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Title: Final Report for the DOE Chemical Hydrogen Storage Center of Excellence

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FINAL REPORT FOR THE DOE CHEMICAL HYDROGEN STORAGE CENTER OF EXCELLENCE

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Summarizing Contributions from Center Partners:

Los Alamos National Laboratory (LANL)
Pacific Northwest National Laboratory (PNNL)
Millennium Cell, Inc.
Northern Arizona University
Rohm and Haas/Dow Chemical Company
University of Alabama
University of California, Davis
University of California, Los Angeles/University of Missouri
University of Oregon
Pennsylvania State University
University of Pennsylvania
University of Washington
U.S. Borax Corporation
Intematix Corporation

This final report was prepared with the assistance of Tom Autrey (PNNL), and Fran Stephens (LANL) who prepared the drafts of Chapter 1 and Chapter 2 respectively.

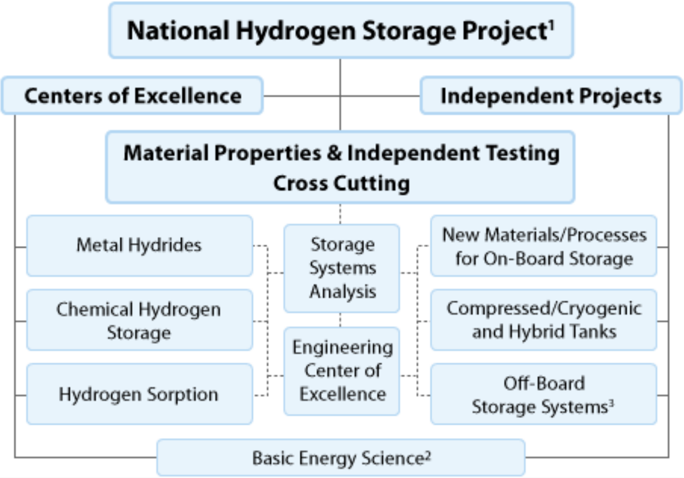
Executive Summary. Chemical Hydrogen Storage Center of Excellence

Contents, Executive Summary

1.0 Overview of the Chemical Hydrogen Storage Center of Excellence and High Level Recommendations[ξ]

This final report documents the successes, lessons learned, recommendations, and overall outcomes of the research and development of the Chemical Hydrogen Storage Center of Excellence. The report is in three sections and is comprised of an Executive Summary and two Chapters, one on hydrogen release from chemical hydrogen storage materials, and the second chapter is on the off board regeneration of spent chemical hydrogen storage fuels.

The Chemical Hydrogen Storage Center of Excellence (henceforth referred to as CHSCoE, or the Center) arose from a competitive solicitation in 2004 through the U.S. Department of Energy's (DOE) Energy Efficiency and Renewable Energy (EERE) Hydrogen Program. It was one of three Hydrogen Storage Materials Centers of Excellence, and joined the Metal Hydride Center and the Sorption Center as integral contributors to the National Hydrogen Storage Project. This national project represented the first time that such large-scale concerted effort was undertaken in the area of materials-based on board vehicular hydrogen storage R&D. These Centers explored a wide variety of materials compositions and configurations with a goal to discover and develop viable hydrogen storage materials with potential to meet DOE technical targets for on board vehicular applications.



1. Coordinated by DOE Energy Efficiency and Renewable Energy, Office of Fuel Cell Technologies
2. Basic science for hydrogen storage conducted through DOE Office of Science, Basic Energy Sciences
3. Coordinated with Delivery Program element

Chemical hydrogen storage is defined as the release of hydrogen from covalent chemical compounds, and their subsequent regeneration. Regeneration of many of these materials must be

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[ξ] Detailed information that supports the conclusions and high level recommendations given here is presented in the subsequent chapters on hydrogen release and spent fuel regeneration and also in the various Final Reports from the Partners of the CHSCoE.

performed off board for reasons related to the thermodynamics of the chemical processes that interconvert spent fuel and fuel.

As the Center was in it's formative stages, little was known about the potential for storing hydrogen in covalent chemical bonds. Some work had been done on 'activated' hydrocarbons systems by researchers at Air Products; and the release of hydrogen from ammonia borane was known largely through it's utility as a precursor to the ceramic, boron nitride. Much of the literature of chemical hydrogen storage was from the area of hydrolysis of sodium borohydride (SBH), performed by researchers at Millennium Cell, who at the time was developing an on board hydrogen storage system demonstration with Daimler-Chrysler. A plot of the materials weight fraction of hydrogen versus temperature for all of the materials known to store hydrogen in covalent molecular bonds is shown in Figure 1, and discussed in a little more detail below in section 1.2.1. The DOE system target lines are estimates of the temperature regime where the storage system must perform, being -20 to 100 °C.

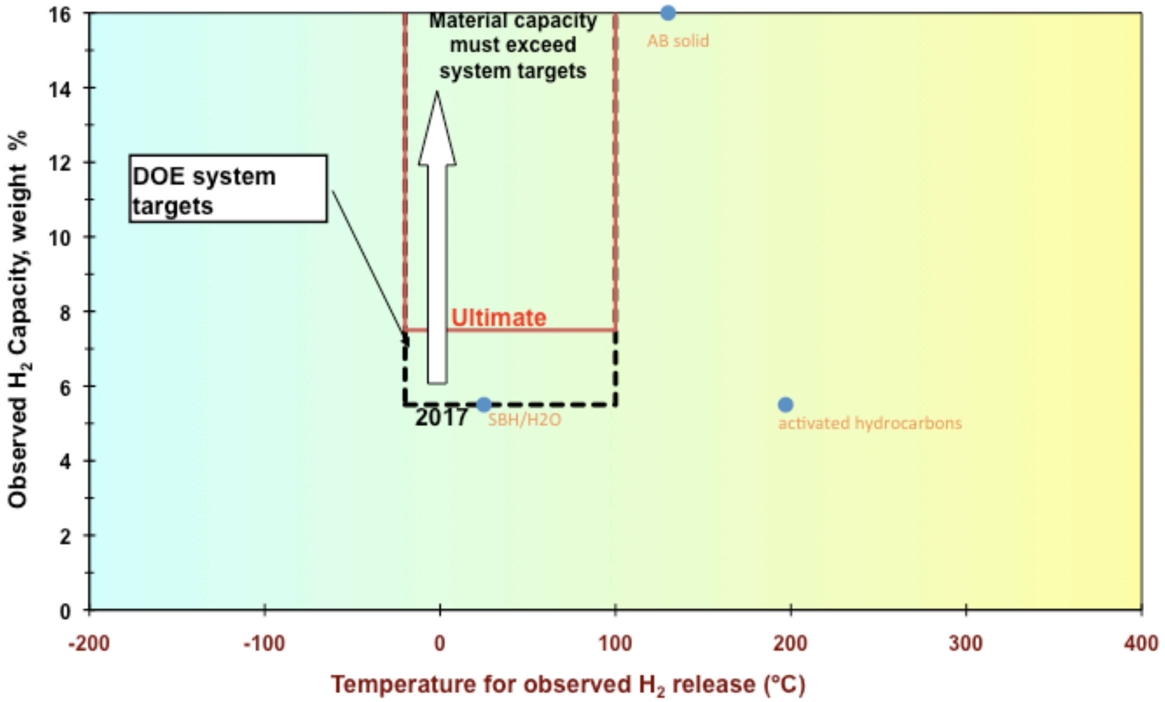


Figure 1. State of chemical hydrogen storage in 2005, before the Center started it's work.

The Chemical Hydrogen Storage Center of Excellence began its work in spring of 2005, and completed its research in the fall of 2010. The Center was comprised of two national laboratory partners, originally four companies, and originally seven academic institutions. The Center's work focused primarily around the chemistry of boranes, and thus many of the partners in the Center were experts in boron chemistry and catalysis, or processing of boron compounds.

During the tenure of the Center, its partners discovered or explored 12 major classes of compounds having over 130 materials or materials combinations. Many of the materials classes examined were chosen because of their potentially very high hydrogen storage capacity coupled with their typically high rates of hydrogen evolution related to their exothermic release of hydrogen. Material gravimetric capacities up to 16% were demonstrated, and many other candidate materials demonstrated capacities in excess of 9 wt. %; these materials capacities are consistent with what will be needed to meet the stringent DOE system capacity requirements for an engineered storage system. Two plots are shown below that illustrate the progress made during the Center's tenure; the plot made after the Center's R&D was completed does not contain all of the data points, as it would be too crowded, but rather shows representative data from several of the various families of chemical hydrogen storage materials explored by the Center.

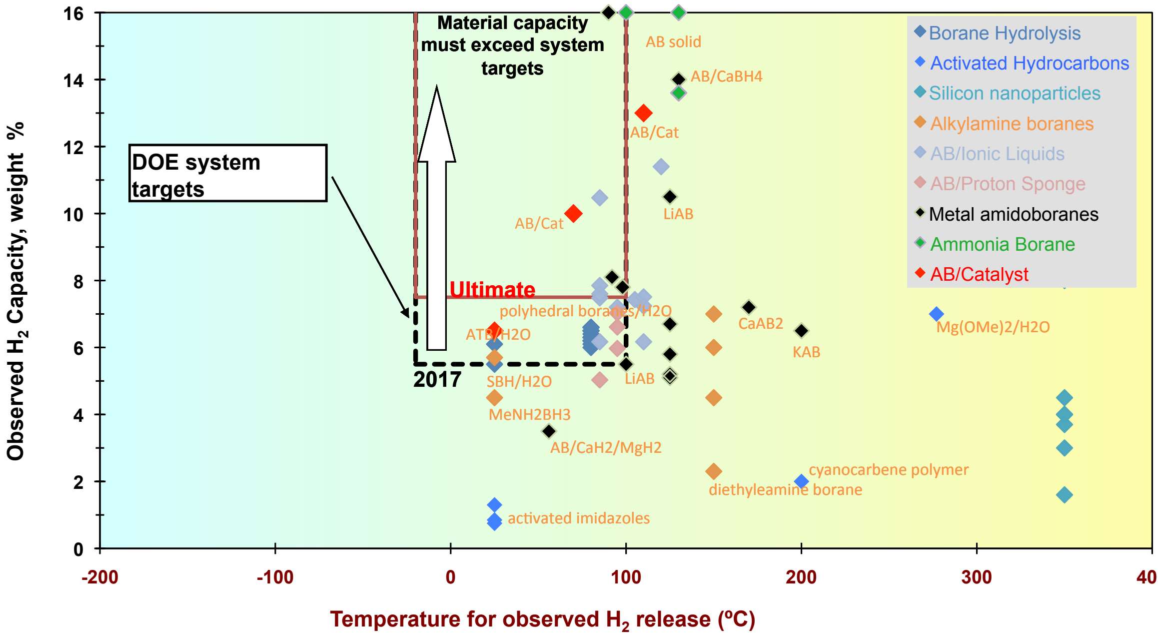
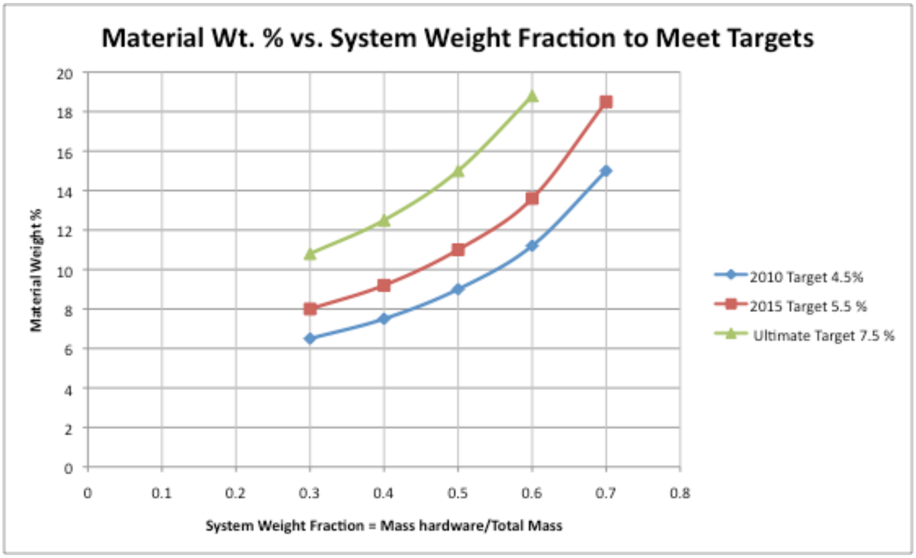


Figure 2. State of chemical hydrogen storage in 2010 after completion of the CHSCoE activities. The plot indicates the general types of families of hydrogen storage materials the Center contributed, and the temperature span over which the various materials release the indicated quantity of hydrogen.

In Figure 2, data for release from some materials are shown at multiple temperatures to indicate the temperature range over which hydrogen can be released. For example, catalysed release of hydrogen from AB is shown as three distinct points (red diamonds) ranging in temperature from 25 °C to 110 °C, a range over which hydrogen can be released with high rates with the potential to meet DOE targets. Similarly, AB in ionic liquids (gray diamonds) also indicate a broad temperature range for fast hydrogen release in the temperature regime of practical application for vehicular applications. From this plot, it can be seen that a number of materials fall close to the gravimetric and temperature ranges considered necessary for vehicular applications. Others, such as silicon nanoparticles release hydrogen at too high a temperature, and do not release hydrogen with adequate gravimetric capacity.

In 2007, the Center developed a robust decision tree process for logical down selection of the broad range of storage materials that were being discovered or developed by the Center. The Center's primary down select criterion was the materials gravimetric capacity. This criterion was based upon a simple plot (below) of the algebraic relationship between system wt. % and materials wt. % with varying system hardware mass contributions. The Center assumed, based upon Millennium Cell's aggressive system design for on board hydrolysis of sodium borohydride, and our additional experience, that the system hardware mass is likely to represent about 50% of the total system. The plot below shows graphically ***that to be able to meet the 2010 and 2017 system targets, that any storage material must contain greater than 7 or 9 wt. % hydrogen respectively.*** This analysis is described in more detail in Chapter 1, Section 1.5.1. Many scientifically interesting, but technologically inferior materials were set aside as a result of the Center's continuous decision tree driven down select process. Of the materials examined, 95% were not down selected for further development as they were considered unable to meet all of the DOE technical targets simultaneously. The remaining 5% of these materials or classes of materials that had the potential to meet all the targets simultaneously are considered as candidates for continued research. These include members of the family of solid ammonia borane with additives, potentially liquid fuels consisting of ammonia borane dissolved in ionic liquids or liquid cyclic carbon-boron-nitrogen heterocyclic materials, and certain metal amidoboranes, a class of materials wherein potentially reversible hydrogen storage materials may be discovered. A preliminary system capacity analysis by Argonne National Laboratory (ANL) showed a system gravimetric capacity of 4.9 wt. % and a system volumetric capacity of 49.5 g H_2/l for an ammonia borane/ionic liquid mixture. While preliminary, this analysis indicated that such a chemical hydrogen storage system was able to achieve the 2010 hydrogen capacity targets[i].



The candidate materials down selected have been demonstrated to have the potential to meet all of the DOE 2010 technical targets (the complete listing of technical targets and a description of DOE's hydrogen storage multiyear program plan may be found online[1]) for on board vehicular storage and they also have been demonstrated to have the potential (with the exception of the metal amidoboranes) for efficient off board regeneration. The metal amidoboranes, while not off board regenerable by energy efficient chemical processes, have shown that they have significant potential to yield new discoveries of near-thermoneutral release materials that in principle can be rechargeable on board a vehicle.

Recommendations: Hydrogen release. Our analysis indicates that to achieve system capacity targets, *any* hydrogen storage material must be able to achieve > 9 wt. % while also achieving the target rate of hydrogen release. Even with aggressive hardware budgets, a material < 9 wt. % H_2 will be challenged to fulfill a 4.5 wt. % system target. Discovery of high capacity materials that release hydrogen less exothermically (nearly thermoneutral) is required to simplify on board heat rejection, and to enable the material to be potentially on board rechargeable. High capacity materials that produce negligible gas-phase impurities under hydrogen release conditions are still required.

In the area of off board regeneration of spent fuel, the Center has made remarkable progress. Five years ago, no concepts existed for the regeneration of a spent borane-based fuel. In a relatively short period, the Chemical Hydrogen Storage Center of Excellence conceived of 10 distinct schemes for the chemical regeneration of spent fuel arising from dehydrogenation of ammonia borane. Of these 10 schemes, the Center demonstrated eight complete cycles in the laboratory. Two of these demonstrated processes were assessed for both cost and energy efficiency by Dow Chemical Co. (Dow) and ANL, respectively. TIAX, LLC provided independent validation of the Dow and ANL assessments. In one of the eight completely demonstrated regeneration process, Center partner Dow developed a cost estimate for spent fuel regeneration of between $7 and $8 per kilogram of hydrogen. This was for a process that is far from optimal, but provided the proof-of-principle that spent fuel could be regenerated, and at a cost that was not beyond reasonable. A second more chemically simple process was also assessed, and in this instance, the process and capital costs not including raw materials were found to be significantly lower ($2/kg H_2) relative to the first process estimate ($6.5/kg H_2), again providing proof-of principle that simpler regeneration schemes may provide a cost effective route to off board regeneration.

Recommendations: Regeneration. The Center has demonstrated that given a spent fuel from a chemical hydrogen system, that efficient process chemistries can be devised and implemented for off board regeneration. The chemistries that should be considered must have the minimal number of separations steps, and any separations should be of low energy intensity (e.g. crystallization). The reagent that transfers the hydrogen to the spent fuel should be inexpensive to recycle. Ideally, the incorporation of hydrogen into the spent fuel cycle should involve an efficient catalytic approach that can be directly coupled into a spent fuel regeneration scheme. Raw materials costs must be minimal, or there must be processes to make currently expensive reagents less expensive when practiced on a world scale.

While regeneration costs represent a critical contribution to the overall fuel costs, also important are the costs of the ‘first fill’ of storage material. Center partner Dow expended significant effort in analyzing first fill costs, and along with partner PNNL, they developed improved ‘first fill’ chemistries and processes for the preparation of ammonia borane. Dow’s analysis indicates that the cost of sodium borohydride (SBH) is the major contributor to the first fill cost. Dow estimates that to achieve the DOE target of \$2-4/kg H_2, the a SBH cost of \$5/kg is required to achieve an ammonia borane first fill cost of around \$9.1/kg; at \$5/kg, SBH represents roughly 2/3 of the first fill cost.

Recommendations: First Fill of Storage Material. For *any* storage material, the cost of the material is central to the overall cost of the fuel. Many storage materials, whether they are a chemical hydrogen storage material, a sorbent, or a complex metal hydride, are derived from currently expensive starting materials. Our Center’s work on sodium borohydride has shown that reducing raw materials costs is required to reduce the overall fuel cost. The Center’s work on first fill also has implications for the Metal Hydride Center of Excellence, as many of the storage materials they have examined are borohydride based, and the cost of these fuels will also rely upon cost effective synthesis of borohydride intermediates.

More emphasis on process analysis and process research is needed to determine whether there is a path forward for a given material type to achieve cost targets. If so, more emphasis is required on research to develop energy and chemically efficient syntheses of first fill hydrogen storage materials of all types.

The Center has made remarkable progress in the last five years in addressing materials needs for viable chemical hydrogen storage. Many challenges remain. Further reductions in cost of borohydride production are necessary to minimize overall fuel cost for any borane or borohydride fuels. While the Center has demonstrated a quite simple ‘one pot’ regeneration of ammonia borane using hydrazine, substantially reducing the costs of hydrazine and other raw materials used in the off board chemical regeneration of spent fuel are also necessary to reduce the cost of fuel. Dramatic improvements in the efficiency of raw materials production is also required to improve the overall spent fuel regeneration process efficiency.

Another important contribution of the Center was in the evaluation of US and global reserves of borate minerals. Center partner US Borax analyzed non-proprietary borate mining data, and concluded[ii] that the proven US borate reserves are sufficient to sustain the US light duty fleet operating on boron-based fuels without displacing existing borate markets. The world reserves of borates are substantially greater than the US reserves, with a significant reserve in Turkey. This reserve evaluation is also important to the Metal Hydride Center, as their main research focus also involved boron-based storage materials.

Recommendations: Resource Availability. When large-scale hydrogen storage materials needs are considered, resource availability studies should be performed at an early stage to ensure that there is enough U.S. and/or global resource available at a reasonable cost to accomplish the scale at which the implementation of the storage material is intended.

After five years, the Chemical Hydrogen Storage Center of Excellence demonstrated that chemical hydrogen storage is a viable materials-based approach. The Center made significant advancements in the understanding the chemistry and materials properties of boron-based chemical hydrogen storage materials, and developed the relationship between what is required of an engineered chemical hydrogen storage system and the materials properties required to achieve the system targets. The root cause of this Center's achievements may be traced to the Center concept that brought together the best boron chemists, boron process chemists, modelers, and chemical engineers into a focused team. The Center concept enabled efficient, quality communication and collaboration among all of the scientists and engineers, and allowed a Center culture to develop that inspired the Center participants to maintain scientific and technical momentum and drive towards progress on many fronts of chemical hydrogen storage. The Center concept encouraged being accepting and responsive to the substantial peer review input and external engineering assessments the Center received, catalyzing rapid progress along the critical path to demonstrating that chemical hydrogen storage in covalent chemical compounds is a viable materials-based hydrogen storage approach.

1.1 Introduction

The Chemical Hydrogen Storage Center of Excellence (hereafter referred to as the CHSCoE or as the 'Center') was one of three 'materials' Centers of Excellence initiated by DOE's Office of Fuel Cell Technologies in early 2005. The Center's missions were to conduct exploratory R&D and demonstrate feasibility of what were considered the three most promising areas of hydrogen storage materials research for on board vehicular applications. These three Centers were to provide focused efforts either on sorption of hydrogen on materials (the Hydrogen Sorption Center), storage of hydrogen in metal hydrides (The Metal Hydrides Center), or 'chemical hydrides' (the Chemical Hydrogen Storage Center). All three Center's technical targets were directed at achieving high hydrogen storage capacity that will allow a hydrogen powered vehicle a >300 mile of range while preserving all of the positive attributes of vehicle electrification and without compromising passenger or cargo space. A government – industry partnership of U.S. automotive and fuel companies known at the time as the FreedomCAR and Fuel Partnership (now referred to as U.S. DRIVE) had developed a set of technical targets for hydrogen storage *systems*. A storage *system* includes the storage material, and also all of the associated containers, valves, and associated on board hardware required to generate the hydrogen and deliver the hydrogen to the propulsion system at a rate to achieve a specified power. These systems targets encompass challenging volumetric and gravimetric targets to hydrogen purity specifications to shelf-life stability among many others that will be discussed in the body of this report. All of the targets need to be met *simultaneously*, in other words, a high capacity material that does not release hydrogen rapidly enough, or that does not have adequate stability is of marginal technical interest. Only those materials that have the chemical and physical properties that allow them to meet, or have the potential to meet system targets are of interest for further development into viable storage systems.

High pressure hydrogen tanks, systems that store hydrogen in a cryocompressed state, or liquid hydrogen storage systems that are more technologically mature may not be able to meet the long-term storage system targets were not topics of study for these three materials Centers. Rather, the materials Centers were tasked to explore materials that had the potential to exceed the capacities available by strictly physical methods of hydrogen storage.

These three Centers thus set out to seek out and develop hydrogen storage materials that have the potential to meet the specified DOE technical targets for an engineered system. The Sorption Center set out to explore the utility of sorption of molecular hydrogen onto novel carbons at cryogenic temperatures, an approach significantly different than the Metal Hydride or the Chemical Hydrogen Centers. These latter two Centers focused on storing hydrogen by compound formation either as ‘complex metal hydrides’ or as ‘chemical hydrides’, respectively.

Some introduction to hydride materials is needed at this point. A common approach to describing the spectrum of ‘hydride’ materials is to organize them into the bins based on chemical properties. A convenient classification system is to classify hydrides into the three groups: 1). Ionic hydrides, 2). Covalent hydrides, and 3). Interstitial metal hydrides.

Ionic hydrides are the true salts like sodium hydride, etc. where there is little covalent bonding between hydrogen and the metal, and thus a high degree of ionic character in the M-H bonding. These tend to be quite thermally stable toward releasing hydrogen.

Covalent hydrides encompass compounds such as MgH_2, AlH_3, the boranes and borohydrides and related derivatives, hydrocarbons, amines and ammonia complexes, etc. where the bonding is highly localized between the hydrogen and the central element (Al, B, C, N, etc). Many of these materials are known to release hydrogen at temperatures above room temperature and up to several hundred degrees Celsius, and can release > 9 and up to 20 wt. % hydrogen such that when placed into a system these compounds have the potential to meet DOE’s 2010 and 2017 gravimetric system targets of 4.5 and 5.5 wt %, respectively.

The interstitial hydrides are distinct from these two classes of ‘hydrides’, in that there is usually not discrete compound formation, in other words, interstitial hydrides may form where H atoms reside in tetrahedral or octahedral interstices within the metal or alloy framework over a wide range of M/H ratios; solid solution formation is common. The bonding between the metal(s) and the hydrogen atom is highly delocalized, with multi-center, multi-electron bonding similar to that in metals occurring. These hydrides can release hydrogen and re-hydride at temperatures that range from sub-ambient to several hundred degrees Celsius depending on the specific composition. Interstitial hydrides by their nature are composed of high atomic number transition metals, and therefore contain a low mass fraction of hydrogen of only a few percent and are not capable of meeting the strict gravimetric system targets set forth by DOE for on board vehicular applications.

In the class of covalent 'hydrides', many of these materials do not contain only hydridic hydrogen atoms, but in many instances also protonic hydrogen atoms, and so we prefer not to use the terminology of 'chemical hydride storage', but rather we use the term 'chemical hydrogen storage' to delineate the storage of hydrogen in covalent molecular solids.

1.2 Mission and scope of the Chemical Hydrogen Storage Center of Excellence

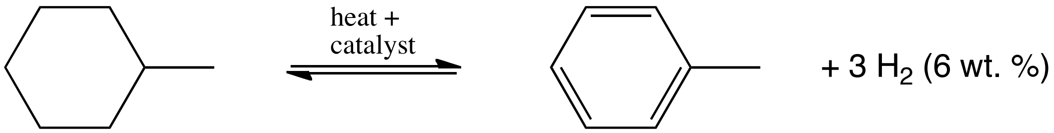
In the topical area of hydrogen storage, a goal of the DOE Office of Fuel Cell Technologies is to develop viable hydrogen storage materials and engineered sub-scale prototypes for a variety of applications ranging from personal power, storage for 'niche' vehicles such as forklifts, to onboard hydrogen storage for light duty vehicles. In the latter area, a key goal is to discover and develop materials for onboard hydrogen storage and propulsion systems that enable hydrogen powered vehicles a range of 300+ miles between refueling without compromising performance or space. The mission of the Chemical Hydrogen Storage Center of Excellence was to discover potential hydrogen storage materials and explore the feasibility of using chemical hydrogen storage materials for on board vehicular storage to enable DOE's goals for hydrogen-fueled vehicles. A major expectation of the Center was to down select and/or rank from the multitude of candidate materials the most promising material(s), release process(es), and regeneration process(es) for more detailed study, with an overarching goal of moving the most promising material(s) from all of the 'materials Centers' that meet all of DOE's technical targets for hydrogen storage toward sub-scale prototype demonstration.

The scope of the Center included all aspects of materials development and assessment activities, ranging from first principles theory and modeling of materials, modeling of the thermodynamics of chemical reactions and reaction sequences, to chemical synthesis and characterization of storage materials, characterization of hydrogen release kinetics and mechanisms and thermodynamics, to catalysis of hydrogen release, to engineering assessments and process modeling studies of regeneration of spent fuels. The scope did not include the problems of hydrogen production and distribution, or of fuel distribution or fueling infrastructure. With the formation of the Hydrogen Storage Engineering Center of Excellence, the Center's initial task of demonstrating a sub-scale prototype was transferred to the Engineering Center. Thus, the CHSCoE's focus was strictly on the discovery and development of high capacity hydrogen storage materials having rapid release, adequate storage stability, and acceptable levels of impurities, among other properties that were defined by DOE technical targets that will be described in more detail below. First, we describe the 'state of the art' for chemical hydrogen storage prior to the Center's formation.

1.2.1 Storage of hydrogen in covalent chemical bonds

At the time DOE requested proposals for a 'chemical hydrides' Center in the period of 2004 - 2005, the science of removing hydrogen 'stored' in covalent bonds of molecular species was relatively undeveloped. The few examples were the reversible dehydrogenation-rehydrogenation of hydrocarbons, e.g. methylcyclohexane ‘releases’ 3 moles of hydrogen to yield toluene as shown schematically in Figure 1. This is an endothermic process that occurs at very low rates in the absence of a catalyst and/or at low temperatures. More recently, in support of DOE’s Hydrogen Storage Program, scientists from Air Products Inc. explored a wide series of heterocyclic molecules that are activated toward hydrogen release and re-uptake.

Figure 1. Catalytic, reversible dehydrogenation of a hydrocarbon storage material. Here, the example is the dehydrogenation of methylcyclohexane to toluene to generate 6 wt. % hydrogen.



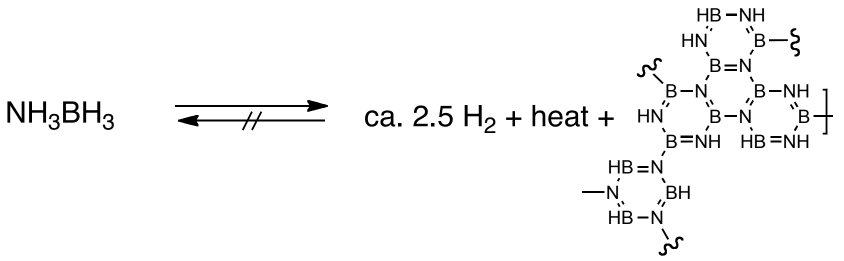
There was also some prior work from Millennium Cell in the highly exothermic, irreversible hydrolysis of sodium borohydride to release hydrogen and sodium borates in aqueous solution. Here, a significant fraction of the hydrogen derives from the water, and the product contains very strong B-O bonds that would require a chemical process to chemically reduce the B-O bonds to B-H bonds and regenerate the borohydride. Millennium Cell’s work was incorporated into the CHSCoE, and is discussed at length in Chapter 1 of this report.

Figure 2. Catalytic hydrolysis of aqueous sodium borohydride (SBH) to generate hydrogen.

$$NaBH_4\text{ (aqueous)} \underset{\not\longleftarrow}{\xrightarrow{\text{catalyst}}} NaBO_2\text{ (aqueous)} + 4\ H_2 + \text{heat}$$

It had also been reported that the molecule ammonia borane released hydrogen when heated to form BNHx polymers. This process was known to be moderately exothermic, and could not be reversed simply with the application of hydrogen pressure. There was no chemical process that had been conceived of to regenerate the spent fuel, completing the cycle.

Figure 3. Thermal decomposition of ammonia borane to release hydrogen and form polymeric



polyborazylene.

1.3 The partners of the Chemical Hydrogen Storage Center of Excellence

During the period of 2004 to early 2005, LANL and PNNL partnered together to assemble a technical team to respond to the Request for Proposals for the ‘chemical hydride’ Center. The original proposed concept of the Center was to explore the feasibility of a few well-specified classes of chemical hydrogen storage materials with a near- or medium term prospects for success. Many of the materials that were of interest to us at that time were boron-based compounds, e.g. boranes and borohydrides for reasons that will be explained in more detail below in Section 1.5. A number of innovative concepts 'beyond boron' were also developed and tended to be potentially more risky, but with high benefit if the chemistry could be worked out. Materials in this class included activated hydrocarbons, nano-scale main group compounds, metal alkoxides, and polymeric carbenes, among others. With these focus areas, LANL and PNNL engaged additional partners that brought together all of the necessary scientific capabilities to address the key scientific and engineering questions surrounding storage of hydrogen in covalent bonds. As the focus of the proposed Center's work had a large focus on boron chemistry, partners that could bring boron chemistry and materials expertise were sought. Indeed, in the final analysis, the Center assembled a 'who's who' of boron chemistry in the US as a portion of the proposal team. This included prominent boron chemists from academia and companies that had business interests and technical experience in boron chemistry and boron process chemistry, as well as experts in boron chemistry at the two national laboratories.

The proposal and eventual Center partners (and principals) and the capabilities they brought were:

1. Los Alamos National Laboratory: Molecular synthesis, inorganic and organometallic chemistry, kinetics and mechanism, boron chemistry, chemical characterization, gas-solid reaction characterization, homogeneous and heterogeneous catalysis.

2. Pacific Northwest National Laboratory: Chemical engineering, theory and modeling, nuclear magnetic resonance characterization, materials synthesis and characterization, catalysis, kinetics and mechanism.

3. Millennium Cell, Inc.: Sodium borohydride hydrolysis systems and experience, chemical and mechanical engineering (discontinued in FY2008).

4. Northern Arizona University (Prof. C. Lane, deceased May 2007): Chemical synthesis, chemical safety, chemical process experience.

5. Rohm and Haas (now Dow): Chemical process engineering and assessment, chemical synthesis, borohydride process chemistry.

6. University of Alabama (Prof.s D.A. Dixon, A. J. Arduengo): Theory and modeling, organic synthesis and characterization

7. University of California, Davis (Prof.s S. M. Kauzlarich and P.P. Power): Main group organometallic and solid state chemistry and characterization, nano-phase chemistry and characterization

8. University of California, Los Angeles (now University of Missouri) (Prof. F. Hawthorne): Boron chemistry, organometallic chemistry.

9. University of Oregon (Prof. Liu): Organic synthesis and characterization of cyclo-CBN compounds (added as partner in September, 2008)
10. Pennsylvania State University (Prof. D. McDonald): Electrochemistry and electrochemical synthesis.
11. University of Pennsylvania (Prof. L. Sneddon): Boron chemistry, kinetics and mechanism of organometallic and inorganic reactions.
12. University of Washington (Prof.s K. Goldberg, M. Heinekey): Organometallic chemistry and catalysis, molecular synthesis.
13. US Borax Corporation: Boron chemistry, boron process chemistry, borate mining and resource assessment (informal participant of Center, added as a funded partner in October, 2009).
14. Intematix Corporation: Rapid throughput screening of chemical processes, catalyst library design and synthesis (discontinued in FY2008).

After successfully competing for the CHSCoE and the final negotiation of work scope with DOE, the Center began its work in March 2005.

1.4 Overview of the principles to the Center's research

The CHSCoE formally kicked off its activities in March 2005. The Center's work initially focused on chemical hydrogen storage in a three-tiered approach to storage materials development that is described in Section 1.6. How we developed this strategy is described in the following paragraphs and Sections.

To determine the promise of a hydrogen storage material, the Center's approach was to synthesize storage materials, characterize the materials both chemically and physically, and determine parameters relevant to their use as hydrogen storage media. A partial list of materials parameters that are required of a potentially interesting storage material include high hydrogen capacity, adequate kinetics and thermodynamics of hydrogen release, impurities (i.e. characterization of the products of release in the gas phase and the solid state), shelf life and thermal stability of the storage material, and regenerability of the 'spent fuel' resulting from the dehydrogenation of the storage material. A subset of the DOE technical targets for hydrogen storage that were in place in 2005 is shown below in Table 1.4.1. In addition to the many materials-related parameters, system related parameters such as cost of the production of the fuel (i.e., the 'first fill'), the cost of regeneration of the fuel, and the overall energy efficiency of the storage cycle from fuel to spent fuel and regeneration back to fuel were also crucial to consider when determining if a particular storage concept was of potential interest to down select for further study. As the research in the three materials Centers evolved, a few of the DOE technical targets for hydrogen storage also evolved, particularly in the volumetric and gravimetric capacity targets. These updated targets are indicated in Table 1.4.1.

1.4.1 Guiding principles and technical targets of the CHSCoE

A key goal of the DOE Office of Fuel Cell Technologies has been to develop a viable onboard hydrogen storage system that enables hydrogen powered vehicles a range of 300+ miles between refueling without compromising performance or space. There are a number of considerations that need to be addressed to achieve DOE's goal. The overall system weight and volume are of particular importance. Since gravimetric and volumetric hydrogen capacities are key contributors to the overall system mass and volume, they have been the primary drivers of our research. Our Center also considered kinetics of H_2 release *not a target, but a requirement fundamental to viable system operation*. Therefore we have focused considerable attention on the measurement of the rates of hydrogen release within temperature ranges of likely vehicle operation; our Center did not work on any material that did not have the potential to release hydrogen with rates approaching the H_2 flow rate target at temperatures below 150 °C, preferably not above 120 °C (caveat – an exception would be given for a material discovered that could be on board rechargeable with H_2). At the same time, it is imperative that the material not release hydrogen under normal ambient conditions (<50 °C) the vehicle will experience during normal operation or while parked; therefore, fuel stability is another challenge we addressed by experimental measurements of stability from hours to days at 50 °C. The next major consideration is how to recharge or regenerate the spent fuel once hydrogen has been released. There must be a chemically and energetically efficient method for regeneration of the spent fuel (a topic that is so important that we address it in a separate section of this report). Since off boarding spent fuel and fuel loading are impacted by the fuel form, the physical form of the fuel (fresh and spent) is a parameter of note. The fuel must be durable enough to the refueling and off boarding as well as normal automotive operations. Finally, the fuel cost is very important. Should the fuel be too expensive, no matter how good it is, it will not be acceptable to consumers. Thus, our Center expended significant effort at developing both efficient 'first fill' syntheses of chemical hydrogen storage fuels, regeneration schemes for spent fuels, proving these processes in the laboratory, and working with our industrial partner to develop preliminary regeneration and first fill cost estimates.

What our Center considered to be the key technological barriers and DOE targets for On-Board Hydrogen Storage are described below and are tabulated in

Table 1.4.1. In addition the regenerationof spent fuel or refueling efficiency must be taken into account. DOE set efficiency goals for on board reversible storage systems and off board regenerable systems. For systems generated off-board, 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 during regeneration. This efficiency is defined as the onboard efficiency of 90 percent multiplied by the "well-to-tank" efficiency of regenerating the chemical hydrogen storage material. The target total efficiency to the power plant for off-board regenerable systems is 60 percent.[1] Thus, for systems regenerated *off-board*, the energy efficiency target includes an allowance of only 40% of the total energy in the fuel for the energetic 'expense' of regeneration.

All of the technical targets including those discussed above are found in the DOE's Multiyear Program Plan (MYPP) for hydrogen storage. The MYPP also includes a list of technical barriers that must be overcome to provide viable on board hydrogen storage systems. This Center's work addressed the following barriers for hydrogen storage (the letters refer to barriers described in the MYPP):

(A) System Weight & Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging & Discharging Rates
(J) Thermal Management
(K) System Life-Cycle Assessments
(R) Regeneration Processes
(S) By-Product/Spent Material Removal

Table 1.4.1 Summary of Selected Material Related Targets from 2007 with Feb. 2009 Updates

Storage Parameter	Units	2007	2010	2017	Ultimate
System Gravimetric Capacity	Wt.% H_2 (updated)	4.5 (--)	6 (4.5)	9 (5.5)	(7.5)
System Volumetric Capacity	g H_2/cc (updated)	0.036 (--)	0.045 (0.028)	0.081 (.040)	(.070)
Operability (Operating ambient T)	°C	-20/50	-30/50	-40/60	-40/60
Operability (Min/max delivery T)	°C	-30/85	-40/85	-40/85	-40/85
Discharge Rate (min full flow rate)	g H_2 /sec/kW	0.02	0.02	0.02	0.02
Hydrogen Purity	% H_2	99.99	99.99	99.99	99.99
Storage System Cost (& fuel cost)	\$/kWh net (\$/kg H_2) \$/gge @ pump	6 (200) ----	4 (133) 2-3	2 (67) 2-3	TBD 2-3

1.5 Motivation of the Center's choice of classes of compounds for study

In the lifetime of the Center from 2005 – 2010, the CHSCoE explored, discovered or developed a rather vast expanse of chemical hydrogen storage landscape where the proper choice of molecular properties or processes was shown to lead to facile release of hydrogen from covalent bonds in molecules. Nearly all of the compounds we eventually focused on were borane amines, and all contained B-H bonds. Why is this? This is a result of several boundary conditions driven by the gravimetric and volumetric targets that require that much of the molecular mass of a storage material must be hydrogen, restricting the search for high gravimetric capacities to elements of low atomic number such as B, N, C, etc.. Boron hydrides, and *especially boron amine compounds are quite unique compared to any other class of compounds, as more than 2 atoms of hydrogen per B atom may be readily released*, and in principle, hydrogen weight fractions of up to 20% could be realized. In the series of analogous, isoelectronic carbon-carbon bonded systems (hydrocarbons), only one hydrogen can be released per carbon atom (without going to extremes of temperature). This limits hydrocarbons to releasing at most 1H/CH_2 unit, or a weight fraction of at most 1/14 or 7% wt. % hydrogen. Ammonia borane, on the other hand, can release up to 3 moles of hydrogen, or a weight fraction of about 6/31 or around 20 wt. % hydrogen (in practice, this would generate the rather stable ceramic BN, and it is doubtful this material could be readily regenerated). It is well demonstrated now, however, that ammonia borane can readily release 2.0 – 2.5 moles of hydrogen, or 13-16 wt. % hydrogen depending on the conditions chosen for release, and generate regenerable BNHx polymeric spent fuel. In another remarkable achievement, researchers at PNNL found that the 'unstable' compound ammonium borohydride can be stabilized and handled. This compound releases an additional mole of hydrogen compared to ammonia borane, and so ammonium borohydride is able to release up to 3.5 moles of hydrogen, or a weight fraction of about 7/33 = 21 wt %! As we will discuss in this report, if ammonium borohydride could be stabilized further, it would represent a potentially very high capacity hydrogen storage material. These are just a few examples of why the Center initially focused on and continued to work on these B-N-H compounds and why the B-N-H compounds are superior as a storage media to many other analogous chemical hydrogen storage systems such as the hydrocarbons.

While the release properties of the B-N-H compounds were known to be of interest, the regeneration of spent fuel was an open question. For vehicular applications on a world scale, it is required that a storage material be efficiently and cost-effectively regenerated to minimize total energy expended, and to recycle *all* of the spent fuel back to active fuel. Certain metal hydrides have been demonstrated to be on board rechargeable with hydrogen, and some covalent chemical hydrogen storage materials may be regenerated directly with hydrogen (which can in principle be done on board the vehicle but has not been demonstrated). However, many chemical hydrogen storage materials, particularly those that release hydrogen very exothermically, are not able to be recharged directly with hydrogen, and must be chemically reprocessed off board. As this report will detail in subsequent chapters, as it became apparent that ammonia borane had interesting release properties, it also became necessary to demonstrate that regeneration is chemically possible in an energetically acceptable process. If the feasibility of chemical regeneration of spent fuel was not proven, it was obvious that the amine boranes would not survive any down select decision, and the Center would move on to other more promising materials. This report outlines the significant expenditure of resources on exploring and then demonstrating the regeneration of spent fuel from ammonia borane.

In the formative stage of the Center, Center researchers recognized that the nature of any regeneration route would depend strongly on the thermodynamics of the release process. For example, in the case of the endothermic dehydrogenation of hydrocarbons, such as the conversion of methylcyclohexane to toluene and hydrogen, the regeneration is performed by reversing the reaction by the well-known and industrially practiced exothermic catalytic rehydrogenation of cyclic aromatic hydrocarbons to yield hydrogen saturated cyclic compounds. For exothermic release systems, particularly strongly exothermic systems like ammonia borane, the simple reverse rehydrogenation is far too endothermic, and not even extreme hydrogen pressure can force the direct regeneration of spent fuel in a practical sense. Instead, it was understood that regeneration of spent fuel from ammonia borane would require a potentially chemically complex regeneration scheme to replace the B-H bonds while maintaining the B-N bond, avoiding loss of ammonia from the system, and avoiding the formation of diborane and subsequent loss of B from the system. Thus the Center was motivated to develop wholly new chemistries and for the first time attempt to demonstrate the resynthesis of a storage material such as ammonia borane from it's dehydrogenation product. Without such concepts in place, it was felt that there was no path forward for the general class of off board regenerable hydrogen storage materials.

1.6 Organization of the Center's research and it's evolution

As discussed above, the Center began with three tiers of materials research ranging from an assessment of current technology, to a mid-term assessment of a variety of non-hydrolytic borane chemistry, to higher risk approaches that were 'beyond boron'. These three tiers are described in the following subsections. As the Center matured, and successfully passed through several down selection or go/no go processes, the organization of the Center evolved from the three-tiered materials-centric organization to an organization focused on the Center's chosen down selected materials. The Center organization then focused on two major tasks, those being 1). hydrogen release properties (capacity, kinetics of release, impurities, thermochemistry), and 2). the regeneration of spent fuel from ammonia borane.

1.6.1 Tier 1. SBH hydrolysis and regeneration of B-O to B-H

We began investigating the hydrolysis of sodium borohydride and the regeneration of the product borates back to borohydride in Tier 1. This work involved Millennium Cell. Their work was to engineer the SBH and build a prototype hydrogen storage system based upon SBH hydrolysis. In addition, processes for the energy and cost efficient regeneration for the spent sodium borate back to SBH were assessed. This research area was focused on achieving progress in advance of a DOE Go/No Go decision process in Fall 2007. As will be discussed in greater detail in Chapter 1, the SBH Go/No Go process resulted in terminating hydrolysis of SBH as well as polyhedral boranes and amine boranes as a viable storage mechanism, and Tier 1 research was ended, and resulted in the discontinuation of Millennium Cell's research as part of the Center. As the work on conversion of sodium borate to SBH was needed as part of the Center's 'first fill' strategy for synthesis of key boron hydride intermediates, this aspect of the Center's research was continued.

1.6.2 Tier 2. Alternative Boron Chemistry for Hydrogen Storage

In Tier 2, research was performed that was focused mainly on non-hydrolytic pathways to hydrogen release. The Center recognized early on that regeneration of the very stable B-O bonds of borates from hydrolysis of borohydrides was going to be energy intensive and difficult, and so we explored non-hydrolytic approaches to release hydrogen from amine boranes and polyhedral boranes and other similar B-N compounds. Some hydrolysis work on polyhedral boranes was carried out in the task and this was ended with the SBH No Go. The primary focus of this Tier was the class of compounds that can release hydrogen to form BNHx polymeric spent fuels that are less thermodynamically stable than the borates that result from hydrolysis. Thus it was felt that these BNHx polymers had a more likely chance of being able to meet the energy efficiency and chemical efficiency targets set forth for spent fuel regeneration. This area evolved into the major focus area of the Center's research.

1.6.3 Tier 3. Advanced concepts for hydrogen storage in covalent compounds

In Tier 3, we explored higher risk approaches such as the coupling of exothermic and endothermic processes to hydrogen release in compounds such as the metal alkoxides, the dehydrogenation of activated hydrocarbons, as well as the release of hydrogen from hydrogenated nanoparticles of main group elements such as Si. This Tier was also informally referred to as 'beyond boron', where we planned to explore hydrogen release from C-H and Si-H bonded covalent materials, among others. As the Center matured, most of these advanced concepts did not show enough promise, and were not down selected for additional study. At the conclusion of the Center, two classes of materials remained, one being the metal amidoboranes (the focus of an International Partnership for Hydrogen in the Economy (IPHE) collaboration and a few Center partners), and the other being the so-called cyclo CBNs. These are both discussed in detail in Chapter 1, and both materials classes continue to show promise.

As the Center's work evolved and as a result of a major Center down select process and milestone in late 2007, it became apparent that the Center's research had coalesced into two major areas of 1). Hydrogen release from B-N-H compounds and 2). Chemical regeneration of spent fuel from ammonia borane. Each of these major areas continued to be informed by theory and modeling and guidance from internal and external engineering assessments of materials and processes. These two large organizational units remained with the Center to its conclusion in 2010.

1.7 The general approach of the Center to performing hydrogen storage research

The general approach of the CHSCoE was to combine experimental,computational chemistry, and engineering expertise from all of the Center partners to develop viable storage materials and processes. Even before the Center was operating, the nascent Center had in place a robust intellectual property (IP) agreement ready to promote free and open discussions among the Center partners. This enabled communication to brainstorm on new ideas, solve problems, share samples and data, and to provide for a path to generating a 'patent estate' for Chemical Hydrogen Storage materials. The Center maintained an excellent chemical synthesis capability, particularly in the area of boron chemistry that enabled the ready manipulation of a variety of boron compounds and derivatives, but also in solid state and solution chemistry of other main group elements. The Center often utilized mechanistic understanding of hydrogen release from chemical hydrogen storage materials to guide our efforts in developing improved materials, additives, and catalysts. The Center also maintained a distributed engineering capability to provide assessments of materials in a systems context, and engaged the industrial partners early and often to provide engineering assessments of chemical processes, particularly for estimating regeneration and 'first fill' materials costs. These assessments provided crucial guidance to the chemists and materials experts in our search for improved regeneration pathways and processes.

The Center also capitalized on the broad spectrum of additional expertise that the partners brought to the Center in theory and modeling, manufacturing, borate minerals processing and boron chemical speciation, chemical characterization, gas speciation and quantification, catalyst design and discovery, electrochemistry, structure and bonding, chemical kinetics and mechanisms, and safety analysis. Certainly all of these contributions were important. Of particular importance was the theory and modeling capability that helped to guide much of the experimental research the Center accomplished. The Center used computational chemistry approaches to predict the thermodynamic properties of a wide range of compounds containing boron, nitrogen, hydrogen, and other elements as appropriate including carbon. These calculations were done in most cases with high-level molecular orbital theory methods that have small error bars on the order of ± 1 to 2 kcal/mol. The results were used to benchmark more approximate methods such as density functional theory for larger systems and for database development. We predicted reliable thermodynamics for thousands of compounds for release and regeneration schemes to aid/guide materials design and process design and simulation. In many cases the values predicted for several critical classes of materials are the first reliable computed values for these compounds and for many represent the only available values as experimental data for many compounds we worked with was simply unavailable.

Even with this tremendous capabilities within the Center, if the capabilities couldn't communicate among themselves, they were valueless. The communication plan for the Center, which had as it's hub the robust multilateral intellectual property agreement that encompasssed all partners, was critical in ensuring that the geographically dispersed partners all knew what the research goals of the Center were, and what each partner's tasks were. This was communicated in a variety of face-to-face meetings, brain storming meetings, topical conference calls among sub-team members coordinated through single points of contact that informed the Center Director, and peer-to-peer phone calls and emails. Students at the academic institutions were able to spend time at PNNL performing research and accessing unique characterization tools and facilities that accelerated information exchange and experimental progress.

As the Center matured beyond it's formative period, a "fail fast" culture was developed to down select to the most promising materials quickly, leaving behind materials where we felt there was no viable path forward to a storage system, and refocusing the Center's resources on the most promising materials. The Center's computational capability provided substantial guidance in rapidly responding to experimentalists needs to quickly make informed experimental choices.

The theory and modeling capability was largely provided by the University of Alabama, and to a lesser extent PNNL. The computational chemists used highly accurate and validated first principles computational chemistry approaches on advanced computer architectures to predict the electronics structure of molecules to obtain thermodynamics and reaction pathway information as well as to predict materials physical properties in support of the design of hydrogen storage materials and regeneration processes. Trends in reactivity or in complex equilibria were often rapidly assessed by computation, which informed the experimentalists choice of chemistries to probe first, or to help explain complex experimental results. Computational approaches were benchmarked when necessary against known chemical and physical properties. In the end, the Center's successful partnerships between experimentalists and theorists demonstrated time and again the value of theory in helping to make rapid experimental progress.

1.8 Major technical accomplishments of the Center

In this section are listed high-level outcomes of the Center that allowed the Center to move ahead efficiently throughout it's lifetime. Positive outcomes that led to down selections for continued study, as well as no go decisions and major findings that de-selected systems for further study and that also taught significant lessons are captured here. More detailed accomplishments are found in the following Chapters, and in the individual partner's final reports.

A most significant accomplishment of the Center was to demonstrate, multiple times over, that chemical reprocessing of spent fuel is feasible. At the start of the Center in 2005, the storage community at large felt that the completely undeveloped notion of spent fuel regeneration represented a daunting and significant technical barrier to the acceptance of the concept of off board regenerable storage materials. Lacking a demonstration of feasibility, it is unlikely that such off board regenerable systems would ever find acceeptance. Five years ago, Center researchers had only the very vaguest of notions as to how to proceed to regenerate BNHx spent fuel. Because of this, the Center dedicated a significant amount of research effort, transfering significant effort from the materials discovery tasks to the regeneration effort during years 2-5. This decision accelerated the Center forward in filling in our knowledge gaps in regeneration chemistry, and led to our eventually successfully demonstrating the regeneration of spent fuel from ammonia borane. The early concepts of 'bootstrapping' the reformation of B-H and B-N bonds using chemical methods to add H^+ and H^- in stepwise fashion to BNHx were proven, and subsequently improved upon multiple times over. Five years hence, after the input of a great deal of creativity from both experimentalists and theorists, the Center demonstrated multiple pathways to ammonia borane regeneration, and have provided preliminary cost and efficiency estimates for two of these pathways. These accomplishments are described in detail in Chapter 2. Along the way, we have learned a great deal about what the key features of a successful off board chemical regeneration scheme must be. We believe that after 5 years of research into off board regeneration processes, the Center has demonstrated that if presented with a spent fuel, it is feasible to conceptualize and demonstrate in the laboratory efficient regeneration schemes, and off board regeneration is in principle no longer the major technical barrier for acceptance of the concept of off board regeneration.

In the area of hydrogen release, a major accomplishment of the Center has been to show that the exothermic nature of amine borane compounds and derivatives can release hydrogen at high rates at temperatures as low as room temperature. The Center developed catalysts and additives that further increase the rate of release and decrease the release temperatures. These accomplishments enable a variety of possible approaches to engineered release systems that the Hydrogen Storage Engineering Center is currently studying and analyzing to determine which has the greatest potential for further system development.

In addition to these major areas of accomplishment, the Center made significant advances to the field of hydrogen storage by either discovering and developing new storage materials and processes, or in defining materials and processes that are unlikely to achieve the technical targets for hydrogen storage systems. These accomplishments are listed below:

1. An early no go decision on SBH hydrolysis system and the termination of all related hydrolysis routes and set the Center on the path to focus on amine boranes, which in the long term was fruitful.
2. Early on, the Center developed an engineering-guided approach to materials development and down selection. This enabled the Center to move quickly to successes, and discard scientifically interesting but technically flawed storage materials in an efficient and rational manner. This approach is evident in each of the following accomplishments.
3. The Center demonstrated time and again that progress in hydrogen storage materials research was accelerated by the deliberate and judicious use of theory to make predictions of chemical reaction outcomes, or to aid in the interpretation of experiments. The utilization of high-level computational chemistry is evident in each of the following accomplishments.
4. Demonstration that ammonia borane releases 2-2.5 moles of hydrogen, equivalent to 13-16 wt. % hydrogen at temperatures below 200 °C. This was, and still is the lowest temperature, highest capacity release material that has adequate shelf life stability (ammonium borohydride has a higher capacity, but as a solid, is quite thermally unstable).
5. Understanding of influence of additives on nucleation and growth kinetics of ammonia borane (AB) dehydrogenation that led to discovery of additives that mitigated the foaming of neat solid AB, a critical observation for any future solid ammonia borane fuel composite.

6. Impregnation of mesoporous scaffolds with ammonia borane were observed to alter the temperature of hydrogen release onset of the composite underscoring importance of surfaces and length scales on reaction chemistry of AB

7. Homogeneous acids, and subsequently metal complexes were demonstrated to catalyze the release of hydrogen from AB. Certain catalysts were found to release one mole of hydrogen (6 wt. %) rapidly at room temperature. This work inspired our Center's research into gaining additional understanding of the mechanism of the catalysis of hydrogen release from AB that informs present and future catalyst design efforts.

8. Preliminary observations of 'digestion' of spent fuel in acids (HX) to produce processable BX_3 and subsequent reduction of BX_3 with aluminum and silicon hydrides to yield amine boranes provided early proof-of-principle for the digestion – reduction regeneration scheme for BNHx spent fuel derived from dehydrogenation of AB.

9. Addition of lithium amide or –hydride to AB decreased the temperature of hydrogen release from AB mixtures, and altered the overall release-temperature profile and nature of the spent fuel. This was an early 'hint' to the existence of metal amidoboranes that eventually became a significant research interest of the Center.

10. Ionic liquids, and addition of hindered bases to AB substantially altered the rates and extent of AB dehydrogenation. Two moles of hydrogen are lost below 110 °C when AB is heated in an ionic liquid. Subsequently, metal catalysis was observed to be effective in ionic liquids at lower temperatures. These observations led to the Center's interest in developing liquid fuels from ionic liquid/AB mixtures. This was a key observation for the Center, as enabling liquid fuel formulations may contribute significantly to achieving an engineered hydrogen storage system based on AB.

11. Development of a systematic decision tree process for down selection of materials within the Center. This focused subsequent materials discovery and development efforts, and focused the Center's attention on only the most promising materials having materials having >7 wt. % hydrogen, preferably > 9 wt. % hydrogen. This framework for decision-making enabled the Center to move rapidly towards the most promising materials, and thus deserves mention as a significant accomplishment of the Center.

12. The demonstration of a complete regeneration cycle using thiocatechol as the digesting agent and a tin hydride as the reducing agent was a key accomplishment of the Center. This led to the eventual optimization of this regeneration chemistry that was the subject of the first preliminary off board chemical regeneration cost assessment. This resulted in an estimate cost of \$7-8/kg H_2, a significantly promising result. Lessons learned from this analysis drove further improvements and discoveries of regeneration chemistries. One crucial lesson learned from this exercise was that the most thermodynamically efficient process might not be the least costly. Thermodynamic efficiencies that come at the cost

of equilibrium-controlled processes can result in significant separations costs, and significant capital equipment expenditures.

13. The Center demonstrated higher yielding syntheses of SBH and AB with higher purities, and performed preliminary cost analyses indicating that potentially lower costs could be achieved for these two crucial intermediates. This was significant for both our Center and the MHCoE, as the cost of boron starting materials currently dominates the 'first fill' cost.

14. Center researchers discovered and characterized a wide variety of metal amidoboranes; these were synthesized for a variety of metals using both solid state and solution state techniques. Trends in hydrogen release as a function of metal cation lead to a search for thermoneutral release compounds. Metal amidoboranes were subsequently observed to emit substantially lower quantities of borazine into the product gas, although ammonia is still detected in most cases as a gas phase impurity that must be mitigated.

15. The Center completed a preliminary assessment of the world borax reserves indicating that DOE commercialization targets for U.S. hydrogen vehicles can be accommodated using U.S. supplies of borax for boron-based fuels without displacing existing boron markets.

16. The Center demonstrated that AB in liquids could be dehydrogenated with a base metal heterogeneous catalyst. This observation enables a flow reactor configuration for future AB liquid fuels. Heterogeneously catalyzed AB dehydrogenation was subsequently observed to result in reduced quantities of gas-phase impurities relative to the uncatalyzed reaction.

17. Based on earlier experience and lessons learned, the Center developed a chemically simple, one-pot regeneration of spent fuel for AB. A cost assessment of this process suggests that significant savings can be gained in process and capital costs when reducing the number of unit operations, and provided an additional significant lessons-learned for future regeneration efforts.

18. The University of Northern Arizona compiled an early report on the safety of borane compounds as fuels. This helped guide Center's partners safety planning for the safe handling of borane materials.

1.9 Lessons learned from the 'Center concept'

During the 5-year tenure, the Center and its research and development work was the subject of DOE annual merit reviews, and annual technical team reviews by FreedomCAR and Fuel Partnership representatives (the 'storage tech team'). Consensus of these reviews either in written or in verbal comments was that our Center moved science and technology of chemical hydrogen storage forward at a rate far faster and an extent farther than what was anticipated at the beginning of the Center of Excellence ‘experiment’. Clearly, the Center made greater advances than what could have been possible if all the partners had worked, but worked apart. There are a multitude of plausible reasons as to why the Center succeeded. A few of the most important are discussed in the following sections.

1.9.1 The Center success was derived from quality communication and intellectual property management plans

The ease, frequency, and quality of communication among the partners at all stages of the project are the main root causes of the progress that was made. In an area where it was clear that inventions were going to occur, it was also necessary to put into place an intellectual property (IP) management plan that enabled all of the partner’s background and developing IP to be protected, and to be shared with other partners in a timely fashion. Indeed, the Center generated a substantial amount of IP, and the patents and patent applications are described in Table 1.9 at the end of this section.

The high quality of communication among the partners was made possible by having an effective intellectual property management plan in place at the very onset of the Center’s activities which removed the usual barriers encountered among collaborating scientists, engineers, and technologists, where ownership of ideas problems arise that discourage open discussion of ideas and results in a timely manner. This formal structure allowed for trust to develop among the partners, and once trust established, open communication was enjoyed across the Center. Up to the minute results could be discussed, problems brainstormed, and potential solutions plotted within this framework of open and trusted communication among peers.

An important component of our effective communication was with DOE program management. Frequent and detailed communication between the Center’s Director and DOE allowed for consistent communication of program goals to flow to and from partners in an efficient manner. The Center concept allowed DOE to typically have but one conversation, and that was with the Center Director and occasionally members of the Center’s coordinating council.

1.9.2 The Center built the right team having the right capabilities

While the quality of communication was key to our success, clearly building the ‘right’ team was crucial. All the best communication tools in the world won’t make up for deficiencies in team capabilities and experience. The Center’s success also hinged upon putting the right team together of the nation’s best boron chemists coupled with expert experience in the experimental study, engineering, and theory and modeling of reacting chemical systems. The Center concept allowed any major technical gaps to be filled by recruitment of the partners having the best capabilities match for the R&D to be performed. This is most apparent when our Center was compared against single principal investigator (PI) projects. The ability for any Center member to access any of the equipment at any of the Center institutional partners, or to access the intellectual capability or experience of any of the Center researchers, enabled every partner to progress in ways that are not possible in individual PI-based projects.

An important feature of our Center was that we coupled excellent academic scientists and industrial researchers with experienced national laboratory researchers accustomed to working in a milestone and deliverables-driven R&D environment that encompasses most if not all of DOE EERE-funded research. Where many academicians are unaccustomed to working in this type of program environment, the national lab partners worked well with positioning the scientific and technical capabilities of the academic partners within the proper context to take maximal advantage of the teams overall scientific capability, and to ensure that milestones were addressed, deliverable met, and program direction was consistent with program needs, and that the program momentum remained high and program focus remained sharp.

1.9.3 The Center concept promotes collaboration and a drive to accomplish

An aspect of the Center concept that is somewhat harder to capture and define is that when a talented set of R&D scientists and engineers gather to work on a problem, camaraderie develops, and the team's desire to solve the problem at hand grows. Perhaps it is also because of some friendly competition as well, but the Center concept clearly galvanized this team to accomplish much more than what it could have had the Center's PI's worked apart.

1.9.4 The Center concept enables near real-time informal peer review

Related to quality of communication is the aspect of informal peer review that goes on in any gathering of scientists and engineers. It is only natural that results are debated, hypotheses are questioned, and problems are brainstormed. All of these occurred during our frequent Center meetings and phone calls. In the process, an informal peer review occurs. Questions are asked, ideas are sharpened, hypotheses changed, conclusions may be abandoned and subsequently reformulated. Without the Center concept in place, independent projects even if working toward a common goal, are unable to achieve this level of trust in communication and concomitant idea flow that the Center concept promotes.

1.9.5 The Center had strong technical leadership with a vision

From its inception, the Center profited by having strong collective technical leadership, and a vision for making scientific and technical progress in the relatively new field of chemical hydrogen storage. The leadership had the technical background necessary to make any changes in technical direction, and the backing of DOE and the Center researchers to make the hard down select decisions that enabled the Center to move forward. As a result, the Center moved ahead rapidly in most areas that were critical to achieving the Center's goals.

The remainder of this report provides a detailed description of the CHSCoE's research and progress in the two main areas: Hydrogen Release (Chapter 1) and Regeneration of Spent Fuel (Chapter 2).

1.9.6 The Center's R&D resulted in new science

When the Center began, there were but few examples of chemical hydrogen storage materials, and fewer examples of regeneration of spent fuels. The Center's researchers often had to uncover fundamental chemistries of the materials that were focused upon. In exploring how to increase the rates and decrease the temperature of hydrogen release from ammonia borane, much mechanistic work had to be done to understand a few of the details in the molecular pathways involved in hydrogen evolution, and how those details influenced the eventual products (e.g. spent fuel) of dehydrogenation. As examples, Professor Sneddon's group at the University of Pennsylvania explored the use of ionic liquids and non-nucleophilic bases to accelerate the rate of release of hydrogen from ammonia borane, AB. They found new pathways that lead to more facile extrusion of hydrogen form in this class of boron-nitrogen compounds. In exploring the catalysis of hydrogen release from AB and other amine borane compounds, researchers at Los Alamos and the University of Washington discovered new catalytic chemistry as they explored the underlying differences among catalysts that led to substantially different rates and product specificity. Using microporous environments or nanoscale particles, researchers at Pacific Northwest and the University of California-Davis found that the chemistry of hydrogen release is controlled by phenomena occurring at small length scales. In the regeneration chemistry of spent fuels from AB, researchers at Los Alamos, Pacific Northwest, Alabama, and Dow Chemical found new, previously unexplored chemical reactivity between chemical reductants and spent fuels on the pathway to complete regeneration. These are but a few examples of new science that resulted from the Center's R&D; additional examples can be found in the subsequent chapters in this final report, and within the references cited at the end of each chapter. Additionally, as some of this new science also represented new intellectual property, the Center partners applied for and received patents on a number of these observations that resulted from their Center-related R&D. Many of these patents are tabulated below, others that are in process may appear in the future.

1.10 Listing of U.S. Patents and Patent Applications Resulting from CHSCoE R&D

1). United States Patent 7,963,116
Autrey, et al. June 21, 2011
Bulk-scaffolded hydrogen storage and releasing materials and methods for preparing and using same

Abstract
Compositions are disclosed for storing and releasing hydrogen and methods for preparing and using same. These hydrogen storage and releasing materials exhibit fast release rates at low release temperatures without unwanted side reactions, thus preserving desired levels of purity and enabling applications in combustion and fuel cell applications.

2). United States Patent 7,897,129
Autrey, et al. March 1, 2011
Process for synthesis of ammonia borane for bulk hydrogen storage

Abstract
The present invention discloses new methods for synthesizing ammonia borane (NH.sub.3BH.sub.3, or AB). Ammonium borohydride (NH.sub.4BH.sub.4) is formed from the reaction of borohydride salts and ammonium salts in liquid ammonia. Ammonium borohydride is decomposed in an ether-based solvent that yields AB at a near quantitative yield. The AB product shows promise as a chemical hydrogen storage material for fuel cell powered applications.

3). United States Patent 7,316,788
Autrey, et al. January 8, 2008
Materials for storage and release of hydrogen and methods for preparing and using same

Abstract
The invention relates to materials for storing and releasing hydrogen and methods for preparing and using same. The materials exhibit fast release rates at low release temperatures and are suitable as fuel and/or hydrogen sources for a variety of applications such as automobile engines.

4). United States Patent 7,439,369
Thorn, et al. October 21, 2008
Method and system for hydrogen evolution and storage

Abstract
A method and system for storing and evolving hydrogen employ chemical compounds that can be hydrogenated to store hydrogen and dehydrogenated to evolve hydrogen. A catalyst lowers the energy required for storing and evolving hydrogen. The method and system can provide hydrogen for devices that consume hydrogen as fuel.

5). United States Patent 7,544,837
Blacquiere, et al. June 9, 2009
Base metal dehydrogenation of amine-boranes

Abstract
A method of dehydrogenating an amine-borane having the formula R_1H_2N--BH_2R_2 using base metal catalyst. The method generates hydrogen and produces at least one of a $[R_1HN$--$BHR_2]_m$ oligomer and a $[R_1N$--$BR_2]_n$ oligomer. The method of dehydrogenating amine-boranes may be used to generate H_2 for portable power sources, such as, but not limited to, fuel cells.

6). United States Patent 7,645,902
Stephens, et al. January 12, 2010
Acid-catalyzed dehydrogenation of amine-boranes

Abstract
A method of dehydrogenating an amine-borane using an acid-catalyzed reaction. The method generates hydrogen and produces a solid polymeric $[R_1R_2B$--$NR_3R_4]$.sub.n product. The method of dehydrogenating amine-boranes may be used to generate H_2 for portable power sources.

7). United States Patent 7,713,506
Burrell et al. May 11, 2010
Metal aminoboranes

Abstract
Metal aminoboranes of the formula $M(NH_2BH_3)$.sub.n have been synthesized. Metal aminoboranes are hydrogen storage materials. Metal aminoboranes are also precursors for synthesizing other metal aminoboranes. Metal aminoboranes can be dehydrogenated to form hydrogen and a reaction product. The reaction product can react with hydrogen to form ahydrogen storage material. Metal aminoboranes can be included in a kit.

8). United States Patent 7,736,531
Thorn, et al. June 15, 2010
Composition and method for storing and releasing hydrogen

Abstract

A chemical system for storing and releasing hydrogen utilizes an endothermic reaction that releases hydrogen coupled to an exothermic reaction to drive the process thermodynamically, or an exothermic reaction that releases hydrogen coupled to an endothermic reaction.

9). United States Patent 7,837,852
Thorn, et al. November 23, 2010
Energy efficient synthesis of boranes

Abstract
The reaction of halo-boron compounds (B--X compounds, compounds having one or more boron-halogen bonds) with silanes provides boranes (B--H compounds, compounds having one or more B--H bonds) and halosilanes. Inorganic hydrides, such as surface-bound silane hydrides (Si--H) react with B--X compounds to form B--H compounds and surface-bound halosilanes. The surface bound halosilanes are converted back to surface-bound silanes electrochemically. Halo-boron compounds react with stannanes (tin compounds having a Sn--H bond) to form boranes and halostannanes (tin compounds having a Sn--X bond). The halostannanes are converted back to stannanes electrochemically or by the thermolysis of Sn-formate compounds. When the halo-boron compound is BCl.sub.3, the B--H compound is B_2H_6, and where the reducing potential is provided electrochemically or by the thermolysis of formate.

10). United States Patent 7,846,410
Davis, et al. December 7, 2010
Regeneration of polyborazylene

Abstract
Method of producing ammonia borane, comprising providing polyborazylene; digesting the polyborazylene with a dithiol-containing agent to produce a boro-sulfide compound and a byproduct; converting the byproduct to the boro-sulfide product of step (b) by reaction with a first alkyl-tin hydride; and, converting the boro-sulfide compound produced in steps (b) and (c) to ammonia borane by reaction with a second alkyl-tin hydride.

11). United States Patent Application 20090274613
Hamilton; Charles W. ; et al. November 5, 2009
Hydrogen Production Using Ammonia Borane

Abstract
Hydrogen is produced when ammonia borane reacts with a catalyst complex of the formula L_nM-X wherein M is a base metal such as iron, X is an anionic nitrogen- or phosphorus-based ligand or hydride, and L is a neutral ancillary ligand that is a neutral monodentate or polydentate ligand.

12). United States Patent Application 20080175781
Thorn; David L.; et al. July 24, 2008
Bootstrap synthesis of boranes

Abstract
Metal hydride materials react with BZ.sub.3 compounds in the presence of ligand to form BH_3-L compounds. A compound of the formula HBZ_2 is prepared from a compound of the formula BZ.$_3$ by reacting a first amount of a compound of the formula HBZ_2 with a metal hydride material "MH" and a compound "L" to form a material of the formula BH_3-L, and then reacting the BH_3-L thus formed with a compound of the formula BZ_3 to form HBZ_2 in a second amount greater than the first amount of HBZ_2. Z is selected from alkoxy, aryloxy, amido, arylamido, doubly substituted alkoxy, doubly substituted aryloxy, doubly substituted amido, doubly substituted arylamido, alkoxy-amido, and aryloxy-arylamido. When Z is bidentate, then HBZ_2 has a ring structure. "L" is selected from ethers, aromatic ethers, amines, aromatic amines, heterocyclic nitrogen compounds, sulfides, aromatic sulfides, and heterocyclic sulfur compounds. "L" becomes a ligand in the BH_3-L material.

13). United States Patent Application 20100272622
Sutton; Andrew ; et al. October 28, 2010
REGENERATION OF AMMONIA BORANE FROM POLYBORAZYLENE

Abstract
Method of producing ammonia borane, comprising providing a reagent comprising a dehydrogenated material in a suitable solvent; and combining the reagent with a reducing agent comprising hydrazine, a hydrazine derivative, or combinations thereof, in a reaction which produces a mixture comprising ammonia borane.

14). United States Patent Application 20090302269
Choi; Daiwon ; et al. December 10, 2009

Process and Composition for Controlling Foaming in Bulk Hydrogen Storage and Releasing Materials

Abstract
New methods and compositions are disclosed that minimize foaming in hydrogen-releasing materials. Foaming can be minimized during release of hydrogen in composites that include structured forms such as wafers and discs. Change tolerances of from 0% to 25% in solid products described show promise for next-generation fuel elements and devices.

15). United States Patent Application 20110021818
Liu; Shih-Yuan ; et al. January 27, 2011
AZABORINE COMPOUNDS AS HYDROGEN STORAGE SUBSTRATES

Abstract
Selected 1,2-azaborine compounds exhibit utility as hydrogen storage substrates, and are useful as components of hydrogen storage devices.

16). United States Patent Application 20110021735
Liu; Shih-Yuan ; et al. January 27, 2011
SUBSTITUTED 1,2-AZABORINE HETEROCYCLES

Abstract
Aromatic heterocycles incorporating boron and nitrogen atoms, in particular, 1,2-azaborine compounds and their use as synthetic intermediates.

1.11 References

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[i] http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage_explanation.pdf

[2] U.S. Borax, Final Report, Chemical Hydrogen Storage Center of Excellence, 2010.

Chapter 1: Hydrogen Release from Chemical Hydrogen Storage Materials

Contents, Chapter 1

1.1 Summary of recommendations for future work: Hydrogen release from chemical hydrogen storage materials

The Center made substantial progress in identifying materials with promising hydrogen release properties and in understanding the chemical processes that control release. Although materials that meet all the targets separately have been identified, *a single material that fulfils all these criteria has not been discovered*. Consequently there are several avenues to pursue for further investigation:

1. Refine those materials that most closely meet the targets. These are identified in Section 1.5 and discussed in more detail in Section 1.6. Further research should be carried out to meet the following specific needs:

    a. Development of fluid systems suitable for transfer with a fluid pump, such as:

        i. Hydrogen storage materials in high concentrations in solvents such as ionic liquids that maintain the liquid state over a broad range of ambient conditions both before and after hydrogen release are desirable from an engineering perspective. Liquid fuels possess substantial advantages for materials handling on board the vehicle, and the systems identified by the Center so far go a long way toward meeting practical targets but do not remain liquid under all anticipated conditions. Higher concentrations of storage material in a liquid formulation that is enabled by improved solvent properties should result in higher gravimetric and volumetric capacities, and so should remain a focus of future R&D.

        ii. Slurries (non-settling, stable suspensions) of hydrogen storage materials such as AB are desirable. Because of the real or perceived impracticality of on board handling of solids, slurries of solid phase hydrogen storage materials in fluids have been proposed as one mitigation strategy. Little is known of the high temperature chemistry and physical chemistry of hydrogen storage materials with potentially 'inert' fluids. Nothing is known of rheological properties of such slurries, nor is there anything known of the implications of regeneration of materials in slurry form, whether it be regeneration using hydrogen or off board chemical processing. In the case of exothermic hydrogen release materials such as ammonia borane, the fluid medium offers an opportunity to mitigate certain heat transfer issues that are certain to arise in an engineered on board system.

   b. Elimination of impurities (e.g. diborane, borazine and ammonia) in the hydrogen gas. Although some of the materials identified as a result of our research to date produce low impurity concentrations, a mechanistic understanding of impurity formation could help devise strategies to eliminate impurities in a wider range of materials, e.g. the use of higher pressures to take advantage of possible bimolecular mechanisms to mitigate gas-phase impurities. Post-release treatment or trapping is another avenue that merits additional exploration such as using cold spent fuel as an impurity sorbent, etc.

   c. Cost of ‘first fill’ components dominates the cost of chemical hydrogen storage using boranes. Development of new lower cost methods of borate to borohydride conversion, and for AB synthesis needs improvement. This, along with low cost regeneration of spent fuel represents the pathway to reducing total fuel cost.

   d. Continue the cyclo CBN materials research. This area of research is just now emerging, and it appears promising.

2. Continue investigations aimed at new materials discovery. The Center has demonstrated an excellent track record in innovating new storage materials that have potential for meeting stringent DOE targets. But there is much left to do. Among the most promising near-term opportunities for additional materials development include:

   a. Search for on board directly rechargeable storage materials that can be regenerated simply by the addition of hydrogen gas. The most promising chemical hydrogen storage materials this Center has explored (e.g. ammonia borane, metal amidoboranes) all release hydrogen exothermically by more than a few kcal/mole H_2. Reversing these reactions is not practical with hydrogen pressure. The majority of the compounds the Metal Hydride Center has explored are quite endothermic (e.g. borohydrides, amides), leading to thermodynamically favorable regeneration with hydrogen. While some of these compounds have been found to have kinetically competent rehydrogenation pathways, their endothermicity of release requires the input of additional energy to achieve the necessary (high) temperature of release. Therefore, a continued search for materials that release hydrogen closer to thermoneutrality (> -1kcal/mole) while maintaining high capacity and adequate kinetics of release should be a continued focus of hydrogen storage materials research.

b. This Center identified ammonium borohydride as a potentially interesting high capacity storage material, if it could be stabilized in a liquid or solution form. This compound, which has one of the highest gravimetric capacities known, has a very high solubility in ammonia and remains stable in this solvent at low temperatures or high pressures. Increasing this stability could result in a very interesting storage material.

3. Develop for near-term applications some of the materials the Center did not down select for additional research because they were not able to meet the very stringent requirements for on board vehicular storage systems. Many materials were not down selected because they did not have the requisite gravimetric capacity or because they have undesirable physical or chemical properties for an on board system, but otherwise may meet many of the requirements for a viable off board storage system. Such materials may be useful for other applications (e.g. forklifts, auxiliary power, etc.) and are discussed in Section 1.7.

4. Solids handling. Transfer of a solid storage material onto the vehicle, and solids handling on board the vehicle have been challenged as being impractical. Thus, this is an area where innovative new concepts for solids handling could ‘change the game’ for all classes of solids, including many materials that the Metal Hydride Center of Excellence has explored.

1.2 Background

There are three major approaches to releasing hydrogen from covalent compounds that are shown in Figure 1.2.1 below: 1). Hydrolysis including steam reforming, 2). Thermolysis, where heating of the compound leads to release of hydrogen, and 3). Catalytic release, where a catalyst is used to increase the rate of hydrogen release from a covalent compound. The Center has explored all three of these approaches. Hydrolysis, and particularly catalytic hydrolysis, was explored as a way to release hydrogen from covalent chemical compounds such as polyhedral boranes and sodium borohydride. Here, water is used to hydrolyze [element] – H bonds, forming [element] – O bonds and hydrogen. One of the drawbacks of this approach is the formation of very stable [element] – O bonds, while one of the positive attributes is that water contributes hydrogen to the total hydrogen released. Another drawback of the hydrolytic approach is that it requires a second reagent (water) to be carried on board, and is thus a potentially more complex engineering problem.

Thermolysis routes that are endothermic tend to require a high temperature (>150 °C) to sustain hydrogen release are less desirable as the heat to sustain the reaction must come from burning hydrogen, diminishing the amount of hydrogen delivered to the power plant. *Ammonia borane releases hydrogen exothermically.* Here, once reaction is initiated, the heat of reaction drives further release. If there is not means to control the rate of thermolysis, the reaction can ‘run away’ with increasing rates and temperatures. Thus an engineered system that utilizes an exothermic release material such as ammonia borane must utilize a method for control of the rate of reaction, as well as the rejection of the heat of reaction.

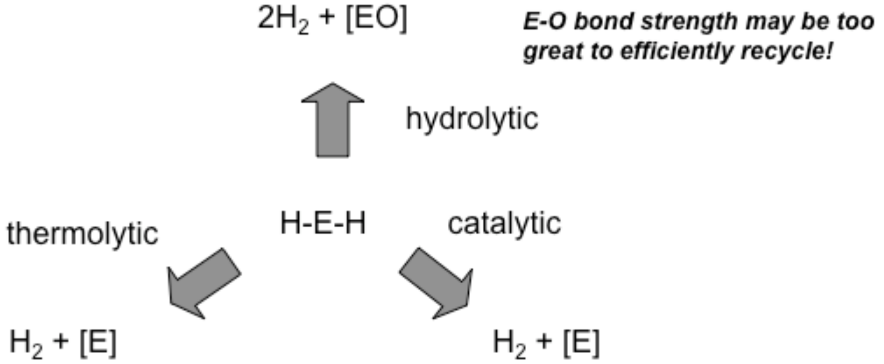


Figure 1.2.1. Three possible routes for release of hydrogen from a chemical hydrogen storage material.

Catalysis of course is the means by which rates of reaction may be increased at a given temperature, or the temperature of reaction may be reduced. Many approaches involving a wide variety of storage materials have attempted to improve temperature or rates of release have involved the use of a catalyst. For exothermic reactions, if the reaction can be initiated at a lower temperature in the presence of a catalyst, such as in a flow reactor, then the residence time in the catalytic zone may help to control the rate of release, and thus the temperature of release, and is thus a means of controlling an exothermic reaction.

1.3 Approach

Our experimental approach to investigating release pathways was to synthesize candidate materials that were felt to have potential to be appropriate to meet the DOE system targets for gravimetric and volumetric densities, characterize the compounds to ensure that the material being studied was in fact the desired material, and then conduct release experiments under a variety of conditions of temperature, concentration, catalysis, etc. to evaluate the rate of release of hydrogen, and the quantity of hydrogen released. The Center's approach also required that a material and a release process give rise to a material that had some chance to be regenerated either off board via a chemical process, or directly with hydrogen gas.

Our Center's approach involved closely coupling experimental work with computational chemistry. Computational modeling of hydrogen release chemistries, kinetics, thermodynamics, and spectroscopic properties of storage materials were used to guide and interpret experiments in the Center's hydrogen release and spent fuel regeneration efforts (Chapter 2). More detail on the computational chemistry methods and tools used are described in Section 1.4.1 below.

As the Center evolved, a substantially detailed down select decision tree was developed to help guide Center decisions on what materials were of substantial promise for further work, and which materials should have additional research discontinued or postponed. This down select decision tree will be discussed in more detail in Section 1.5 below.

1.4 Materials Investigated and Results

Chemical hydrogen storage materials such as ammonia borane and its derivatives offer the potential of high gravimetric and volumetric capacity (Figure 1.3.1), at rapid release rates sufficient to meet or exceed DOE targets at moderate temperatures. Another class of chemical hydrogen storage materials is represented by classical dehydrogenation/rehydrogenation of hydrocarbon compounds. In general, hydrocarbons release hydrogen quite endothermically, and are reasonably limited to release of one hydrogen per carbon atom, or < 7 wt. % hydrogen. Because of these two features, the boranes are potentially more attractive. Ammonia borane readily loses more than 2 hydrogen atoms per B or N, and releases the hydrogen at lower temperatures, albeit exothermically. The Center investigated many more classes of compounds than just the amine boranes, but in the end, this class of compounds appeared the most promising to the Center, and most of our work focused on ammonia borane and its derivatives. The Center also investigated hydrolysis and catalytic hydrolysis of borohydrides, polyhedral boranes, and ammonia triborane. Also studied were various main group nanoparticle hydrides of Si, and 'coupled' endo-exothermic systems such as the magnesium alkoxides. Activated hydrocarbons such as imidazole derivatives and carbenes were explored, but were found to be lacking in hydrogen capacity. Ammonia borane as a pure solid, and also encapsulated within mesoporous scaffolds of silica and carbon, and in the presence of 'inert' additives were explored as means to control the rates of hydrogen evolution and influence the generation of impurities or control the foaming that is observed during hydrogen evolution from pure ammonia borane. Ammonia borane in various solvents (organic ethers, liquid amine boranes, ionic liquids) in the presence of a variety of catalysts (homogenous, acid catalysts, heterogeneous) or initiators (proton sponge, among others) was the focus of considerable attention. Eventually, much focus shifted to the use of ionic liquids and catalysts to effect the rapid evolution of greater than two

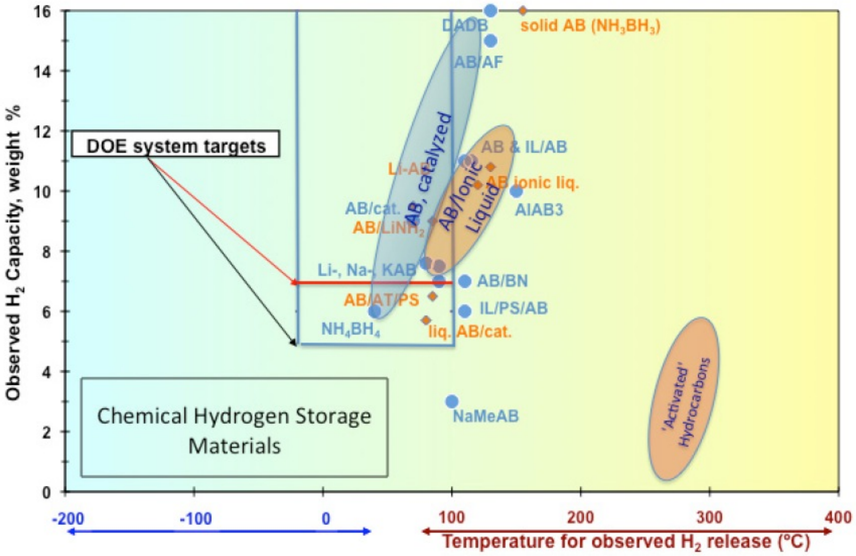


Figure 1.3.1. Representative chemical hydrogen storage materials the material wt% of hydrogen released, and their approximate temperature ranges of hydrogen release. Note, the boxes on the diagram represent *system* targets, and the data plotted are *materials wt. %.*

moles of hydrogen at temperatures as low as 70 °C with the potential of providing a liquid spent fuel form. Another class of catalysts was found to liberate one mole of hydrogen from solutions of AB at room temperature. While this latter approach does not yield the gravimetric capacity requirement for a system, it taught us a great deal about the catalysis of ammonia borane dehydrogenation. It may also represent a 'cold start' option as a rapid heat source for cold weather operation of a hydrogen storage system based upon AB.

This is just a snapshot of the materials the Center explored. Additional descriptions of these classes of materials follows below, and detailed accounts of each material class studied by the Center can be found in the individual partner reports.

1.4.1 Computational Chemistry Support for Center's Activities

Our Center's approach involved closely coupling experimental work with computational chemistry. Computational modeling of hydrogen release chemistries, kinetics, thermodynamics, and spectroscopic properties of storage materials were used to guide and interpret experiments. Thus the theory was not a 'stand alone' project; it was integrated into the fabric of every experimental effort addressed by the Center. The Center made particular use of computational chemistry approaches to provide direction to experimentalists in cases where there were potentially hundreds or thousands of chemical options to choose from; this dramatically accelerated Center progress in the area of selecting regeneration chemistries, for example.

More specifically, the Center's computational chemistry effort used highly accurate and validated first principles computational chemistry approaches on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of regeneration systems. To support engineering assessments of chemical regeneration processes, theory and modeling was used to predict physical properties for reagents, intermediates, or products involved in regeneration cycles where the physical properties data is not known. Parameters such as heats of vaporization and heats of formation were computed for use in engineering calculations of process heat requirements, for example. These computational approaches were successfully benchmarked against experimentally determined values for known compounds.

To accomplish many of these tasks, the Center's theorists used newly developing approaches to the prediction of thermodynamic properties to chemical accuracy based on valence electron calculations. Computations were matched against the problem at hand, and were performed by using the Gaussian 03, MOLPRO 2006, the NWChem suites of programs in addition to G3MP2B3, DFT/B3LYP, Gaussian, ADF, among others. The calculations were performed on a variety of computers including the Cray XD-1 computer at the Alabama Supercomputer Center, a PQS Opteron computer at the University of Alabama, and the 2000 processor HP Linux cluster in the Molecular Science Computing Facility at the William R. Wiley Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory.

1.4.2 Analyses Performed to Characterize Storage Materials

Various synthesis techniques, spectroscopic, calorimetric instruments were used for obtaining characteristic information on materials studied for the Center. The specific synthetic approaches for the various systems the Center explored can be found in the individual partner final reports, as well as in the numerous peer-reviewed journal articles published by Center authors. Both solid state and solution synthetic approaches were used in the preparation of the wide variety of storage materials explored by this Center.

As compared to the analysis for metal hydrides and hydrogen sorbents used by the other two materials Centers, the techniques used by this Center to characterize storage materials were significantly different as our Center dealt mainly with molecular solids and solutions, and so many of the analytical approaches we used were specifically intended to characterize those types of materials.

- **Nuclear magnetic resonance** (NMR) was used extensively to understand the chemical nature of the particular species synthesized or generated. Boron-11 NMR was particularly useful to characterize new materials, and study the evolution of products along the hydrogen release pathways. NMR of other nuclides (H-1, N-15, C-13, Li-7, among others) was also used quite routinely to characterize storage materials, and products from release. NMR was performed on both liquid and solid samples.
- **Differential Scanning Calorimetry** (DSC) was used to determine the enthalpy of hydrogen release reactions.
- **Thermogravimetric analysis** (TGA) was used to determine the amount of hydrogen released from a material as a function of time and temperature, or can be used to study the isothermal stability of a compound by monitoring weight loss over many hours or days. TGA information is useful in determining the gravimetric density of hydrogen in a material. When combined with mass spectroscopy and/or infrared spectroscopy, the speciation and quantification of any impurities may be determined as well.
- **Mass-spectrometry** (MS) was used to identify the identity and concentrations of gas-phase species generated during hydrogen release.
- **Infrared spectroscopy** was used to identify gas-phase impurities and their concentrations. Infrared spectroscopy was also used to study the evolution of species in the solid state as well by employing a diffuse reflectance sample cell. Often, mass spectroscopy and infrared spectroscopy were used in tandem along with thermogravimetric analysis to provide a more comprehensive view of the reacting materials as a function of time and temperature.
- **X-ray diffraction and powder neutron diffraction** was used to identify the crystal and molecular structure of crystalline materials, or was used to monitor the changes in the solid materials of reacting mixtures as a function of time and temperature.
- **Pressure composition isotherm** (PCT) instrumentation was used to measure the pressure of hydrogen released from a storage material as a function of time and temperature from which hydrogen capacity and the kinetics of hydrogen release could be derived.
- **Automated burette systems** were employed to determine the volume of gas released as a function of sample temperature and time. This technique is useful for most bench-top H_2 release tests for storage materials to determine the storage capacity and the kinetics of

release of hydrogen. The use of cooled traps can be used to identify and quantify impurities in the gas(es) released. As this technique became a fairly standard approach for this Center to use for measurements of capacity and kinetics, a more detailed explanation of this technique is given below. PNNL automated a system, and published a description of the approach that is abstracted below.

Automated gas burette system: A gas burette simply collects the gas evolved from a storage material, and provides a straightforward measurement of total gas evolved. Simple gas burettes with manual measurements of gas volume evolved at intervals of perhaps 15 – 30 seconds are easy to set up but are not adequate to study fast kinetics or to carry out high throughput testing. PNNL developed a gas burette system using pressure and temperature sensors, which is capable of continuously recording the gas amount and evolution rate to a computer with sub-second interval time. In this system, the moles of gas generated are calculated from the volume, pressure, and temperature change of the gas phase assuming ideal gas behavior. Our automated gas burette system was modified based on a standard hydride test glassware kit.[1] A schematic of the system is shown in Figure 1.3.2. A heated oil bath was placed on a platform so it could be rapidly raised to immerse the reaction flask by a lever. A condenser was placed on top of the reaction flask to isolate the reaction zone from the rest of the system in the instances where volatile solvents were being used. A series of traps, including one that could be cooled, collected any volatile impurities or sublimed reactants and prevented the downstream burette from being contaminated, and also to condense non-hydrogen species such that only the volume of hydrogen was being measured in the burette gas receiver. The glass bulb trap closest to the burette also isolated the reactor from potential inadvertent overflow of the working fluid in the burette. The automated burette configuration should be applicable and adequate for most bench-top H_2 release tests from potentially any storage material.

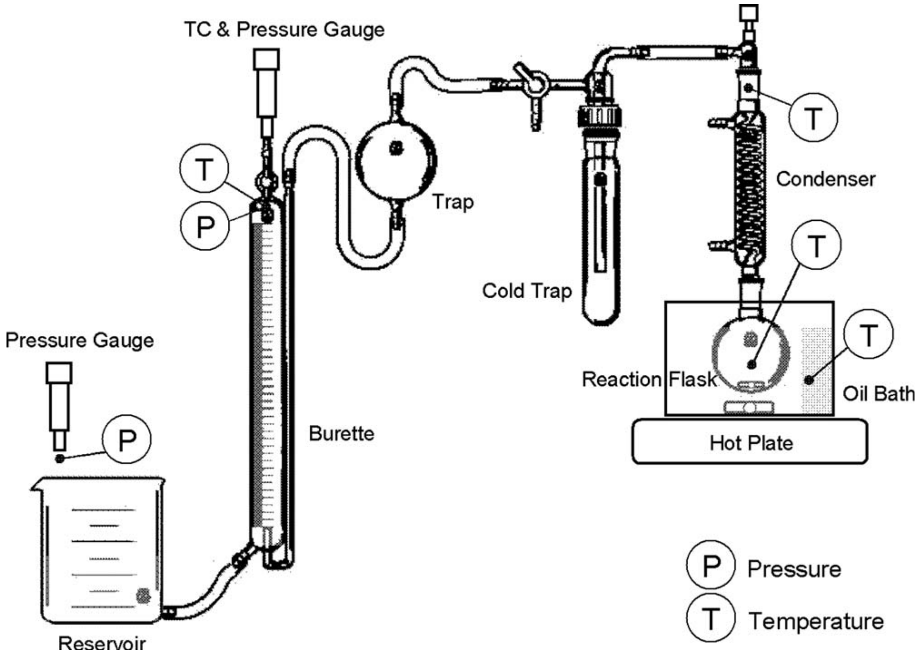


Figure 1.3.2 Schematic system of the burette system for hydrogen evaluation studies.

1.4.3 Endothermic Chemical Hydrogen Storage Materials

The general class of endothermic chemical hydrogen storage materials was explored early during the Center's tenure. As the Center gained experience in these systems, it became apparent that either the capacity, rate of release, or regenerability of endothermic chemical hydrogen storage systems explored by this Center were inadequate to meet the DOE technical targets for onboard hydrogen storage systems. The few areas where we had some early effort were in the areas of 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 Center avoided duplication of effort of the independent DOE project at Air Products & Chemicals Inc. and their work in examining storage in activated hydrocarbon materials.

1.4.3.1 Activated Imidazole Compounds

Summary. The goal of this section of work was to develop materials that could be obtained from common feedstocks such as hydrocarbons and yet would meet all of the DOE targets. These materials were not down selected, as they could not meet gravimetric targets. This work resulted in the issued US patent 7,439,369. More information on this activity can be found in the Final Report from Los Alamos National Laboratory.

For most hydrocarbon compounds, elimination of hydrogen is strongly endothermic, requiring in excess of 250 °C to achieve reasonable rates and extent of release of hydrogen. Spontaneous loss of hydrogen from organic compounds is rare. Formic acid is one compound that readily catalytically decomposes to hydrogen and CO_2, but there are only a handful of other examples.

One class of compounds that was felt to show promise for low temperature spontaneous loss of hydrogen were certain activated imidazole compounds. Early in the Center's tenure, it was recognized the dihydrobenzimidazoles had potential for exothermic release of hydrogen. A few members of this family were synthesized, characterized, and subjected to conditions where catalytic release of hydrogen was thought to be possible. Indeed, hydrogen could be rapidly released from 1,3 dimethyldihydrobenzimidazole in an organic solvent in the presence of acetic acid and a Pd catalyst as shown in Figure 1.3.3 below. The thermodynamic properties of this reaction was studied, and hydrogen release was found to be strongly exothermic and exergonic

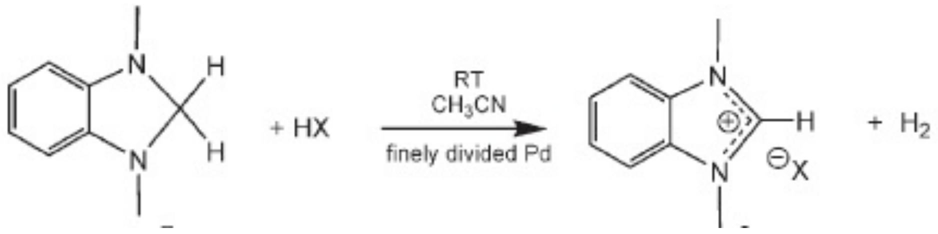


Figure 1.3.3. Reaction scheme indicating the dehydrogenation of a benzimidazole in the presence of a weak acid (acetic acid = HX) and a Pd catalyst to generate hydrogen and a benzimidazolinium salt.

with delta H being -44 ± 12 kilojoules/mole. This is consistent with the reaction proceeding even under 3.5 atm. pressure of hydrogen. Thus these hydrogen release reactions, while facile, are not reversible with hydrogen pressure alone, and so regeneration would also require off board chemical processing. This, in addition to the inability to increase the hydrogen weight fraction substantially above 1.3 wt. %, the Center discontinued this line of research.

1.4.3.2 Coupled Chemistries

Summary. The goal of this section of work was to develop materials that could be tuned to give near thermoneutral hydrogen release and uptake. These materials were not down selected as the temperature of release was too high (> 200 °C) and the gravimetric capacity was too low. This work resulted in the issue US patent 7,736,531. More information on this activity can be found in the Final Report from Los Alamos National Laboratory.

The coupled chemistries focused on the release of hydrogen from $Mg(OMe)_2/H_2O$. This system involves on-board conversion of magnesium methoxide and *in situ* CO_2 capture with the products being H_2 and magnesium carbonate:

$$Mg(OCH_3)_2{\cdot}MgO + 3H_2O \rightarrow 2Mg(CO_3) + 6H_2$$

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.

1.4.3.3 C-N Polymer Systems

Summary. The goal of this section of work was to develop materials that could be obtained from common feedstocks such as hydrocarbons and yet would meet all of the DOE targets. These materials were not down selected, as they could not meet gravimetric targets. More information on this activity can be found in the Final Report from the University of Alabama.

The University of Alabama developed C-N oligomer and carbene-based reversible systems based on thermal release of hydrogen. As for other $C\text{-}H_x$ systems explored, it is difficult to release more than one hydrogen atom per carbon atom, or one H per $–CH_2$- unit, thus it is unlikely that such systems will ever exceed more than 7 wt. % hydrogen, and thus have little potential for achieving DOE's gravimetric targets.

1.4.4 Exothermic Chemical Hydrogen Storage Materials

The majority of the work by the Center has focused on exothermic chemical hydrogen storage materials and ammonia borane / ammonia borane based materials in particular. In this section we review our work dealing with sodium borohydride, metal boron nitrogen materials, metal amidoboranes, ammonia borane, and polyhedral boranes.

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 from AB: 1) thermolysis from the solid state material, 2) thermolysis from nanoporous composites,[2,3] 3) thermolysis in ionic liquids,[4,5] and chemical additives to promote dehydrogenation of AB, and 4) catalytic dehydrogenation of solutions of AB. Center partners published early results from acid,[6] precious metal,[7] and base-metal catalyzed dehydrogenation of AB[8] and have reviewed the topic of catalyzed release of hydrogen from AB.[9]

1.4.4.1 Aqueous Hydrolysis of Boron Hydrides

Sodium Borohydride

Summary: The goal of this work was to determine if hydrolysis of sodium borohydride (SBH) could achieve DOE's 2005 system targets, and to determine whether the spent fuel could be regenerated efficiently. At a high enough concentration of SBH in water to achieve the capacity target, the spent fuel sodium borate precipitated from solution. This resulted in a no go decision for SBH hydrolysis. More information on this decision is available in a report.[10]

An early focus in the Center was an investigation of the *Hydrogen on Demand System* as conceived by Millennium Cell. At the start of the Center it was suggested that Millennium Cell's approach showed promise to meet the rate and mileage targets set by DOE for 2005. A critical technical barrier was determined to be the efficient and economic regeneration of the spent fuel. A report on this approach, and DOE's decision to defer additional research on this approach may be found in the DOE SBH Down Select Report.[9]

Sodium borohydride has long been a topic of active chemical research, primarily because of its utility as a reducing agent in organic and pharmaceutical chemistry.[11] The potential for SBH as a hydrogen storage source was recognized as early as the 1950's.[12] The major use of SBH today is as a reducing agent in many chemical processes. [13,14,15,16,17,18] Millennium Cell reviewed[19] existing synthesis routes to SBH, and concluded that electrochemical routes may be promising to provide SBH in a cost effective process, and suggested that further research be performed in this area.

SBH is stable in dry air for months, however; aqueous SBH solutions tend to decompose slowly such that stabilizers such as NaOH (3 wt%) are added to increase shelf life of SBH solutions.

While the stabilized SBH solutions are caustic they are non-flammable. Passing a solution of SBH across an appropriate catalyst releases hydrogen exothermically. Catalysis is readily initiated at room temperature. The catalytic hydrolysis of SBH results in an aqueous solution of sodium borate that was proposed to be recycled off –board to regenerate the SBH.[20,21,22]

In the exothermic release (ca. ~ 300 kJ/mol SBH) of hydrogen from aqueous solutions of SBH, one half the hydrogen (theoretical 21.6 wt%) is supplied by the water. In practice solubility is a factor and aqueous SBH solutions (20-30 wt%) are capable of providing a gravimetric hydrogen storage density of 4.2-6.5 wt. % hydrogen. If the hydrogen storage material is to be recycled the spent fuel product, sodium metaborate, $NaB(OH)_4$ (or $NaBO_2 \cdot 2H_2O$), must be removed and regenerated off board. The chemistry for SBH regeneration from borate is outlined in the Regeneration chapter of this Center Final Report.

$NaBH_4 + 4\ H_2O = NaB(OH)_4 + 4\ H_2$

Millennium Cell developed a number of *Hydrogen on Demand* systems that included fuel storage and a discharge fuel tank, a catalyst bed reactor and hydrogen ballast tank, a water condenser and gas–liquid separator, a filter and fuel pump designed to provide hydrogen to a fuel cell for power application. In one collaboration, with DaimlerChrysler an experimental FC car, the *Natrium,* was developed and road tested. The H_2 generation is controllable in an exothermic reaction using a proprietary catalyst. The sodium borohydride solution is nonflammable and the H_2 generated is of sufficient purity for fuel cell operation.

In 2007 the U.S. DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program commissioned the National Renewable Energy Laboratory (NREL) to convene an independent review panel to conduct an evaluation of the status of SBH hydrolysis for on-board hydrogen storage. The down select analysis was based on the hydrolysis of an aqueous 30% by weight solution (3% sodium hydroxide as the stabilizer). Three major concerns were outlined in the decision on aqueous SBH as a storage material: (1) Questions remained about engineering a movable diaphragm in the volume exchange, single-tank bladder system, (2) The need for large amounts of water on board the vehicle were a concern and (3) The potential precipitation of SBH from a 30 wt% solution (solubility limit at room temperature) before the reaction and precipitation of sodium borate ($NaBO_2$) from the saturated concentrated aqueous solution at ambient temperatures following the completion of the hydrogen release process. This latter problem could be mitigated by of course using a more dilute SBH starting concentration, but then this results in a reduced hydrogen weight fraction. These concerns resulted in a No-Go decision[9] for SBH and further development was halted.

Significant research into the electrochemical regeneration of sodium borohydride was carried out at PSU in conjunction with Dow and LANL. These studies indicated that no aqueous electrochemical reduction experiment demonstrated convincing evidence of BH_4^- formation. In addition to the typical indirect and direct electrochemical reductions (mostly discussed in patents), attempts were made to overcome electrostatic repulsion of BO_2^- ion from the cathode, considered to be a major issue facing aqueous reduction. This work was discontinued after the SBH no-go decision. Before any additional future work is considered in this area, it should be borne in mind that if the reduction experiments produced any BH_4^-, the current efficiency was well below 1%. Thus, a spectacular improvement would have to be realized even before an aqueous, electrochemically- based process could be considered practical.

Polyhedral Boranes

Summary: Hydrolysis of polyhedral boranes offered a technical alternative to sodium borohydride hydrolysis, particularly in the area of catalysis of the hydrogen release steps. This area of research was linked to the SBH go/no go decision, as many of the same issues regarding borate solubility and regeneration are similar for the polyhedral boranes. This area of research was discontinued with the SBH no go decision. More information on this area can be found in the Final Reports from the University of Missouri and the University of Pennsylvania.

Hydrolysis of polyhedral boranes and ammonia triborane were believed to offer advantages in solubility, reactivity, and catalytic conversion over aqueous sodium borohydride when the Center began this line of research. As the Center evolved and the problems with the hydrolysis of SBH became better understood, 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 in the energetically intensive process of regenerating B-H bonds from B-O bonds of the spent fuel borate materials.

The University of Pennsylvania undertook research on the hydrolysis of ammonia triborane.[23,24] This work demonstrated that iodine oxidation of $B_3H_8^-$ in glyme solution produced (glyme)B_3H_7. Subsequent displacement of the coordinated glyme by reaction with anhydrous ammonia provided a safe and convenient preparation of ammonia triborane, $NH_3B_3H_7$. Studies of the hydrolysis of ammonia triborane to release hydrogen showed that upon the addition of acid or an appropriate transition metal catalyst, aqueous solutions of $NH_3B_3H_7$ rapidly release hydrogen, with 6.1 materials-wt% H_2-release being achieved from a 22.7-wt% aqueous solution of $NH_3B_3H_7$ at room temperature in the presence of 5-wt% Rh/Al_2O_3 (1.1 mol% Rh). The rate of H_2-release was controlled by both the catalyst loadings and temperature.

$$NH_3B_3H_7 + 6H_2O \rightarrow NH_4^+ + 3BO_2^- + 2H^+ + 8H_2 \qquad \textbf{9.7 wt \%}$$

The University of Missouri studied the catalyzed aqueous hydrolysis $B_{10}H_{10}$, $B_{11}H_{14}$ and $B_{12}H_{12}$ salts (5.7, 6.3 and 5.7 wt% respectively for the Na salts) using Rh, Co and Ni based catalysts.[25] The rates of hydrogen release depend on the polyborane concentration and the active surface area of the catalyst with $B_{11}H_{14} > B_{10}H_{10} > B_{12}H_{12}$. The Arrhenius parameters derived from the rates

$$Na_2B_{10}H_{10} + 32\ H_2O \xrightarrow{\text{catalyst}} 2\ NaB(OH)_4 + 8\ B(OH)_3 + 21\ H_2 \qquad \textbf{5.7 wt\%}$$

$$NaB_{11}H_{14} + 34\ H_2O \xrightarrow{\text{catalyst}} NaB(OH)_4 + 10\ B(OH)_3 + 24\ H_2 \qquad \textbf{6.3 wt\%}$$

$$Na_2B_{12}H_{12} + 38\ H_2O \xrightarrow{\text{catalyst}} 2\ NaB(OH)_4 + 10\ B(OH)_3 + 25\ H_2 \qquad \textbf{5.7 wt\%}$$

$$NaBH_4 + 4\ H_2O \xrightarrow{\text{catalyst}} NaB(OH)_4 + 4\ H_2 \qquad \textbf{6.5 wt\%}$$

of the aqueous phase hydrolysis of the polyboranes as a function of temperature suggested that the mechanism was similar to the mechanism of metal catalyzed hydrolysis of metal borohydrides.

The Rh based catalyst ($RhCl_3$ precursor) was the most active for releasing hydrogen. At 80 °C, nearly 90% of the available hydrogen from $B_{10}H_{10}$ or $B_{12}H_{12}$ was released in ca. 10 and 60 min respectively. The advantage of polyborane salts is they are non-toxic and stable in neutral pH aqueous media. While the DOE total-system H_2-storage targets for transportation do not appear to be attainable from hydrolytic-based chemical hydrogen storage systems, they can provide a means of safe hydrogen generation that should be competitive with hydrolysis of either NH_3BH_3 or $NaBH_4$ for other applications having less stringent weight requirements. Full descriptions of this work are included in the final reports of the Center partners: the University of Pennsylvania, University of Missouri and LANL.

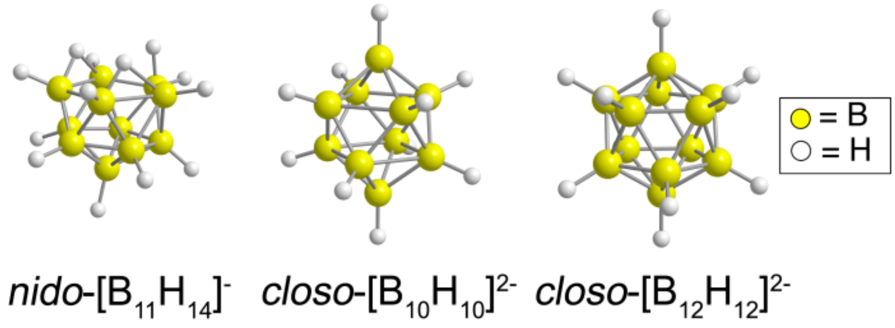


Figure 1.3.5 Polynuclear borane anions investigated in this study.

1.4.4.2 Neat AB Thermolysis to Release H_2.

Summary: Neat, solid AB thermally dehydrogenates. During dehydrogenation, the material foams and evolves gas phase impurities to such an extent that it was felt there was no path toward an engineered system using pure AB as the storage material. Mitigating both of these properties of the neat material are required to meet DOE technical targets. Methods of partial mitigation of impurities generation were identified, and are discussed below in the subsections that deal with 'scaffolds' and 'additives'. See the Final Report from Pacific Northwest National Laboratory for more details.

Solid AB dehydrogenates thermally. The rates are low at 85 °C, but at temperatures above 130 °C, AB releases 9wt.% hydrogen with an average rate of $0.1 gH_2/s/kg$ AB. Hydrogen release via thermolysis is thought to proceed by a series of stepwise reactions each liberating one equivalent of hydrogen per mole of AB:

$n\mathrm{NH_3BH_3} \rightarrow (\mathrm{NH_2BH_2})_n + n\mathrm{H_2}$ (<100 °C)

$(\mathrm{NH_2BH_2})_n \rightarrow (\mathrm{NHBH})_n + n\mathrm{H_2}$ (>100 °C)

$(\mathrm{NHBH})_n \rightarrow n\mathrm{BN} + n\mathrm{H_2}$ (>500 °C)

Our Center's research has shown that these steps overlap to give the release of non-integer equivalents of hydrogen and a complex mixture of straight, branched, and cyclic structures (Fig. 1.3.8). Solid-state 11B NMR spectroscopy shows that the spent fuel contains a mixture of $\mathrm{BH_4}$, -$\mathrm{BH_3}$, =$\mathrm{BH_2}$, =BH-, and $\mathrm{sp^2}$ boron sites.

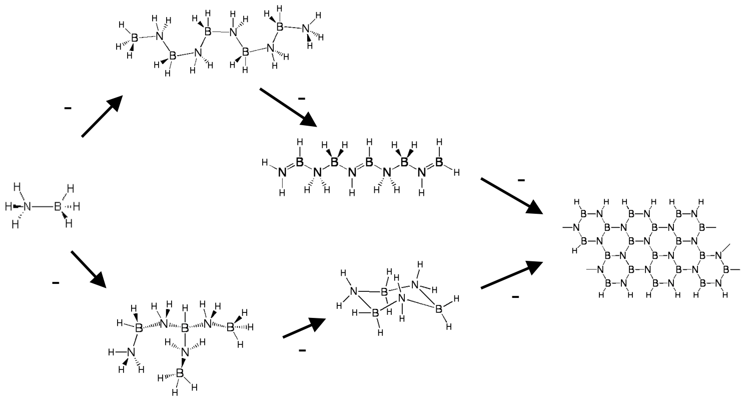


Fig 1.3.8. Schematic representation of AB dehydrogenation to give linear, branched and cyclic products with various hydrogen contents.

Because the onset of dehydrogenation is at a relatively low temperature, an initial concern was whether AB had sufficient shelf life stability at 50 – 60 °C (the DOE 2010 and 2015 targets for shelf life stability, respectively). Extensive shelf life and kinetics studies using thermogravimetry and calorimetry were fit to Avrami nucleation and growth kinetics models, and it was concluded that shelf life is not a significant concern for pure, solid AB. The details of the measurements, models, and results of AB thermal stability in the range of 40-70 °C are found in PNNL's final report.

Solid AB has a volumetric capacity of around 0.12 g $\mathrm{H_2}$/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 $\mathrm{H_2}$/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 equivalents of hydrogen being liberated per mole of AB.

There is a concern over impurities in hydrogen generated from solid AB, particularly ammonia and borazine (BZ). In a scoping experiment, a PEM fuel cell was conditioned using pure hydrogen (99.999%) and stabilized before switching to hydrogen generated from ammonia borane that was known to contain large concentrations of borazine, and likely other contaminants. The fuel cell current was monitored at a constant voltage of 6 V. When the hydrogen from ammonia borane thermolysis was introduced there was an immediate impact on the fuel cell current, with 30 % loss in current observed in the first few minutes after switching. All current is completely lost after 3 hours on stream in hydrogen from AB. This experiment indicated that considerable work had to be done to understand the nature of the impurities, and how to mitigate them. Details may be found in LANL's final report.

Borazine is known as a reversible poison on fuel cell electrocatalysts, and ammonia reacts irreversibly with the acidic polymer electrolyte to form ammonium ions, with concomitant loss in proton transport and fuel cell performance. Thus, both of these impurity components must be mitigated by either physical or chemical means.

Chemical analyses of the impurities and their concentrations in the hydrogen generated from pure solid ammonia borane indicates that a gas scrubbing technology will be required in order to supply fuel-cell grade hydrogen to a PEM fuel cell. It is therefore necessary to accurately quantify these impurities in order to appropriately size the required scrubbing technology. A useful method for simultaneously quantifying ammonia, borazine, and diborane is infrared IR spectroscopy.

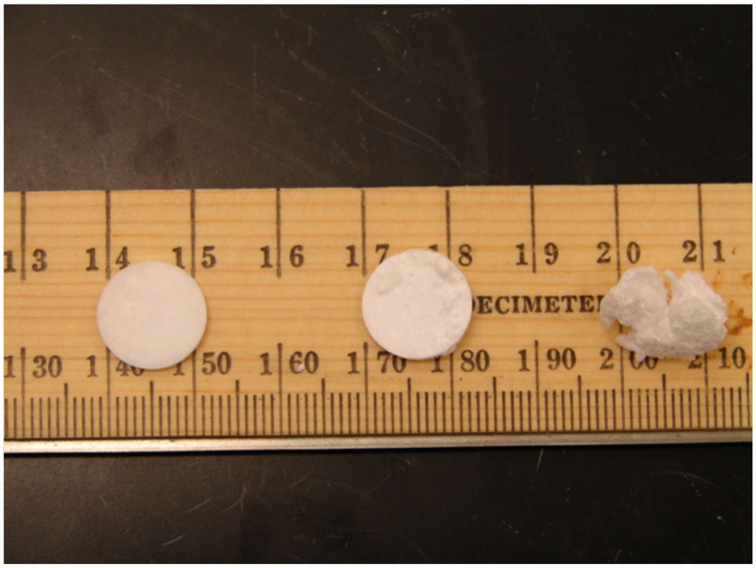
The sampling conditions of diborane and borazine are critical for accurate determination of these impurities. Borazine is known to polymerize easily at temperatures above room temperature and this can lead to quantification errors. It is therefore critical for accurate quantification that the temperature of the analysis cell and all associated hardware is maintained at room temperature. We employed a two-meter IR cell interfaced with a thermogravimetric analysis (TGA) and a mass spectrometer (MS). The system tubing was kept to a minimum and was maintained at room temperature (i.e., unheated) throughout the entire experiment to ensure no borazine was lost by polymerization on the surface of the analytical hardware.

To quantify the levels of ammonia, borazine and diborane, an IR response was calibrated against known concentration standards of ammonia, borazine and diborane gas. Then samples of ammonia borane ranging from 4 – 10 mg were heated in the TGA at a rate of 0.1 ºC per minute, from 30 ºC to 200ºC. Argon at a flow rate of 50 sccm was used as the purge gas to sweep the gas phase products into the room temperature IR cell. The time/temperature dependent IR spectrum was collected to establish the mass of each impurity produced from ammonia borane as it is heated. Based upon the data collected 10-20% of the volatiles released from ammonia borane are impurities that must be efficiently removed by an appropriate scrubbing technology to remove impurities to the level that will not harm a PEM fuel cell membrane or catalyst.

Because of the significant evolution of borazine from solid AB, and the foaming problem, work on pure solid AB was halted in favor of other compositions containing additives that are able to mitigate foaming and partially mitigate evolution of borazine during hydrogen release. These approaches are discussed below.

1.4.4.3 Solid AB with antifoaming additives.

There are several significant issues with solid AB that the Center addressed. One is the increase in volume that the solid undergoes upon liberation of hydrogen. PNNL explored over 50 different mixtures and down selected methyl cellulose (MC) as a most promising antifoaming agent. MC was selected since it was inexpensive, readily available, and did not impact hydrogen release other than suppressing the foaming. PNNL found that 15 wt. % MC/AB essentially eliminated foaming when properly prepared (Figure 1.3.9).



1.3.9 Pellets of 15 wt. % MC/AB essentially eliminate foaming. Left to right: before hydrogen release, post hydrogen release and neat AB upon hydrogen release.

Pure solid AB, as mentioned above, decomposes at temperature after an incubation period. The kinetics of incubation and decomposition fit well with an Avrami model of a nucleation and growth process. Under such circumstances, the nucleation event is related to the generation of a reactive intermediate that upon reaching a critical concentration switches from the ‘incubation’ to a ‘growth’ phase, being then the steady release of hydrogen in the case of AB. Eliminating or minimizing the incubation period is important to achieving the desired control and rates of hydrogen release from AB.

Various additives were shown to reduce or eliminate the induction period and decrease the release temperature. Materials tested included DADB (di-ammoniated diborane, the ionic ‘dimer’ of AB), NH_4Cl, $NaBH_4$ and others. DADB was determined to have the largest impact on increasing the rate of hydrogen release from AB, but at the expense of reducing the stability for shelf life considerations.

As noted earlier, the dehydrogenation of AB is exothermic and so thermal management of the process is crucial to the success of on board solids handling approach. And of course, the handling of solids on board to control hydrogen generation is a challenge, as is the on boarding of fresh fuel and off boarding of spent fuel. These solids handling challenges still require novel solutions to materials engineering and systems engineering that are being addressed to the Hydrogen Storage Engineering Center.

For methylcellulose (MC)/ammonia borane mixtures, the weight loss with respect to ammonia borane mass, was 29% which is similar to that observed with AB samples purchased from Aviobor. However, the relative amounts of the impurities were different. The ammonia released is somewhat larger than with the pure ammonia borane samples. In contrast, there is a reduction in the amount of both borazine and diborane generated.

1.4.4.4 Thermolysis of known intermediates from AB dehydrogenation.

As part of the Center's studies on AB thermolysis, results from known intermediates along the hydrogen release pathway from AB have been incorporated into the summary database in the Appendix. 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-$(BH_2NH_2)_5$,[26] and subsequently on to cyclotriborazine $(BH_2NH_2)_3$.[1] The hydrogen release properties of these compounds have been measured. 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.

1.4.4.5 AB-Scaffold Composites

Silica Based Scaffolds

Summary. The goal of this section of work was to improve the kinetics of hydrogen release from solid ammonia borane using mesoporous supports. These materials were not down selected, as they were less likely to meet the gravimetric targets. The Final Report from Pacific Northwest National Laboratory contains more information on this topic.

Ammonia borane may be impregnated in the mesoopores of a support such as MCM-41 or SBA-

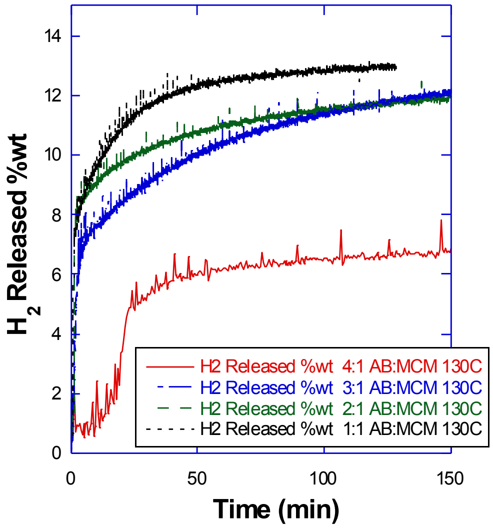


Figure 1.3.10 Isothermal hydrogen release from n:1 AB:MCM-41 normalized to AB at 130 °C

15, two high surface area forms of silica (SiO_2). Center research found that the release of hydrogen from AB within these 'silica scaffolds' at 1:1 mixtures by weight was accelerated dramatically, 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. When the amount of AB was increased to 2:1, 3:1, or more the AB filled all the available mesopores and began sorbing onto the external surface of the scaffolds. As the AB loadings increased, AB/scaffold performance began to resemble the performance of AB (increased temperatures, increased impurities etc) and the stability decreased. Due to the weight penalties AB/silica scaffold work was discontinued as part of the Center. PNNL did continue examining the physical chemistry of these systems, but as part of their DOE-BES program. More information can be found in PNNL's Final Report.

Nano Boron Nitride Scaffolds AB was coated onto nano boron nitride (BN) nanoparticles in an effort to improve the release properties. The coating was done by ball milling AB with hexagonal boron nitride in mixtures ranging from 1:4 to 4:1 AB/BN by weight. The composite mixtures of AB/BN released hydrogen at lower temperatures than neat AB, but not as low as AB in the silica scaffolds and there was a decrease in ammonia production.[27] However, hydrogen released from the composite mixture had higher amounts of BZ. Due to the increase in BZ, work in this area was discontinued. More details about this effort can be found in UC Davis's final report.

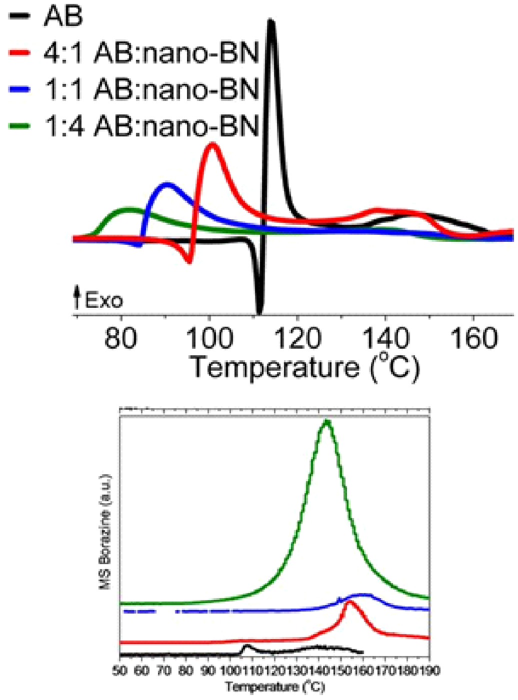


Figure 1.3.11 DSC and MS (m/e=80) Borazine for AB:BN composites showing an increased borazine yield at lower AB concentrations

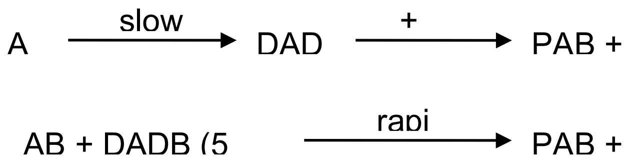
Carbon Cryogel Scaffolds Finally, AB was embedded in porous carbon cryogel. It was believed that the carbon would offer benefits over mesoporous silica such as increased thermal conduction for improved heat transfer, the synthetic procedures could be modified for variable pore diameters, and the carbon matrix would increase the gravimetric hydrogen capacity due to the lower atomic mass of carbon compared to silica. Furthermore, the surface chemistry of the carbon materials can be altered for potential catalytic effects. AB in cryogels showed enhanced hydrogen production rates up to 1.5 hydrogen equivalents at temperatures as low as 90°C while suppressing BZ yields. However, the exothermicity in the dehydrogenation reaction increased from -25kJ/mol for neat AB to -120 kJ/mole for AB in carbon cryogels and AB in the cryogels was destabilized at room temperature. The work in this area was discontinued. Additional information can be found in PNNL's Final Report.

1.4.4.6 Solid AB with Additives

Summary. The goal of this section of work was to improve the kinetics of hydrogen release from solid ammonia borane and to reduce both the foaming and release of impurities. Results look promising but must be considered in conjunction with any regeneration scheme. Additional information is available in Pacific Northwest National Laboratory's Final Report.

The slow release kinetics and presence of copious gas-phase impurities generated during thermolysis of AB prompted the Center to investigate additives to mitigate these drawbacks. This section describes the outcomes of these studies where the material is predominantly AB and the additive (typically less than 10 wt%) is designed to improve the kinetics or hydrogen purity. Further results of mixed systems containing AB (e.g. AB + methylamine borane or AB + metal borohydrides) are described in later sections.

Additives which were found to improve the rate of H_2 release were the diammoniate of diborane (DADB, $[NH_3BH_2NH_3]^+ [BH_4]^-$), ammonium chloride, $LiNH_2$, LiH, Proton Sponge (PS, bis(dimethylamino)naphthalene),$NiCl_2$ and $CoCl_2$. The use of DADB and NH_4Cl was identified by detailed mechanistic studies that showed that DADB was a critical intermediated formed during the induction period before H_2 release. Adding 5 wt % of these additives eliminated the induction period, substantially improving the rate of release at lower temperatures (Scheme 1.3.1). A further advantage of DADB as an additive is that it has exactly the same chemical composition as AB and therefore simplifies regeneration. Center research on the synthesis of AB has discovered methods where DADB can be incorporated directly into AB as a by-product.



Scheme 1.3.1. PAB = polyaminoborane, $(NH_2BH_2)_n$.

The rate-limiting step in hydrogen release from AB appears to be the formation of DADB. Addition of a small quantity of DADB decreases the incubation period, and increases the rate of hydrogen evolution. Other additives have also been shown to work, but the mechanisms of their action are not as well understood.

$LiNH_2$ and LiH promote H_2 release through the formation of $LiNH_2BH_3$ and increase both the rate and extent of release at low temperatures. For example, at 85 °C pure AB released 0.9 equivalents of H_2 which increased to 1.5 equivalents with the addition of 5-10 wt% $LiNH_2$ or LiH. However, these additives also lead to the formation of $LiBH_4$ that limits further H_2 release at higher temperatures by trapping hydrogen in this unreactive compound. This drawback was not observed for base-promoted release using the hindered base known as 'proton sponge' which produced a comparable enhancement in H_2 release at lower temperatures and went on to release more than 2 equivalents at higher temperatures.

Metal boride additives to AB, in particular nano Co or Ni (prepared by a co-precipitation method from the corresponding chlorides) showed three beneficial effects at low levels (<5 wt%): inhibited foaming of AB upon hydrogen release, reduced the borazine yields to below the detection limit and decreased the hydrogen release temperature.[28] While measured yields of BZ heated to 200 °C are reduced significantly, $CoCl_2$ may be too active as there are questions about the thermal stability of AB/$CoCl_2$ over long periods of time at 50°C. Addition of iron chloride salts to neat AB have also been investigated and shown to have similar effects on the hydrogen release properties of neat AB. It is believed that AB reduces the $FeCl_3$ to an iron boride under the reaction conditions and the corresponding FeB catalyzes the decomposition of the first hydrogen release step to form crystalline PAB polymers. The crystalline PAB polymers may be less likely to form borazine than the amorphous PAB polymers formed in the absence of the catalyst.[29]

Further developments of additives to reduce borazine are recommended. Details on solid AB research including these additives are found in the final reports from Center Partners including PNNL, LANL, and the University of Pennsylvania. The effects of these additives on regeneration processes for AB also need to be addressed.

1.4.4.7 Liquid or Solution-based Storage Materials Containing AB

Summary: This section describes the results of the investigations into liquid formulations of ammonia borane. The goal was the development of a fluid ammonia borane system that enables the use of heterogeneous catalysts, and a reactor that is potentially easier to engineer than an onboard solid system. The outcome of the work leaves ionic liquid based systems as the prime candidates for a liquid-based AB fuel. Two patents on homogeneous catalysts for AB dehydrogenation were issued as a result of this work: U.S. 7,645,902, and U.S. 7,544,837. For additional information on these topics, see the Final Reports from Los Alamos National Laboratory and the University of Pennsylvania, and the University of Washington.

Liquid Systems Incorporating AB with Conventional Solvents

Thermal dehydrogenation of AB occurs at rates that can exceed the DOE target only at temperatures above 100 °C. One goal of our research was to develop fuels that could utilize catalysis to increase the rates of hydrogen release from ammonia borane and to substantially reduce the temperature of release while maintaining the hydrogen capacity above 2 equivalents of H_2 released. The only practical means of achieving catalysis is to place AB into solution in order to efficiently contact it with the catalyst. Solvents for AB such as tetrahydrofuran (THF) or diglyme were studied extensively during the early days of the Center, mainly to assist in catalyst screening. As it turned out, the amount of solvent necessary to maintain the precursor and spent fuel in solution renders these conventional solvent-based systems impractical based on gravimetric capacity considerations alone. For this reason, the suitability of AB in solvents against the various DOE targets was not studied. However, solutions of AB were a useful platform for exploring and screening both homogeneous and heterogeneous catalysts. Numerous homogeneous catalysts for the dehydrogenation of AB were examined. Trends in the catalytic dehydrogenation activity of various catalyst compositions were determined and this guided additional catalyst design. Catalyst compositions were 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 were measured. Dramatic differences in catalytic activity were observed among various classes of homogeneous catalysts. For example, a class of catalysts that are based upon Ir or Co coordinated to 'pincer' ligands release only one equivalent of hydrogen per mole of AB, but the rate of release is greater than 10 times the DOE target rate *even at room temperature*. Other classes of ligands result in a wide range of activity, but that release two equivalents of hydrogen. A few of these classes of ligands are discussed below, and are discussed in detail in the LANL and University of Washington final reports.

Numerous examples have now been reported of metal-catalyzed H_2-release from ammonia borane in conventional solvents, many contributions are from this Center.[6,7, 30] Trends in the catalytic dehydrogenation activity of various catalyst compositions were 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 were found that give rise to the release of either one or two equivalents of hydrogen per mole AB (Figure 1.3.12), and the kinetics of these two release pathways have been measured. LANL prepared several different catalytic systems based upon both precious and non-precious metals. This work was instrumental in developing an understanding of the mechanism of metal catalyzed hydrogen release from ammonia borane.

Homogeneous 1st row transition-metal-based catalysts are active for dehydrogenation of ammonia borane. Addition of AB to an active catalyst formed *in situ* from the reaction of $Ni(cod)_2$ and 2 equiv of an appropriate N-heterocyclic carbene (NHC) ligand rapidly evolves H_2 at 60 °C. Using a gas burette to quantify the gas evolved, 29 of a possible 31 mL of H_2 for 3 equiv of H_2 was produced, equating to >2.5 equiv of H_2 from each mole of AB. Kinetic isotope effects of deuterated derivatives of AB suggest that both N-H and B-H bonds are being broken in the rate-determining step(s).

Strong Lewis and Bronsted acids initiate dehydrocoupling of ammonia borane under mild conditions that includes a novel hydride abstraction pathway. The reaction is carried out in the presence of $B(C_6F_5)_3$ or a protonic acid (e.g., trifluoromethanesulfonic acid). The formation of acyclic aminoborane oligomers by chain transfer is followed by facile dehydrocyclization at > 60 °C to yield borazine and additional hydrogen. Boronium borohydride $[BH_2(NH_3)][BH_4]$, implicated in thermolysis of AB in ionic liquids, is structurally similar to the boronium cations discussed in this study. A proposed mechanism is supported by an examination of the reaction thermodynamics using density functional theory, in which non-volatile acids or solid acids are proposed that can initiate dehydropolymerization of AB.

In situ ^{11}B NMR monitoring of reaction solutions, computational modeling, and external trapping studies show that selectivity and extent of H_2 release in metal-catalyzed dehydrogenation of ammonia borane are determined by coordination of reactive aminoborane, NH_2BH_2, to the metal center.

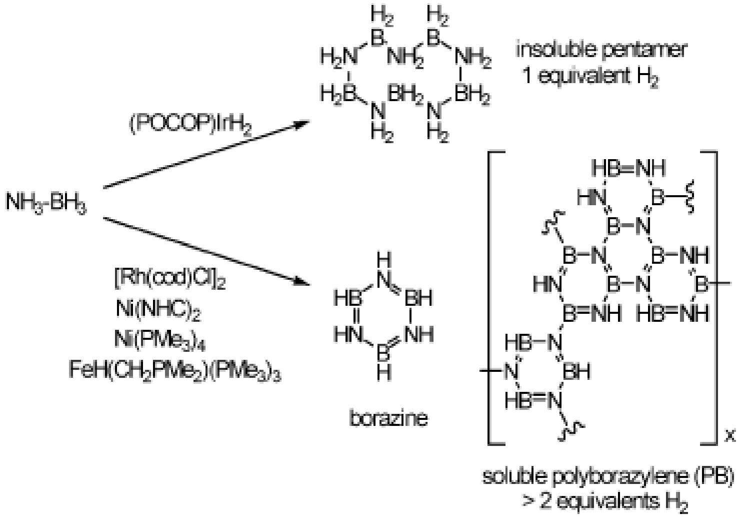
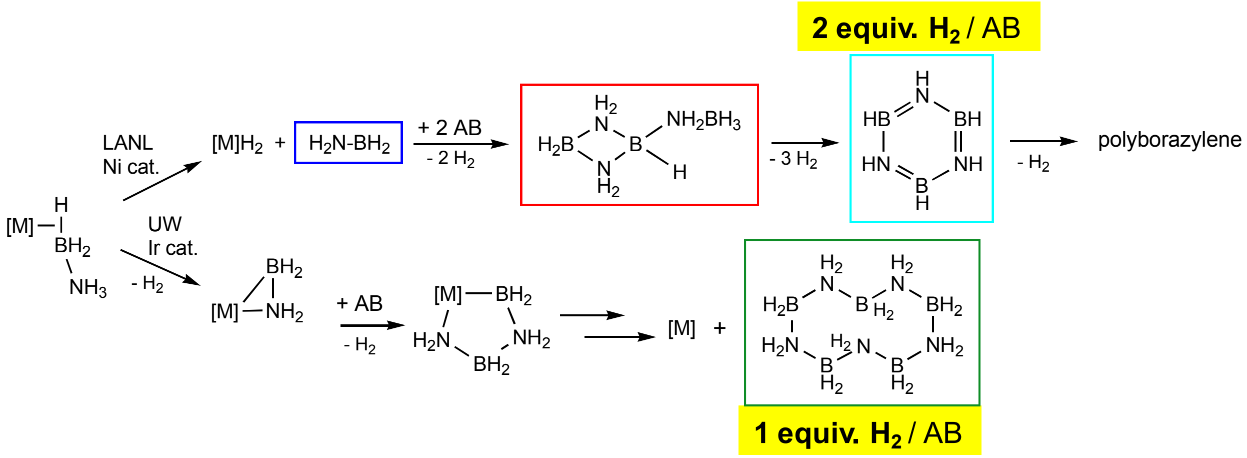


Figure 1.3.12. Selectivity in metal catalysts AB dehydrogenation with different catalysts

Overall this work and the work of other research groups both inside and outside the Center lead to a mechanistic description of metal catalyzed hydrogen release from ammonia borane that proceeds by one of two paths. After coordination to the transition metal the hydrogen releases from the B-N species and either the hydrogen leaves and the BN fragment remains coordinated to the metal or the B-N moiety leaves and the hydrogen remains coordinated to the metal. If the BN fragment remains on the metal it generally undergoes further BN insertion reaction leading to the loss of a single hydrogen molecule per AB. When the B-N moiety leaves the metal center it can undergo further dehydrogenation reactions leading to greater than 2 equivalents of hydrogen released. This mechanistic evidence is shown in the scheme below.



While homogeneous catalysts are of scientific interest, the Center's engineering-guided assessments indicated that a heterogeneous catalytic reactor would be more desirable than a homogeneous reactor system. Ease of catalyst separation from the spent fuel, as well as the simplicity of heterogeneous reactor control were the major reasons for choosing to search for heterogeneous catalysts for the dehydrogenation of ammonia borane.

Heterogeneous catalysts such as platinum supported on alumina were examined. Dehydrogenation of AB catalyzed by transition metal heterogeneous catalysts was carried out in non-aqueous solution at temperatures below the standard polymer electrolyte membrane (PEM) fuel cell operating conditions. The introduction of a catalytic amount (2 mol%) of platinum to a solution of AB in 2-methoxyethyl ether (0.02–0.33 M) resulted in a rapid evolution of H_2 gas at room temperature. In addition, non-precious metal catalysts were also identified. Heterogeneous base metal catalysts for hydrogen release from solvent/ammonia borane systems were prepared and demonstrated to have high rates (2x the DOE target rate) of release and greater than 9 wt% H_2 at 70 °C. However, the spent fuel solutions generated insoluble solid products that would foul the catalyst. While this type of catalyst fouling was reversible, the inability to generate solvents of high enough concentration to meet the gravimetric target led the Center to discontinue this line of research except for catalyst screening purposes. More information about this research can be found in University of Washington's and LANL's final reports.

Thermolysis of ionic Liquid Solutions of AB

A promising AB composite mixture system studied by the Center partner, the University of Pennsylvania, consists of AB dissolved or slurried in ionic liquids, with and without the presence of base additives such as proton sponge or metal-based catalysts. The use of these additives to promote AB H_2-release was motivated by a number of potential benefits, including (1) faster initial H_2-release, (2) better control of release rates, (3) lower temperature reactions, and (4) better control of product structure/composition, and reduced impurities. Details of this work can be found in the final reports of University of Pennsylvania and LANL.

Ionic Liquid/AB Mixtures

Ionic liquids are simply ionic salts that are liquid at around ambient temperatures. Ionic liquids have found utility as useful solvents for a variety of chemical reaction types. Because the cation and the anion chemical properties can be 'tuned' through a diversity of combinations of cation and anion, the physical properties of ionic liquids can be chosen to match the desired property most suitable for the application of interest.

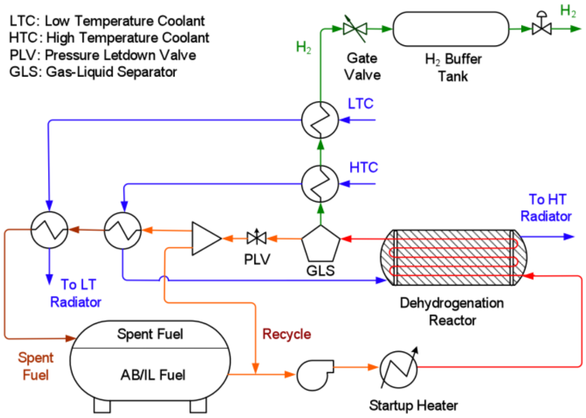
The Center first explored the utility of ionic liquids as a solvent and as an activator of AB towards dehydrogenation reactions. Subsequently, ionic liquids (IL) were found[3,4,31] to promote the rate and extent of H_2-release from ammonia borane (AB). For example, mixtures of AB with 1-butyl-3-methylimidazolium chloride (bmimCl) (50:50-wt%) at 85 °C exhibited no induction period and released 1.0 H_2-equiv. in 67 min and 2.2 H_2-equiv. in 330 min at 85°C. At the same temperature, solid AB released 0.81 H_2-equiv. after 360 minutes, and so the presence of the ionic liquid substantially increases the rate of hydrogen evolution, and removes the incubation period reminiscent of additives to solid AB discussed earlier in this report. Significant rate enhancements for the ionic liquid mixtures were obtained with only moderate increases in temperature, with, for example, a 50:50-wt% AB/bmimCl mixture releasing 1.0 H_2-equiv. in 5 min and 2.2 H_2-equivalents in only 20 min at 110°C. Increasing the AB/bmimCl ratio to 80:20 still gave enhanced H_2-release rates compared to the solid state, and produced a system that achieved 11.4 wt. % H_2-release.

Solid state and solution ^{11}B NMR studies of AB H_2-release reactions indicate that the mechanistic pathway is very similar to that of solid AB: first, ionic liquid promotes conversion of AB into its more reactive ionic diammoniate of diborane (DADB) form, followed by further intermolecular dehydrocoupling reactions between hydridic B-H hydrogens and protonic N-H hydrogens on DADB and/or AB to form neutral polyaminoborane polymers and then polyaminoboranes are dehydrogenated to yield unsaturated cross linked polyborazylene materials. The IL speeds the formation of DADB, dramatically improving the H_2 release rate.

The hydrogen produced from the AB/IL mixtures contained only trace levels of BZ and no detectable diborane as determined by IR spectroscopy. Further analysis indicated that the IL interacts with the BZ, impeding its release from the IL such that subsequent cross-linking reactions can occur, mitigating the loss of volatile BZ.

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. While these AB/IL combinations are promising, challenges remain in keeping the reaction products soluble in the ionic liquids especially when more than 1 equivalent of hydrogen is released at high AB concentrations. This is important, because work by Aardahl et al. showed that in order to meet DOE gravimetric capacity targets a minimum of 2 equivalents of hydrogen must be released from concentrated solutions of 50 wt.% AB. 50 wt% solutions of AB in ionic liquids are about the maximum concentration where the AB remains in solution, and, depending on the ionic liquid employed, the products tend to begin precipitating out. However, we only examined a few ionic liquids out of the hundreds that are available, so there is a lot more research that needs to be done to find the optimal combination. This is an area where a rapid throughput approach would be useful.

Preliminary Engineering Assessment of an On Board AB/IL System. Argonne National Laboratory prepared a preliminary assessment of an AB/IL fluid hydrogen release system. Their assessment assumed a volume exchange tank for storing fresh and spent fuel, a hydrogen buffer tank for cold start and transients, and an electrically heated startup reactor. Because of the exothermicity of the release reaction of AB, heat rejection subsystems were also sized for the reactor system. The dehydrogenation reactor was sized to enable significant recycle of cooled spent fuel through the reactor for heat removal. A schematic of the system configuration is shown below.



Argonne's preliminary assessment yielded a gravimetric system capacity of 4.9 wt. % (meets 2010 target), and a volumetric system capacity of 49.5 g H_2/L (exceeds 2015 target).

Ionic Liquid/AB Mixtures with Additives

Similar to the work with solid state AB, proton sponge (PS, 1,8-dimethylaminonaphthalene) was added to AB solvated in ionic liquids. This addition was found to be effective in increasing both the rate and extent of H_2 release and borazine levels relatively low. Reaction of AB in bmimCl containing 5.2 mol% PS showed a significantly increased H_2 release rate at 85°C, with 1.40 H_2 equiv. released within 1 h and 2.10 H_2 equiv. released at 3 hrs. Even when the amount of PS was decreased to only 0.5 mol% PS, the rate of H_2 release was found to be 0.83 equiv. at 1 hrs, 1.65 equiv. at 3 hrs., and 2.1 equiv. at 6 h. These values are high compared to those of the reaction without PS, but these rates at 85 °C are still too low to meet the DOE targets, therefore higher temperatures are required. Increasing the temperature to 110°C decreased the release time to 9 minutes for 2 equivalents. *In-situ* ^{11}B NMR studies of PS-promoted reactions in progress suggest a reaction pathway involving initial AB deprotonation to form the $H_3BNH_2^-$ anion, similar to the pathway proposed for reaction of solid-state AB with PS. The boraneamido anion can then initiate AB dehydropolymerization to form polyaminoborane polymers. Subsequent chain branching and dehydrogenation reactions lead ultimately to a cross-linked polyborazylene-type product. Model studies of the reactions of $[Et_3BNH_2BH_3]^-Li^+$ with AB show evidence of chain growth providing additional support for a PS-promoted AB anionic dehydropolymerization H_2-release process.

The Center has studied a number of metal catalysts in ionic-liquid solvents and found enhanced H_2-release from ammonia borane and Me_2NHBH_3.[32] While significant increases in the initial H_2 release rates of the catalyzed reactions for 50-wt% AB/ionic-liquids solutions were observed at 65°C, H_2 release from these concentrated solutions essentially stopped after the release of only ~1 H_2-equivalent. A higher degree of AB H_2 release was observed for the metal-catalyzed reactions with more dilute (~10-wt%) AB/ionic-liquid solutions with the release of over 2 H_2 equivalents at 65°C. *In-situ* ^{11}B NMR studies suggest that there are different mechanistic pathways for H_2 release in the uncatalyzed and metal-catalyzed reactions in ionic-liquids. Because the reactions in ionic-liquids yield lower amounts of borazine, a potential fuel cell poison, ionic-liquid solvents are favored over conventional solvents for metal catalyzed AB H_2-release. There are several challenges to using a homogeneous metal catalyst in this system. If a homogeneous catalyst is used, separation of the catalyst from the spent fuel mixture prior to regeneration is a challenge. Also, if the homogeneous catalyst is mixed with fresh fuel and ionic liquid, then it may be a challenge to meet the 50 °C shelf life target. Heterogeneous catalysts avoid many of these challenges by enabling physical separation of the fuel mixture and the catalyst, and are therefore preferred in many situations. However, reactor design becomes more difficult because there is now three phases involved- solid (catalyst surface), liquid (AB in ionic liquid) and gas (hydrogen produced). Designing reactor systems that mitigate the challenges of such three-phase is expected to be difficult. In addition, reaction products can precipitate onto the catalyst surface blocking active sites, reducing catalyst activity. Further work is required to identify the best combination of fuel form and catalyst. Further details are available in LANL's and University of Pennsylvania's final reports.

Liquid fuels based upon ammonia borane dissolved in liquid amine boranes

Summary. The goal of this research was to provide a liquid fuel using a hydrogen donating solvent, e.g. a liquid amine borane that could also be dehydrogenated either thermally or catalytically. To date, no amine boranes having the proper physical and chemical properties to solubilize both AB and spent fuel have been found. For more information, see the Final Report from Los Alamos National Laboratory.

As we found from our experience with the SBH go/no go decision, it is crucial that a liquid fuel system does not result in precipitating solids in the spent fuel system – the fuel, spent fuel mixture must remain liquid throughout to avoid plugging of flow systems, etc. Therefore the Center searched for compositions of ammonia borane mixed with liquid amine boranes that have the widest liquid range possible, 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.% H_2:

$n\mathrm{CH_3NH_2BH_3} \rightarrow (\mathrm{CH_3NBH})_n + 2n\mathrm{H_2}$ (8.8 wt% H_2)

A mixture of 20%MeAB/AB containing impurities or additives has been shown to be a liquid down to 30 °C, which was 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 shelf life stability target. Another liquid amine borane is ethylenediamine bis borane, EDBB:

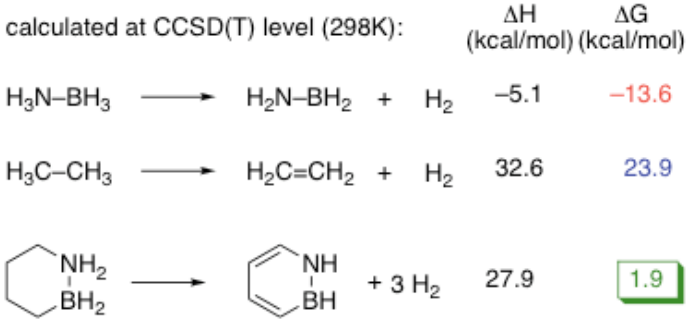
$n\mathrm{BH_3NH_2CH_2CH_2NH_2BH_3} \rightarrow (\mathrm{BHNCH_2CH_2NBH})_n + 4n\mathrm{H_2}$ (9.2wt% H_2)

Cyclo-CBN Hydrogen Storage Materials

Summary. The goal of this research was to develop coupled endo/exothermic release materials that were also potentially liquid. This research is ongoing, but has provided promising early leads. As this project continued past the end of the Center, for more information on this topic, see the scientific literature from Prof. Liu's group at the University of Oregon. A Final Report will be available upon completion of Oregon's project.

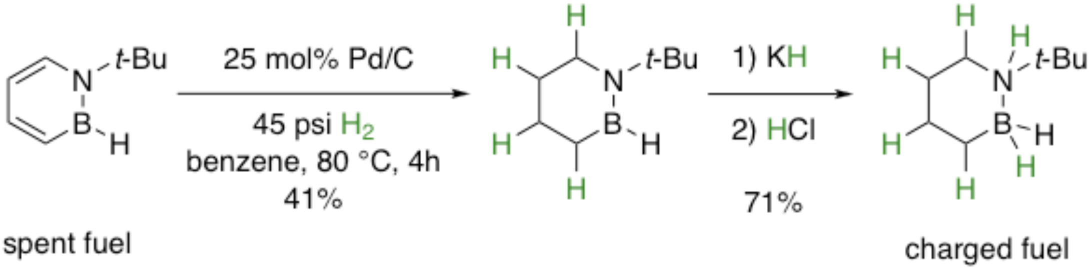
Late in the Center's tenure, the University of Oregon was added as a partner. Professor Liu contributed his research on heterocyclic boron nitrogen compounds that are composed of -H_2C-CH_2- segments and -H_2N-BH_2- segments in cyclic structures referred to as cyclo-CBN compounds. The structure of the parent cyclo-CBN compound is shown at the bottom of Figure 1.3.13. The concept for studying these materials is that even though the weight fraction of hydrogen of 7 wt. % is lower than compounds such as ammonia borane, the potential coupling of the endothermic release of hydrogen from the hydrocarbon section with the exothermic release of hydrogen from the aminoborane segment could lead to storage materials having near thermoneutral release of hydrogen. If successfully demonstrated, this approach could lead to potentially reversible storage materials. In addition, this class of compounds has the potential to provide storage materials that are liquid fuels and spent fuels.

Figure 1.3.13. Computed thermodynamics of ammonia borane, ethane, and the parent 1,2-azaborine indicating its near-thermoneutral release of hydrogen



Synthetically, the parent material as shown in Figure 1.3.13 is challenging to prepare. The t-butyl derivative is readily prepared for study as a model compound. This compound has 4.1 wt. % hydrogen. This compound has been used to address the spent fuel regeneration challenge for this class of compounds. A simple three-step process to regenerate spent fuel has been devised and demonstrated (Figure 1.3.14).

Figure 1.3.14. Demonstrated spent fuel regeneration scheme for the t-butyl derivative



Although this class of compounds exhibits overall near-thermoneutral release of hydrogen, both the forward and reverse reactions are stepwise, with the C-C segment re-hydrogenating under fairly mild conditions, whereas the B-N segment requires more forcing conditions and utilizes H^+/H^- rather than hydrogen, similar to the regeneration of spent fuel from AB.

The first fill synthesis of the t-butyl derivative has also been demonstrated in the laboratory, and simplified syntheses are being explored. The details of this chemistry for this class of cyclic CBN storage materials will be described in the University of Oregon's final report, but is also available in the chemical literature.[33]

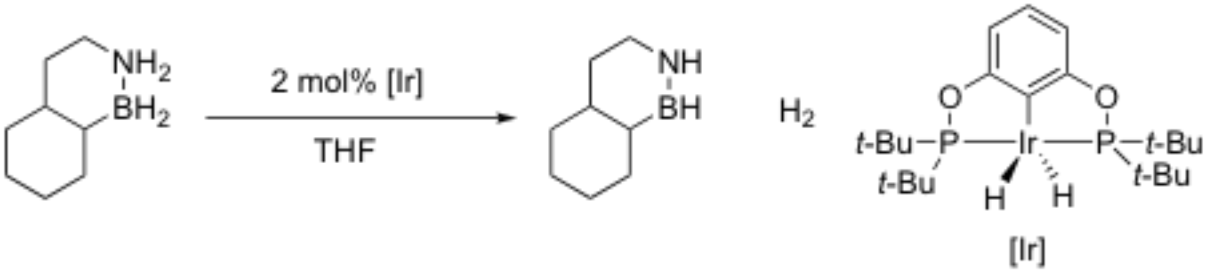


Figure 1.3.15. Dehydrogenation of a model 1,2-azaborine compound releases 1 equivalent of hydrogen at room temperature using homogeneous transition metal catalysts.

Dehydrogenation of 1,2-azaborine compounds at room temperature with homogeneous transition metal catalysts having pincer-type ligands is similar to the dehydrogenation of AB, in that 1 equivalent of hydrogen is readily released, as is shown in Figure 1.3.15 above. Additional research is needed to discover a catalyst or combination of catalysts that will dehydrogenate both the B-N and C-C segments of this class of molecules.

1.4.4.8 Storage Materials Derived from Ammonia Borane Reactions with Metal Hydrides and Metal Amides

Summary: This section describes the results of the investigations into the development of new materials that may have displayed less exothermic hydrogen release. All of the single metal amidoboranes were found to release hydrogen exothermically, and therefore cannot be regenerated on board. However, the results were promising enough that further work in specific types of metal amidoboranes is warranted. This work resulted in the issued US patent 7,713,506. For more information on these topics, see the Final Reports from Los Alamos National Laboratory, Pacific Northwest National Laboratory, and the University of Missouri.

Two approaches were investigated in which AB was combined with metallic hydrides or metal amides. In the first, physical mixtures of AB with metal hydrides, amides or borohydrides were prepared to develop new composite systems. The second approach used more reactive hydrides that reacted with AB to form new amidoborane ($NH_2BH_3^-$) complexes. One of the goals of this line of research was to search for materials that released hydrogen at near thermoneutrality. Such materials would then be likely to be directly regenerable on board with hydrogen pressure. Thus the potential benefit of discovering an on board reversible storage material was felt to justify the risk of this approach.

Ammonia Borane - Metal Hydride Composites

Mixtures containing AB which releases hydrogen exothermically, and endothermic hydrogen release complexes, metal borohydrides (MBH) and/or metal hydrides (MH), were prepared with a goal developing new hydrogen storage materials that were less exothermic than AB, and less endothermic than the metal hydrides, or borohydrides, etc. A wide diversity of reactions of AB with metal hydrides (MH = MgH_2, CaH_2, TiH_2 and/or ZrH_2), borohydrides (BH = $LiBH_4$, $NaBH_4$, KBH_4, $Ca(BH_4)_2$ or $Mg(BH_4)_2$), and lithium amide, $LiNH_2$ were explored.

The ultimate goal of this approach was to prepare new compounds that might allow of control over the thermodynamics and kinetics of high capacity hydrogen storage materials for on board vehicular storage applications. For example, in the case of reacting AB with metal borohydrides, the Center explored a wide variety of reaction conditions for the following example reactions:

$$AB + Ca(BH_4)_2 \rightarrow H_2 + ??$$

$$AB + Mg(BH_4)_2 \rightarrow H_2 + ??$$

For these AB+$Ca(BH_4)_2$ and AB+$Mg(BH_4)_2$ mixtures, experiments using TG/DSC/MS analysis indicated that hydrogen release occurred less exothermically relative to pure AB, had lower gas phase impurity levels, and did not foam during hydrogen release. This is in contrast to mixtures of AB and alkali metal borohydrides where there did not appear to be any beneficial additive effects on the enthalpy of hydrogen release. The impurity levels of borazine and ammonia were lower but not as low as in the Ca and Mg borohydride mixtures.

Combinations of AB mixed with TiH_2 (0.1 equivalent) show a remarkable drop in impurity levels of borazine and ammonia, <1% compared to neat AB. No foaming is observed during hydrogen release but there was little difference in the enthalpy for hydrogen release. Similar effects were observed for a ternary mixture of AB containing 0.5 eq. MgH_2 and 0.1 eq. TiH_2, however the hydrogen release onset temperature was lowered by ca 20°C.

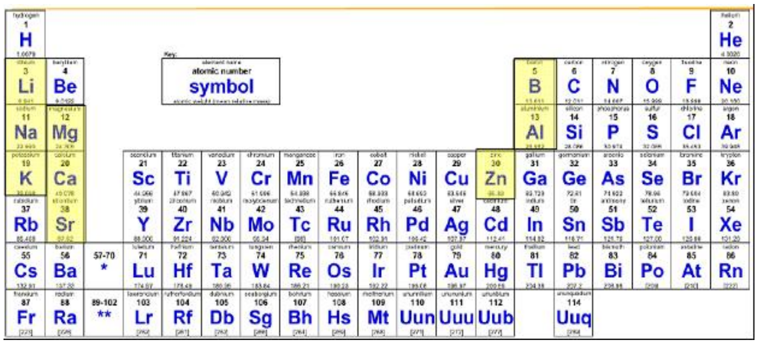
These findings suggested that this approach is a viable approach for discovering new hydrogen storage material composites with favorable properties.

Metal Amidoboranes

It was felt that one or more of the hydrogen atoms in AB could be replaced with a metal and/or other functional groups resulting in less exothermic hydrogen release relative to pure AB, perhaps to the extent that near thermoneutral release and hence on-board regeneration could be achieved. As part of the International Partnership for Hydrogen Economy (IPHE) efforts coordinated with the Center’s activities, PNNL and LANL collaborated 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, metal amidoboranes (MAB), which exhibit improved hydrogen release reactions relative to the parent compound AB. In general, MAB materials were found to have lower release temperatures, lower reaction enthalpies, no induction period, and decreased borazine (BZ) impurities.

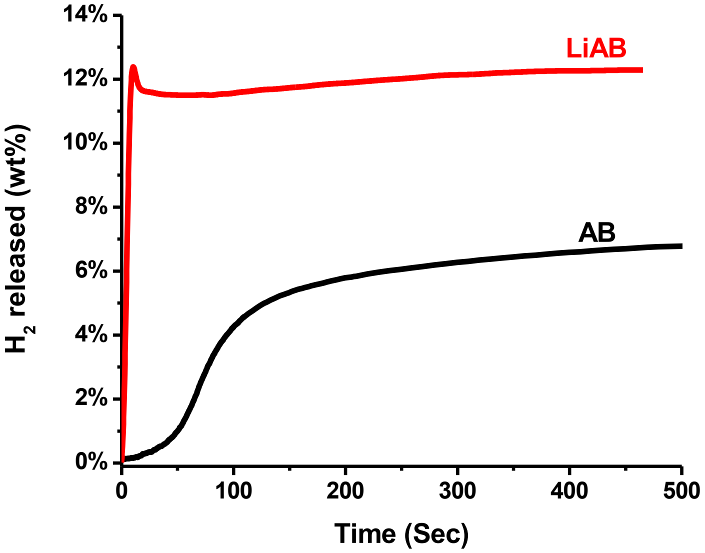
Metals explored included Li, Ti, Mg, Sc, Zn, Ca, Na, K, Sr, and Al (Figure 1.3.16). The faster reaction kinetics of release compared to AB can be seen in Figure 1.3.17 below for Li amidoborane. LiAB releases more than 11 wt% H_2 at 130 °C in approximately 7.5 s, a rate of 15 g H_2/kg/s corresponding to the reaction:

$LiNH_2BH_3 \rightarrow LiNBH + 2H_2$ 11.9 wt% H_2



1.3.16 Metals considered for M-AB studies Li, Ti, Mg, Sc, Zn, Ca, Na, K, and Al

All the monometallic MAB's studied to date were too exothermic for onboard regeneration and no path forward was identified for direct chemical regeneration so work in monometallic MAB's was discontinued. However, the results demonstrate that the properties can be tuned using this approach so the search should continue with adjustments to the strategy. Details of the MAB work are contained in the final reports by university of Missouri, LANL and PNNL.

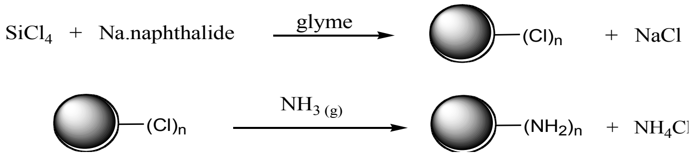


1.3.17 Hydrogen release from $LiNH_2BH_3$ (LiAB) at 130 °C compared to ammonia borane (AB).

1.4.4.9 Light Element Nanomaterials

Summary: This section describes the results of the investigations into nanoscale light element hydrides that could have met the DOE targets. None of these materials had high enough capacities, and also released hydrogen at > 200 °C, and so none were down selected. For more information on this topic, see the Final Report from the University of California, Davis.

The Center's research on hydrogen storage in and on nanomaterials involved three classes of materials studied at UC Davis: boron nanoparticles,[34] silicon nanoparticles and clathrates.[35] The target for this work was to approach the bulk composition, SiH_2, corresponding to a weight fraction of nearly 6.5 weight percent hydrogen. This value could in principle be reached in the limit as the silicon particle size decreases to the point where the material exists as $(SiH_2)_n$ clusters, and all the Si atoms of the clusters are exposed to the surface. Silicon nanoparticles were found to store hydrogen in a chemisorbed state, as discrete Si-H and SiH_2 species were observed spectroscopically. In the silicon clathrates, molecular hydrogen is physisorbed in cages at moderate (atmospheric) pressure. The targets for the silicon nanomaterials work were different size nanoparticles with compositions: $M_{1.0}H_{1.0}$, $M_{1.0}(NH_2)_{1.0}$, $M_{1-x}M'_xH_{1.0}$, $M_{1-x}M'_x(NH_2)_{1.0}$ with M, M' = B, C, Si, and C. Hydrogen capped silicon nanoparticles of the average diameter 60 nm, 10 nm, 5 nm, and 4 nm were prepared via a low temperature chemical method in order to explore the release of hydrogen from the surface as a function of size. The 60 nm and 10 nm diameter particles have only hydrogen on the surface. The 60 nm diameter particles are crystalline and the 10 nm diameter particles are amorphous by powder X-ray diffraction. The 5 and 4 nm diameter particles have both hydrogen and solvent molecules on the surface and are more resistant to oxidation while washing and when exposed to air. Weight percentages of approximately 3.5 % at 350˚C are observed for the 10 nm diameter particles. The largest weight loss is observed for the amorphous 4 nm diameter particles that show a weight loss of approximately 4.5 % that is attributed primarily to hydrogen. The silicon-doped materials were found to release hydrogen above 180°C for the 20% wt. C doped Si nanoparticles. The preparation of Si nanoparticles by room temperature reduction of $SiCl_4$ with sodium naphthalide in solution has been adapted to synthesize amine-capped silicon nanoparticles.



Infrared analysis of the material shows hydrolytic decomposition of the Si-(NH_2) interactions to form Si-O(H) bonds upon exposure to air. Amine capped materials showed significant weight loss at temperature above 100˚C. However when the resulting gas was qualitatively analyzed with a pH indicator, the gas is basic and it is presumed to be predominantly ammonia.

The synthesis of amorphous, surface-functionalized boron nanoparticles has been achieved *via* the reduction of boron tribromide with sodium naphthalenide and subsequent reaction with octanol. These B nanoparticles have not been further pursued. This work was discontinued since there was no discernable path to increasing the gravimetric capacity or reducing the release temperatures.

1.4.5 Synthesis of ammonia borane for 'first fill'

Summary. For ammonia borane to be considered a viable storage material, the cost of AB must be minimized to an acceptable level. New approaches to sodium borohydride and subsequent conversion to AB with improved yield and purity were developed. Cost analyses were performed. For more information on this topic, see the Final Report from Dow Chemical Co.

Cost efficient synthesis of ammonia borane for the 'first fill' of fuel is crucial to determining the overall life cycle costs for ammonia borane. Analysis by Center partner Dow indicated that a crucial element of fuel cost is the cost of SBH, and to a lesser extent, the subsequent conversion of SBH to ammonia borane.

There are four procedures for preparing AB described in the literature:

1. Ligand exchange of NH_3 with BH_3:THF.
2. Metathesis of NH_4X and MBH_4 in organic ethers.
3. Direct formation of diborane through I_2 and MBH_4 in organic ethers followed by complexation to *N, N*-dimethylaniline, followed by transamination with NH_3 in toluene.
4. Cryogenic metathesis of NH_4X and MBH_4 in liquid NH_3 followed by extraction and purification of AB using organic ethers.

The first approach requires making BH_3:THF using stoichiometric quantities from B_2H_6 and THF followed by ligand exchange of THF with NH_3 to yield AB. This method provides nearly quantitative yields of pure AB. However, this procedure is relatively expensive and utilizes pyrophoric and highly toxic diborane. Furthermore the production of diborane from $NaBH_4$ is inefficient and hazardous. The second method utilizes metathesis of NH_4X and MBH_4 salts which are reacted in ether solvents under dilute reaction conditions. The metathesis is the most common method to produce AB with yields up to 95%. One drawback of the metathesis method is the prohibitive costs associated with large volumes of ether solvents needed to prevent side reactions by dilution of the metathesis salts. A third approach utilizes the direct reaction of MBH_4 and I_2 to make diborane that is then complexed with *N,N*-dimethylaniline to form dimethylaniline-borane. Dimethylaniline-borane is then trans-aminated with NH_3 in toluene to form AB in quantitative yield. This method can be advantageous because the anilineamineborane does not undergo side reactions like NH_4X metathesis systems; however this system utilizes pyrophoric and highly toxic diborane. The fourth method developed at PNNL involves the metathesis of NH_4X and MBH_4 at low temperatures in liquid NH_3 to produce NH_4BH_4, which was shown to quantitatively convert to AB and H_2 when treated with organic ethers. This method produces AB in near quantitative yields and purity under concentrated conditions for both the metathesis and treatment with organic ethers. The details of this work appear in PNNL's final report.

Dow performed several process analyses examining different methods for AB synthesis. The two primary methods were metathesis of ammonium salts and SBH in organic solvents and base displacement of borane complexes with ammonia. Three metathesis processes and one base displacement processes were analyzed. All processes had advantages and disadvantages. The metathesis processes were favored over the base displacement primarily since multi-step reactions that were required are cost disadvantaged relative to the metathesis processes. The costs for the metathesis processes were all approximately the same, with SBH costs dominating the overall cost of AB production. Dow's analysis indicated that the PNNL high pressure process was more advantageous than the other processes analyzed because of the higher purity and slightly higher yield offered by this route. Full details of the analysis of AB first fill costs are included in the Dow final report.

As mentioned above, Dow identified that low cost SBH production is crucial to low cost AB first fill production. SBH is prepared by the conventional Schlesinger process (Figure 1.3.6) that is a multi-step synthesis using expensive NaH as a reductant of expensive trimethylborate resulting in byproducts, and significant energy utilization (Figure 1.3.6, lower right panel) in the production of sodium and the recycle of sodium methoxide. As mentioned earlier, Millennium Cell had suggested that electrochemical routes to the production of SBH might be cost-effective.[19] Our partners at Penn State University explored direct electrochemical methods, and were unable to achieve but minor yields of borohydride product. Details of this work can be found in the Penn State final report.

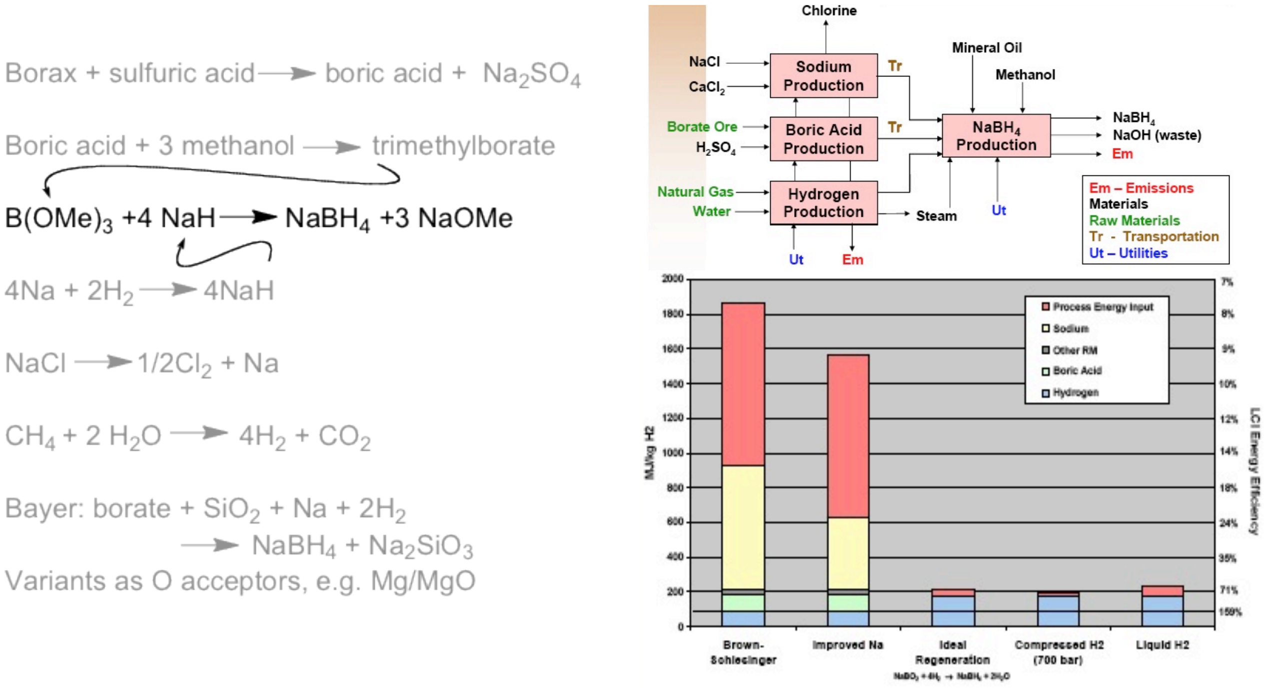


Figure 1.3.6. Schematic of the Schlesinger and Bayer processes for manufacture of $NaBH_4$ (left), and the process flow sheet and overall energy (right panels).

To avoid the use of expensive reagents, and simplify the process chemistry, Dow examined two potentially simpler processes: (i) Carbothermal reduction of borate, and (ii) metal reduction of borate. A carbothermal borate reduction process had been reported as having been developed at Idaho National Laboratory. This process consisted of reacting methane with sodium borate in a plasma reactor to form SBH with conversion of at least 40%. The presumed reaction is as follows:

$NaBO_2 + 2CH_4 \rightarrow NaBH_4 + 2CO + 2H_2$

Dow worked with INL to reproduce this chemistry, and was able to produce unidentified water reactive materials, but was not able to reproduce the SBH synthesis as originally reported by INL. After extensive troubleshooting failed to resolve the issue, a no-go decision was made for carbothermal reduction.

Dow then focused on the metal reduction of borate in a high-energy laboratory scale ball mill. A number of metal reductants were analyzed for their potential as reductants in this process. The most promising reductant appeared to be alane that reacts with sodium borate to generate sodium borohydride and aluminum metal in the presence of the appropriate ligand ‘L’. Recycling the aluminum oxide to aluminum and then to the alane-ligand complex completes the cycle. The process is shown in Figure 1.3.7.

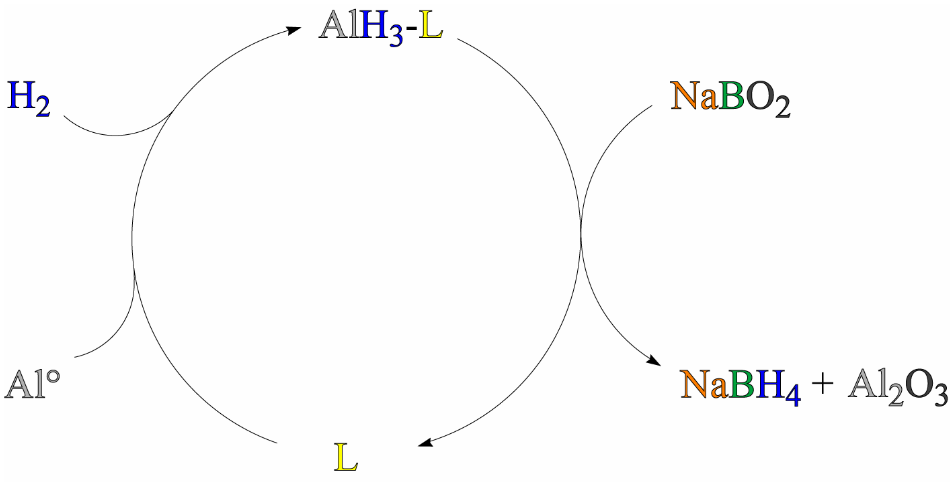


Figure 1.3.7 Metal Reduction of Borate.[36]

In the laboratory, the process had a good material balance, full accountability for all products, no intractable by-products, and isolation and purification steps were identified. High yields of 99% SBH at 99% purity were achieved. However, scaling the process in larger mills proved to be very difficult as only low SBH yields were achieved. **Dow concluded that large-scale production by reactive balling milling was problematic and examined other approaches to avoid using ball mills. Since many metal hydrides propose using reactive ball milling to make their compounds, this scale up challenge has implications for metal hydrides as well as SBH**. Other approaches examined included slurry milling, and the used of conventional solution routes and reactors. The solution based results showed the most promise. Further details are found in Dow's final report.

It is important to note that this process of cycling aluminum oxide to aluminum to alane may be amenable to 'first fill' of SBH, in other words, it may be inexpensive enough to do one time for the very first fill of AB, but it is likely not economically viable to cycle aluminum oxide to alane as a storage concept or as part of a regeneration concept.

1.5 Down Selection of Chemical Hydrogen Storage Materials

1.5.1 Down Selection Criteria

The Center developed criteria based on DOE's targets that enabled a consistent Center-wide process for down selection of the most promising materials for continued development. Selection of chemical hydrogen storage materials must be based on some criteria that are different than those for reversible systems. As an example, the majority of the Center's 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 Center, we gained experience from the sodium borohydride (SBH) go-no go decision process that took place in September 2007.[9] 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. The regeneration of borate to borohydride was also felt to be too energy intensive, as confirmed by an ANL regeneration system analysis. Thus another decision was to avoid any formation of B-O type spent fuels. This eliminated hydrolysis as a viable path forward for this Center's research.

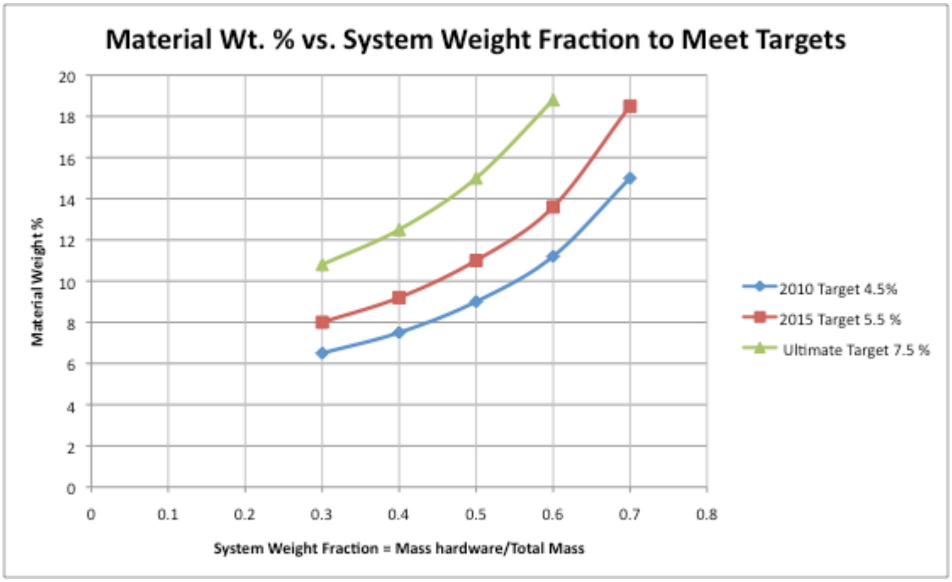
On-board system considerations and off-board regeneration were considered equally during the development of our down selection decision process. If we assume that system hardware mass is independent of material wt%, we can use the following equation to relate material wt% to system wt% for *any* hydrogen storage material:

Equation 1.5.1

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

Figure 1.5.1 below shows one way to display the system targets as a function of the materials wt. % hydrogen.

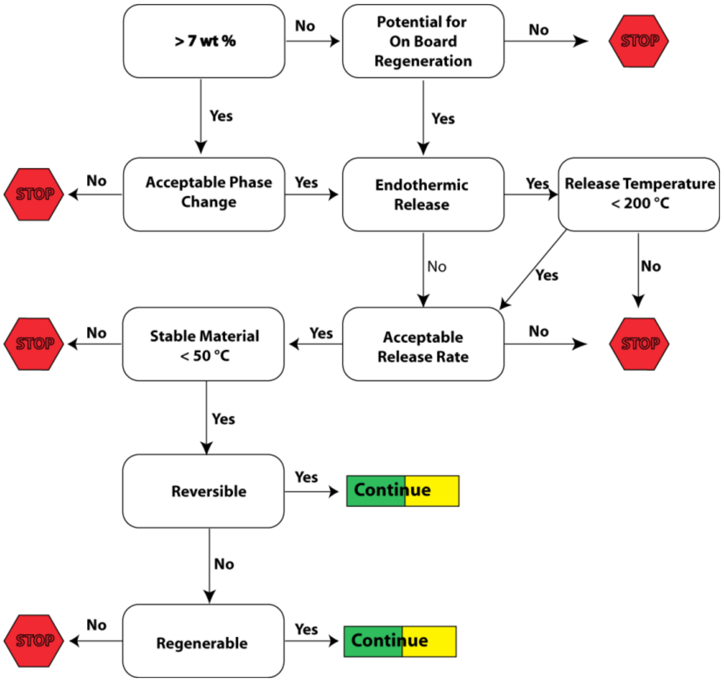
Figure 1.5.1 System Weight % vs. Material Wt. % using Equation 1.5.1



This is shown for the three target scenarios for 2010, 2015, and the ultimate target. Based upon this simple algebra, it can be seen that to meet the 2015 target, and assuming that the system weight fraction is around 50% of the total system mass which is the system hardware plus the mass of the storage material, that the material wt. % hydrogen is required to be above 10 wt. %. Based on a very aggressive system design where perhaps only 40% of the total system mass is system hardware, then to meet the 2015 target will require a material having greater than around 9 wt. % hydrogen, or 7 wt. % to meet the 2010 target. This analysis is what led the Center to set the Center's primary down select criterion for wt. % hydrogen to the value of greater than 7 wt. % hydrogen.

From this metric we developed a decision tree to consider all materials under investigation within the Center. The decision tree (Figure 1.5.2, below) includes additional criteria based on rates of release, phase changes, fuel stability, reversibility or 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. For some materials, 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, continued development is recommended, but with the requirement that necessary data for a down select be obtained first. Also, those materials that are identified as borderline cases can be considered of lower priority for future research.

Figure 1.5.2 Decision Tree for the Center’s Materials Down Selection Process



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 1.5.1 that are most relevant to the materials discovery phase of the Center’s activities.

Storage Parameter	Description	Metric
Gravimetric Capacity	Maximum calculated hydrogen weight fraction	>7 wt. %
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/maybe
Regenerability	Ability to chemically reprocess spent fuel off board	yes/no/maybe
Acceptable Phase Change	Problematic liqquid to solid phase change, or volatile byproducts	yes/no/maybe
Acceptable Release Rate	Maximum rate of hydrogen release, T< 125°C	0.02g 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 1.5.1 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 recharged 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. 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 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. PNNL's work focused on solid AB, so this decision point was not a factor in PNNL's part of the Center's work. It was included here for completeness.

Acceptable H_2 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 experiments; 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 where power = 80kW; rate = 0.02g/s/kW; mass of H_2 required for 300 mile range = 5 kg. The required rate of hydrogen release for a material to meet the kinetics target, for a 7 wt. % H_2 material, the required rate of release per kg of material is:

$$80\text{kW x } 0.02\text{g/s/kW]/5kg x } 0.07 = 0.022 \text{ g } H_2\text{/s/kg of material}$$

Note that the rate of release required for the system is a function of the weight % H_2 in the material. For a 10 wt. % H_2 material, the rate of release to achieve the technical target is 0.032 g H_2/s/kg of material.

Stable Material at 50 °C: The storage material must be stable to premature hydrogen release under storage conditions. The 2010 target for the upper end of ambient storage temperature for automotive applications is 50 °C; any material that releases hydrogen (or other contaminants/by-products) at readily measurable rates below this temperature does likely not have sufficient stability. An acceptable rate of hydrogen release under storage conditions has not been specified by DOE, however any release rate that eventually exceeds the system pressure capacity and must be vented at rates > 0.1g/h/kg H_2 stored will exceed the acceptable H_2 loss rate target.

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 thermally initiated 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 lower temperature *catalyzed* endothermic release, then this criterion is 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, the Center did not wish to deselect materials based upon impurity release. In future work, impurity levels may become more crucial in down select decisions not only because of hydrogen purity issues, but because of the additional systems that may be incurred, and also from the aspect that loss of fuel materials from the system must be readily recovered for the regeneration to be overall chemically efficient.

1.5.2 Down-Selection Process

The down select milestones were a focal point for many of the Center's activities. The Center collected materials storage performance data on a frequent basis to track progress and aid in the planning of future work. It is important to point out that the fuel regeneration processes was considered. 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.

1.5.3 Results of Down Selection of Chemical Hydrogen Storage Materials

This section summarizes the materials investigated by the Center, focusing on the significant advantages of each class and their remaining challenges. More detail can be found in the preceding section (1.3) and in the individual partner reports. A larger table with more quantitative summary data is included at the end of this report.

Down Select Decision	Materials Class	Principal Advantages	Outstanding Issues
Go	***Solid ammonia borane with additives***	• Good gravimetric and volumetric capacities • Additives mitigate foaming • Good release rates with suitable additives • Additives mitigate, to an extent, deleterious gas phase impurities • Stable at ambient conditions • Exothermic release drives high release rates	• Impurities in gas stream detrimental to fuel cell performance • Lack of solids handling technologies may limit AB and other solid storage materials that must be taken off board for regeneration • Treatment or separation of additives during regeneration needs to be demonstrated • Exothermic release generates heat that must be managed
Go	***AB in IL systems***	• Fast release possible in ionic liquid systems • Borazine is either not formed or rapidly consumed by bimolecular processes promoted by the IL • IL heat capacity contributes to heat	• Spent fuel is solid or suspension in high capacity systems • Not all ILs may be stable to regeneration conditions, and so separation of the IL from spent fuel would add to process complexity • Stability of ILs at high temperature during exothermic

		management • Regeneration demonstrated - Certain ILs compatible with regeneration conditions, mitigating need to separate IL from spent fuel • Catalysis of AB dehydrogenation in ILs demonstrated	release during long periods of usage • Heterogeneous catalysts need to be developed for the ionic liquid environment
Go	***AB with metal hydrides, metal amidoboranes,***	• Good gravimetric capacities • Good release rates • No foaming eliminates need for specific anti-foam additives • Less heat evolved during release • Gas impurities reduced or eliminated • Lower temperature of release for many M-ABs relative to AB • Opportunities to discover new compositions that are thermoneutral	• Regeneration too exothermic to enable direct regeneration with H_2 • Lack of solid handling technology for on board transfer • Feasibility of chemical regeneration unlikely; requires re-synthesis of M-H or M
Go	***Cyclo-CBN materials***	• Favorable thermodynamics, near thermoneutral release calculated • Potentially liquid fuel and spent fuel • Potentially regenerable with H_2 • Regeneration demonstrated using H_2 and chemical reagents • First fill synthesis demonstrated	• Preliminary work, more research required to better define release chemistry • Impurities not yet determined for this class of compounds
No Go	***Imidazole***	• Good rate of release at room temperature • Liquid both before and after H_2 release	• Low gravimetric and volumetric capacities with no path forward to increased capacity • Release too exothermic; regeneration requires off board chemical regeneration
No Go	***Coupled chemistries***	• Potential to use exotherms to drive endothermic	• No demonstration of mechanistically coupling to

		release	drive the thermodynamics of release
No Go	***C-N polymers***		• Theoretical weight fraction no greater than 6-7 wt. % hydrogen
No Go	***Aqueous hydrolysis***	• Good rates of H_2 release • No detrimental impurities in gas stream	• Spent products insoluble, introducing potential fuel system plugging issues • Must carry water onboard • Energy intensive regeneration of borates to borohydrides or boranes
No Go	***Pure solid AB***	• Good gravimetric and volumetric capacities • Good release rates • Stable at ambient conditions • Exothermic release drives high release rates • Off board regeneration demonstrated	• Impurities in gas stream detrimental to fuel cell performance • Lack of solids handling technologies may limit AB and other solid storage materials that must be taken off board for regeneration • Exothermic release generates heat that must be managed
No Go	***Light element nanomaterials***	• Good gas purity possible without amine capping groups	• Low gravimetric capacity • High release temperatures

1.5.4 Most Promising Categories Investigated by the Center

From our studies of chemical hydrogen storage materials, the Center has identified three materials types that show considerable promise for further development. (1) Solid AB with additives, (2) AB ionic liquid mixtures, and (3) AB with metal hydrides all possess sufficient storage capacity to suggest that system targets can be met while also showing high hydrogen release rates. These are the most promising systems of all the systems we investigated under the scope of this project. This should not be considered an all-inclusive list since we have not examined every perturbation that is possible.

(1) Solid AB with additives (to mitigate foaming and partially mitigate impurities) has many positive attributes to commend it as a viable storage compound, including one of the highest demonstrated storage capacities, and good safety and stability under ambient conditions. Consequently the Center has developed an excellent understanding of hydrogen release from AB, including identification of several major drawbacks - slow release kinetics, foaming during H_2 release, and deleterious impurities (principally borazine) in the H_2 stream. Additives such as methylcellulose

have been identified which ameliorate all of these. Further efforts are required to separate or otherwise deal with these additives during the regeneration pathways developed for AB. A large challenge remains, and that is in developing innovative solids handling technologies for moving the solids in an on board system, and in off boarding of a solid material. Chemical regeneration of spent fuel from pure AB has been demonstrated, and it is likely that the presence of methylcellulose (which is anticipated to be inert under regeneration conditions) will not provide process chemistry barriers that cannot be overcome.

(2) Solutions or slurries of AB in ionic liquids represent another class of hydrogen storage materials. IL/AB mixtures accelerate H_2 release, eliminate the incubation time, and have reduced gas phase impurities relative to other materials we have explored. On- and off boarding of liquid fuel and spent fuel appears to be more straightforward than solids handling. Liquids also enable the use of catalytic reactors, and allow for more options in heat management of these very exothermic release materials. The storage capacity is reduced by the additional weight of ionic liquid but is still sufficiently high (> 7 wt%) to offer considerable promise. Regeneration of spent fuel in the presence of ionic liquid has been demonstrated. Considerable compositional variation is yet to be explored to find the optimal ionic liquid (perhaps in combination with other reagents) to yield the broadest temperature range over which the fuel and spent fuel remain fluid. Long-term stability of an ionic liquid during repeated exothermic release cycles is a concern.

(3) AB/metal hydride systems (including amidoboranes) have been demonstrated to deliver > 10 wt% H_2 with good rates and purity. These materials are too exothermic to be regenerated with hydrogen pressure, and it is likely that chemical regeneration will require re-synthesis from the corresponding metal or metal hydride, which is known to be a very energy intensive process. However, the Center believes that breakthroughs in the search for new M-AB materials having near thermoneutral release is promising, and such a search should be undertaken.

(4) Cyclo-CBN compounds have shown some promise at an early stage of research. Much more work is required to better define the conditions for hydrogen release. Regeneration using hydrogen for the C-C segments of the molecules is readily accomplished; the B-N segment still requires chemical processing using H^-/H^+ reagents. If these materials continue to prove interesting, then clearly they are among the handful of promising chemical hydrogen storage materials this Center has explored that warrant additional research and development.

1.6 Remaining Issues and Recommendations for Future Research

Chemical hydrogen storage materials discovered and/or investigated by the Center can meet all of the DOE targets; however, no single material can yet meet all the targets. It should be emphasized that the Center's analysis showed that a minimum material gravimetric capacity of 9 wt.% is required to meet the DOE's system hydrogen capacity targets. **In other words, in our analysis, any material (chemical hydrogen storage material, metal hydride, sorbent, etc.) below 9 wt.% hydrogen cannot meet the DOE targets**. Overarching issues remain for hydrogen purity, thermal management, regeneration, and cost. Overcoming these issues will require a mixture of material discovery and engineering. In our experience, we believe the Center approach used by the DOE may be an effective mechanism to expeditiously resolve the remaining issues. This Center demonstrated that by working together, the right team of academics, industrial researchers, and national lab researchers could make far more and more rapid progress than by working apart.

The most promising candidate materials include solid AB + additives, metal amidoboranes, AB in ionic liquids with heterogeneous catalysts, and depending on the outcome of the continuing research on cyclo CBN compounds, this family of storage materials may also be worth further investigation. The Center has developed solutions to most of the challenges, but several issues remain for each candidate. We will discuss those issues in more detail.

1.6.1 Solid AB + Additives

The primary challenges for ammonia borane included release rate, foaming, gas phase impurities (principally borazine and ammonia), high exothermicity of release, solids handling (both on board and off-board), reactor design, regeneration, and cost. As detailed in PNNL's Final Report, additives have been shown to decrease ($CoCl_2$) or eliminate foaming (methylcellulose), lower the release temperature (DADB, $CoCl_2$, …), and decrease impurities ($CoCl_2$, $FeCl_3$). The University of Pennsylvania's contribution indicated that the presence of ionic liquids significantly mitigates gas phase impurities. Ideally, we would like the impurities to be completely eliminated, or at a minimum reduced to the sub ppm level from the <1% levels currently attained with $CoCl_2$ and other catalysts. In addition, $CoCl_2$ may reduce the release temperature too much, causing concern over long-term stability at moderate temperatures (50°C). Similar catalysts need to be found to further reduce impurities while maintaining stability. The kinetics of AB plus these new additives need to be understood for reactor design and modeling. The impact of inclusion of catalysts in solid AB on the regeneration of spent fuel is another unresolved issue at this time.

The high exothermicity of hydrogen release is an area that needs to be addressed. Since the exothermic release is independent of the release route (i.e. it won't be reduced with catalysts), other routes must be explored to manage the thermal energy release. For example, we have mixed endothermic materials, such as metal hydrides, with AB and found reduction in release temperature, exothermicity, impurities, and foaming while maintaining a high hydrogen capacity. Further exploration in this direction may find a set of materials that lower the exotherm to moderate levels. Alternatively, the reactor system could be engineered to manage the thermal energy rather than allow an adiabatic reaction. The Engineering Center is exploring ideas to increase heat rejection enabling nonadiabatic operation. Understanding of the heat capacity and thermal conductivity of both the fresh and spent fuel is needed. Finally, one solution is to either dissolve the AB in solution or to make a slurry mixture. The liquid provides very high thermal transfer rates making heat rejection from the reactor to a coolant easier, but the heat must still be rejected from the system that may necessitate a large radiator. AB in liquids will be discussed in the next subsection.

For a solid fuel system solids handling both on-board and off-board is an issue that needs to be addressed. The Engineering Center is engaged in understanding the system and developing solutions. Some remaining issues for study would be to determine if the fuel becomes “sticky” at elevated temperatures and developing appropriate solutions. Neat AB foams and does become sticky or tacky; however, there is evidence that AB/methyl cellulose does not. This needs to be further investigated, as does the impact of other additives. The tackiness will impact how the materials is moved both internally and during refilling where the spent fuel must be removed and fresh fuel added within an acceptable time period. Finally, the form factor (powder, compressed pellet, cartridge,…) of the fuel needs to be determined. Each form has advantages and challenges. Determining the optimum form will require a trade-off study. The Engineering Center is looking at these issues.

Associated with the solids handling, would be the development of a reactor design suitable for solid fuel. The kinetics, foaming, thermal conductivity, thermal management, form factor and materials handling all need to be considered in the design of the reactor. The Engineering Center is examining these issues and will model various reactor designs to address these issues. Another issue that remains is regeneration. AB regeneration will be dealt with in the Regeneration portion of this report. For solid AB plus additives, an additional issue will be the impact of the additives on the regeneration scheme. Questions such as, “Can the spent fuel be regenerated with the additives present? If not, how will we separate out the additives?” need to be examined. If the additives must be separated from spent fuel prior to regeneration, this will add unit operation(s) and increase regeneration complexity, efficiency, and cost.

The Center has done considerable research on understanding and lowering the price of AB. Research scale quantities of AB may be procured at a cost of around $5,000/kg. Dow has projected world scale production of fresh AB cost to be approximately $9/kg AB, with the largest cost component being sodium borohydride. It has been hypothesized that regenerating spent fuel would cost less than production of fresh fuel; however, this has not been demonstrated at scale. Additional reductions in the costs of SBH and first fill of AB are required, and needs further research. The Center Partners limited the AB synthesis approach to processes based on sodium borohydride. Other processes using different boron starting materials may be less expensive. PNNL proposed but did not demonstrate one alternative that would by-pass sodium borohydride and more efficiently use the hydrogen and other compounds in AB synthesis. This approach may also be applicable to spent fuel regeneration. If it can be applied to regeneration, then the same capital equipment used for production could be used for regeneration, saving infrastructure costs. Development of new innovative ideas to decrease AB synthesis cost needs to be examined.

1.6.2 Metal Amidoboranes

Metal amidoboranes (MAB) are solid chemical hydrogen storage material materials with many advantages: no foaming, reduced quantities of gas-phase impurities, etc. that have been detailed in previous sections. The most significant issue with this class of compounds is that the hydrogen release from these compounds is still too exothermic to enable direct rehydrogenation. Chemical regeneration must proceed through either the re-reduction of the metal M and/or the re-synthesis of the metal hydride, M-H in order to complete the regeneration cycle. Clearly, if one must resynthesize the M and/or M-H for each regeneration cycle (which we know from Dow's work on first fill synthesis of AB is costly and energetically inefficient) that re-reduction of the metal and/or resynthesis of the M-H is untenable. (NOTE: Attempted regeneration of M-AB spent fuels with hydrazine should NOT be attempted without firm knowledge of the M – hydrazine chemistry. Many metal hydrazides are shock sensitive). Because there is not a chemically reasonable, energetically efficient means of regeneration of the known M-AB spent fuels (Li, Na, K, Al, etc.) that the Center did not down select the currently known M-AB compounds for continued work for onboard vehicular applications. Of course, for other applications, some of the M-ABs may find application where the cost of spent fuel regeneration is not so critical, and more work may be required to follow those leads.

While the Center did not down select any of the known M-AB compounds for further work, the Center recommends the investigation of remaining strategies that may lead to the discovery of near-thermoneutral M-AB compounds that the Center did not have the time to follow up on. Finding the 'right' M, or rather the right combination of M and M' in more complex structures containing the amidoborane anion may lead to the discovery of reversible hydrogen storage materials.

For any additional work along this line, discovering M-ABs that release hydrogen at near thermoneutrality is the key materials screening criterion. Beyond this crucial release parameter, determining the identity and amount of impurities, the long-term stability of the M-AB, its physical properties that impact onboard vehicular reactor design (again, for solids), and cost should all be addressed.

1.6.3 AB in Ionic Liquids

AB in ionic liquids offers many advantages that make the chemistry attractive for use in on-board hydrogen storage: a mixture of 50 wt. % AB in IL can still achieve the gravimetric target. These mixtures offer fast hydrogen release, and as liquid fuels they enable the use of catalytic approaches to control rate and extent of release. AB/IL mixtures also give rise to reduced levels of gas-phase impurities, among other advantages that have been previously outlined. While these are all advantages of this storage material class, the Center's work did not complete by the end of the Center an in-depth assessment at the level required for subsequent engineering design studies. Thus, there is still a need to understand and control release rates especially at low temperature and at cold start conditions, more information on impurities is required, optimal catalysts, and more information on the influence of various ionic liquids on regeneration schemes. Of the perhaps hundreds of reasonable ionic liquids that are candidates for this application, the Center looked at but a few. Continuing research directed at selecting the optimal ionic liquid to optimize gravimetric capacity, to provide phase stability and thermal stability, and coupled with an exploration of the impacts of the presence of IL on regeneration costs are all areas that the Center recommends as a path forward in this area.

AB/IL mixtures have achieved the desired minimum release rates by thermolysis and by homogeneous and heterogeneous catalysis. Heterogeneous catalysis has the usual advantages over homogeneous catalysts in the separation of the catalyst is not an issue for the heterogeneous case, which is a large advantage for any regeneration process. Catalytic release appears to significantly reduce the quantity of borazine produced, relative to pure AB. Ammonia is released in either case, and thus more understanding is needed to either shut this reaction pathway down, or minimize it to the extent that any residual can be readily removed from the gas stream. Catalyst stability and lifetime are remaining issues, and must be optimized and quantified to enable engineering analyses to go forward on such a process.

The use of a heterogeneous catalytic system may necessitate some additional efforts in reactor design. The preferred arrangement would be a supported catalyst in a fixed bed where the AB would react to release hydrogen on the catalyst surface and spent fuel would de-sorb from the catalyst surface, thus allowing another catalytic cycle to take place. This three-phase reaction system (solid catalyst, liquid reactants and products, and hydrogen gas) presents significant catalyst and reactor design challenges at high rates of hydrogen evolution, where hydrodynamic effects of the expanding hydrogen gas can prevent liquid mass transfer to occur, decreasing the catalyst efficiency. This has been observed in a similar hydrogen release system studied by Air Products, where they have been interested in releasing hydrogen from a liquid carrier carbazole over a heterogeneous catalyst.[37] They determined that the high gas flow rate from hydrogen release inhibited the liquid reactants from contacting the catalyst decreasing performance. They concluded that a new reactor design that minimized diffusion resistance needed to be invented; this may also bear out for AB/IL mixtures that as suggested above may have similar challenges. Alternative reactor design needs to be further developed for this topical area of hydrogen storage materials research.

A second significant challenge in the reactor design is thermal management. The heat generated from dehydrogenation of AB/IL needs to be removed from the system, just as the heat from solid AB dehydrogenation must be dealt with in a solids handling reactor as discussed earlier in this report. The heat capacity and thermal conductivity of the IL/AB mixture offer some advantage in heat management over a solids AB reactor design, but both reactors must deal with heat rejection from the system. Doing this with minimal volume and weight is a substantial engineering challenge.

Finally, cost is an issue that will need to be addressed. AB synthesis cost was described in the solid AB section previously. AB/IL have the added cost of the ionic liquid, which currently can be very expensive at the research quantity scale. Therefore, once the optimum ionic liquid(s) are identified, an assessment of how low a cost can be achieved in large scale production of the IL is required on the path to a go/no go decision on AB/IL as a storage material.

1.7 Materials for Early Markets

1.7.1 Market Definitions

Near term markets (exclusive of on board vehicle applications) for fuel cells and corresponding hydrogen storage systems, can be divided into two classes: (1) motive and (2) non-motive. Motive applications include all non-vehicle applications where the system is moving and the fuel cell is the principle power source. Examples of motive applications would include: materials handling equipment (forklifts), airport tugs (similar to material handling equipment), golf carts, lawn mowers, and wheel chairs. Non-motive applications would be portable, stationary or auxiliary power units. Examples of non-motive applications would include: portable electronics (laptops), remote power, back-up power, auxiliary power for boats and RV's, auxiliary power for hotels and/or cooling loads on class 8 trucks, mobile lighting, and stationary power / combined heat and power (CHP), among others. Although specific requirements for these applications have not been defined, generally they may require the following.

(1) Motive Applications

  a. Volumetric and gravimetric hydrogen capacity lower than what vehicles may need, but higher than stationary applications
  b. Low concentrations of impurities in the released hydrogen since there will be limited space for purification technologies
  c. Moderate hydrogen production rates.
  d. Either on board regeneration or fast materials exchange
  e. Low cost

(2) Non-motive applications

a. Volumetric and gravimetric hydrogen capacity will vary depending on the specific application, but it is generally considered to most likely be lower than requirements for on-board vehicle applications and for motive applications

b. Impurities - lower is always better, but there may be a larger operation window for some applications.

   i. Portable, auxiliary power, and other applications with constrained volume will require low concentrations of impurities

   ii. Stationary, back-up power, and applications with reduced constraints on volume may be able to accommodate larger cleanup components (i.e. larger filters etc).

   iii. Low to moderate hydrogen generation rates, depending on the application

   iv. On-board regeneration may not be required

   v. Low cost is always preferred, but many of these applications are in specialty niches that may be able to tolerate a higher cost.

1.7.2 Materials For Early Market Recommendations

Since the requirements are different, many chemical hydrogen storage materials that are not suitable for on-board vehicle hydrogen storage may be suitable for these near-term market applications. Table 1.8.1 lists classes of chemical hydrogen storage materials and indicates if we feel they may be suitable for use in particular Motive and Non-motive applications. The number of 'plus's, with a maximum of three, indicates how suitable the material is, no 'plus's indicates that a material is not likely to be suitable.

Material	**Motive Applications**					**Non-Motive Applications**					
	Fork-lifts	Golf carts	Lawn mower	Wheel-chair	Motor-cycles / bikes	Portable Power (<100W)	Portable Power (<1kW)	Mobile lighting	Gen. Sets/ Back-up Power (>1kW)	Aux. Power	CHP
Endothermic Chemical Hydrogen Storage											
Imidazole	++	++	+			+	++	+	+		
Coupled reactions											
Carbenes	+++	++	++	+	++		+++	+++	+++	+++	+
Exothermic Chemical Hydrogen Storage											
Sodium borohydride	++	++	+	+	+	+++	+++	+++	+++	+++	+
Polyhedral boranes	++	++	+	+	+	+++	+++	+++	+++	+++	+

Neat AB											
AB+ silica						++	++	+	++		
AB + carbon											
AB + BN											
AB + additives	++	+++	+	+		+++	+++	+++	+++	++	+
AB / Ionic liquid (thermal)	++	+++	++	++	++	++	+++	+++	+++	++	+
AB / Ionic liquid (catalytic)	+++	+++	++	++	++	+++	+++	+++	+++	++	+
AB / MeAB / EDBB (thermal)											
AB / MeAB / EDBB (Catalytic)	++	++	+	+		+++	+++	+++	+++	++	+
Metal amido-boranes	++	++	+	+		+++	+++	+++	+++	+++	+
Nano-particles						+	+	+	+	+	

Table 1.8.1 Chemical Hydrogen Storage for Near Term Applications.

Notes:
“+++” = strongly recommend investigation into use of this chemical in this application
“++” = recommend investigation into use of this chemical in this application
“+” = this chemical may be suited for this application
No marks indicate we do not believe the chemical is likely to be successful in this application.

1.8 Tables of Down Select Information for Chemical Hydrogen Storage Materials

Endothermic Chemical Hydrogen Storage Materials

Material	**Measured Wt.%**	**Vol. %**	**Onboard Spent Fuel Regeneration**	**Off board Spent Fuel Regeneration**	**Phase Change**	**Rate @ T (g H**	**Stability**	**Release T**	**Decision Summary: Disadvantages and Comments**	**Decision Summary: Advantages and Comments**	**Go/No-Go**
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	l/l	<.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	l/l	<.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	l/l	<.01 @ RT	Good	Room temp	Low gravimetric capacity	Rates of release good at room temperature.	No-Go
Coupled reactions											
$Mg(OMe)_2/H_2O$	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 %.	No-Go
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	No-Go
Main Group Nanoparticles and Clathrates											

Material	Measured Wt.%	Vol. %	Onboard Spent Fuel Regeneration	Off board Spent Fuel Regeneration	Phase Change	Rate @ T (g H	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/No-Go
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 >300°C	---	No-Go
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-NH2	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

Exothermic Chemical Hydrogen Storage Materials

Aqueous Hydrolysis

Material	Measured Wt.%	Vol. % g H2/cc (target - .045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H2/sec/kg) (target - .020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/No-Go
Sodium Borohydride											
$NaBH_4$	6.5		Not feasible	Not demonstrated	l/s		Good	< 80 °C	Precipitaion	Excellent rates at 80 °C	No-Go
Polyhedral Boranes (Rh catalyzed aqueous hydrolysis):											
Li2B10H10	6.5	0.08	Not feasible	Not demonstrated	l/s	ca.04 @ 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
(NH4)2B10H10	6.3	0.08	Not feasible	Not demonstrated	l/s	ca.04 @ 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
Na2B10H10	6.2	0.08	Not feasible	Not demonstrated	l/s	ca.04 @ 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
K2B10H10	6	0.08	Not feasible	Not demonstrated	l/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
LiB11H14	6.6	0.08	Not feasible	Not demonstrated	l/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
(NH4)B11H14	6.55	0.08	Not feasible	Not demonstrated	l/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
NaB11H14	6.5	0.08	Not feasible	Not demonstrated	l/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
KB11H14	6.4	0.08	Not feasible	Not demonstrated	l/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
Li2B12H12	6.5	0.08	Not feasible	Not demonstrated	l/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
(NH4)2B12H12	6.3	0.08	Not feasible	Not demonstrated	l/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

Material	Measured Wt.%	Vol. % g H2/cc (target -.045)	Onboard Spent Fuel Regeneration	Offboard Spent Fuel Regeneration	Phase Change	Rate @ T (g H2/sec/kg) (target -.020)	Stability	Release T	Decision Summary: Disadvantages and Comments	Decision Summary: Advantages and Comments	Go/No-Go
Na2B12H12	6.2	0.08	Not feasible	Not demonstrated	l/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
K2B12H12	6	0.08	Not feasible	Not demonstrated	l/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	l/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

AB-Based Materials/ Thermolysis and Catalytic Release

Material	Measured Wt.%	Vol. %	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
Solid AB and AB with Additives											
Solid, neat 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	No-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	
AB + Additives	13.6	0.10	Not feasible	Not demonstrated but likely	s/s	Similar rates to neat solid AB	Good	> 50 °C	Impurities and decreased capacity compared to neat AB	No foaming	Go
1:1 AB/MCM scaffold	8		Not feasible	Not demonstrated	s/s	TBD		> 50 °C	TBD	Low but acceptable wt. %, 3:1 more promising	No-Go

Material	Measured Wt.%	Vol. %	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
3:1 AB/MCM scaffold	12		Not feasible	Not demonstrated	no foam	TBD	Not yet determined	> 50 °C	Stability	Demonstrated 14 wt % hydrogen at 85 °C; reduced gas phase impurities relative to AB.	No-Go
AB/ cat. Amt. NH4X	16		Not feasible	Not demonstrated, but likely	s/s	N/A	Not determined	> 50 °C	Stability questionable,	Demonstrated 6 wt % at 90°C. Fast rates on release; no foaming	No-Go
AB/PS (5mol%)	5	3.8	Not feasible	Not demonstrated, but likely	s/s				Stability questionable, needs work. Impurities	Demonstrated fast rates	No-Go
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	No-Go
Liquid AB systems (excludes IL systems)											
MeAB	8.8 (2 equivalent)		Not feasible	Not demonstrated	l/s	Similar to AB	Evolves H2 < 50 °C	> 50 °C	Stability at room temperature not adequate; volatile	Low melting point, good rate	No-Go
20%MeAB/AB	12 wt % (2 equivalent)		Not feasible	Not demonstrated	l/s	Similar to AB	Evolves H2 < 50 °C	> 50 °C	Stability at room temperature not adequate; volatile	Low melting point, good rate	No-Go
EDBB with catalyst	9.1 (2 equivalent)		Not feasible	Not demonstrated	l/l	Similar to AB	Promising	> 50 °C	Slight weight fraction penalty from hydrocarbon linkage	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.	No-Go

Material	**Measured Wt.%**	**Vol. %**	**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	l/l	TBD	Promising	> 50 °C	None/TBD	Liquid composition, liquid to liquid potential, good rate to 6 wt% with catalyst; stability needs to be verified. Additional components e.g. ionic liquieds 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	l/s	.0003 @ 60°C	Good	> 50 °C	Poor hydrogen capacity, very slow.	---	No-Go
20% AB/% BPh3/diglyme	3.9		Not feasible	Same as for AB	l/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	l/s	Rates good to 1st equivalent down to room temp	Good	> 50 °C	Insufficient solubility in THF, glymes	---	No-Go
AB/tetraglyme (50wt%)	7 wt% (@368 K)								Insufficient solubility in THF, glymes		No-Go
AB/tetraglyme (50wt%) PS(1 mol%)	6.6 wt% (@368 K)				l/l				Insufficient solubility in THF, glymes		No-Go
MeAB and THF (xM) with catalyst	ca. 1 @ 1.5 M		Not feasible	Not demonstrated	l/l	Not determined	Not determined	> 50 °C	Insufficient solubility in THF, glymes	---	No-Go
Ionic Liquids											
AB/IL (20 wt% bmimCl)	10.5% @ 80 wt.% (3 eq) @120 C	*0.1 (3 eq)*	Not feasible	Regeneration demonstrated in presence of IL	l/s				Need to tune IL properties to improve phase stability, increase	With optimal IL, liquid systems may be found	Go
AB/IL (50 wt% bmimCl)	7.6% @ 50 wt.% (3 eq)	0.07 (3 eq)	Not feasible	Regeneration demonstrated in presence of IL	l/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 °C, demonstrated 7.2 wt. % H2 at 50% IL, needs lower mp IL	Go

Material	Measured Wt.%	Vol. %	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/IL/PS	8.3% @ 5 mol% PS (3 eq.)	.08 (3 eq)	Not feasible	Regeneration demonstrated in presence of IL	l/s	Avg rates: .011 @ 85 °C, .018 @ 100 °C	Not determined	> 50 °C	Questionable solubility of spent fuel; requires optimal IL	Good rates at 100, demonstrated 6.2 wt. % H2 at 50% IL, needs lower mp IL	Go
AB/IL/5 mol%Rh cat	7.8	0.09	Not feasible	IL/cat separation potentially an extra step	l/s	avg rate: .077 @ 85 °C	Not determined	> 50 °C	Adequate capacity, but capacity of other mixtures is higher , need to identify a heterogeneous catalyst to avoid the separations problem in regen	Good rates above 100 °C	Go
DADB/IL (50wt% bmimCl)	7.9 wt% @85C		Not feasible	Regeneration possible based on AB experience	l/s				Stability needs to be determined	Good rates at 100, demonstrated 7.2 wt. % H2 at 50% IL, needs lower mp	TBD
AB intermediates, and related:		Not feasible									
DADB, neat	19.6		Not feasible	Regeneration possible based on AB experience	s/s	1.8 @ 145°C 0.48 @ 130°C 0.2 @ 100°C		> 50 °C	Stability is a question, impurities similar to AB are anticipated	Work in progress, no foaming, high rate, high capacity	No-Go
PAB	10@150C		Not feasible	Not known	s/s	Not determined		> 50 °C	Slow release <120 °C	Adequate weight fraction, no foaming	No-Go
cyclic Pentamer	4.5@150 C		Not feasible	Not known	s/s	Not determined		> 50 °C	Slow release <120 °C	Same as PAB	No-Go
NH4BH4	24.5		Not feasible	Not known	s/s	Not determined	Decomposes at room temp	> 20 °C	Stability needs further demonstration.	Low foaming, very high capacity > 20 wt%	TBD

AB with Metal Hydrides and Metal Amidoboranes

Material	Measured Wt.%	Vol. %	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/Hydride composites											
AB + Ca(BH4)2	14wt% <150°C		TBD	Not demonstrated	s/s	Similar to AB	Good	> 130 °C	Borazine, ammonia and diborane release observed, regeneration need further demonstration	Significantly less exothermic, high capacity, reduced levels of borazine, ammonia and diborane, no foaming, good rate	No-Go
AB + Mg(BH4)2	16wt% <150°C		TBD	Not demonstrated	s/s	TBD	Good	> 90 °C	Borazine, ammonia and diborane release observed, regeneration need further demonstration, stability is questionable; powder changes into paste	Significantly less exothermic, high capacity, reduced levels of borazine, ammonia and diborane, low foaming	No-Go
2AB + MgH2 + 0.1TiH2	7.5 wt% @ 200°C		TBD	Not demonstrated	s/s	.12 @ 150°C for 2AB+MgH2+0.1TiH2; .08 @ 150°C for AB	Good	> 86°C	Stability and regeneration need further demonstration, adequate capacity	Less exothermic than AB as is, low foaming, no gas phase impurities, good rates below 100°C	No-Go
2AB + MgH2 + 0.1TiH2 + 0.1CaH2	8.1 wt% @ 200°C		TBD	Not demonstrated	s/s	TBD	Good	> 92°C	Stability and regeneration need further demonstration, adequate capacity, impurities (ammonia, borazine, diborane)	Less exothermic than AB as is, no foaming, reduced gas phase impurities relative to AB, good rates @100°C	No-Go
6AB + 3CaH2 + MgH2 + 0.1TiH2	3.5 wt% @ 200°C		TBD	Not demonstrated	s/s	TBD	Good	> 56°C	Poor hydrogen capacity, significant level of ammonia	Less exothermic than AB as is, no foaming, low release temperature (> 56°C)	No-Go
3AB + TiH2	8.4 wt% @ 200°C (theoretical)		TBD	Not demonstrated	s/foam	TBD	Good	> 115°C	Foaming, impurities (ammonia, diborane, borazine), slow release <120 °C	Slightly less exothermic than AB	No-Go

Material	Measured Wt.%	Vol. %	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 + 0.1TiH2	11.2 wt% @ 200°C (theoretical)		TBD	Not demonstrated	s/foam	TBD	Good	> 114°C	Foaming, impurities (ammonia, diborane, borazine), slow release <120 °C	Relatively high theoretical capacity	No-Go
2AB + CaH2	7.8 wt% @ 200°C		TBD	Not demonstrated	s/s	TBD	Good	> 98°C	Significant level of ammonia	Less exothermic, no foaming, no diborane and borazine	No-Go
Metal amidoboranes									Regeneration has not been investigated	Promising materials with high rates low impurities	
LiAB	11	0.052	Not feasible	Not demonstrated, unlikely to be energy efficient	s/s	1.76 @ 130°C 0.44 @ 100°C 0.08 @ 90°C	TBD	10 wt % @ < 90 °C	Regeneration not yet determined.	Good rate to 11 wt%	TBD
NaAB	7.6	0.043	Not demonstrated	Not demonstrated, unlikely to be energy efficient	s/s	0.44 @ 80°C	TBD		Regeneration not yet determined. Stability issues	Good rate to 7.6 wt%	No-Go
Ca(AB)2	10	Density not determined	Not demonstrated	Not demonstrated, unlikely to be energy efficient	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	No-Go
Li2Zn(AB)4	10	Density not determined	Not demonstrated	Not demonstrated, unlikely to be energy efficient	s/s	>.02	Good	Room temp	Regeneration not yet determined	Good release temperature and rate	No-Go
LiZn(AB)3	9	Density not determined	Not demonstrated	Not demonstrated, unlikely to be energy efficient	s/s	Not determined	Not stable at room temp.	Room temp	Releases H at too low a temperature	High capacity	No-Go
Ti(AB)4	12	Density not determined	Not demonstrated	Not demonstrated	s/s	TBD	TBD	< 160 °C	Regeneration pathway not yet determined.	Demonstrated 11.9 wt % H2 released.	No-Go

Material	**Measured Wt.%**	**Vol. %**	**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**
Al(AB)3	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	No-Go
NaMeNHBH3	3	Density not determined	Not demonstrated	Not demonstrated	s/s	0.43 @ 100°C			Low capacity		No-Go
KMeNHBH3	2	Density not determined	Not demonstrated	Not demonstrated	s/s				Low capacity		No-Go
K(t-Bu)NHBH3	1.5	Density not determined	Not demonstrated	Not demonstrated	s/s				Low capacity		No-Go
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 % H2	No-Go
9 mol% LiNH2/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 % H2	No-Go

1.9 References for Chapter 1: Hydrogen Release

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Chapter 2. Regeneration of Spent Fuel from Ammonia Borane Dehydrogenation

Contents, Chapter 2

1.1 Summary and Recommendations for Future Work: Regeneration

Within the first year of the Center's lifetime, it became apparent that ammonia borane (AB) in it's various forms was a potentially viable chemical hydrogen storage material. The question that needed to be answered quickly was, How can the polymeric BNH_x spent fuel be regenerated in high chemical and energy efficiency resulting in pure AB at low cost? The Center subsequently directed a great deal of resources to answering this question. After a significant level of effort, the Center demonstrated (on a laboratory scale) that chemically efficient regeneration of amine-borane-based chemical hydrogen storage systems is possible via a number of approaches. Given the large number of chemical regeneration processes possible, which are the 'best'?

An acceptable regeneration scheme must be (1) high yielding, (2) competent for a variety of spent fuel types, (3) energy efficient, and (4) low cost (no order of importance is implied). The Center's research on regeneration encompassed a great deal of experimental work, applied modeling, theory, and engineering assessments. Through its work, the Center determined that high yielding, low-mass regeneration reagents and fewer regeneration steps can dramatically lower the cost of a regeneration process. We assert that treatment of spent AB fuel with hydrazine in liquid ammonia is currently the best chemical process to accomplish regeneration because it can accommodate a variety of spent fuel forms and can occur in a single vessel thereby simplifying the separations requirements and reducing capital costs. However, the cost and energy efficiency of hydrazine production dominate, and thus significantly lower cost, more energy efficient routes to industrial scale production of hydrazine are required for this strategy to meet the DOE cost and efficiency metrics.

As stated in Chapter 1 of this report, one of the challenges for chemical hydrogen storage and complex metal hydride storage (which are both in the same class of covalent compounds) is to find near thermoneutral release materials that release hydrogen at less endothermic heats of reaction than the existing complex metal hydrides or so-called 'liquid carriers', and that are far less exothermic than the materials addressed in this report. This would drive toward potentially viable on board recharging of chemical hydrogen storage materials that could have potentially high weight fractions of hydrogen. The current state of our knowledge of many chemical hydrogen storage and complex metal hydride materials is that most of these will need to be regenerated in off board processes either due to the lack of practical reversibility of the compounds discussed in this Final Report, or in the case of some of the so-called complex metal hydrides that can be recharged with hydrogen but because of the complexity of the conversion must be taken off board (e.g. alane, AlH_3).

The Center has demonstrated using several different approaches for off board regeneration of spent fuel. Given a spent fuel that requires off board processing, this Center has demonstrated that it is likely that skilled chemists will be able to conceptualized and demonstrate chemical processes for regeneration. The Center's recommendation is that given this 'existence proof', that further research on off board regeneration for vehicular application be postponed until a firmer understanding of what the potentially final fuel form(s) will be becomes known, and that the focus in regeneration research be placed on regeneration with high pressure hydrogen – e.g. that work be devoted to discovering storage materials that release hydrogen with near-thermoneutral thermodynamics.

A summary of the several successfully demonstrated regeneration processes is given in Section 1.7 and 1.8, and additional details are given in the LANL, Penn, and PNNL final reports. Several of these demonstrated approaches have been the subjects of preliminary engineering assessments by Dow, ANL, and TIAX. These assessments are summarized in Section 1.8, and in the final reports of LANL and Dow.

1.2 Approach

Discussion of chemical hydrogen storage regeneration schemes must start with a quantitative description of the free energy of hydrogen release from the storage material. The dehydrogenation of AB (2-2.5 equiv H_2 released, generating polyborazylene) is exothermic by ca. -14.3 kcal mol^{-1} (Equation 1). While this is certainly closer to thermoneutral than hydrolysis of AB (ΔH = ca. -227 kcal/mol) or sodium borohydride, for example, the reaction is quite exergonic due to the increase in entropy contributed by the evolved H_2 gas. The reverse, endergonic reaction (Equation 2) requires a tremendous hydrogen pressure, on the order of 100,000 atmospheres, too great to be feasible on an industrial scale. Instead, we have considered several regeneration schemes that involve stepwise reactions of spent fuel with proton (H^+) and hydride (H^-) sources. Addition of H^+ and H^- has the same net result as direct H_2 addition, but the former is mechanistically and thermodynamically feasible as we describe in this Report. Schemes of this sort are the best way to efficiently overcome the intrinsic energy barrier in chemical hydrogen storage regeneration by separating the large thermodynamic and entropic barriers into achievable steps. Because of this processing strategy, the chemical hydrogen storage materials generated to date by the Center must be regenerated off-board in a chemical processing facility.

(1) $AB \Rightarrow \geq 2\ H_2 + BNHx$

(2) $BNH_x + \geq 2\ H_2 \nRightarrow AB$

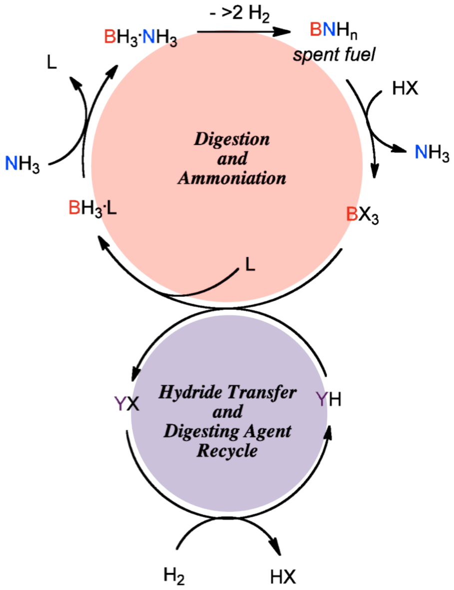
Another important concept to consider is that the extent of dehydrogenation of AB, methods for which were discussed in the previous sections of this Report, may impact the effectiveness of a regeneration scheme. While AB has an ultimate H_2 capacity of 19 wt. % corresponding to storage of three molecules of H_2, in practice we find that release of 2-2.5 equivalents of H_2 is an achievable, realistic goal. This is 13-16 material wt% hydrogen. The rationale for "incomplete" dehydrogenation is that it lends itself to greater ease of regeneration. Loss of three molecules of hydrogen from AB will generate boron nitride (BN, a ceramic material). Whether this material is ordered or amorphous, the generation of BN is extremely exothermic ($\Delta_f H^\circ$ = -107 kcal mol^{-1}).

Furthermore, BN is quite unreactive, requiring strong acids or strong oxidants for even partial digestion.[1] Herein spent fuel refers to the material produced when 2-2.5 H_2 is released from AB.

1.2.1 Regeneration Process Design Principles

The Center presented its first strategy for regeneration to DOE's Hydrogen Storage Tech Team in February 2006. It consisted of three major steps: Digestion, reduction, and ammoniation (Figure 1). These steps may also be considered as addition of H^+ using a digesting agent HX; addition of H^- using a reducing agent YH and addition (i.e. reuse) of NH_3. The Center exploited the propensity for incompletely substituted boranes to disproportionate to generate the necessary intermediates during these three steps. Computational work at Alabama and PNNL using similar approaches and tools as outlined in Chapter 1, Section 1.3 dramatically guided the experimental work to successful completion by calculating reaction thermodynamics, permitting early elimination of unfavorable reaction or reagent types. As discussed above, reactions near thermoneutral are favored; thus, reactions shown by computational means to be energy intense were eliminated from consideration. Specific examples of computed results will be given as appropriate in the following sections.

Figure 1: General Center scheme for regeneration.



1.2.2 Regeneration Down Selection Approach and Criteria

The Center is acutely aware that an off-board regeneration scheme faces energy efficiency and cost hurdles to its large-scale implementation. This required the Center to develop an engineering-focused mindset when we considered regeneration process chemistries to ensure that time and resources were directed at the most promising pathways from an engineered regeneration system perspective. Early on, the Center utilized thermodynamics of proposed processes to guide our research, and then as we found useful chemistries for regeneration, the

Center utilized more complex analyses brought to us through our industrial partner's extensive experience (Dow) in process chemistry, engineering, and cost assessment, and also engaged ANL's extensive energy efficiency assessment capability to help guide our regeneration research toward both cost and energy efficient pathways.

Because some forecourt costs and the cost of hydrogen are fixed in our calculation of system cost, we can instead consider the overall thermodynamic efficiency of our processes and the cost of required reagents and processes as variables to optimize. The energy required to regenerate an ideal hydrogen storage system would simply be the lower heating limit of H_2, 57.8 kcal mol^{-1} at 25 °C. However, any hydrogen storage system deviates from the ideal, and the thermodynamic efficiency of the regeneration system can be computed using Equation. 3.

$$\frac{(\text{Equiv. H}_2\text{ stored})(57.8)}{(\text{Equiv. H}_2\text{ used})(57.8)+\sum(\Delta H_{endo})-(\%\text{ heat recovery})\sum(-\Delta H_{exo})}=\mathit{efficiency} \tag{3}$$

The variables are:

1. Equivalents of hydrogen stored: This is the amount of H_2 released from the storage material by heating, catalysis, etc.

2. Equivalents of hydrogen used to effect regeneration: This is the amount of H_2 used to regenerate the storage material; this value may be more than (1) due to the steps required in the regeneration process (vide infra)

3. The sum of the endothermic steps

4. The sum of the exothermic steps

5. The percent heat recovery: This is a value related to the ability to recover and reuse heat generated in the exothermic regeneration step

It can be seen that high efficiency (values approaching 1) can be achieved when the amount of H_2 stored and the amount required for regeneration are equal or nearly so; and when all chemical steps required for complete regeneration are nearly thermoneutral. When the Center examines regeneration schemes using Equation 3, *all* chemical steps except the production of H_2 are considered. In other words, when all of the chemical steps required for regeneration are summed, the total should simply be H_2 and energy. In practice, this also means all reactions should be close to 100% yield; the experimental yield of regeneration steps was not included in Eqn. 3, but has been an informal criteria for the down-selection of regeneration methods. Furthermore, while Equation 3 can give us an estimate of the thermodynamic efficiency, it does not include the entropic components of the reactions in the form of reaction free energies. Evaluation of reaction free energies was done for reactions presented in the following sections, and was used as qualitative criteria for down selection; reactions with large positive free energies would not be feasible without tremendous pressure and/or temperatures.

For a hydrogen storage technology to be accepted by industry and successfully commercialized it should offer benefits superior to what is currently available and must have an acceptable cost. The Center has focused largely on efficiency as a figure of merit as directed by the DOE goals; many factors determine a technology's cost with efficiency being one of the major contributors. However, it is not always the case that the most efficient process has the lowest cost. A prime example is the use of hydrogen fuel cell for energy storage as reported by NREL.[2] They examined eight energy storage technologies for a energy storage scenario consisting of charging during off-peak hours (~18 hrs a day, and all day on weekends) and discharge at a rate of 50 MW for 6 hours during peak time weekdays. Even after assuming some improvement in the fuel cell and electrolyzer technologies, hydrogen fuel cell technologies had the lowest round trip efficiency[2] of 34-35% of all the technologies examined. However, the projected levelized cost for the hydrogen fuel cell system was lower than that of NiCd batteries (efficiency = ~59%) and comparable to NaS batteries and vanadium redox batteries (efficiency = 77% and 72%, respectively). This clearly illustrates that higher efficiency does not guarantee lower costs. It was for this reason that the Center added projected cost into consideration as a down select criterion when examining regeneration schemes. Dow has calculated costs required to scale up several of the Center's leading regeneration candidates. Factors such as capital costs, chemical costs, and process costs such as utilities and natural gas to supply heat or cooling for various separations or gas compression were examined. These assessments highlighted various process strategies that were favorable or highly unfavorable that the Center subsequently attempted to address by redesigning the process chemistries. The Center's down select process for regeneration was thus an ever-evolving one, where as engineering assessments came in form Dow or from ANL, Center researchers responded to the various challenges that came our way.

The engineering assessments that resulted in process costs and efficiencies complemented Eqn. 3 by considering not only the thermodynamic efficiencies but also the process efficiencies. Process efficiencies effectively consider the entropic demands of a set of reactions, thereby giving the Center down selection criteria where the simple thermodynamic assessment was lacking. The Center initially believed that a regeneration system based on a series of equilibria (i.e. $\Delta G \approx 0$) would be the best way to achieve a high efficiency. This is indeed true when only considering thermodynamic efficiencies. For example, in practice and as evaluated by Dow, equilibrium processes may result in difficult or energy intensive separations (e.g. distillation). Hence, the product of an equilibrium optimally will precipitate from the reaction to allow for a low cost separation process or the reaction must proceed to a single product with $K_{eq} > 1$. Reagent cost also was considered in Dow's assessments, and for example led the Center to discontinue work on rhodium-containing catalysts for regeneration, instead focusing on lower cost catalysts based on cobalt and nickel. The details the Center down selection process for regeneration entailed a variety of inputs, but relied heavily on cost assessments performed by Dow and of engineering efficiency calculations performed by Argonne National Laboratory, and these are discussed in this Chapter, Section 1.7.

1.3 Regeneration Chemistries Investigated

As described in Section 1.2.1, the Center developed a digestion-reduction paradigm for regeneration. Table 1 gives the general reagent classes for the required steps.

Table 1: Overview of Regeneration Reagent Types

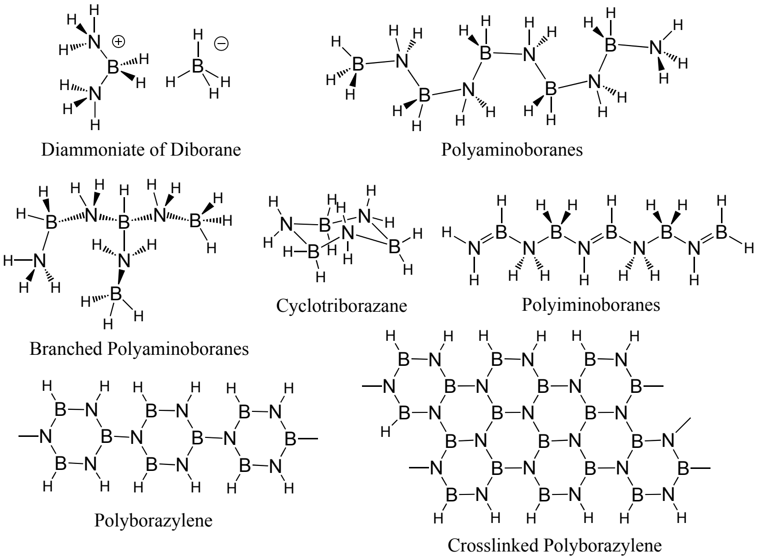
Reagent Class	***Contributing Partners***	***Report Section***
Digesting Agent		Digestion 1.5.1
Strong Acids	Penn	Digestion with Strong Acids 1.5.1.1
Alcohols	PNNL, US Borax, LANL	Digestion with Alcohols 1.5.1.2
Amines	LANL	Digestion with Amines 1.5.1.3
Thiols	LANL	Digestion with Thiols 1.5.1.4
Reducing Agent		Reduction 1.5.2
Transition metal hydrides	PNNL	• Reduction with transition metal hydrides 1.5.2.1
Tin hydrides	LANL, Davis	Reduction with tin hydrides 1.5.2.2
Other main group hydrides	Penn, Davis, LANL	Reduction with other main group hydrides 1.5.2.3
Combination Agents Hydrazine	LANL	One-pot Regeneration using a Dual Digesting/Reducing Agent 1.6

1.3.1 Characterization of spent fuel

Wolf and coworkers published the systematic thermolysis of AB.[3] A variety of oligomeric products were observed, including polyaminoborane $H_3N[H_2BNH_2]_xBH_3$, cyclotriborazane $(H_2BNH_2)_3$, cyclopentaborazane $(H_2BNH_2)_5$, borazine $(HBNH)_3$, and polyborazylene (Figure 2). When solid-state thermolysis was monitored by ^{11}B nuclear magnetic resonance (NMR) spectroscopy by the Center, the ionic isomer of AB $[BH_2(NH_3)_2][BH_4]$ was formed before hydrogen loss initiated.[4] The Center has broadly used solid state and solution nuclear magnetic resonance (NMR) spectroscopies to characterize the components of spent fuel. Various methods have been used by the Center to quantify the amount of hydrogen generated in reactions of interest. These include Toepler pump (cryogenic separation of gases followed by volumetric measurement);[5] gas burettes, the most efficient of which was published;[6] gravimetric methods such as TGA; and pressure transducer methods such as PCT. In combination with NMR methods, the Center can identify the chemical characteristics and extent of dehydrogenation in spent fuel; typically spent fuel has a polyborazylene-like structure and has evolved 2-2.5

equivalents of H_2. It is not uncommon for multiple spent fuel types to be generated from different AB release processes (e.g. thermolytic vs. catalytic release generates spent fuels of differing characteristics), and regeneration schemes should ideally be effective for all molecules present in a spent fuel sample.

Figure 2: Types of materials present in spent fuel mixtures. Distribution of species varies and is dependent on hydrogen release conditions.



1.4 Non-Center Regeneration Schemes

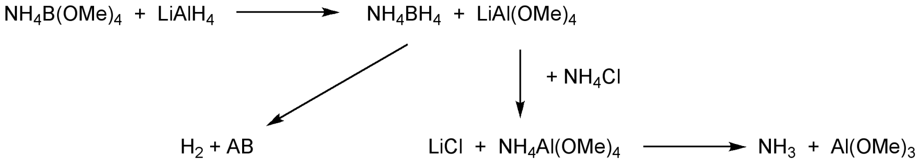
To allow the reader to put the Center's accomplishments into context, here we describe two literature examples of regeneration of borane spent fuels. One example of regeneration of methanolyzed ammonia-borane has appeared in the literature.[7] The authors used lithium aluminum hydride ($LiAlH_4$, LAH) and ammonium chloride as reagents to regenerate ammonia-borane from ammonium tetramethoxyborate (Eqn. 4). The reported yield (81%) of this reaction when run in a pressure vessel is modest (in terms of yield required for successful industrial scale-up), and the resulting AB purity is good (98%).

(4) $NH_4B(OMe)_4 + NH_4Cl + LiAlH_4 \rightarrow AB + Al(OMe)_3 + MeOH + H_2 + LiCl + NH_3$

The authors report using excess (1.2-1.5 equivalents) reducing agent and additional ammonium equivalents to obtain modest yields of AB. Although the authors do not discuss the mechanism of this regeneration, we believe that the mechanism shown in

Figure is likely: LAH will reduce $[B(OMe)_4]^-$ to BH_4^-, and the resulting ammonium borohydride will lose H_2 at the reaction temperature utilized to generate AB. This process is similar to the Schlesinger process[8] for synthesis of borohydride from trimethylborate; details on the Center's analysis of the Schlesinger process can be found in the First Fill section of this report, Chapter 1, Section 1.3.3.2.

Figure 3: Likely regeneration pathway for methanolyzed AB using LAH.



The authors make no quantitative statements about this scheme's efficiency, but do qualitatively call the scheme efficient. This assertion is likely based upon the yield and purity of the AB product. The authors did not report the *overall* efficiency including the energy requirements for synthesis of their reagents, a *critical* component of an accurate efficiency calculation. In this case use of LAH will dramatically lower the overall scheme efficiency because LAH is made industrially from the high temperature, high pressure reaction of sodium metal, aluminum metal, and hydrogen followed by metathesis using lithium chloride. Sodium metal is generated industrially by the electrolysis of sodium chloride solutions, and aluminum metal is generated industrially by the electrolysis of a mixture of alumina, cryolite, and aluminum fluoride. The Center (based on DOE guidance) generally considers electrolysis methods for regeneration or synthesis of required reagents to be untenable due to the inefficiency of the electrical energy generation and transmission via the U.S. electrical grid. Using Eqn. 3, we calculated the thermodynamic efficiency of this process. Table 2 contains tabulated energies for each required step for the scheme to sum to H_2 and energy; it can be seen than this process has a thermodynamic efficiency, assuming quantitative yield in each step, of less than 50%. The Center's progress toward transition metal hydrides for energy efficient, mild reduction of B-O bonds is detailed in Section 1.5.1.2.

Table 2: Computed energy efficiency of Ramachandran et al. regeneration scheme (enthalpies in kcal mol^{-1}).

$NH_4B(OMe)_4$ (s) + NH_4Cl (s) + $LiAlH_4$ (s) → NH_3BH_3 (s) + $Al(OMe)_3$ (l) + MeOH (l) + H_2 (g) + LiCl (s) + NH_3 (g)	-65.4
NaCl (s) + electricity → Na (s) + ½ Cl_2 (g)	98.2
½ Cl_2 (g) + ½ H_2 (g) → HCl (g)	-22.1
HCl (g) + NH_3 (g) → NH_4Cl (s)	-42.1
$Al(OMe)_3$ (l) + 3/2 H_2 (g) + electricity → Al (s) + 3 MeOH (l)	48.0
Na (s) + Al (s) + 2 H_2 (g) → $NaAlH_4$ (s)	-27.6
LiCl (s) + $NaAlH_4$ (s) → $LiAlH_4$ (s) + NaCl (s)	2.4
Overall reaction: $NH_4B(OMe)_4$ (s) + 3 H_2 (g) → NH_3BH_3 (s) + 4 MeOH (l)	**-8.6**
Sum of exothermicities	*-157.2*
Sum of endothermicities	*148.6*

Efficiency with 0% heat recovery	46%
Efficiency with 20% heat recovery	50%

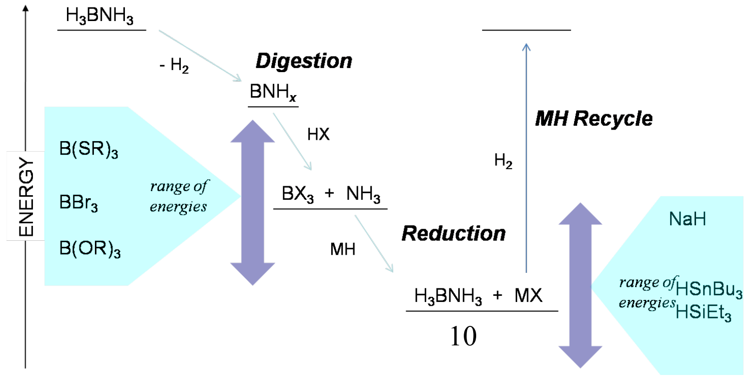
After initial communication of the Center's results at the DOE Annual Merit Review in 2007 (Section 1.5.1.1), Mertens and coworkers published a similar regeneration scheme in which spent fuel was digested by hydrochloric acid or $HCl/AlCl_3$ to generate boron trichloride, BCl_3.[9] These reactions were done in anhydrous organic solvents, and required 16 hours at 23 °C to achieve, in the authors' words, "nearly complete digestion." Subsequently, the authors suggested coordination of BCl_3 to a tertiary "helper" amine, followed by hydrodechlorination by H_2 gas to generate $BH_3{\cdot}NR_3$ and $NR_3{\cdot}HCl$. The tertiary amine hydrochloride and the ammonium chloride would then be roasted to separate the amine and ammonia from the HCl(g), and the $BH_3{\cdot}NR_3$ would undergo ammoniation to generate AB. The authors noted, as we have indicated above (Section 1.5.1.3), that the identity of the helper amine can dramatically affect the facility of the required reaction steps. They concluded that weak bases, such as $NPhEt_2$ ($pK_a = 6.56$) or NPh_2Et, would balance the need for rapid hydrodechlorination (which was inhibited by the strong bases NMe_3 ($pK_a = 9.76$) and NEt_3 ($pK_a = 10.65$)) and facile amine hydrochloride roasting. Center partner Penn attempted to repeat Mertens' results and were unsuccessful; Penn showed that these superacids gave low yields of digested product (Section 1.5.1.1).

Both of these processes while viable on the laboratory scale, would be unlikely to result in a chemically and energy efficient process, and would likely have high cost associated with the associated separations steps resulting from low yielding steps, and the expensive reagents required for reduction.

1.5 Multi-step Regeneration Protocols from Center Research

As outlined in Section 1.2, the Center investigated regeneration schemes composed of three steps: Digestion (H^+ addition), reduction (H^- addition), and ammoniation. In the following sections, we describe specific findings and conclusions related to the effectiveness of various reagent types and their ability to be efficiently recycled. The observations in this Section are exemplary of the back-and-forth process Center researchers employed to develop a functioning regeneration scheme: The identity of the digesting agent dramatically impacts the success or failure of the subsequent regeneration steps.

Figure 4: Digestion and reduction agents' potentials were varied to arrive at an overall energy efficient regeneration process.



1.5.1 Digestion

Summary. Digestion of spent fuel to generate a more readily processable, reducible chemical intermediate was sought. Both experimental and computational chemistry approaches were used to select the most promising pathways that enabled the most chemically and energy efficient conversion of spent fuel. Of the many thousands of potential digestion agents, several classes of reagents were screened. Thiols and the combination of hydrazine in liquid ammonia are particularly promising. Detailed discussions of digestion processes appear in the final reports from Los Alamos National Laboratory, the University of Alabama, the University of Pennsylvania, and Pacific Northwest National Laboratory.

Spent fuel generated during hydrogen release from AB has an oligomeric or polymeric structure (Figure 2). Because the integral B-N bonds are relatively strong, digestion of spent fuel into small units is nontrivial. The Center considered several types of digesting agents (H^+ sources): Strong acids, alcohols, amines, and thiols. Each agent type (HX) has advantages and disadvantages related to their competency as digesting agents and their impacts on subsequent reduction chemistry and reducing agent recycling. Generally it was found that more acidic digesting agents (X = Cl, Br, OR) could be monofunctional, while less acidic digesting agents (X = NR_2, SR) were only able to effectively digest spent fuel when bifunctional. The acidity correlates to B-X bond strength in the BX_3 product of the digestion reaction; B-S bonds are weaker than B-O bonds making them easier to reduce in the subsequent regeneration step. Specific examples and conclusions are provided in the following sections.

Table 3: Summary of digesting agent reactivity.

Digesting Agent	**Molecular Formula**	**pK_a (H_2O)**	**Result**
Trifluoroacetic Acid	CF_3COOH	0.23	Products of digestion can be reduced using aminoalanes, but resulting $NR_3{\cdot}BH_3$ does not generate AB when treated with NH_3; Consideration of other reducing agents in conjunction with this strong acid may be warranted
Trifluoromethanesulfonic Acid	CF_3SO_3H	ca. -15	Generates BX_3/BX_4^- mixture that is difficult to separate from excess CF_3SO_3H
Hydrochloric Acid	HCl	-9.3	No reaction at standard pressure. In a pressure vessel, HCl appeared to reversibly add across the BN bonds in spent fuel, but did not break apart the larger spent fuel polymer into smaller units
Hydrochloric Acid/Aluminum Chloride	$HCl/AlCl_3$	< -19	Spent fuel was digested, but isolation of the products from the reaction mixture by distillation or extraction were unsuccessful
Hydrobromic Acid/Aluminum Bromide	$HBr/AlBr_3$	< -19	Low yield (ca. 40%) of BBr_3; Also generates an oil that contains $(H_2NBBr_2)_3$ and $AlBr_3$ and was not reducible to $BH_3{\cdot}L$
Formic Acid	HCOOH	3.77	Generates BX_3/BX_4^- mixture that is difficult to separate from excess HCOOH
Chlorosulfonic Acid	HSO_3Cl	-6.0	Generates BX_3/BX_4^- mixture that is difficult to separate from excess $ClSO_3H$
Methanol	CH_3OH	15.5	Digests a variety of spent fuel types; residual B-H can be preserved depending on digestion reaction conditions; product of digestion can undergo transesterification with PhOH to make a reducible species
Ethanol	CH_3CH_2OH	15.9	Digests a variety of spent fuel types; residual B-H can be preserved depending on digestion reaction conditions; product of digestion can undergo transesterification with PhOH to make a reducible species

tert-Butanol	$(CH_3)_3COH$	19	Digests a variety of spent fuel types; residual B-H can be preserved depending on digestion reaction conditions; Generates some insoluble material during digestion, affecting overall yield; product of digestion can undergo transesterification with PhOH to make a reducible species
Phenol	C_6H_5OH	9.95	$B(OPh)_3 \cdot NH_3$ product undergoes undesirable side-reactions
Catechol	o-$C_6H_4(OH)_2$	9.48	B_2Cat_3 product was not reducible using mild reducing agents; residual B-H is not preserved
Phenylenediamine	o-$C_6H_4(NH_2)_2$	4.5	Digestion is slow, but residual B-H is preserved; the resulting 1,3,2-benzodiazaborolane is not reducible with mild reductants
Ammonia	NH_3	36	Does not add H^+ to spent fuel, but can extract residual B-H from spent fuel to generate AB
Benzenethiol	C_6H_5SH	8.2	No digestion was demonstrated with PhSH, but $B(SPh)_3$ can be reduced easily with mild reductants
o-Benzenedithiol	o-$C_6H_4(SH)_2$	ca. 6.0	Digests a variety of spent fuel types; residual B-H is preserved; products of digestion can be reduced using tin hydrides

1.5.1.1 Digestion with Strong Acids

Spent fuel was successfully digested by some strong acids to produce materials containing tetrahedral boron atoms devoid of remaining hydrogen; no residual B-H in spent fuel is preserved. Trifluoroacetic acid (CF_3COOH, TFA) digested spent fuel to generate $[B(O_2CCF_3)_4]^-$ as the primary product. Excess TFA was easily separated from the products of digestion by distillation. Other oxyacids, such as trifluoromethanesulfonic acid (CF_3SO_3H, HOTf), formic acid (HCOOH), and chlorosulfonic acid ($ClSO_3H$), were also able to digest spent fuel, but the resulting BX_3/BX_4^- mixture was difficult to separate from excess acid and/or was difficult to reduce using mild reductants.

Anhydrous hydrogen chloride (HCl) was not able to digest spent fuel. While HCl did react with spent fuel under pressure, it appeared to simply add across the B-N bonds of spent fuel reversibly and HCl was not able to digest the polymeric structure of spent fuel. In contrast, superacidic systems generated by addition of Lewis acids to HX were able to digest spent fuel. The addition of 55 mol% $AlCl_3$ to the 1-butyl-3-methylimidazolium chloride (BmimCl) ionic-liquid has previously been shown to greatly enhance the acidity and the reactivity of dissolved HCl as a result of the reactions given in Eqns. 5 and 6.[107]

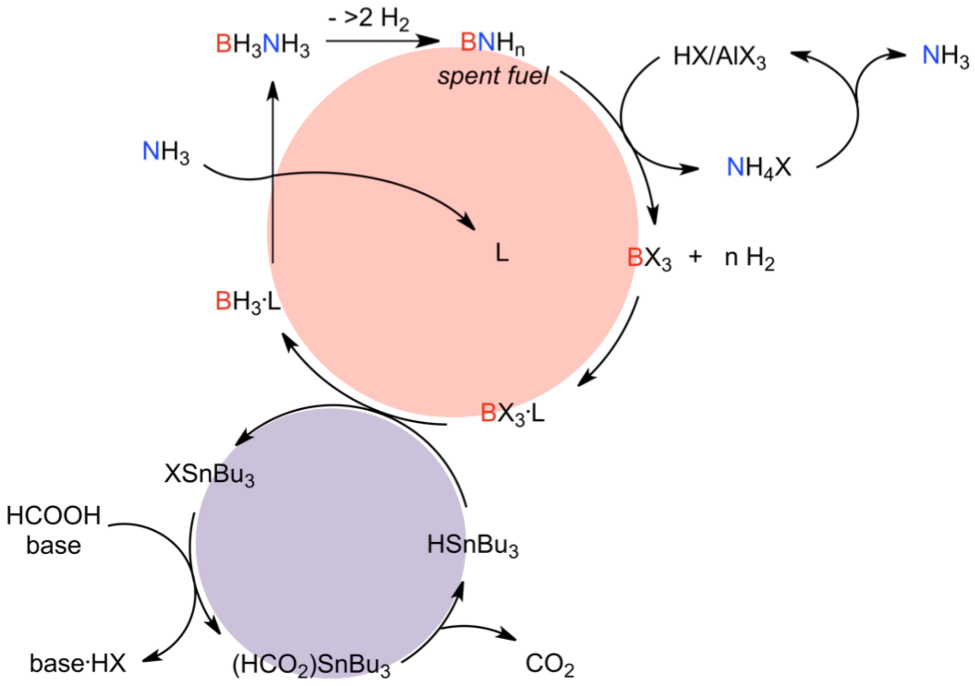
$$(5)\quad \mathrm{BmimX} + 2\mathrm{AlX_3} \rightleftarrows [\mathrm{Al_2X_7}][\mathrm{Bmim}]$$

$$(6)\quad [\mathrm{Al_2X_7}]^- + \mathrm{HX} \rightleftarrows 2\,\mathrm{AlX_4}^- + \mathrm{H}^+$$

When spent fuel was stirred at 65 °C in an $AlCl_3$/bmimCl mixture saturated with HCl, spent fuel readily dissolved with vigorous bubbling. Analysis indicated complete digestion to form $(H_2NBCl_2)_3$, NH_3BCl_3 and $(HNBCl)_3$. For reactions at 90 °C, only the former two products were observed. In these reactions, it was not possible to separate the chloroborane products from the BmimCl ionic-liquid, leading us to investigate alternative superacidic systems, such as superacidic $HBr/AlBr_3/CS_2$ solutions,[10] that could potentially allow product separation. Analysis of the reaction mixture confirmed the formation of BBr_3, which was vacuum distilled from the reaction mixture and then reacted with triethylamine to form its $Et_3N{\cdot}BBr_3$ complex to allow a gravimetric determination (ca. 40% conversion to BBr_3). The remaining balance of material appeared to have been transformed into $[H_2NBBr_2]_3$, but this material was difficult to separate from residual $AlBr_3$ making its reduction to $BH_3{\cdot}L$ impossible. Furthermore, these superacids were only competent in the digestion of singly dehydrogenated spent fuel; these superacids did not digest spent fuel in which ≥2 eq. H2 had been evolved.

While this project was in progress, an encouraging report by Mertens et al appeared[9] claiming that AB spent-fuel digestion was achieved by superacidic $HCl/AlCl_3$/toluene to produce BCl_3 in yields up to 60%. However, we were unsuccessful in reproducing the results reported in the Mertens publication. We explored a number of reactions conditions, but in no case was BCl_3 formation observed in the reactions of superacidic $HCl/AlCl_3$ with spent fuel.

Figure 5: General Penn regeneration scheme using a strong acid to digest spent fuel, combined with the Davis/LANL [Sn] recycling protocol; X = Cl, Br.



The most recent attempts to generate BX_3 (X = Cl) using an acidic digesting agent have focused on chlorosulfonic acid, HSO_3Cl. It is known that thermolysis of $NaB(O_3SCl)_4$ liberates SO_3 and forms $NaBCl_4$,[11] a compound that could be incorporated into the reduction schemes established by the Center (Section 1.5.2). Initial results show that spent fuel is indeed digested by chlorosulfonic acid to generate $[B(O_3SCl)_4]^-$. Chlorosulfonic acid can be industrially prepared by the reaction of hydrochloric acid with sulfur trioxide; hydrochloric acid can be industrially prepared by electrolysis of brine followed by reaction of the resulting chlorine with hydrogen, or as a byproduct of the chlorocarbon industry. Further study is required to determine the energy efficiency of this digestion process, and how it will integrate into successful reduction and ammoniation protocols.

1.5.1.2 Digestion with Alcohols

Spent fuel may be digested using aliphatic alcohols such as methanol (MeOH), ethanol (EtOH) and *tert*-butanol (^{t}BuOH), thereby generating $B(OR)_3$. Ammonia is released during this digestion and may be recaptured for reintegration into later ammoniation processes. Digestion with phenol (PhOH) is also possible; however, PhOH digestion generates $B(OPh)_3\cdot NH_3$, which can undergo unwanted side reactions (Eqns. 7 and 8).

(7) $(PhO)_3B\cdot NH_3 + PhOH \rightarrow [NH_4][B(OPh)_4]$

(8) $(PhO)_3B\cdot NH_3 \rightarrow (PhO)_2B{=}NH_2 + PhOH$

As described in Section 1.5.1.2 and Figure 7, $B(OPh)_3$ is easier to reduce than $B(OR)_3$ so transesterification is a necessary process to make the overall regeneration scheme shown in Figure 9 viable. Addition of PhOH to $B(OR)_3$ and distillation of the lower boiling aliphatic alcohol (HOR) from the mixture produces triaryl borates via transesterification. Since the Lewis acidity of alkyl borates is low, digestion with aliphatic alcohols allows ammonia to be removed from the system prior to transesterification. This avoids generating the troublesome $(PhO)_3B\cdot NH_3$ adduct.

When aliphatic alcohols were used to digest spent fuel, a small amount of fluffy white solid remained after digestion. The identity of the solid was not conclusively determined, however it is consistent with incompletely digested spent fuel containing multiple BN units substituted with alkoxy groups. Haworth observed a similar white non-volatile solid was formed when the 3:1 methanol adduct of borazine was pyrolyzed.[12] This white solid converts to boric acid on treatment with aqueous HCl. Digestion of model compounds borazine and borazine-derived polyborazylene were also performed. Qualitatively, the rates and ease of conversion trended with the decrease in H content of the material. Of the aliphatic alcohols used, ethanol generated the least residual white solid; approximately 80% of boron in spent fuel from AB heated to 150 °C could be recovered as $B(OEt)_3$.

Catechol (o-$C_6H_4(OH)_2$, H_2Cat) reacts with spent fuel model compound borazine ($B_3N_3H_6$) to generate B_2Cat_3. As anticipated, this ortho-diol is a good digesting agent, however the stability imparted to the product of digestion by the five-membered BO_2C_2 ring contained therein makes subsequent steps of the regeneration cycle difficult. Furthermore, the diol is acidic enough to protonate the residual B-H moieties in spent fuel, releasing H_2. Reduction of B_2Cat_3 to a $BH_3\cdot L$ compound was not demonstrated with mild reductants, so this digesting agent was eliminated from consideration.

1.5.1.3 Digestion with Amines

The reaction of *ortho*-phenylenediamine with spent fuel model borazine was examined and the formation of 1,3,2-benzodiazaborolane was observed when a 1:1 ratio of borazine and ortho-phenylenediamine were heated at 60 ˚C in THF for 3 days.[13] The presence of free NH_3 in the reaction vessel was confirmed by the addition of BH_3-THF, resulting in the immediate formation of AB. Although this reaction appeared promising for the selective extraction of B-H bonds within spent fuel, the very slow reaction rate led us to investigate other phenylenediamines. The more electron withdrawing 3-trifluoromethylphenylene-diamine was observed to react significantly faster (6h at 60 ˚C), producing the analogous product 3-trifluoromethyl-benzodiazaborolane in high yield. Attempts to reduce these benzodiazaborolanes with mild reducing agents (i.e. tin hydrides) proved unsuccessful.

Residual B-H moieties can effectively be extracted out of spent fuel using Lewis bases. When polyborazylene is heated at 90 ˚C in excess dimethylaminopyridine (DMAP) for days to weeks, $BH_3 \cdot$DMAP is observed. Excess ammonia reacts in a similar fashion at 25 ˚C to generate AB. In both cases residual, presumably hydrogen-deficient, boron products were observed by ^{11}B NMR. Use of simple Lewis bases like these to extract residual B-H from spent fuel may be used to improve the overall process efficiency of a regeneration process in conjunction with another digesting agent, but they cannot on their own effectively digest spent fuel in high yield.

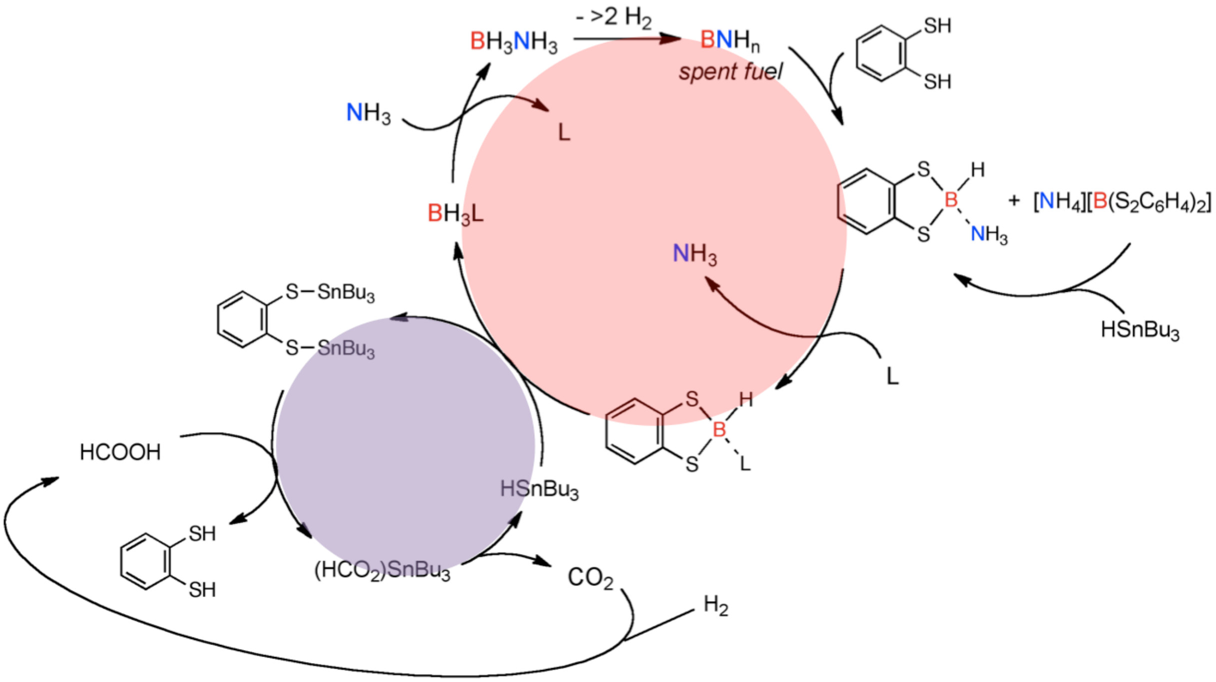
1.5.1.4 Digestion with Thiols

Benzenethiol (C_6H_5SH) does not digest spent fuel while *ortho*-benzenedithiol (o-$C_6H_4(SH)_2$) does digest a variety of spent fuel types. Monothiols have been shown to catalyze dehydrogenation and dehydrocoupling of alkylamine-boranes; we found that the residual hydrogen in spent fuel was protonated to H_2 by monothiols. This inability of benzenethiol to successfully digest spent fuel is likely due to a more favorable entropy of reaction in the case of the bifunctional digesting agent. Calculations estimated that the enthalpy of reaction of digestion of borazine with benzenethiol is 42.2 kcal mol^{-1} (298K, condensed phase); with the expected decrease in entropy, this reaction is unlikely to proceed near room temperature and pressure. While we demonstrated that $B(SPh)_3$ can be readily reduced to $BH_3 \cdot L$ (L = “helper” base) using mild reducing agents (see Section 1.5.2), it was not possible to generate $B(SPh)_3$ from spent fuel through digestion with benzenethiol. Attempts to transesterify alkyl borates with thiophenol were made, but those reactions were unsuccessful.

When o-benzenedithiol is used to digest spent fuel, two products are generated: $(C_6H_4S_2)BH \cdot NH_3$ and $[NH_4][B(S_2C_6H_4)_2]$ (Figure 6).[14] The regenerated ammonia molecule remains coordinated to the boron-containing digestate, in contrast to the similar digestion using o-phenylenediamine. This difference is due to the weaker basicity of the sulfur chelate. Calculations estimated the enthalpy of reaction for digestion of borazine with o-benzenedithiol, generating only $(C_6H_4S_2)BH \cdot NH_3$, to be -20.4 kcal mol^{-1} (298K, condensed phase). When o-benzenedithiol and PB were heated at reflux in THF, 90% of the PB reacted within 12 h.

Observations made in the course of these reactions suggest that $[NH_4][B(C_6H_4S_2)_2]$ might originate from reaction of benzenedithiol and $(C_6H_4S_2)BH{\cdot}NH_3$ as well as any H-depleted boron contained within the spent fuel. This process does not generate NH_4^+ salts that require thermal cracking to release and recycle NH_3.

Figure 6: LANL regeneration scheme using a dithiol digesting agent and a tin hydride reductant.



1.5.2 Reduction

Summary. Choice of the optimal reducing agent is crucial to optimize the chemical yield, and energy efficiency of the recycle of the reducing agent, and thus the overall energy efficiency of the regeneration cycle. Each digestion agent results in digested spent fuel that has differing requirements for strengths of reducing agent. Through the combination of computational chemistry guidance, engineering assessments and experiment that the use of the mildest reducing agent, and the reducing agents with the lowest formula weight per hydrogen transferred were preferable. Detailed discussions regarding reduction of digested intermediates appear in the final reports from Los Alamos National Laboratory, the University of Alabama, the University of Pennsylvania, and Pacific Northwest National Laboratory.

Recycle of the reducing agent is a critical component of an efficient regeneration scheme. The reducing agent can be thought of as a reagent for the transfer of hydrogen equivalents to the spent hydrogen storage material, just as the hydrogen carrier material itself is a storage medium for H_2 before its release at the fuel cell. Thus, the reducing agent must not only be competent for the reduction of spent fuel (or digested spent fuel), but must also have an accessible, relatively low energy recycling pathway.

The Center chose to ignore “traditional” reducing agents such as sodium hydride and lithium aluminum hydride because their preparations require energy intense electrolytic methods via the metal (Na and Al, respectively). Furthermore, these reducing agents have reducing potentials far exceeding that required for regeneration of spent fuel. Reaction with trimethoxyborane ($B(OMe)_3$), for example, results in formation of borohydride (BH_4^-) using either NaH or LAH;[8] this is an over reduction of the boron, instead of simply generating the required BH_3 functionality. Instead of these strong reducing agents, the Center considered transition metal hydrides, tin hydrides, and other main group hydrides.

Table 4: Summary of Center's reducing agent results.

Reducing Agent	**Result**
Dihydrogen	Direct reaction of H_2 with spent fuel is not possible at accessible pressures; H_2 did not react with $XSnR_3$ to regenerate $HSnR_3$ and HX
Transition metal hydrides	Reduction demonstrated, but catalyst turnover not demonstrated
$HRh(dmpe)_2^{*}$	Transfers H^- to BX_3 (X = OPh, SPh, F, Cl), but deemed too expensive
$HCo(PP)_2$	Cannot transfer H^- to $B(OPh)_3$, but can transfer H^- to halogenated derivatives and $B(SPh)_3$
$[HNi(dmpe)_2]^+$	Can transfer H^- to $B(SPh)_3$, but formation of $(H_2)Ni(dmpe)_2^+$ is unfavorable so catalyst turnover may be difficult
Tin hydrides	Reduction demonstrated, but engineering analysis showed that this reductant type is too massive to be cost effective
$HSnBu_3$	Unable to reduce $NH_3{\cdot}HB(S_2C_6H_4)$, but does effectively reduce $L{\cdot}HB(S_2B_6H_4)$ to $BH_3.HNEt_2$ (L = alkylamine); can convert $[NH_4][B(S_2C_6H_4)_2]$ into $NH_3{\cdot}HB(S_2C_6H_4)$
H_2SnBu_2	Can reduce $NH_3{\cdot}HB(S_2C_6H_4)$ to AB, but no efficient recycling pathway was found to regenerate H_2SnBu_2 from the X-Sn products of reduction; H_2SnBu_2 is thermally unstable
Other main group hydrides	While able to reduce B-X bonds, generally were difficult to recycle
Alanes	Can reduce $B(O_2CCF_3)_3$, but efficient recycle was not demonstrated
Silanes	Can reduce some B-X types, but efficient recycle was not demonstrated
Germanes	Thermodynamic calculations indicated Ge-H compounds would be effective reductants, but synthesis and recycling was low-yielding

- PP = dmpe, dedpe ($Et_2PCH_2CH_2PPh_2$)

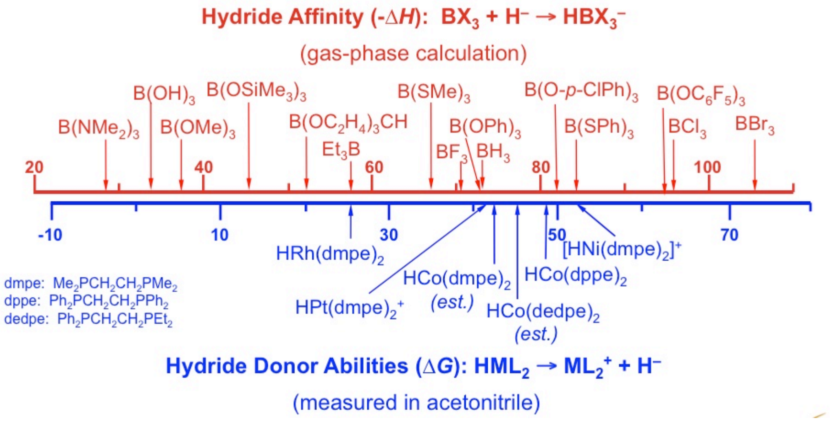
1.5.2.1 Reduction with transition metal hydrides

The Center has designed a scheme that aims to incorporate H_2 directly into the regeneration scheme in a catalytic fashion. We investigated transition metal catalysts (L_nM^+) for the activation and transfer of hydride. Eqn. 9 generally describes this process.

$$(9) \qquad H_2 + \text{base} + BX_3 \xrightarrow{L_nM^+} [HBX_3][Hbase]$$

These catalysts must be able to coordinate H_2, to be deprotonated by a base, to transfer the resulting H^- ligand to BX_3, and to accept X^- with a modest to weak bond that can be broken when another H_2 molecule enters the coordination sphere. The general formula of these complexes is $[M(PP)_2]^{n+}$ where M = Rh (n = 1), Co (n = 1), Ni (n = 2); PP = a diphosphine. In collaboration with Alabama, the hydride affinities of a variety of BX_3 compounds were calculated (Figure 7).[15]

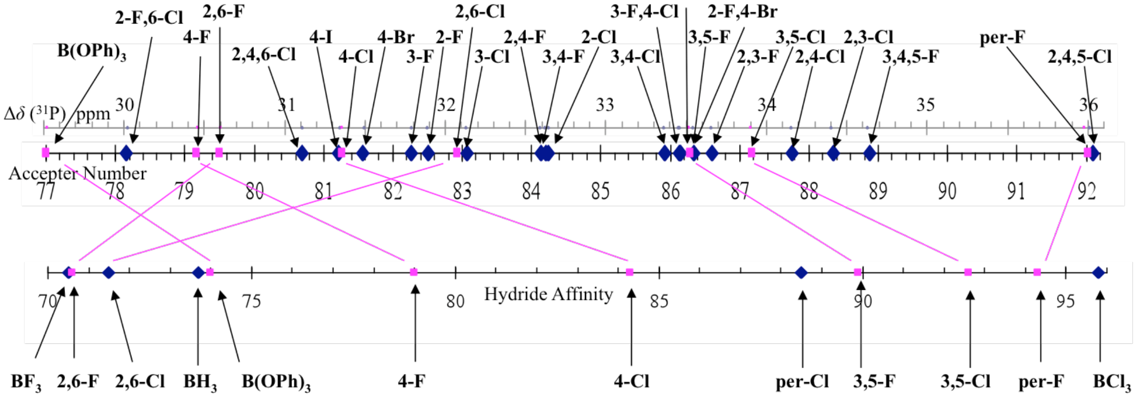
Figure 7: Scales of hydride donor abilities of selected transition-metal hydride complexes (blue, bottom) and the calculated gas-phase hydride affinity values for selected BX_3 compounds (red, top). Reactions of HML_2 with BX_3 compounds to its right are predicted to be favorable.



Coordination and deprotonation of H_2 is facile for M = $Rh(dmpe)_2^+$ and base = *tert*-butoxide. Deprotonation of $H_2Rh(dmpe)_2^+$ was demonstrated with Verkade's super base. Subsequently the reaction of $HRh(dmpe)_2$ with a variety of BX_3 compounds was investigated, showing facile hydride transfer to BX_3 (X = OPh, SPh, F, Cl). Hydride transfer to $B(OPh)_3$ generated $[HB(OPh)_3]^-$ and $[B(OPh)_4]^-$; the latter compound is thought to be formed by ligand redistribution between $[HB(OPh)_3]^-$ and $B(OPh)_3$. Residual phenol could not be eliminated as a contributor to $[B(OPh)_4]^-$ formation. When $HRh(dmpe)_2$ was allowed to react with $B(OPh)_3$ and Et_3N in ether solvent, both Et_3NBH_3 and $dmpeBH_3$ were observed; the latter compound is formed via ligand dissociation from the transition metal catalyst. The reactions between excess $HRh(dmpe)_2$ and BX_3, where X = F, p-methoxyphenyl, or perfluorophenyl, result in the formation of B-H containing products, but are accompanied by formation of BX_4^- to which hydride transfer does not occur. In contrast to these findings, when X = SPh or Cl the major products contain multiple B-H bonds; neither $[B(SPh)_4]^-$ nor BCl_4^- were observed as final products. The reaction of $HRh(dmpe)_2$ with $B(SPh)_3$ in the presence of Et_3N forms Et_3NBH_3 in high yields, a reaction in which all B-S bonds are cleaved.

The high cost of $Rh(dmpe)_2^+$ makes it impractical for large-scale use. Thus, efforts were focused on exploring the feasibility of using non-precious transition metal complexes. It was found that $HCo(dmpe)_2$ is not strong enough of a hydride donor to transfer a hydride to $B(OPh)_3$. However, it readily transfers H^- to $B(OC_6F_5)_3$, which has greater H^- affinity compared to $B(OPh)_3$. On the basis of these observations and recent theoretical analyses, the use of chlorophenols and fluorophenols in place of phenol in the above process with complexes of Co and Ni was considered. Theory was used to identify aromatic borate esters with hydride affinities greater than that of $B(OPh)_3$.[16] Hydride affinities vary over a wide range depending on the type, position and number of halogen substitutions (Figure 8). Approximately 25 compounds were synthesized and their relative Lewis acidities were determined.[17] It was found that Co hydrides dechlorinate chlorophenyl borates instead of generating the desired BH_3-containing product. Furthermore, the reactions of $HCo(dmpe)_2$ with partially fluorinated phenyl borates are complex; esters of monofluorophenols do not have high enough hydride affinities to reaction with cobalt hydrides. $HCo(dmpe)_2$ did react with the borate ester of 3,5-difluorophenol, but the reaction was complicated by side reactions that consumed B-H products and partially decomposed the $Co(dmpe)_2^+$ complex.

Figure 8: Comparison of acceptor number (top) and hydride affinity (bottom) scales for halogenated phenyl borates. Acceptor number correlates with Lewis acidity and is determined from effect of the Lewis acid on ^{31}P NMR chemical shift of triethylphosphine oxide.



Reactions of $B(SPh)_3$ with $HCo(dmpe)_2$ and $HNi(dmpe)_2^+$ were investigated to assess the range of boron compounds that could be reduced with these hydrides. For the Co complex, facile reduction of all B-S bonds to B-H bonds occurs. Reactions in the presence of triethylamine produced triethylamine borane as the sole boron-containing product (Eqn. 10). Recycle of $PhSCo(dmpe)_2$ or $PhSNi(dmpe)_2^+$ may be accomplished by treating with an acidic reagent such as H^+base (Eqn. 11).

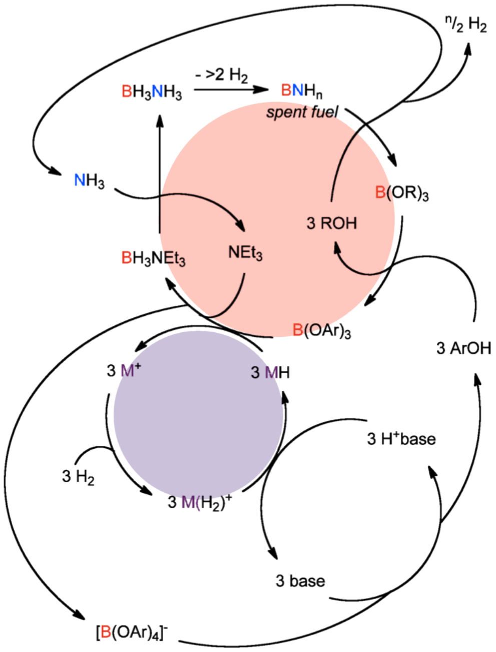
(10) $3\ HCo(dmpe)_2 + B(SPh)_3 + 70\ NEt_3 \longrightarrow H_3B{\cdot}NEt_3 + 3\ Co(dmpe)_2(SPh)$

(11) $PhSCo(dmpe)_2 + H^+base \rightarrow PhSH + Co(dmpe)^+$

A more thorough understanding of reactions of fluorinated phenyl borates with Co hydrides and of fluorinated and chlorinated phenyl borates with Ni^+ hydrides is required. It was observed that Et_3N inhibited hydride transfer from $HCo(dmpe)_2$ to perfluorophenyl borate. For esters that are more Lewis acidic than $B(SPh)_3$ with hydride affinity of ~86 kcal mol^{-1}, it may be necessary to use a more hindered base to carry BH_3 through the process. It is anticipated that deprotonation of the H_2 adduct of $Ni(dmpe)_2^{2+}$ with tertiary amines will be favorable. However, formation of the $(H_2)Ni(dmpe)_2^+$ complex is unfavorable, making the rate too slow; high pressures of H_2 may be required. This or alternate routes to nickel(II) hydride need to be investigated.

As a part of this proposed regeneration scheme (Figure 9), it is critical that $[Hbase]^+$ react with $[B(OPh)_4]^-$ to reform the digesting agent (or transesterification agent) and the base required for MH formation. Thermal gravimetric/differential scanning calorimetric (TG/DSC) and mass spectrometric (MS) analysis on a crystal of the protonated Verkade's super base paired with $[B(OPh)_4]^-$ was completed. The analysis showed that the crystal melts (endotherm with onset at ~214 °C) and subsequently loses 95% of its mass during a second endothermic event culminating at ~360 °C. The mass spectral analysis shows phenol (M+ = 94) to be in the vapor above the sample over this same temperature range. The data suggest that although this reaction is thermodynamically unfavorable it may be driven by distillation of phenol from the products.

Figure 9: PNNL regeneration scheme using an alcohol for digestion and a transition metal hydride for reduction.



1.5.2.2 Reduction with tin hydrides

Trialkylstannanes such as tri-*n*-butylstannane (Bu_3SnH) are known to be mild reducing agents. The Center successfully employed Bu_3SnH in the reduction of several B-X bond types, principally B-Br and B-S bonds. Reaction of Bu_3SnH with $BBr_3{\cdot}S(C_2H_5)_2$ at 0 ^{o}C was complete in minutes to generate $BH_3{\cdot}S(C_2H_5)_2$ and Bu_3SnBr. This reaction required only 3 Bu_3SnH equivalents and no solvent, thus simplifying product isolation. Since both Bu_3SnH and tributyltin bromide (Bu_3SnBr) are nonvolatile at room temperature, the volatile $(C_2H_5)_2S\text{-}BH_3$ product was isolated by distillation.

Tin hydrides were used to reduce the products of ortho-benzenedithiol digestion to $BH_3{\cdot}L$. When Bu_3SnH is added to the mixture of digestion products in Figure 6, $[NH_4][B(C_6H_4S_2)_2]$ is transformed into $(C_6H_4S_2)BH{\cdot}NH_3$ with concomitant generation of $C_6H_4SH(SSnBu_3)$. Follow-on reduction of $(C_6H_4S_2)BH{\cdot}NH_3$ with Bu_3SnH was not successful. Computations indicated that the reaction of dibutyltin dihydride (Bu_2SnH_2) with $(C_6H_4S_2)BH{\cdot}NH_3$ is thermodynamically viable. Experiments subsequently confirmed that $(C_6H_4S_2)BH{\cdot}NH_3$ was transformed into AB using a slight excess of Bu_2SnH_2, with concomitant formation of $Bu_2Sn(C_6H_4S_2)$. Tributyltin hydride *may* be used as the reductant when other Lewis bases replace ammonia. The Lewis basicity requirements of these “helper” amines to facilitate both reduction and the necessary ammoniation are described in Section 1.5.1.3.

tri-*n*-Butyltin formate (Bu_3SnO_2CH) has been previously shown to eject CO_2 and form Bu_3SnH when heated.[18] Thus, we envisioned a recycling strategy in which Bu_3SnH reduced the spent fuel digestate, and the resulting Bu_3SnX (where HX is the digesting agent) can be transformed into Bu_3SnO_2CH by treatment with formic acid and base. The stepwise regeneration of Bu_3SnH from Bu_3SnBr is shown in Figure 5.[19] In the specific case of tin thiolates, treatment with HCl releases ortho-benzenedithiol and generates Bu_3SnCl. Use of either sodium hydroxide or triethylamine in concert with formic acid generates the desired tin formate quantitatively and in one pot. Distillation of the tin formate through a column of 3 mm Raschig rings at reduced pressure (112 ˚C, 0.3 Torr) generated Bu_3SnH in 60% isolated yield. Use of base (sodium hydroxide or triethylamine) in this recycling reaction is necessary to lower the free energy of reaction (Table 5). However, base use effects the overall reaction efficiency since energy is required to recycle these reagents.

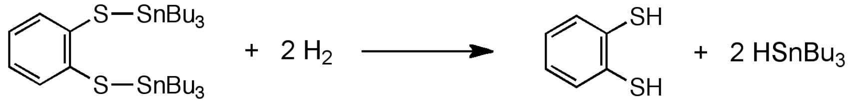
Table 5: Reaction energies (kcal mol^{-1}) for reaction of Bu_3SnX with formic acid to generate the corresponding tin formate and HX.

Bu_3SnX + HCOOH	ΔH	ΔG
X = Cl	12.4	13.0
X = Br	15.6	15.4

While dibutyltin dihydride was able to effectively generate AB from $(C_6H_4S_2)BH{\cdot}NH_3$, it is somewhat unstable at room temperature and no literature methods exist for its recycle. We prepared dibutyltin diformate, and it has an oligomeric structure. No evolution of CO_2 from this diformate was detected at temperatures up to 200 ˚C, presumably because some additional stability is conferred by the oligomeric structure. Computations indicated that $Ar_2Sn(O_2CH)_2$ (Ar = mesityl or 2,6-diisopropylphenyl) would have a mildly exergonic CO_2 release (ΔG = -2 to -6 kcal mol^{-1}) to generate diaryltin dihydride, but these compounds were difficult to prepare.

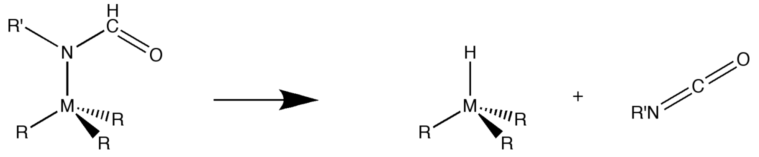
Direct hydrogenolysis of Bu_3SnX to recycle the reducing agent and release the digesting agent was considered. A computational investigation of the condensed phase reaction between hydrogen and Sn-S bonds in $(o\text{-}C_6H_4S_2)(SnBu_3)_2$ indicated that the reaction has a free energy of ca. 4.2 kcal mol^{-1}, mildly endergonic and potentially achievable with heating (Figure 10). Experimental reaction of $(o\text{-}C_6H_4S_2)(SnBu_3)_2$ with excess H_2 at 70 ˚C in a pressure vessel (80 psi) was inconclusive, however; a catalyst may be required. It can be expected that isolation of the products from one another will be somewhat challenging here, since the reverse reaction is thermodynamically favored and neither product has a conveniently low boiling point to facilitate separation via distillation. While hydrogenolysis of other Sn-X molecules was not attempted, it is probable that Sn-S is more susceptible to cleavage than Sn-O or Sn-halogen bonds because Sn-S bonds are the weakest of the three types.

Figure 10: Hydrogenolysis of Sn-S bonds.



Engineering analysis (Section 1.7) by ANL and Dow of the tin-based reduction chemistry indicated two points of concern. First, synthesis of formic acid is energy intensive due to the required compression of CO_2. Thus, LANL investigated (with computational input from Alabama) replacement of CO_2 with isoelectronic dicyanamides ($C(NR)_2$) or isocyanates (OCNR) (Figure 11). Isocyanates and dicyanamides are liquids or solids at standard temperature and pressure, making the compression requirements described for CO_2 moot. While calculations indicated that the tin formate analogs (Figure , left) would be energetically accessible, and would generate the tin hydride with modest heating, experimentally the required compounds were not easily accessible.

Figure 11: Strategy to replace CO_2 with isocyanate RNCO in tin hydride generation; M = Sn.



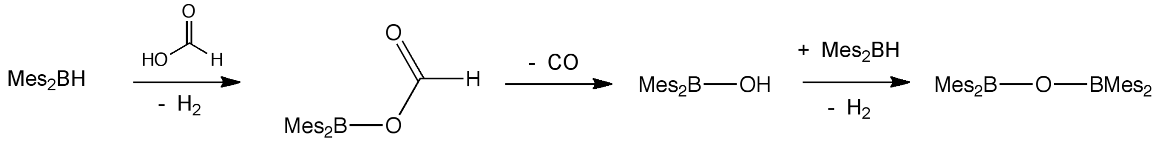
Secondly, engineering analysis showed that a less massive reducing agent would be favorable; the energy required to move the significant mass of a tin-based reducing agent (relative to AB) through a chemical process caused the Center to consider regeneration schemes that utilize reducing agents of as low molecular weight as possible.

1.5.2.3 Reduction with other main group hydrides

Trialkylsilanes (R_3SiH; R = Et) can be used in a manner analogous to trialkyltin hydrides to reduce B-X bonds. In the particular case of B-Br bonds, reduction of $R_2S\text{-}BBr_3$ with Et_3SiH generated $R_2S\text{-}BH_3$ complexes.[20] The reaction rate varied depending on the identity of the coordinated R_2S base. Reactions with R = *n*-alkyl (dimethyl, dibutyl, etc.) required >12 h and 55 ˚C for complete reduction, but the diisopropyl derivative was complete in only 3-4 h. Because of its low-volatility, which enabled efficient isolation of the $(C_6H_{13})_2S\text{-}BH_3$ adduct, the dihexylsulfide was employed in the optimized process. The Et_3SiBr coproduct and any remaining Et_3SiH were then vacuum distilled from the reaction mixture and separated by trapping at -25 ˚C and -78 ˚C, respectively. Because of its low volatility, the $(C_6H_{13})_2S\text{-}BH_3$ adduct remained in the reaction flask. While this process had a high yield, we have no energy efficient method to recycle Et_3SiH from Et_3SiBr, so silanes were eliminated from consideration.

We postulated that other Group 13 and Group 14 formates analogous to the tin formates discussed in Section 1.5.2.2, and their resulting hydrides, would be possible substitutes for the tin reductants. While it was possible to generate a boron formate $R_2B(O_2CH)$, thermolysis of this compound resulted in ejection of CO, not CO_2, and concomitant formation of a B-OH moiety (Figure 12). Computational analysis indicated that heavier congeners (Si, Ge, Ga) would have more favorable formation of M-H than the boron congeners (that prefer to eject CO, thereby forming M-OH). However, silicon, germanium, and gallium formates were difficult to prepare, required large protecting groups (thereby increasing the reagent mass unacceptably), or did not form the desired hydride upon thermolysis.

Figure 12: Generation of a boron formate and its release of CO.



Nanoparticulate silicon with surface hydride moieties was investigated as a reductant (Table 6). Mixtures of sodium silicide, ammonium bromide, and spent fuel or digested spent fuel were heated to and AB was observed among the products. We explored the regeneration of B–H bonds from B–O and B-Cl model systems, by reacting nanoparticles of hydrogen terminated Si nanoparticles with $B(OPh)_3$, $B(OBu)_3$ and BCl_3 in solution. However, AB appeared to be unstable in the product mixture and separation of AB from the mixture was not optimized.

Table 6: Regeneration reactions using hydrided silicon nanoparticles.

$NaSi + NH_4Br + B(OR)_3 \rightarrow Si_y(OR)_xH_{1-x} + BH_x(OR)_{3-x} + H_2 + NH_3 + NaBr$ (THF, 60˚C), R=Ph, tBu
$Si)H + NH_4Br + B(OR)_3 \rightarrow Si_y(OR)_xH_{1-x} + BH_x(OR)_{3-x} + H_2 + NH_3 + HBr$ (THF, 60˚C), R=Ph, tBu
$SF + NaSi + NH_4Br \rightarrow H_3NBH_3 + NaBr + H_2 + NH_3 + Si_y(OR)_x$ (THF, 60˚C), SF = BNH_x (x=1-2)
$SF + Si)H + NH_4Br \rightarrow H_3NBH_3 + HBr + H_2 + NH_3 + Si_y(OR)_x$ (THF, 60˚C), SF = BNH_x (x=1-2)
$CTB + NaSi + NH_4Br \rightarrow H_3NBH_3 + NaBr + H_2 + NH_3 + Si_y(OR)_x$ (THF, 60˚C), CTB = $N_3B_3H_{12}$
$CTB + NaSi + NH_4Br \rightarrow H_3NBH_3 + NaBr + H_2 + NH_3 + Si_y(OR)_x$ (THF, 60˚C), CTB = $N_3B_3H_{12}$
$BCl_3 + NaSi + NH_4Br \rightarrow H_3NBH_3 + NaBr + H_2 + NH_3 + Si_yCl_x$

The digestate from the reaction of spent fuel with TFA was found to react with dimethylethylamine-alane ($Me_2EtN{\cdot}AlH_3$) to form dimethylethylamine-borane ($Me_2EtN{\cdot}BH_3$). However, dimethylethylamine could not be displaced from $Me_2EtN{\cdot}BH_3$ by ammonia to produce AB. Furthermore, the Center has no route to efficiently regenerate the alane reducing agent from the AlX_3 or $[AlX_4]^-$ coproducts, so this reductant class was eliminated from consideration.

1.5.3 Ammoniation

Summary. Ammoniation reactions were often necessary to complete a regeneration cycle. Certain aspects of the digestion and reduction steps often required that the ammonia ligands of boron intermediates be replaced with amines or other ligand types to achieve higher conversions and/or higher rates of conversion. Replacement of these 'helper' ligands with ammonia was thus necessary to complete the regeneration cycle and produce ammonia borane. Study of amine replacement, and re-ammoniation reactions using both computational chemistry tools and experiment enabled the Center to choose the most chemically and energetically efficient pathways. Additional detail on the ammoniation processes appear in the final reports from Los Alamos National Laboratory, the University of Alabama, the University of Pennsylvania, and Pacific Northwest National Laboratory.

Ammoniation reactions were some of the first studied by the Center in the context of regeneration development. In the 2006 Annual Progress Report, the Center presented the use of diethylaniline (NEt_2Ph) as a "helper" amine to encourage disproportionation of reduced spent fuel.[21] Ammonia can readily displace diethylaniline from $BH_3{\cdot}NEt_2Ph$; K_{eq} (298K) >> 1, $t_{1/2} <$ 30 min. Using a combination of experimental calorimetry and computations, the relative $BH_3{\cdot}L$ bond strengths for a variety of Lewis bases were measured (Table 7).[22] The similarity between the solution thermodynamic values of AB and $BH_3.{\cdot}NEt_3$ indicates that the ammonia and triethylamine may form an equilibrium with BH_3 in solution. This was verified, and the reaction of NEt_3 with AB has $K = 0.2$ at 25 °C.

Table 7: Experimental enthalpies (kcal mol^{-1}) for reaction of Lewis bases with 0.5 M $THF{:}BH_3$ in THF solution and calculated gas phase reaction enthalpies.

Lewis base (L)	**ΔH° (solution)**	**ΔH° (gas phase, calculated)**
NH_3	-14.9 ± 0.1	-5.3
NH_2Pr	-19.1 ± 0.5	-12.3
$NHEt_2$	-16.9 ± 0.3	-13.6
NEt_3	-14.6 ± 0.1	-15.2
NPh_3	No exotherm	2.3
Pyridine	-12.7 ± 0.3	-11.8
Lutidine	-5.4 ± 0.5	-10.1
PEt_3	-16.6 ± 0.3	-18.1
PPh_3	-12.4 ± 0.3	-16.1
SMe_2	-3.3 ± 0.1	-3.6

The Center examined experimentally and computationally a variety of Lewis bases that may facilitate disproportionation reactions and may be replaced by ammonia. It was discovered, as described in Section 1.5.2.2, that Bu_3SnH was unable to reduce $(C_6H_4S_2)BH\cdot NH_3$. However, other bases can replace ammonia, and in some cases this facilitates subsequent reduction of the boron to $BH_3\cdot L$. Some of these results are presented in Figure 13 and Table 8. Experimentally it was found that diethylamine readily displaced ammonia in Reaction A and was displaced by ammonia in Reaction C; however, the reduction chemistry in Reaction B was low yielding when $L = HNEt_2$.

Figure 13: Computational examination of "helper" base L participation in reduction of B-S bonds by tin hydrides.

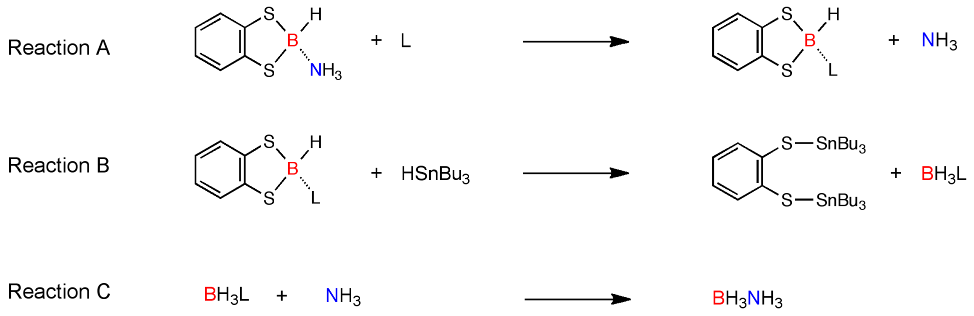


Table 8: Computed enthalpies and free energies of reaction for Figure 13.

	Reaction A		**Reaction B**		**Reaction C**	
	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
Triethylamine NEt_3	6.2	9.2	-4.7	5.6	-1.3	1.0
Diethylamine $HNEt_2$	-1.0	1.0	0.1	10.0	-3.7	-2.8
n-Propylamine H_2N^nPr	-4.5	-3.3	2.7	13.0	-4.6	-4.1
Piperidine $C_5H_{11}N$	-5.5	-3.7	1.5	11.6	-6.8	-5.9
Dimethylaminopyridine $4\text{-}(NMe_2)C_6H_5N$	-5.4	-4.5	2.1	11.5	-6.0	-6.7
Phosphine PH_3	14.4	13.7	-4.7	6.7	-5.2	-6.7
Trimethoxyphosphine $P(OMe)_3$	7.3	8.0	-10.2	1.1	5.7	4.6
Methyldimethoxyphosphine $P(OMe)_2Me$	4.7	5.3	-8.5	2.1	6.9	6.2
Dimethylmethoxyphosphine $P(OMe)Me_2$	0.8	2.9	-6.2	3.5	8.2	7.4
Trimethylphosphine PMe_3	-0.7	0.0	-3.9	6.2	7.4	7.6

Trialkylamine borane produced in the PNNL scheme can be converted to AB using ammonia recovered from digestion of spent fuel. The thermochemistry of the formation of Lewis adducts of BH_3 in tetrahydrofuran (THF) solution and the gas phase and the kinetics of substitution of ammonia on triethylamine borane were performed. The results show that Et_3NBH_3 is suited to displace NH_3 when reacted in THF solution. Kinetic and equilibrium data on the ammoniation reaction of NEt_3BH_3 were measured by letting solutions of Et_3N and AB in THF come to equilibrium in sealed tubes (Eqn. 12).

(12) $NH_3BH_3 + Et_3N \longrightarrow Et_3NBH_3 + NH_3$

The relative concentrations of Et_3NBH_3 and AB were monitored by ^{11}B NMR spectroscopy as a function of time for temperatures of 23-50 °C. The reaction exhibits a strong temperature dependence evidenced by the Arrhenius rate parameters: $E_a = 28$ kcal mol^{-1} and log A =15. $K_{eq} = 0.2$ at 25 °C and it's variation with temperature is small suggesting that $\Delta S°$ is small for the reaction such that $\Delta H° \approx \Delta G° = 1$ kcal mol^{-1} at 25 °C.

Investigation of factors affecting Lewis acidity of BH_3 and $B(OPh)_3$ suggest that tertiary amines such as triethylamine are suitable carriers for BH_3. They exhibit weak interactions with $B(OPh)_3$ due to front strain and so should not block H^- transfer. Conversely, they exhibit strong interactions with BH_3, which will favor it formation by ligand redistribution reactions, and yet the interaction is comparable to that for ammonia such that ammonia should be able to displace triethylamine in the ammoniation step.

A tertiary "helper" amine is used to drive production of an amine:BH_3 adduct instead of BH_4^- in reaction of $HM(PP)_2$ with spent fuel. Aprotic trialkylamine boranes are volatile and do not suffer H_2 loss like AB. These are desirable properties because the overall unfavorable thermochemistry for regeneration of AB requires the use of heat to drive reactions and overcome sluggish kinetics. The thermochemistry of forming dative bonds to BH_3 and $B(OPh)_3$ were elucidated by PNNL and Alabama using computational methods and experimental calorimetry. The results show that Et_3N binds weakly to $B(OPh)_3$ and does not hinder H^- transfer. Conversely, Et_3N binds strongly to BH_3, which favors its formation over BH_4^-. Finally, it was observed that Et_3N inhibited hydride transfer from $HRh(dmpe)_2$ to $B(OC_6F_5)_3$. Here it seems that the much greater Lewis acidity of $B(OC_6F_5)_3$ with HA ~ 95 kcal mol^{-1} requires a BH_3 carrier that is more sterically hindered than Et_3N to frustrate dative bond formation. 2,6-Lutidine may in this case be preferable to Et_3N.

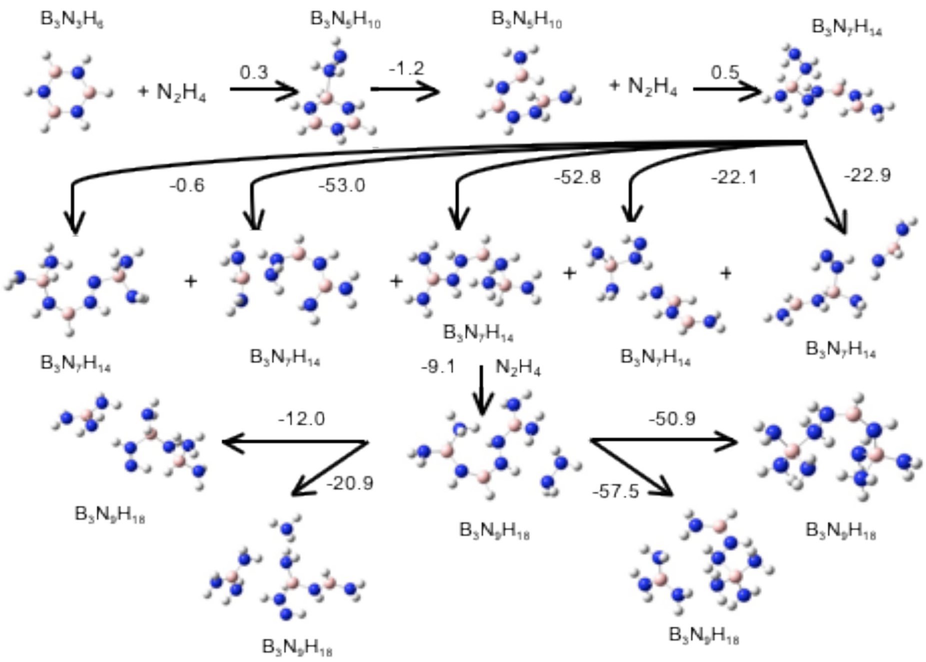
1.6 One-pot Regeneration using a Dual Digesting/Reducing Agent

Summary. The complexity of the demonstrated thiocatechol-based regeneration schemes discussed in Sections 1.5.1.4 and 1.7.2 that were subjected to engineering cost analysis (Section 1.8.1.1) suggested that simpler processes using lower molecular weight reducing agents were necessary to reduce capital and operating costs. Hydrazine represents the lowest molecular weight reducing agent per hydrogen delivered, other than H_2 and other metal hydrides that are not efficiently recycled (e.g. LiH, MgH_2, $LiAlH_4$, etc). This motivated the exploration using hydrazine as a reducing agent, and led to the discovery that spent fuel could be regenerated in a

single step using a combination of hydrazine in liquid ammonia. More detailed discussion of the hydrazine reduction process appears in the final report from Los Alamos National Laboratory.

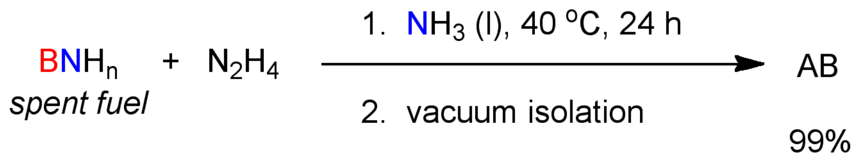
Anhydrous hydrazine (H_2NNH_2) reacts with spent fuel (several types) in liquid ammonia to generate AB directly.[23] Hydrazine is a strong reducing agent, transferring its hydrogen atoms to an acceptor and releasing dinitrogen. Here we propose that hydrazine initially reduces the boron in spent fuel. A mechanism for this digestion and reduction was investigated computationally, starting with addition of hydrazine to a borazine-like boron center, followed by generation of a new B_{ring}-NH_2 moiety in near thermoneutral reaction steps. This is followed by ring opening reactions and further digestion into monomeric units in exothermic reactions.

Figure 14: Energies (ΔH_{298}) in kcal/mol of one of the ten 2nd addition products of trans-$B_3N_3H_6(NH_2)_2$ and a limited set of 3rd addition products.



Subsequently, the reaction proceeds via an observed $BH_3{\cdot}H_2NNH_2$ intermediate that undergoes ammoniation. This process was computationally determined to be modestly exothermic ($\Delta H_{298K} = -6.95$ kcal mol^{-1}) and exergonic ($\Delta G_{298K} = -22.88$ kcal mol^{-1}). Hydrazine can also effectively digest $[BH_2NH_2]_5$ to generate a mixture of $BH_3{\cdot}H_2NNH_2$ and AB. Substituted hydrazines were examined, but were incompetent in this regeneration reaction. Furthermore, spent fuel generated in an ionic liquid system can also be regenerated using hydrazine. *Please note here that hydrazine-bis borane ($H_2NNH_2{\cdot}2BH_3$) is explosive*;[24] we always use excess hydrazine to avoid its formation and hydrazine-bis borane has never been observed in our reaction mixtures.

Figure 1: LANL One-pot, hydrazine-based regeneration of spent fuel.



$$\underset{\text{spent fuel}}{BNH_n} + N_2H_4 \xrightarrow[\text{2. vacuum isolation}]{\text{1. } NH_3 \text{ (l), 40 } ^{o}\text{C, 24 h}} \underset{99\%}{AB}$$

Regeneration using a slight excess hydrazine can occur in a one-pot process.[23] While initially it was believed that a "helper" base would be required just as in the dithiol-based Figure 6, use of a slight excess of hydrazine led to isolation of 99% AB in purity comparable to commercially available material. This process requires the use of a pressure vessel to keep the ammonia liquid above its boiling point. A baseline cost estimate of this process was performed by Dow and is detailed in Section 1.7.1.3.

Note: do not attempt using the hydrazine process to regenerate spent fuels from M-AB compounds! Alkali and certain other metal hydrazides are potentially explosive!

1.7 Summary of Demonstrated Spent Fuel Regeneration Schemes

This section outlines all of the complete regeneration schemes that were demonstrated at a laboratory scale. All chemical steps were shown to occur at reasonable rates and with high yields. In many cases, spent fuel was added to a reaction vessel, pure AB was extracted, and chemistry for the recycle of the reductant was either demonstrated or well-known from literature precedent and/or industrial practice.

Many variants of the benzenethiocatecholate digestion route were demonstrated in the laboratory as the Center gained both experience from laboratory results, guidance from theory, and guidance from engineering assessments provided by Dow, ANL, and TIAX. Significant improvements in this iterative process are captured in the following sub sections.

The sub sections below appear roughly in chronological order of development.

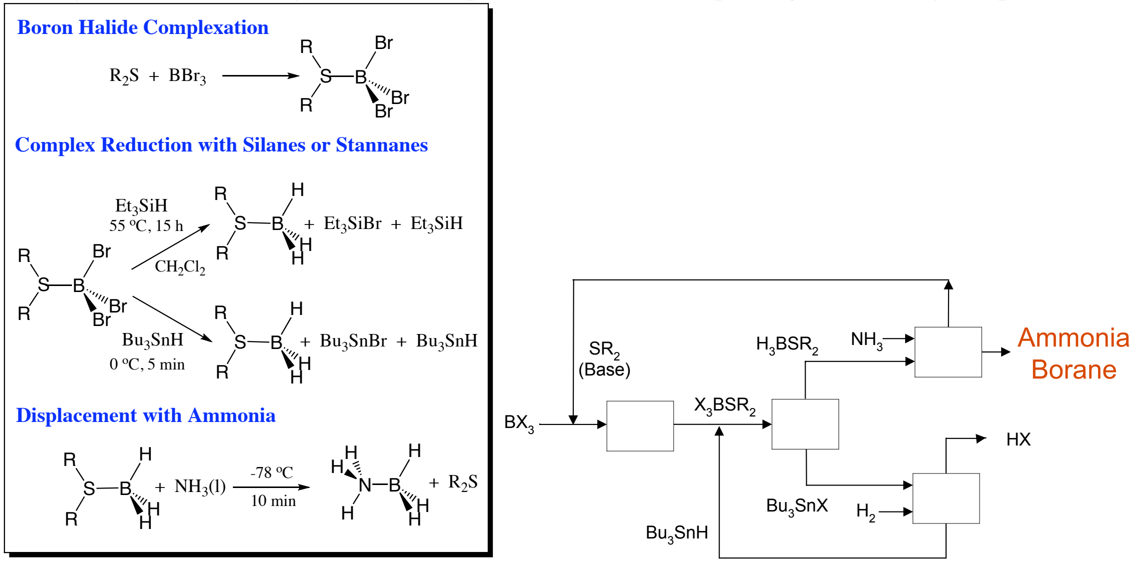
1.7.1 Strong acid digestion

Our partner, Professor Larry Sneddon at the University of Pennsylvania, accomplished the first and second demonstrations of regeneration of ammonia borane from a spent fuel BNHx.

1). The first successful approach is discussed in Section 1.5.1.1, and involved the use of the strong acid trifluoroacetic acid. Trifluoroacetic acid completely digests spent fuel to generate boron trifluoroacetate, and all residual B-H bonds are removed as H_2. Subsequent reduction of the boron trifluoroacetate with a strong aluminum hydride reducing agent in the presence of a 'helper' amine ligand generated an amine-borane complex that could subsequently be trans-amminated to AB. While the Center was pleased to have demonstrated chemical regeneration for the first time, the Center recognized that recycle of the metal reduction product, an aluminum trifluoroacetate, would be difficult, and would most likely have to be recycled back via hydrolysis to trifluoroacetic acid and alumina that would have to be recycled back to aluminum metal, and then to the aluminum hydride. This recycle of the aluminum hydride was though impractical, and so aluminum hydrides for regeneration were not down selected for further study. It was also felt at the time that the use of trifluoroacetic acid could be cost prohibitive as well. These lessons learned led to the *second* demonstrated chemical process for spent fuel regeneration:

2). As it was known that the reduction of BX_3 could be carried out with less potent reducing agents than aluminum hydrides, routes to digestion that resulted in BBr_3 were sought as discussed in Section 1.5.1.1. The super acid mixture of $HBr/AlBr_3$ was demonstrated to produce BBr_3 that was subsequently reduced through a series of steps result in very high yields of AB. This chemistry is shown schematically in Figure 5 and is also shown schematically below in Figure 16 along with a hypothetical process flow sheet generated by our partners at Dow.

Figure 16. Outline of the Center's second demonstrated chemistry of BX_3 reduction with either silicon or tin hydrides followed by ammonia displacement of the 'helper' ligand R_2S to yield pure AB.



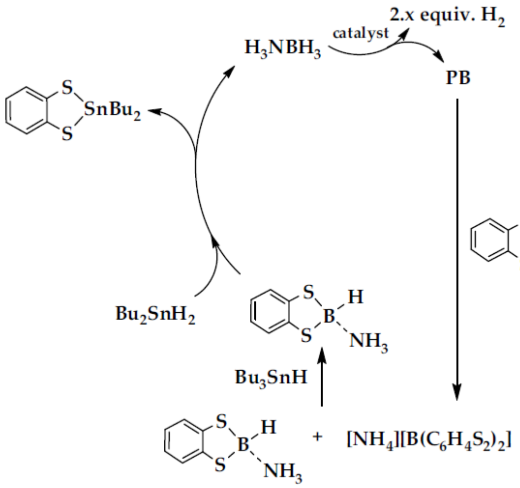
While the chemistry of reduction of BBr_3 was chemically very efficient resulting in near-quantitative yields of AB from BBr_3, the digestion of spent fuel with $HBr/AlBr_3$ was found to give only moderate yields of BBr_3 in addition to significant intractable byproducts that could not readily be reduced to B-H products. Because this regeneration scheme, although complete, did not have sufficiently high overall yields of AB, it was not down selected for further development. The Center did learn, however, that the reduction chemistry of tin hydrides with boron- X bonds could be high yielding, and this finding inspired subsequent additional successes in spent fuel regeneration outlined below.

1.7.2 Thiocatechol-based regeneration

The *third through seventh* demonstrated chemical processes for spent fuel regeneration involved digestion of spent fuel with thiocatechol as discussed in Section 1.5.1.4.

3). Reduction of the mixture of boron products from thiocatechol digestion was first attempted with a tin dihydride, as shown below in Figure 17.

Figure 17. Schematic of the Center's third demonstrated regeneration scheme using tin dihydride as reductant. PB = polyborazylene, spent fuel.



The resulting tin product of reduction, a tin thiocatecholate, was recyclable via reaction with formic acid and subsequent thermal decomposition of a bis formato-tin complex back to the tin dihydride via a literature method. It was found that the tin dihydride was too thermally labile to be useful for this chemistry, and its use was discontinued.

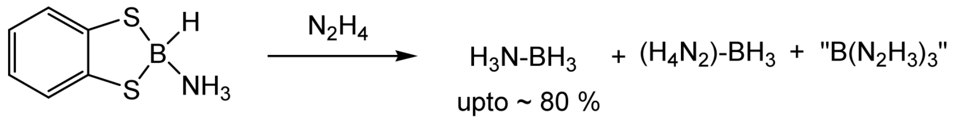
The knowledge gained from the tin dihydride approach led to the *fourth* demonstrated regeneration cycle that is shown schematically in Figure 6 in Section 1.5.1.4.

4). The fourth scheme was demonstrated using spent fuel, and recovered AB in greater than 70% yield at a laboratory scale. ANL performed a preliminary energy efficiency analysis of this scheme, and it was found that the formic acid recycle consumed a substantial fraction of the overall regeneration energy budget. Details of this analysis are given in Section 1.8.1.1 below. Re-compression of the CO_2 to re-synthesize formic acid was the major source of the energy cost. Because of this, alternatives to formic acid-based recycle of the tin hydride were sought. These lessons learned led to the *fifth* demonstrated spent fuel regeneration scheme.

5). The *fifth* successfully demonstrated regeneration scheme was identical to the fourth as shown in Figure 6 with the exception that the formic acid recycle of the tin hydride was replaced with a metal catalyzed hydrogenolysis of the tin thiocatecholate byproduct to give thiocatechol and tin hydride. Dow performed a cost analysis on this particular regeneration scheme that is discussed in further detail in Section 1.8.1.1. Dow's assessment of this scheme led to an estimated regeneration cost of \$7-8/kg H_2 at an industrial scale.

Dow's assessment of this scheme indicated that much of the cost was in the utilities and capital related to the numerous separations steps required of the equilibria limited transamination steps, and also because of the very significant amount of mass of tin compounds that were being used to simply move hydrogen equivalents through the reaction sequence. Dow recommended that other regeneration schemes that used lower mass reductants be explored in addition to schemes that required fewer reaction steps, and hence fewer unit operations. These lessons in turn led to the *sixth* regeneration scheme demonstrated by the Center.

6). In the search for a lower mass reductant to address the opportunities indicated in Dow’s analysis of the thiocatecholate/tin hydride scheme, the use of hydrazine (N2H4 FW= 32) to reduce a spent fuel digested with thiocatechol was attempted. This scheme is indicated in the reaction scheme in equation 13.



(13)

When hydrazine was reacted with the major component of thiocatechol-digested spent fuel, the boron mono(thiocatecholato)boron complex shown in Equation 13, up to 80% AB is formed. The remainder of the boron exists as hydrazine borane complex, and a small quantity of a boron species that contains hydrazine. Unfortunately, hydrazine did not react with the other major component of thiocatecholate spent fuel, a bisthiocatecholateboron compound. While this latter complex is converted to the mono(thiocatecholate) complex with tin hydride, this was felt to be too complex. Instead, in the seventh complete regeneration process demonstrated by the Center, spent fuel was digested and reduced with hydrazine in THF solvent.

1.7.3 Direct Digestion and Reduction with Hydrazine

7). When spent fuel is digested and reduced by hydrazine in THF solvent, AB is recovered in good yields along with the hydrazine borane complex and a small amount of the unknown boron species first seen in the thiocatecholate reduction with hydrazine. This seventh process is shown below in Figure 18.

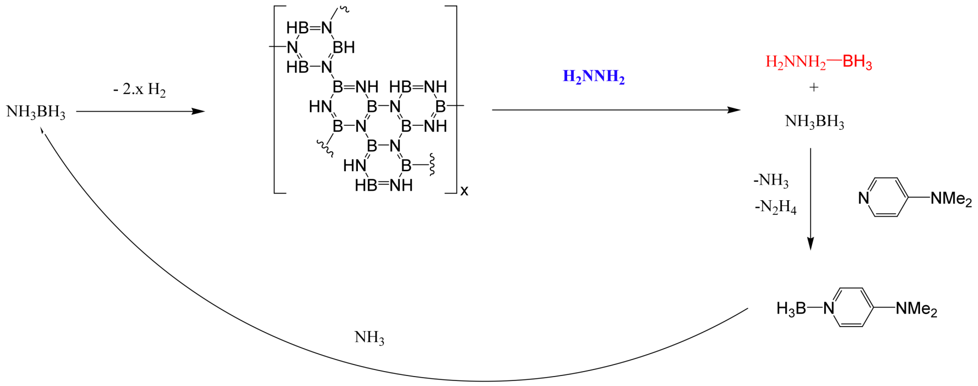
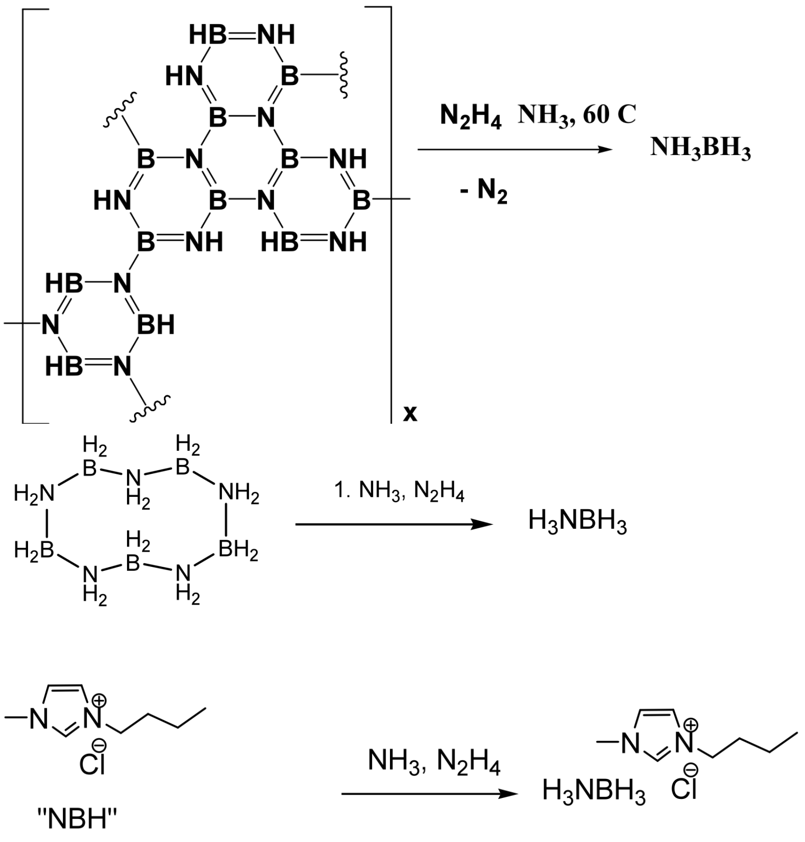


Figure 18. Direct digestion and reduction with hydrazine in THF solvent.

The challenge for this seventh scheme is the conversion of the co-product hydrazine borane. Replacing the hydrazine with ammonia was found to be surprisingly slow, and so once again, ‘helper’ ligands were used to first displace the hydrazine, to form in this case the dimethylaminopyridine borane complex that could be readily converted to ammonia borane with ammonia. This was felt to be too complex. It also appeared that there is an opportunity to force the transamination reaction by replacing the THF solvent with liquid ammonia solvent to drive the transamination of the hydrazine borane complex directly to AB without the use of a ‘helper’ ligand. This idea led to the *eighth* demonstrated regeneration cycle.

8). By digesting and reducing spent fuel with hydrazine to generate mostly ammonia borane and hydrazine borane and then subsequently converting the hydrazine borane to ammonia borane with high concentrations of ammonia, it became obvious that the entire reaction could be run in ‘one pot’. Digesting and reducing spent fuel in liquid ammonia at 60 °C in a pressure vessel sped the reaction to completion, yielding ammonia borane in high yield that could be isolated by removing the liquid ammonia solvent, as is shown below in Figure 19. This approach works equally well with the so-called ‘pentamer’ that results from certain catalytic processes that release only one equivalent of hydrogen from AB, and it also works well in the presence of ionic liquids. Thus ‘one pot’ hydrazine regeneration offers a significant amount of process flexibility, which is a significant advantage over all other methods the Center explored.

Figure 19. ‘One pot’ direct digestion and reduction of spent fuel, ‘pentamer’, and IL/spent fuel to AB.



This regeneration scheme addressed both of the lessons learned from the thiocatecholate/tin hydride route analyzed by Dow. It lowers the mass of reagents used substantially, and it minimizes the number of steps. Dow performed a preliminary cost assessment of this process, and the details appear in Section 1.8.1.3. This analysis indicated that these improvements result in significant decrease in capital and operating costs, but that the raw materials costs of hydrazine dominate the overall cost. ANL also performed a preliminary 'well-to-tank' energy efficiency analysis, which indicated that the energy intensity of hydrazine production dominates the overall energy intensity of the regeneration process. Thus, to make this 'one pot' regeneration scheme feasible from both a cost and an energy efficiency standpoint, dramatic improvements in the process of hydrazine manufacture must be accomplished.

1.8 Analyses Performed – Engineering Assessments

Summary. Engineering assessments were conducted on promising, demonstrated regeneration chemistries, and on hypothetical on board release systems to provide guidance to the experimental work, and provide confirmation that both off board regeneration and the chemical hydrogen storage are potentially viable approaches to on board vehicular storage. Engineering assessments helped this Center to make down select decisions and make rapid progress. More information on the engineering assessments of the regeneration processes appear in the final reports from Los Alamos National Laboratory, Pacific Northwest National Laboratory, and Dow Chemical Company.

Engineering and cost assessments of potential regeneration schemes were initiated as viable regeneration chemistry was developed. Argonne National Laboratory has completed engineering assessments; baseline cost assessments have been completed by Center partner Dow and verified by TIAX (as an independent assessment for DOE). The regeneration schemes assessed were: (A) dithiol digestion / tin hydride reduction; (B) alcohol digestion / transition metal hydride reduction; and (C) treatment with hydrazine. For (A), (B), and (C), the Center provided ANL engineers with full cycles including recycle of all necessary reagents. Dow's assessment of (A), (B), and (C) made appropriate assumptions to create a conceptual process, establishing the necessary material and energy balances, and scaled up to a commercial plant producing AB at a rate equivalent to 100 metric ton per day of H_2 delivered as AB. TIAX verified Dow's methodology, assumptions, and cost estimates.

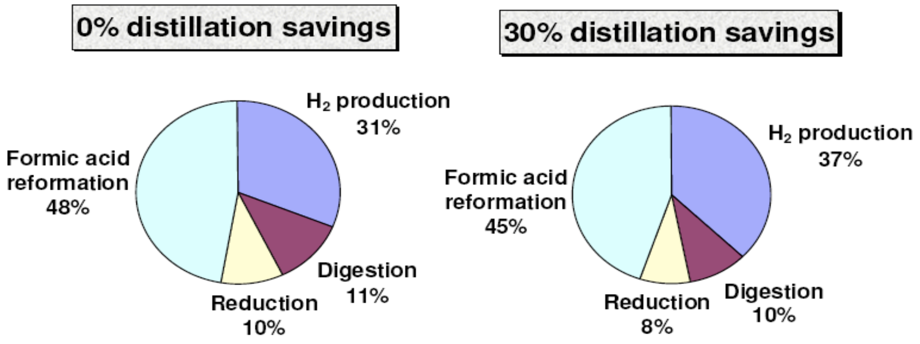
1.8.1 Assessment of ortho-benzenedithiol digestion and tin hydride reduction

LANL provided ANL and Dow with a list of reactions (Table 9) that represent chemistry similar to that shown in Figure 6. The reactions in Table 9 are consistent with the chemistry published by Davis et al. in *Angewandte Chemie, International Edition*;[14] two separate tin hydrides, a monohydride and a dihydride, are used while no "helper" amine is employed. Readers will see herein that the results of engineering analysis on the process detailed in Table 9 led to modification of the process to the one that is shown in Figure 6. Step C3 is synthesis of formic acid, which is used to regenerate the reducing agent precursor in Steps C1 and C1'. ANL assessment indicated that the required compression of carbon dioxide during the synthesis of formic acid would be energy prohibitive; the estimated well-to-tank efficiency was 20-33%. Thus, LANL investigated (with computational input from Alabama) replacement of CO_2 with isoelectronic isocyanides (OCNR) and dicyanamides ($C(NR)_2$), as described in Section 1.5.2.2.

Table 9: Dithiol / tin hydride scheme used for engineering analysis. (D = digestion; R = reduction; C = recycle of reductant)

D1	$BNH_2 + {}^3/_2\ SCatH_2 \rightarrow$ ½ "$NH_4\ B(SCat)_2$" ["A1"] + ½ $HBSCat{\cdot}NH_3$ ["A2"] + ½ H_2
R1	½ A1 + ½ $HSnBu_3 \rightarrow$ ½ A2 + ½ $SCatH(SnBu_3)$ ["B1"]
R2	A2 + $H_2SnBu_2 \rightarrow$ AB + $SCat(SnBu_2)$
C1	$SCat(SnBu_2) + 2\ HCOOH \rightarrow SCatH_2 + (COOH)_2SnBu_2$
C1'	½ B1 + ½ HCOOH → ½ $SCatH_2$ + ½ $COOHSnBu_3$
C2	$(COOH)_2SnBu_2 \rightarrow H_2SnBu_2 + 2CO_2$
C2'	½ $Bu_3Sn(COOH) \rightarrow$ ½ $HSnBu_3$ + ½ CO_2
C3	${}^5/_2\ CO_2 + {}^5/_2\ H_2 \rightarrow {}^5/_2\ HCOOH$
Net	**$BNH_2 + 2\ H_2 \rightarrow AB$**

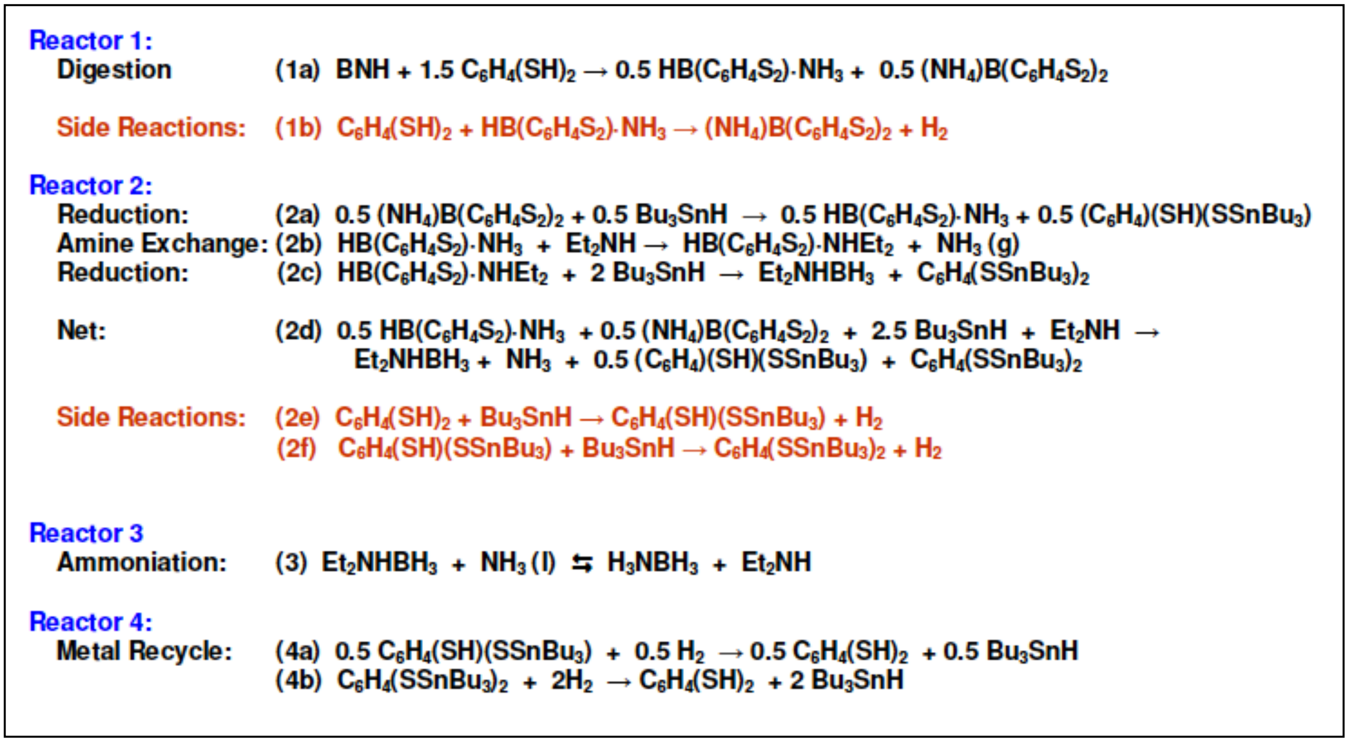
Figure 20: Argonne National Laboratory-completed engineering assessment of ortho-benzenedithiol / tin hydride regeneration scheme.



	0% Distillation Savings		30% Distillation Savings	
Process Step	**Percent Contribution**	**Energy Consumption (MJ/kg)**	**Percent Contribution**	**Energy Consumption (MJ/kg)**
Digestion	**13%**	**66**	**11%**	**47**
Reduction	**9%**	**46**	**8%**	**34**
Formic Acid Reformation	**43%**	**218**	**41%**	**171**
Hydrogen Production	**35%**	**177**	**40%**	**175**
Total		**507**		**427**

Dow completed a baseline cost assessment of the improved dithiol/tin hydride regeneration scheme, using diethylamine as a "helper" amine and using only tributyltin hydride as the reductant and catalytic hydrogenolysis to regenerate the tin hydride and the thiocatechol (similar to Figure 6, but with hydrogenolysis replacing the formate-based tin hydride recycle scheme). The cost of this process was found to be \$7.90/kg H_2 (scale up to 200 metric ton/day H_2 delivered as AB resulted in a decrease in cost to around \$7.00/kg H_2). Dow identified several opportunities to lower the cost of this process, including elimination of separation steps (use of mixed streams); less stringent separation targets (e.g. 99% vs. 99.9% separation); use of lower boiling solvents; use of a lower molecular weight reducing agent; and implementation of heat integration.

Figure 21: Dithiol / tin hydride process analyzed for baseline cost estimate.



Reactor 1:

Digestion (1a) $BNH + 1.5\ C_6H_4(SH)_2 \rightarrow 0.5\ HB(C_6H_4S_2)\cdot NH_3 + 0.5\ (NH_4)B(C_6H_4S_2)_2$

Side Reactions: (1b) $C_6H_4(SH)_2 + HB(C_6H_4S_2)\cdot NH_3 \rightarrow (NH_4)B(C_6H_4S_2)_2 + H_2$

Reactor 2:

Reduction: (2a) $0.5\ (NH_4)B(C_6H_4S_2)_2 + 0.5\ Bu_3SnH \rightarrow 0.5\ HB(C_6H_4S_2)\cdot NH_3 + 0.5\ (C_6H_4)(SH)(SSnBu_3)$

Amine Exchange: (2b) $HB(C_6H_4S_2)\cdot NH_3 + Et_2NH \rightarrow HB(C_6H_4S_2)\cdot NHEt_2 + NH_3\ (g)$

Reduction: (2c) $HB(C_6H_4S_2)\cdot NHEt_2 + 2\ Bu_3SnH \rightarrow Et_2NHBH_3 + C_6H_4(SSnBu_3)_2$

Net: (2d) $0.5\ HB(C_6H_4S_2)\cdot NH_3 + 0.5\ (NH_4)B(C_6H_4S_2)_2 + 2.5\ Bu_3SnH + Et_2NH \rightarrow Et_2NHBH_3 + NH_3 + 0.5\ (C_6H_4)(SH)(SSnBu_3) + C_6H_4(SSnBu_3)_2$

Side Reactions: (2e) $C_6H_4(SH)_2 + Bu_3SnH \rightarrow C_6H_4(SH)(SSnBu_3) + H_2$

(2f) $C_6H_4(SH)(SSnBu_3) + Bu_3SnH \rightarrow C_6H_4(SSnBu_3)_2 + H_2$

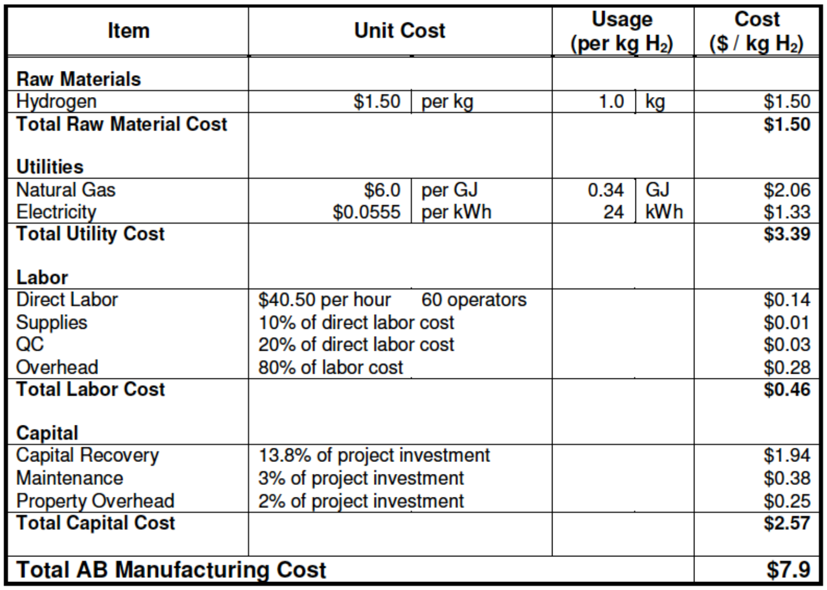
Reactor 3

Ammoniation: (3) $Et_2NHBH_3 + NH_3\ (l) \leftrightarrows H_3NBH_3 + Et_2NH$

Reactor 4:

Metal Recycle: (4a) $0.5\ C_6H_4(SH)(SSnBu_3) + 0.5\ H_2 \rightarrow 0.5\ C_6H_4(SH)_2 + 0.5\ Bu_3SnH$

(4b) $C_6H_4(SSnBu_3)_2 + 2H_2 \rightarrow C_6H_4(SH)_2 + 2\ Bu_3SnH$



Item	Unit Cost		Usage (per kg H_2)		Cost ($ / kg H_2)
Raw Materials					
Hydrogen	$1.50	per kg	1.0	kg	$1.50
Total Raw Material Cost					**$1.50**
Utilities					
Natural Gas	$6.0	per GJ	0.34	GJ	$2.06
Electricity	$0.0555	per kWh	24	kWh	$1.33
Total Utility Cost					**$3.39**
Labor					
Direct Labor	$40.50 per hour	60 operators			$0.14
Supplies	10% of direct labor cost				$0.01
QC	20% of direct labor cost				$0.03
Overhead	80% of labor cost				$0.28
Total Labor Cost					**$0.46**
Capital					
Capital Recovery	13.8% of project investment				$1.94
Maintenance	3% of project investment				$0.38
Property Overhead	2% of project investment				$0.25
Total Capital Cost					**$2.57**
Total AB Manufacturing Cost					**$7.9**

process.

1.8.2 Assessment of alcohol digestion and transition metal hydride reduction

ANL analyzed the hypothetical scheme (B), alcohol digestion and transition metal hydride reduction (Table 11). ANL estimated a well-to-tank efficiency of 25-47%. In the analysis, the base and transition metal complex were left undefined and the energy for separations in the recycle of $B(OPh)_4^-$ was not considered. Nonetheless the analysis provided useful insights. It showed that efficiency is sensitive to stoichiometry, separations and heat integration of the process. Specifically, two digestion approaches were analyzed, one in which residual B-H was protonated by the digesting agent to release H_2 (Eqn. 14) and one in which residual B-H was preserved (Eqn. 13, Table 11).

(13) $BNH_2 + 2\ t\text{-}BuOH \rightarrow NH_3 + HB(O\text{-}t\text{-}Bu)_2$

(14) $HB(O\text{-}t\text{-}Bu)_2 + {}^{1}/_{3}\ Et_3N \rightarrow {}^{1}/_{3}\ Et_3NBH_3 + {}^{2}/_{3}\ B(O\text{-}t\text{-}Bu)_3$

The analysis showed that the latter approach, preserving spent fuel's residual B-H, is ~10% more efficient than B-H conversion to H_2. However, this differential is somewhat dependent on the amount of hydrogen atoms retained in the spent fuel. For spent fuel with composition of BNH obtained by releasing 2.5 equiv. of H_2 from AB, the decreased efficiency in releasing residual hydrogen as H_2 would be smaller than that calculated for spent fuel from release of 2 H_2.

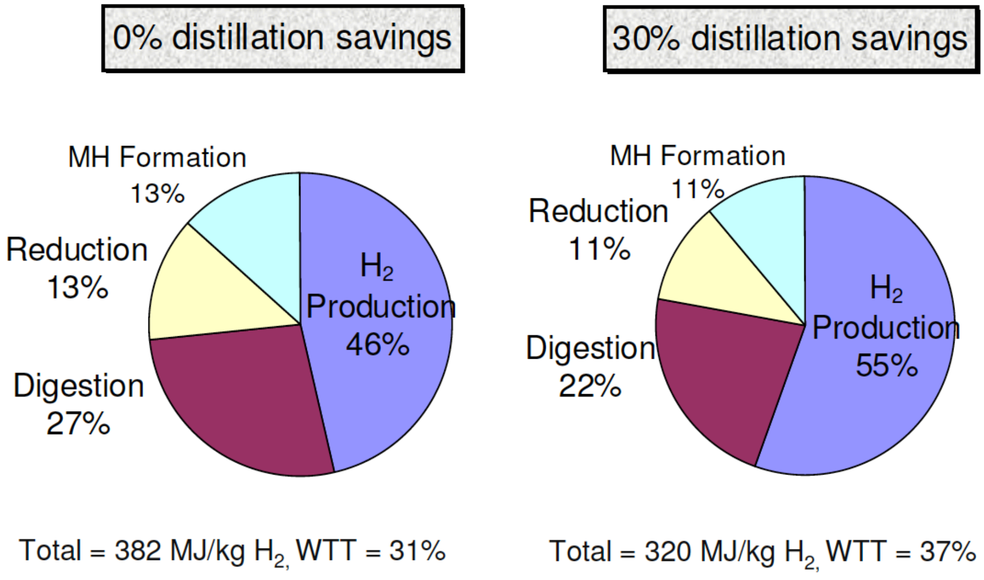
ANL analysis also showed that the energy requirements for regeneration are largely due to hydrogen production (a factor outside of the Center's scope of control) and to digestion processes. The discovery that digestion (and the associated transesterification) contribute over 20% of the energy requirements can be used to guide the future process refinement by, for example, exploring other digesting agents that permit adequate digestion while meeting the hydride affinity requirements described in Section 1.5.2.2.

Table 11: Alcohol / transition metal hydride scheme used for engineering analysis. (D = digestion; M = MH formation; R = reduction; A = ammoniation).

D1	$BNH_2 + 2\ t\text{-}BuOH + \alpha\ THF \rightarrow HB(O\text{-}t\text{-}Bu)_2 + NH_3 + \alpha\ THF$
D2	$HB(O\text{-}t\text{-}Bu)_2 + \alpha\ THF + 1/_3\beta\ A \rightarrow 1/_3\ ABH_3 + 1/_3(\beta-1)\ A + \tfrac{2}{3}\ B(O\text{-}t\text{-}Bu)_3 + \alpha\ THF$
D3	$1/3\ (\beta-1)A + \tfrac{2}{3}\ B(O\text{-}t\text{-}Bu)_3 + \alpha\ THF + 2\gamma\ PhOH \rightarrow$ $\tfrac{2}{3}\ B(OPh)_3 + 1/3(\beta-1)\ A + 2\ t\text{-}BuOH + 2(\gamma-1)\ PhOH + \alpha\ THF$
M1	$2\ MX + 2\delta\ Y + (\lambda+2)\ H_2 + 2\sigma\ Z \rightarrow 2\ HYX + 2\ MH + 2(\delta-1)\ Y + \lambda\ H_2 + 2\sigma\ Z$
R1	$\tfrac{2}{3}\ B(OPh)_3 + 1/3(\beta-1)A + A + 2\ t\text{-}BuOH + 2(\gamma-1)\ PhOH + 2\ MH + 2(\delta-1)Y + 2\ B(OPh)_3 \rightarrow$ $2\ MB(OPh)_4 + \tfrac{2}{3}\ ABH_3 + 1/3\ \beta\ A + 2(\delta-1)\ Y + 2\ t\text{-}BuOH + 2(\gamma-1)\ PhOH$
R2	$2\ MB(OPh)_4 + 2(\delta-1)\ Y + 2\ t\text{-}BuOH + 2(\gamma-1)\ PhOH + 2\ HYX \rightarrow$ $2\ t\text{-}BuOH + 2\gamma\ PhOH + 2\ MX + 2\delta\ Y + 2\ B(OPh)_3$
A1	$ABH_3 + (\phi+1)\ NH_3 + \varepsilon\ A \rightarrow BH_3NH_3 + \phi\ NH_3 + (\varepsilon+1)\ A$
Net	**$BNH_2 + 2\ H_2 \rightarrow BH_3NH_3$**

A = amine, phosphine, or sulfide; X = BF4, halogen, PhO, etc.; Y = base; Z = non-polar solvent (e.g. hexane)

Figure 21: Argonne National Laboratory-completed engineering assessment of alcohol / transition metal hydride regeneration scheme.

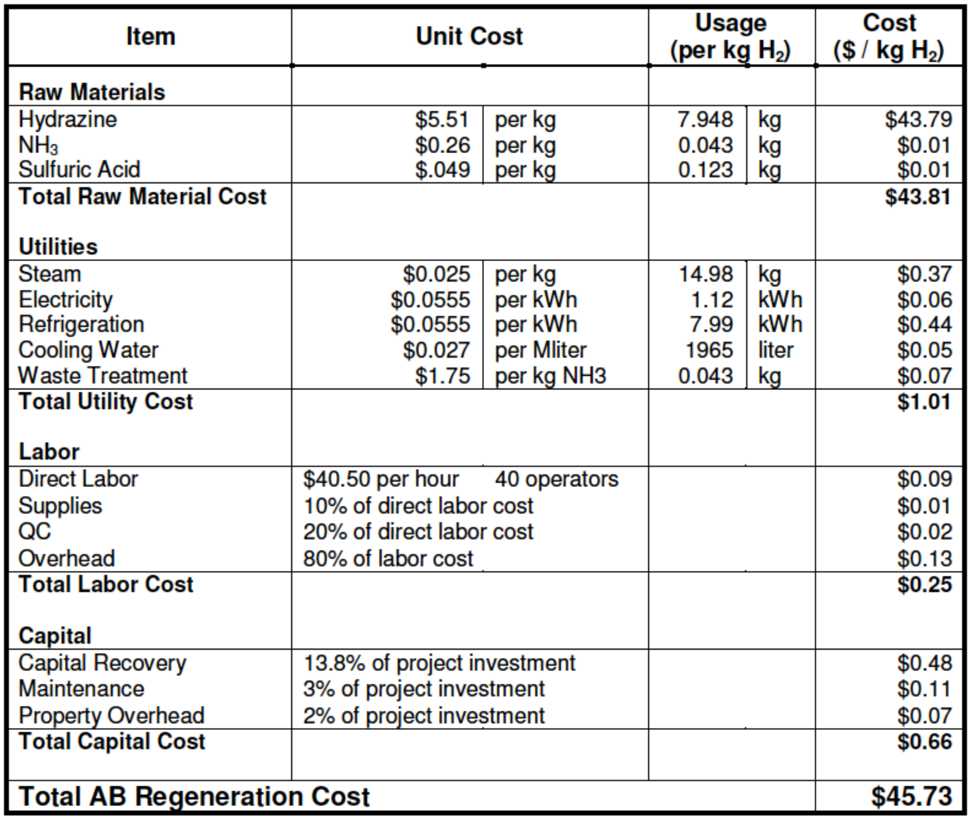


Cost analysis by Dow of this process confirmed what had been anticipated: rhodium-based catalysts are cost prohibitive. Furthermore, lessons can be drawn from cost analysis of the dithiol process: high molecular weight reagents and multiple separations are a disadvantage. Consequently, process optimization will require research into whether reactions can happen in a single vessel and whether lower stoichiometries of reagents can be employed.

1.8.3 Assessment of hydrazine as a dual digesting/reducing agent

Dow's assessment of the dithiol/tin hydride process (Section 1.7.1.1) (particularly the findings that separations and tin-containing reagent flows dramatically increased the process cost) led the Center to consider alternative chemical routes to regenerate AB. As was described in Section 1.6, hydrazine can be used to both digest and reduce spent fuel in the presence of excess ammonia, and has a significantly reduced molar mass relative to the tin and transition metal hydrides used in other regeneration schemes. This process was analyzed by Dow, and was found to substantially simplify the engineering requirements and associated costs of separation. However, due to the current cost of hydrazine ($5.51/kg; $43.79/kg H_2), this process is substantially more expensive than the tin hydride approach; the total AB regeneration cost of the hydrazine process is $45.73/kg H_2 (Table 12). However, unlike the tin hydride process, most of the resulting cost of AB is related to the raw material cost (hydrazine is over 95% of the total cost), not to the regeneration process itself. If the hydrazine raw material cost is excluded, this process would be less than $2/kg H_2. Thus, the total cost will be dramatically lowered when a lower cost method for hydrazine preparation is developed; hydrazine costs need to be below $0.20/kg to meet the DOE cost target of $3/kg H_2. This is a major research need to take this process to commercialization. ANL completed a preliminary 'well-to-tank' and green house gas assessment of this regeneration cycle, and it is discussed below in Section 1.8.1.4.

Table 12: AB manufacturing cost for hydrazine-based regeneration process.



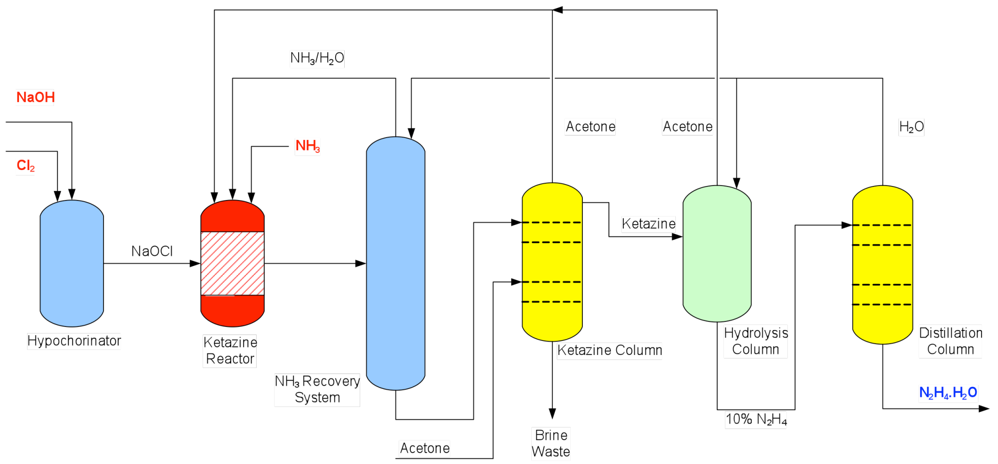
Item	Unit Cost		Usage (per kg H_2)		Cost ($ / kg H_2)
Raw Materials					
Hydrazine	$5.51	per kg	7.948	kg	$43.79
NH_3	$0.26	per kg	0.043	kg	$0.01
Sulfuric Acid	$.049	per kg	0.123	kg	$0.01
Total Raw Material Cost					**$43.81**
Utilities					
Steam	$0.025	per kg	14.98	kg	$0.37
Electricity	$0.0555	per kWh	1.12	kWh	$0.06
Refrigeration	$0.0555	per kWh	7.99	kWh	$0.44
Cooling Water	$0.027	per Mliter	1965	liter	$0.05
Waste Treatment	$1.75	per kg NH3	0.043	kg	$0.07
Total Utility Cost					**$1.01**
Labor					
Direct Labor	$40.50 per hour	40 operators			$0.09
Supplies	10% of direct labor cost				$0.01
QC	20% of direct labor cost				$0.02
Overhead	80% of labor cost				$0.13
Total Labor Cost					**$0.25**
Capital					
Capital Recovery	13.8% of project investment				$0.48
Maintenance	3% of project investment				$0.11
Property Overhead	2% of project investment				$0.07
Total Capital Cost					**$0.66**
Total AB Regeneration Cost					**$45.73**

1.8.3.1 Energy efficiency assessment by ANL of hydrazine as a dual digesting/reducing agent

ANL performed a preliminary ‘well-to-tank’ primary energy analysis and green house gas assessment for the direct hydrazine spent fuel regeneration process. This assessment assumed current technology for hydrazine manufacture, which is known to be energy intensive. ANL performed a review of the chemical process literature for hydrazine manufacture, and performed their assessment of the overall regeneration process based upon this information and on materials inputs information for the spent fuel regeneration steps from both LANL and Dow.

ANL considered two hydrazine manufacturing options. One is the PCUK process, based upon hydrogen peroxide oxidation of ammonia to yield hydrazine. Hydrogen peroxide for this process is generated by way of an energy intensive process using hydrogen. The second hydrazine manufacturing process ANL analyzed is the Bayer Ketazine process, where bleach is used as an oxidant to react with ammonia and acetone to form ketazine, which is subsequently hydrolyzed to hydrazine. Bleach is derived from electrolysis of brine to form chlorine, another process that is highly energy intensive. These two current commercial processes are shown in Figure 22.

Figure 22. Process schematics and chemistry of the Bayer Ketazine process (top) and the PCUK process (bottom) for the commercial production of hydrazine (courtesy of ANL).

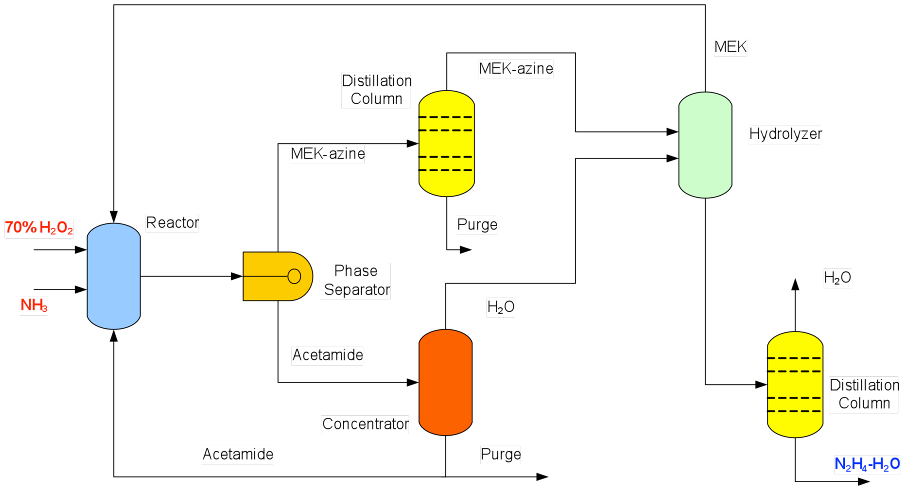


– $2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$

– $2NH_3 + NaOCl + (CH_3)_2CO \rightarrow (CH_3)_2CNNH_2 + NaCl + 2H_2O$

– $(CH_3)_2CNNH_2 + (CH_3)_2CO \rightarrow (CH_3)_2CNNC(CH_3)_2 + H_2O$

– $(CH_3)_2CNNC(CH_3)_2 + 2H_2O \rightarrow 2(CH_3)_2CO + N_2H_4$



– $NH_3 + H_2O_2 + (CH_3)(C_2H_5)CO \rightarrow (CH_3)(C_2H_5)CONH + 2H_2O$
– $NH_3 + (CH_3)(C_2H_5)CONH \rightarrow (CH_3)(C_2H_5)CNNH_2 + H_2O$
– $(CH_3)(C_2H_5)CNNH_2 + (CH_3)(C_2H_5)CO \rightarrow (CH_3)(C_2H_5)CNNC(CH_3)(C_2H_5) + H_2O$
– $(CH_3)(C_2H_5)CNNC(CH_3)(C_2H_5) + 2H_2O \rightarrow 2(CH_3)(C_2H_5)CO + N_2H_4$

ANL's analysis of these two processes, and the energy inputs needed for the subsequent spent fuel regeneration process resulted in the overall energy inputs shown in Table 13.

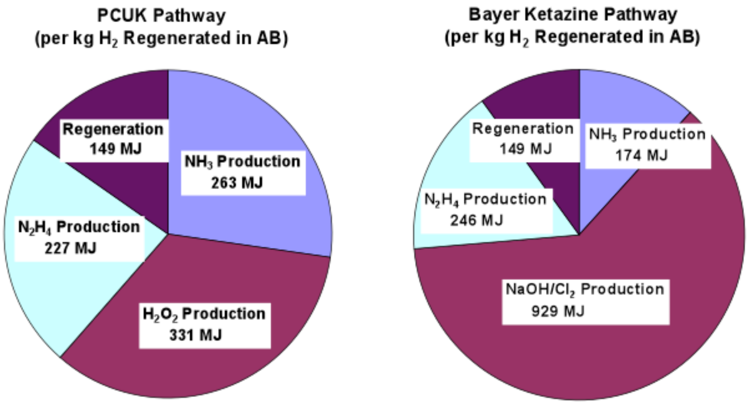
Table 13. Well to tank efficiency of hydrazine regeneration of spent fuel using the two commercial hydrazine manufacturing processes.

Process	**PCUK**		**Bayer**	
	NG	Electricity	NG	Electricity
NH_3 Production (1)	258	5	169 (2)	5
H_2O_2 Production	331	-	-	-
NaOH/Cl_2 Production (3)	-	-	65	870
Hydrazine Production	227	-	246	-
AB Regeneration (4)	45	104	45	104
Total Primary Energy (MJ)	861	109	525	979
WTT Efficiency (%)	**12.4**		**8.0**	

(1) Uhde plant data
(2) Includes credit for H_2 co-produced in NaOH/Cl_2 production
(3) E. Worrell et al., LBNL-44314, 2000
(4) L. Klawiter and A. Chin, Personal Communication, 2010

The overall 'well-to-tank' efficiency for hydrazine regeneration is dominated by the energy intensity of hydrazine production from ammonia and either oxidation agent, with the hydrogen peroxide route being slightly favored. But the overall energy intensity of hydrazine production, which includes the energy 'costs' of ammonia, the oxidant, and the hydrazine synthesis, overwhelms the AB regeneration 'costs' as shown below in Figure 23.

Figure 23. Contributions of process steps to overall regeneration energy intensity.



The high energy intensity of hydrazine production is consistent with its current cost as was shown above in Section 1.8.1.3.

Either route using current commercial technology results in unacceptably low overall energy efficiency for regeneration compared to DOE's target of 60% energy efficiency. To achieve a value of 50%, the energy intensity of the PCUK process would have to be reduced by 80%, which represents a scientific and technological challenge.

1.8.3.2 Summary of hydrazine processes and potential future opportunities for hydrazine-based regeneration of spent fuel

Industrial methods for the production of hydrazine are generally variations of the Raschig process, which uses the oxidation of ammonia by hypochlorite, or the PCUK process, which uses hydrogen peroxide oxidation of ammonia in the presence of a ketone.[25] Worldwide production of hydrazine was estimated at about 50,000 mt/yr in 2004, most of this in the form of hydrazine-hydrate, N_2H_4-H_2O.[26] Arch Chemicals is currently the only US producer of hydrazine with its plant in Lake Charles, LA.[27] Thus, hydrazine is only produced in small quantities currently, and construction of new facilities will be required to support a hydrazine-based AB regeneration process.

The direct reduction of nitrogen to form ammonia is exothermic by -33 kJ mol^{-1} while reduction of N_2 to form H_2NNH_2 is endothermic by 158 kJ mol^{-1}. Thus, the development of wholly new processes for the production of hydrazine in high yield and low energy intensity is a significant scientific challenge. New methods that exceed the efficiency of the Raschig process (ca. 60%

yield) and the PCUK process (ca. 66% yield) and thus deliver hydrazine at a lower cost are a significant research need.[28] The N_2 gas released in our proposed process may be captured for reprocessing into NH_3 (and then N_2H_4) at the same facility as regeneration occurs. Thusly, hydrazine industrial synthesis and AB regeneration could potentially be co-located for cost savings.

1.8.4 Summary of regeneration costs and efficiency for demonstrated processes

Dow and ANL completed two preliminary cost and energy efficiency assessments of the thiocatecholate/tin hydride (Section 1.8.1.1) and 'one pot' direct digestion/reduction process using hydrazine (Sections 1.8.1.3 and 1.8.1.4). The results are tabulated in Table 14, and indicate that as mentioned earlier, that while the hydrazine has a markedly lower process cost relative to the dithiocat process, the hydrazine cost and energy intensity dominate the overall regeneration cost and well-to-tank efficiency.

Process	Process Cost ($/kg H_2)	Raw Materials Cost ($/kg H_2)	WTT Efficiency, %
Dithiocat/tin formate	n/a	n/a	20-33
Dithiocat/tin hydride	6.42	1.50	n/a
Hydrazine one pot	1.92	43.81	12

Table 14. Summary of process and raw materials costs ($/kg H_2) and well to tank efficiencies (%).

1.9 Emerging questions

The Center has identified one very promising method and other developing methods for AB regeneration. Remaining questions that must be addressed before commercialization include:

1. What is the effect on regeneration efficacy of anti-foaming agents used in solid AB formulations?
2. What is the effect on regeneration efficacy of solvents like ionic liquids or fuels containing a mixture of amine-boranes?
3. To what extent does the presence of residual dehydrogenation catalyst affect the regeneration effectiveness?
4. Is the quality of fuel affected by repeated regeneration cycles?
5. Can the scientific challenges of reducing the energy intensity and cost of hydrazine be met to enable the simple, one-pot regeneration of spent fuel using hydrazine?

These questions must be included in any future program to address transportation-based chemical hydrogen storage.

1.9.1 New Concepts in Chemical Hydrogen Storage: Direct Rehydrogenation?

The Center has designed two new types of chemical hydrogen storage materials that combine the exothermic hydrogen release of AB with endothermic processes in an effort to generate near-thermoneutral, on-board regenerable molecules. The specific design principles and syntheses of metal amidoborane and carbon-boron-nitrogen compounds are detailed in other sections of this report. Here we simply state that more work is needed in this area to determine if the envisioned, near-thermoneutral regeneration using H_2 gas is possible and what mechanistic pathway is taken to achieve this refueling.

Because metal amidoborane compounds such as LiAB are not regenerable with hydrogen, regeneration schemes for the metal amidoboranes such as Li-AB must involve the regeneration of the equivalent of LiH or Li metal, which are likely too energy inefficient. Also, using hydrazine is out of the question for many metal-based systems: *Please note: regeneration of spent fuel from Li-AB should not be attempted using the hydrazine process! Certain metal and alkali metal hydrazides are shock sensitive!*

1.10 References for Chapter 2: Regeneration

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