical, but knowledge of their reactivity and hydrogen release behavior is integral to the Center's understanding of the AB system including the release of hydrogen from AB-scaffold materials.

2) Thermolysis of AB-scaffold composites. Ammonia borane may be infiltrated within the micropores of a support such as MCM-41 or SBA-15, two highly porous silica-based materials. Center research found that the release of hydrogen from AB within these 'scaffolds' was accelerated dramatically, and that the quantities of impurities were reduced, and that foaming was mitigated. At a given temperature, the rate of release of hydrogen from the AB in scaffold is approximately six times greater than AB by itself. Even though there is a weight penalty because of the mass of the scaffold, AB-scaffold mixtures can still achieve > 9 wt. % H_2 released at high rates exceeding the DOE target rate.

3) Thermolysis of Ionic Liquid/AB mixtures and additives. A promising AB composite mixture system studied by the Center consists of AB dissolved or slurried in ionic liquids, with and without the presence of base additives such as proton sponge or Rh catalysts. A 50 wt % AB solution in an ionic liquid solvent may liberate up to 9.8 wt. % hydrogen (including the mass of the solvent), if all three equivalents H_2 per mole AB are released. The Center has demonstrated > 7 wt % hydrogen evolution from these systems within 15 minutes at 120 °C, and adequate rates of ca. 0.02 g/s/kg have been measured at 100 °C. Maintaining the spent fuel in solution, or using the ionic liquid as an activating additive at lower concentrations of ionic liquids (which will also increase hydrogen capacity) remain as potentially interesting possibilities for these hydrogen release systems. A systematic study is underway on the interaction of AB and its derivatives with a range of ionic liquids that remain liquid over a range of temperature conditions and needs to be continued.

Another related additive system that has been explored is the addition of ionic solids such as ammonium halides to solid AB which results in fast release up to 90 °C to yield 6 wt % hydrogen without foaming of the solid. Additional studies of solid additives to reduce foaming and control the rate of release are ongoing. Balancing the need to obtain good rates above 50 °C with the need to have negligible rates below 50 °C are a challenge in this and all hydrogen release systems.

4) Catalytic release from AB. Dehydrogenation of AB by the thermolytic pathway occurs at rates that can exceed the DOE target only at temperatures above 100 °C. The goal of our search for homogeneous catalysts is to discover catalysts that substantially reduce the temperature of release.

Numerous homogeneous catalysts for the dehydrogenation of AB have been examined. Trends in the catalytic dehydrogenation activity of various catalyst compositions have been determined. A variety of combinations of ligand properties and transition metal ions have been screened for hydrogen release rates and extent of AB dehydrogenation. Catalyst compositions have been found that give rise to the release of either one or two equivalents of hydrogen per mole AB, and the kinetics of these two release pathways has been measured. The class of catalysts (Ir and Co pincer ligands) that release only one equivalent of hydrogen per mole of AB release this hydrogen at rates > 10 times the DOE target rate even at room temperature. The other class of catalysts that release nearly two equivalents of hydrogen do so much more slowly, approximately five times slower than the required DOE target rate. Mechanistic information has been obtained that attempts to explain these differences, and to guide additional catalyst design concepts to improve the rate and capacity that these catalysts can promote. Through this work, certain guiding principles of catalyst design have been uncovered that may provide the basis for the design of heterogeneous catalysts, which will be necessary for onboard catalytic release systems. Another requirement for a catalytic release system is that the fuel and the spent fuel must be liquid to avoid complex, and likely inefficient multiphase reactions. Therefore the Center has been searching for compositions of ammonia borane mixed with liquid amine boranes that have a wide liquid range, and that release hydrogen in quantities and at rates that will meet or exceed DOE targets.

One such liquid amine borane compound is methylamine borane (MeAB). If MeAB releases two moles of hydrogen, it has a material-based gravimetric capacity of 8.8 wt.% H₂. A mixture of 20% MeAB/AB containing impurities or additives has been shown to be a liquid down to 30 °C, which is a promising preliminary result, indicating that perhaps liquid fuel compositions can be developed. Work from this Center has shown that the catalysts that are active for AB dehydrogenation also dehydrogenate MeAB and MeAB/AB mixtures at similar rates. One problem with MeAB is that it is volatile, but more detrimentally, it decomposes to hydrogen slowly even at room temperature, so it does not meet the stability criterion. Another liquid amine borane is ethylenediamine bis borane, EDBB. Mixtures of EDBB with AB have shown catalytic release of 11.3 wt% hydrogen. Mixtures of EDBB, AB, and diethylamine form liquids that are more stable than MeAB. Appropriate catalysts for these mixtures with potentially larger liquid ranges relative to the MeAB/AB system are being developed.

Liquid mixtures in which a typical ether solvent such as THF or diglyme is employed to provide a solution of AB have been much studied by the Center, mainly to assist in catalyst screening and development. The amount of solvent necessary to maintain the precursor and spent fuel in solution renders these conventional solvent-based systems impractical on gravimetric capacity

considerations. However, these systems continue to provide the platform necessary for catalyst discovery that is required for continued improvements in catalyzed AB dehydrogenation. Heterogeneous catalysts are also under investigation and preliminary results appear promising. Heterogeneous base metal catalysts for hydrogen release from liquid ammonia borane systems have been prepared and demonstrated to have high rates (2x the DOE target rate) of release and greater than 9 wt% H₂ at 70 °C. This work is new and were not considered during the down-select process (see results presented at the 2008 Annual Merit Review and Peer Evaluation Meeting at http://www.hydrogen.energy.gov/pdfs/review08/st_6_burrell.pdf)

Down Select Results

1) Thermolysis of solids. AB continues to be a promising candidate hydrogen storage material and should be continued. The work toward mitigating foaming and minimizing gas phase impurities should continue. In Phase II, a focus area of this work will be to generate innovative ideas for the design of reactor systems and associated solid handling concepts necessary to accommodate an onboard solid fuel/spent fuel process.

2) Thermolysis of AB-scaffold composites. As for AB-scaffold composites, work should continue. AB-scaffold composites have demonstrated that they continue to have promising capacities, very high release rates capable of exceeding DOE targets, and the AB-scaffold materials mitigate to a significant extent the formation of volatile impurities in the hydrogen gas stream. Work should continue to demonstrate optimal AB to scaffold weight fraction, and continue to improve the kinetics of release, already greater than five times faster than AB, with higher extent of release at lower temperature.

3) Thermolysis of ionic liquid/AB mixtures and additives. It is recommended this work be continued. For the ionic liquid-based additive system, a diversity of ionic liquids and additives such as proton sponge and ammonium halide need to be investigated to extend the range of release conditions, and continue to improve the kinetics and extent of release.

4) Catalytic release from AB. Liquid fuels are necessary to enable catalytic processes for onboard release systems. Conventional solvent-based liquid systems for AB are unlikely to be practical at currently accessible concentrations and are not recommended to be studied further except for work on solvents necessary as model systems for catalyst screening work while liquid fuel systems are being developed. Liquid systems such as AB/EDBB mixtures and related alkyl amine borane mixtures are recommended for continuation. These mixtures have high capacities, good rates of hydrogen release, and good stability below 50 °C. Greater liquid range must be sought, and ever more effective catalysts must still be developed, especially heterogeneous catalysts.

3) Polyhedral Boranes; Rh-catalyzed Aqueous Hydrolysis

Background

Hydrolysis of polyhedral boranes and ammonia triborane were believed to offer advantages over sodium borohydride when the Center began this line of research. As the Center evolved, it became obvious that the SBH go/no-go decision would have to be tied to the decision for these

hydrolysis systems because of similarities relating to both the physical properties of the spent fuel borates, and the need to regenerate borane B-H bonds from borate B-O bonds.

Current Status

Rh effectively catalyzes the hydrolysis of polyhedral boranes and ammonia triborane. The polyhedral boranes exhibit excellent rates of 0.3 g H₂/s/kg (15 times the DOE target rate) of hydrogen release at 80 °C, but unfortunately do not release greater than 7 wt. % hydrogen. Hydrolysis of ammonia triborane (AT) is similar, but somewhat slower than the polyhedral boranes, and again only releases about 6 wt. % hydrogen¹³.

Down Select Results

Work on these systems is being discontinued. In spite of the fact that these hydrolysis systems have excellent rates of hydrogen release, none will exceed 7 wt.% hydrogen and involve the problematic regeneration of borate spent fuels. Many of these same issues were identified for SBH hydrolysis in the SBH go/no-go decision. The solubility of the resulting borate spent fuel is a problem because of potential crystallization in the fuel system, and energy efficient regeneration of the borate is difficult. Because of these issues and consistent with DOE's no go decision on sodium borohydride hydrolysis, the Center will not perform further work on these hydrolysis systems. However, this does not rule out polyhedral boranes that may occur as intermediates in some other, as yet undiscovered hydrogen release process from a borane-based fuel.

Spent Fuel Regeneration

Spent fuel from dehydrogenation must be efficiently recycled back to fuel in order for chemical hydrogen storage systems to be acceptable hydrogen storage media. Currently, ammonia borane is (or is contained within) the most promising chemical hydrogen storage systems the Center is investigating. Because of this, the Center has dedicated a great deal of resource and effort at developing and demonstrating the chemistries necessary to recycle spent fuel back to AB.

The Center's AB regeneration processes currently take the following general form:

- A. Digestion of spent fuel BNH_x by a digesting agent (using a reagent HX, X= OR -- alcohol, SR -- thiol, or halide – bromide, chloride, etc.) to dissolve and pretreat the spent fuel to a chemical form that is susceptible to reduction by hydride reagents
- B. Addition of hydride by a reducing agent (using MH) to form BH₃ units
- C. Addition of ammonia to complete the formation of NH₃BH₃ (AB)
- D. Recycle of the reducing agent (from MX to MH) to complete the regeneration cycle

In the section below, three current regeneration pathways under consideration by the Center are outlined. These pathways are at various stages of development, and all show promise. In the course of developing these regeneration strategies, a large number of down selects have been done on individual steps, and this will continue as the Center identifies more favorable chemistries for each individual step or as steps are integrated. It is likely that hybrids of these

three approaches may form the basis for an even more chemically and energetically efficient regeneration process for AB. Thus it is too early to make any down select decisions regarding overall selection of pathways.

Thermodynamic efficiencies were calculated as shown below from the summation of positive enthalpies of the steps. Enthalpies of formation of each of the components were either from literature values, or were calculated using quantum mechanical techniques. The energy of the hydrogen input and hydrogen released is based upon the lower heating value of hydrogen of 57.8 kcal/mole H₂. For this report, we assume no heat recovery, in other words, heat given up from exothermic steps is lost. The efficiencies given do not include the efficiency of hydrogen production. In other words, the energy efficiencies quoted above are not well-to-tank energy efficiencies. The CHSCoE will be working with Argonne National Laboratory to assess these efficiencies during FY08.

The efficiency is defined in equation 2 below:

$$\text{Equation 2. } \frac{(\text{Equiv. H}_2 \text{ stored})(57.8)}{(\text{Equiv. H}_2 \text{ used})(57.8) + \sum (\Delta H_{\text{endo}}) - (\% \text{ heat recovery}) \sum (-\Delta H_{\text{exo}})} = \text{efficiency}$$

Scheme 1 (being developed at PNNL. Preliminary estimate of thermodynamic efficiency > 75%)

1. $\frac{1}{3} \text{B}_3\text{N}_3\text{H}_6 + 2 \text{HO-}t\text{-Bu} \rightarrow \text{NH}_3 + \text{HB(O-}t\text{-Bu)}_2$
2. $\text{HB(O-}t\text{-Bu)}_2 + \frac{1}{3} \text{NH}_3 \rightarrow \frac{1}{3} \text{H}_3\text{NBH}_3 + \frac{2}{3} \text{B(O-}t\text{-Bu)}_3$
3. $\frac{2}{3} \text{B(O-}t\text{-Bu)}_3 + \frac{2}{3} \text{NH}_3 + 2 \text{H}_2 \rightarrow \frac{2}{3} \text{H}_3\text{NBH}_3 + 2 \text{HO-}t\text{-Bu}$

This methodology preserves residual B-H bonds in the spent fuel, converting them directly back into AB. However, the co product B(O-*t*-Bu)₃ contains strong B-O bonds and its reduction to AB is prohibitively endothermic (ca. 28 kcal/mol). To improve this process, multidentate alcohols such as glycerol are being considered since the steric strain in B(O₃C₃H₅) dramatically reduces the endothermicity of its reduction (by at least 20 kcal/mol). The ultimate reduction of the B(OR)₃ or the strained borate esters is anticipated to be mediated by silanes, alanes, or possibly by RhH₂⁺ complexes. These specific details for step 3 are not yet determined.

Scheme 2 (being developed at U. Penn. Calculated overall thermodynamic efficiency = 38%)

1. "Spent Fuel" + 4 HAlBr₄ → NH₄Br + BBr₃ + H₂ + 4AlBr₃
2. BBr₃ + 3 HSnBu₃ + R₂S + NH₃ → H₃NBH₃ + 3 BrSnBu₃ + R₂S
3. NH₄Br → HBr + NH₃

4. $\text{BrSnBu}_3 + \text{NEt}_3\text{H}^+ \text{OOCH} \rightarrow \text{NEt}_3\text{H}^+\text{Br} + \text{HCOOSnBu}_3$
5. $\text{HCOOSnBu}_3 \rightarrow \text{HSnBu}_3 + \text{CO}_2$
6. $\text{H}_2 + \text{CO}_2 \rightarrow \text{HCOOH}$
7. $\text{HCOOH} + \text{NEt}_3 \rightarrow \text{NEt}_3\text{H}^+ \text{OOCH}$

This pathway to regeneration of spent fuel goes through volatile BBr_3 that is readily separated from the reaction mixture, and then reduced with a mixture of an alkyl disulfide and a tin hydride. The tin hydride is reformed via a formic acid route shown in steps 4-7.

Scheme 3 (being developed at LANL – calculated overall thermodynamic energy efficiency = 75%)

1. $\frac{1}{3} \text{B}_3\text{N}_3\text{H}_6 + \text{C}_6\text{H}_4(\text{SH})_2 \rightarrow \text{B}_2(\text{SCat})_3 \cdot 2\text{NH}_3 + \text{H}_2 + \text{HB}(\text{SCat}) \cdot \text{NH}_3$
2. $\frac{1}{2} \text{B}_2(\text{SCat})_3 \cdot 2\text{NH}_3 + \frac{1}{2} \text{H}_2\text{SnBu}_2 \rightarrow \text{HB}(\text{SCat}) \cdot \text{NH}_3 + \frac{1}{2} (\text{SCat})_2\text{SnBu}_2$
3. $\text{HB}(\text{SCat}) \cdot \text{NH}_3 + \text{H}_2\text{SnBu}_2 \rightarrow \text{H}_3\text{NBH}_3 + (\text{SCat})_2\text{SnBu}_2$
4. $\frac{3}{2} (\text{SCat})_2\text{SnBu}_2 + 3 \text{HCOOH} \rightarrow \frac{3}{2} \text{C}_6\text{H}_4(\text{SH})_2 + 3 (\text{HOOC})_2\text{SnBu}_2$
5. $\frac{3}{2} (\text{HOOC})_2\text{SnBu}_2 \rightarrow 3 \text{CO}_2 + \frac{3}{2} \text{H}_2\text{SnBu}_2$
6. $3 \text{H}_2 + 3 \text{CO}_2 \rightarrow 3 \text{HCOOH}$

This regeneration scheme uses a dithiol ligand for the digestion step, and tin hydride as the reducing agent that is recycled through the synthesis of formic acid from hydrogen and carbon dioxide as shown in steps 4-6.

The Center makes no formal down select decision for the spent fuel regeneration schemes at this time, as the research indicates that there is a great deal of synergy among the potential regeneration schemes. For example, all of the schemes have used concepts from one another to help improve either the yield or the thermodynamic efficiency of various steps. It is likely that a hybrid approach will emerge from the Center's investigations of these three regeneration approaches. The Center will make a spent fuel regeneration down select decision in the future as the research matures so that the overall well-to-tank energy efficiency target of 60% can be met.

Conclusions

This report documents the materials that have been investigated by the CHSCoE since its inception, and gives the “Go” and “No-Go” decisions for these materials. The report summarizes the Center's progress with respect to the DOE technical targets for hydrogen storage, and against

the materials performance metrics developed by the CHSCoE upon which the down select decisions were based. Of the more than 60 materials the CHSCoE investigated, the results summarized in this Down Select Report indicate that the Center is discontinuing more than 50% of the materials examined to date. Approximately 30% of the materials show promise, but require near-term answers or solutions to potential problems to remain in the Center's portfolio for its Phase II activities. The remaining materials investigated to date, approximately 20%, show high potential to meet or exceed DOE's 2010 technical targets, and remain high priority. The Center is also addressing regeneration of spent fuel derived from dehydrogenation of ammonia borane, and has developed three pathways that are under current development and are in various stages of demonstration. As all of the current regeneration schemes have substantially positive attributes and may lead to hybrid approaches, the Center will continue all of the work directed towards regeneration of ammonia borane while continuing the practice of constant selection and rejection of potential chemical reaction pathways or reagents. A final assessment will be provided to the DOE within the next two years.

Appendix 1. Chemical Hydrogen Storage CoE Materials Database Template

Example for Solid Ammonia Borane:

Storage Parameter	Units	Demonstrated @ 150-155 C	Estimated or Measured @ 85 C	Estimated or Measured @ 120 C
Gravimetric Capacity H ₂	g H ₂ /g material or wt%	16-17% (in 60 min)	6.5% (in 20 hr)	7.6% (in 60 min)
Volumetric Capacity	g H ₂ /cc material	0.05-0.12	0.02-0.048	0.023-0.056
Density (indicate if estimate)	g/cc	0.3-0.74	0.3-0.74	0.3-0.74
Discharge Rate of H ₂	g H ₂ /sec/(kg Material)	~3.8 peak & 1.4 avg. (~50 sec duration; 7.3 wt% released)	~0.005 peak	~0.3 peak
Catalyst 1 (or 'none')		none	none	none
Catalyst 2 (if >1 cat. studied)				
Catalyst 3 (if >2 cat. studied)				
Fuel Form (liq. solid, solution,)		solid: powder, or pressed pellet	solid: powder, or pressed pellet	solid: powder, or pressed pellet
Spent Fuel characteristics (solids, liq. foam, etc.)		frothed solid	solid	frothed solid
Known or potential impurities	ppm	NH ₃ , borazine	NH ₃ , borazine	NH ₃ , borazine

Appendix 2. Decision Summary Spreadsheet

(color code: red -- discontinue work; yellow – continue but resolve short-term issues or discontinue; green – continue with high priority)

I) Endothermic Chemical Hydrides

Material	Measured Wt.%	Vol. % g H ₂ /cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H ₂ /sec /kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/No-Go
Endothermic Chemical Hydrides											
Imidazolines											
Hexahydrotriazine	6.9								Not demonstrated -- hypothetical	Not demonstrated -- hypothetical	
N,N-9-dimethyl dihydrobenz-imidazole/Pd	0.75	0.06	No	Not demonstrated, but likely	I/I	<.01 @ RT	Good	Room temp	Low gravimetric capacity	Rates of release good at room temperature.	No-Go
1,3-dimethyl-2-phenylbenz-imidazoline/HoAc/Pd	0.85		No	Not demonstrated, but likely	I/I	<.01 @ RT	Good	Room temp	Low gravimetric capacity	Rates of release good at room temperature.	No-Go
1,3-dimethylbenz-imidazoline	1.3		No	Not demonstrated, but likely	I/I	<.01 @ RT	Good	Room temp	Low gravimetric capacity	Rates of release good at room temperature.	No-Go
Coupled reactions											
Mg(OMe) ₂ /H ₂ O	7% @ 20 wt% catalyst		No	Not demonstrated	s/s	.03g/s/kg @ 260 °C	Good	Onset 160 °C, max 260 °C	Endothermic, temperature release too high (>200°C), requires water, CO ₂ loss, not directly regenerable	---	No-Go
Organocarbenes											
Carbene	6.3 - 7.3 (theoretical)	0.098	No	Not demonstrated	s/s	TBD	Good	room temp to 50°C	Awaiting validation of free hydrogen release, synthesis of polymer not demonstrated	Demonstrated 1-3 wt % by hydrogen transfer, potential for > 6 wt %.	TBD
Cyanocarbene	6.3 - 7.3 (theoretical)	0.092	No	Not demonstrated	s/s	TBD	Good	room temp to 50°C	Awaiting validation of free hydrogen release, synthesis of polymer not demonstrated	Demonstrated 1-3 wt % by hydrogen transfer; potential for > 6 wt %. Awaiting validation of free hydrogen release	TBD
Main Group Nanoparticles and Clathrates											
4nm Si	4.5	0.1	Potential	Yes	s/s	Not determined	Good	> 300 °C	Low gravimetric capacity, non-reversible, release T > 300°C	---	No-Go
8nm Si	3.7	0.08	Potential	Yes	s/s	Not determined	Good	> 300 °C	Low gravimetric capacity, non-reversible, release T	---	No-Go

Material	Measured Wt. %	Vol. % g H ₂ /cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H ₂ /sec /kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/No-Go
									> 300°C		
10nm Si	3	0.06	Yes	Yes	s/s	Not determined	Good	> 300 °C	Low gravimetric capacity, non-reversible, release T > 300°C	---	No-Go
60nm Si	1.6	0.037	Potential	Yes	s/s	Not determined	Good	> 300 °C	Low gravimetric capacity, non-reversible, release T > 300°C	---	No-Go
Si-NH ₂	8		Potential	Yes	s/s	Not determined	Good	Not measured	Non-reversible	---	No-Go
Na Si Clath	4	0.08	Potential	Yes	s/s	Not determined	Good	Not measured	Low gravimetric capacity	---	No-Go
K Si Clath	4	0.08	Potential	Yes	s/s	Not determined	Good	Not measured	Low gravimetric capacity	---	No-Go
TypeII Si Clathrate	4	0.08	Potential	Yes	s/s	Not determined	Good	Not measured	Low gravimetric capacity	---	No-Go

II) Exothermic Chemical Hydrides

1) Metal-Boron-Nitrogen Materials

Material	Measured Wt. %	Vol. % g H ₂ /cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H ₂ /sec/kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/No-Go
Exothermic Chemical Hydrides											
Metal-Boron-Nitrogen Materials:											
LiAB	11	Density not determined	Not demonstrated	Not demonstrated	s/s	Not quantified	TBD	10 wt % @ < 90 °C	Regeneration not yet determined.	Good rate to 11 wt%	Go
Ca(AB) ₂	10	Density not determined	Not demonstrated	Not demonstrated	s/s	Not quantified	Good	7.2 wt % @ 170 °C	Temp release too high in solid state; regeneration pathway not yet determined	Catalytic release demonstrated, could lower temperature of release	TBD
Li ₂ Zn(AB) ₄	10	Density not determined	Not demonstrated	Not demonstrated	s/s	>.02	Good	Room temp	Regeneration not yet determined	Good release temperature and rate	Go
LiZn(AB) ₃	9	Density not determined	Not demonstrated	Not demonstrated	s/s	Not determined	Not stable at room temp.	Room temp	Releases H at too low a temperature	High capacity	TBD
Ti(AB) ₄	10-12	Density not determined	Not demonstrated	Not demonstrated	s/s	TBD	TBD	< 160 °C	Regeneration pathway not yet determined.	Demonstrated 11.9 wt % H ₂ released.	Go
Al(AB) ₃	10-12	Density not determined	Not demonstrated	Not demonstrated	s/s	Not determined	Not stable at room temp.	Room temp	Unstable at room temperature	High capacity	TBD
17 mol %LiH/AB	10	Density not determined	Not demonstrated	Not demonstrated	s/s	.006 @ 85°C	Good	> 50 °C	Generates borohydride, ammonia	Demonstrated 9.5 wt % H ₂	No-Go
9 mol% LiNH ₂ /AB	10	Density not determined	Not demonstrated	Not demonstrated	s/s	.005 @ 85°C	Good	> 50 °C	Generates borohydride, ammonia loss	Demonstrated 9.5 wt % H ₂	No-Go

2) Ammonia Borane-Based Materials

Material	Measured Wt. %	Vol. % g H ₂ /cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H ₂ /sec /kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/ No-Go
Ammonia Borane-based Materials											
Solid AB	17% in 1 hr @ 150 °C	.12 @ 150 °C	Not feasible	Steps demonstrated	s/foam	.005 @ 85°C; .30 @ 120°C (peak rate)	Good	> 50 °C	Foaming requires solution, solid impurities may impact stability, borazine impurities in gas	High capacity, solid to solid transformation, rates to 7 wt% good, work in progress on foaming	Go
AB 3 equivalent	19.6	0.145	Not feasible	Yes	s/foam		Good	> 50 °C	For Reference Only -- not experimental data	For Reference Only -- not experimental data	
AB 2.5 equivalent, fully dense	16.3	0.121	Not feasible	Yes	s/foam		Good	> 50 °C	For Reference Only -- not experimental data	For Reference Only -- not experimental data	
AB 2.5 eq. packed pellet 60% voids	16.3	0.049	Not feasible	Yes	s/foam		Good	> 50 °C	For Reference Only -- not experimental data	For Reference Only -- not experimental data	
AB 2.5 eq. packed pellet 30% voids	16.3	0.085	Not feasible	Yes	s/foam		Good	> 50 °C	For Reference Only -- not experimental data	For Reference Only -- not experimental data	
1:1 AB/MCM scaffold	8		Not feasible	Yes	s/s	TBD		> 50 °C	TBD	Low but acceptable wt. %, 3:1 more promising	TBD
3:1 AB/MCM scaffold	14.7	0.0735	Not feasible	Not demonstrated	no foam	TBD	Not yet determined	> 50 °C	None/TBD	Demonstrated 14 wt % hydrogen at 85 °C; reduced gas phase impurities relative to AB.	Go
MeAB	8.8 (2 equivalent)		Not feasible	Not demonstrated	l/s	Similar to AB	Evolves H ₂ < 50 °C	> 50 °C	Stability at room temperature not adequate; volatile	Low melting point, good rate	TBD
20%MeAB/ AB	12 wt % (2 equivalent)		Not feasible	Not demonstrated	l/s	Similar to AB	Evolves H ₂ < 50 °C	> 50 °C	Stability at room temperature not adequate; volatile	Low melting point, good rate	TBD
EDBB with catalyst	9.1 (2 equivalent)		Not feasible	Not demonstrated	l/l	Similar to AB	Promising	> 50 °C	None/TBD	New work, appears promising liquid composition, liquid to liquid, good rate to 6 wt% with catalyst; stability needs to be verified. EDBB has potential for mixture with AB for higher capacity.	Go

Material	Measured Wt. %	Vol. % g H ₂ /cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H ₂ /sec /kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/ No-Go
EDBB/AB with catalyst	11.3		Not feasible	Not demonstrated	I/I	TBD	Promising	> 50 °C	None/TBD	New work, appears promising liquid composition, liquid to liquid, good rate to 6 wt% with catalyst; stability needs to be verified. Additional components may be added to increase liquid range. EDBB has potential for mixture with AB for higher capacity.	Go
20%AB/diglyme, Bronsted acid catalyst	3.5		Not feasible	Not demonstrated	I/s	.0003 @ 60°C	Good	> 50 °C	Poor hydrogen capacity, very slow.	---	No-Go
20% AB/% BPh ₃ /diglyme	3.9		Not feasible	Same as for AB	I/s	.0004 @ 65 °C	Good	> 50 °C	Poor hydrogen capacity, very slow.	---	No-Go
AB, THF/or glymes (xM) with tm catalyst	ca. 1 @ 1.5 M		Not feasible	Steps demonstrated	I/s	Rates good to 1st equivalent down to room temp	Good	> 50 °C	Insufficient solubility in THF, glymes	---	No-Go
MeAB and THF (xM) with catalyst	ca. 1 @ 1.5 M		Not feasible	Not demonstrated	I/I	Not determined	Not determined	> 50 °C	Insufficient solubility in THF, glymes	---	No-Go
AB/IL	9.8% @ 50 wt.% (3 eq)	0.09 (3 eq)	Not feasible	IL separation potentially an extra step	I/s	Avg rates: .006 @ 85 °C, .019 @ 100 °C, .080 @ 120 °C	Not determined	> 50 °C	Questionable solubility of spent fuel	Good rates at 100, demonstrated 7.2 wt. % H ₂ at 50% IL, needs lower mp IL	TBD
AB/IL/PS	8.3% @ 5 mol% PS (3 eq.)	.08 (3 eq)	Not feasible	IL, PS separation potentially an extra step	I/s	Avg rates: .011 @ 85 °C, .018 @ 100 °C	Not determined	> 50 °C	Questionable solubility of spent fuel	Good rates at 100, demonstrated 6.2 wt. % H ₂ at 50% IL, needs lower mp IL	TBD
AB/IL/5 mol%Rh cat	7.8	0.09	Not feasible	IL/cat separation potentially an extra step	I/s	avg rate: .077 @ 85 °C	Not determined	> 50 °C	Adequate capacity, but capacity of other mixtures is higher	Good rates above 100 °C	TBD
AB/AT/5 mol% PS	17		Not feasible	Not demonstrated	s/s	.004 @ 85°C	Not determined	> 50 °C	Adequate capacity, but capacity of other mixtures is higher	Demonstrated 6.9 wt % @ 85°C	TBD
AB/ cat. Amt. NH ₄ X	18 (theoretical)		Not feasible	Not demonstrated, but likely	s/s	N/A	Not determined	> 50 °C	Stability questionable, needs work	Demonstrated 6 wt % at 90°C. Fast rates on release; no foaming	TBD

Material	Measured Wt. %	Vol. % g H ₂ /cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H ₂ /sec /kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/ No-Go
AB intermediates, and related:			Not feasible								
DADB	19.6		Not feasible	Yes	s/s	Not determined		> 50 °C	Stability is a question	Work in progress, no foaming, high rate, high capacity	TBD
PAB	7-10		Not feasible	Yes	s/s	Not determined		> 50 °C	Slow release < 120 °C	Adequate weight fraction, no foaming	TBD
cyclic "Pentamer"	7-10		Not feasible	Yes	s/s	Not determined		> 50 °C	Slow release < 120 °C	Same as PAB	TBD
NH ₄ BH ₄	24.5		Not feasible	Yes	s/s	Not determined	Decomposes at room temp	> 20 °C	Stability needs further demonstration.	Very high capacity > 20 wt%	TBD

3) Polyhedral Boranes; RH-Catalyzed Aqueous Hydrolysis

Material	Measured Wt. %	Vol. % g H ₂ /cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H ₂ /sec/kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/No-Go
Polyhedral Boranes (Rh catalyzed aqueous hydrolysis):											
Li ₂ B ₁₀ H ₁₀	6.5	0.08	Not feasible	Not demonstrated	I/s	ca.04 @ 5 mol % Rh _i	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
(NH ₄) ₂ B ₁₀ H ₁₀	6.3	0.08	Not feasible	Not demonstrated	I/s	ca.04 @ 5 mol % Rh _i	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
Na ₂ B ₁₀ H ₁₀	6.2	0.08	Not feasible	Not demonstrated	I/s	ca.04 @ 5 mol % Rh _i	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
K ₂ B ₁₀ H ₁₀	6	0.08	Not feasible	Not demonstrated	I/s	.3 @ 80 °C, 5 mol % Rh	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
LiB ₁₁ H ₁₄	6.6	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
(NH ₄)B ₁₁ H ₁₄	6.55	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
NaB ₁₁ H ₁₄	6.5	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
KB ₁₁ H ₁₄	6.4	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
Li ₂ B ₁₂ H ₁₂	6.5	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
(NH ₄) ₂ B ₁₂ H ₁₂	6.3	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
Na ₂ B ₁₂ H ₁₂	6.2	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
K ₂ B ₁₂ H ₁₂	6	0.08	Not feasible	Not demonstrated	I/s	Similar to above	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go
22.7 wt% AT/Hydrolysis, Rh catalyst	6.2	.09 @ 4 hrs, rt	Not feasible	Not demonstrated	I/s	.004 @ 85 °C	Good	< 80 °C	Potentially solid spent fuel products and regen similar to SBH, < 7 wt%	Excellent rates at 80 °C	No-Go

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