Low-Cost Precursors to Novel Hydrogen Storage Materials

Final Report

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1 Executive Summary

From 2005 to 2010, The Dow Chemical Company (formerly Rohm and Haas Company) was a member of the Department of Energy Center of Excellence on Chemical Hydrogen Storage, which conducted research to identify and develop chemical hydrogen storage materials having the potential to achieve DOE performance targets established for on-board vehicular application. In collaboration with Center co-leads Los Alamos National Laboratory (LANL) and Pacific Northwest National Laboratory (PNNL), and other Center partners, Dow's efforts were directed towards defining and evaluating novel chemistries for producing chemical hydrides and processes for spent fuel regeneration.

In Phase 1 of this project, emphasis was placed on sodium borohydride ($NaBH_4$), long considered a strong candidate for hydrogen storage because of its high hydrogen storage capacity, well characterized hydrogen release chemistry, safety, and functionality. Various chemical pathways for regenerating $NaBH_4$ from spent sodium borate solution were investigated, with the objective of meeting the 2010/2015 DOE targets of \$2-3/gal gasoline equivalent at the pump (\$2-3/kg H_2) for on-board hydrogen storage systems and an overall 60% energy efficiency.

With the September 2007 No-Go decision for $NaBH_4$ as an on-board hydrogen storage medium, focus was shifted to ammonia borane (AB) for on-board hydrogen storage and delivery. However, $NaBH_4$ is a key building block to most boron-based fuels, and the ability to produce $NaBH_4$ in an energy-efficient, cost-effective, and environmentally sound manner is critical to the viability of AB, as well as many leading materials under consideration by the Metal Hydride Center of Excellence. Therefore, in Phase 2, research continued towards identifying and developing a single low-cost $NaBH_4$ synthetic route for cost-efficient AB first fill, and conducting baseline cost estimates for first fill and regenerated AB using a variety of synthetic routes.

This project utilized an engineering-guided R&D approach, which involved the rapid down-selection of a large number of options (chemical pathways to $NaBH_4$) to a smaller, more manageable number. The research began by conducting an extensive review of the technical and patent literature to identify all possible options. The down-selection was based on evaluation of the options against a set of metrics, and to a large extent occurred before experimentation was initiated. Given the vast amount of literature and patents that has evolved over the years, this approach helped to focus efforts and resources on the options with the highest technical and commercial probability of success. Additionally, a detailed engineering analysis methodology was developed for conducting the cost and energy-efficiency calculations. The methodology utilized a number of inputs and tools (Aspen PEA™, FCHTool, and H2A).

The down-selection of chemical pathways to $NaBH_4$ identified three options that were subsequently pursued experimentally. Metal reduction of borate was investigated in Dow's laboratories, research on electrochemical routes to $NaBH_4$ was conducted at Pennsylvania State University, and Idaho National Laboratory researchers examined various carbothermal routes for producing $NaBH_4$ from borate. The electrochemical and carbothermal studies did not yield sufficiently positive results. However, $NaBH_4$ was produced in high yields and purities by an aluminum-based metal reduction pathway. Solid-solid reactive milling, slurry milling, and solution-phase approaches to metal reduction were investigated, and while both reactive milling and solution-phase routes point to fully recyclable processes, the scale-up of reactive milling processes to produce $NaBH_4$ is expected to be difficult. Alternatively, a low-cost solution-phase approach to $NaBH_4$ has been identified that is based on conventional process unit operations and should be amenable to scale-up.

Numerous advances in AB synthesis have been made in recent years to improve AB yields and purities. Process analysis of several leading routes to AB (Purdue's formate-based metathesis route and PNNL's NH_4BH_4–based route) indicated the cost to produce first-fill AB to be on the order of \$9-10/kg AB, assuming a $NaBH_4$ cost of \$5/kg for a 10,000 metric tons/year sized AB plant. The analysis showed that the dominant cost component for producing first-fill AB is the cost of the $NaBH_4$ raw material. At this AB cost and assuming 2.5 moles hydrogen released per mole of AB, it may be possible to meet DOE's 2010 storage system cost target, but the 2015 target will likely require lower cost AB and demonstrates the importance of having a low-cost route to $NaBH_4$.

Substantial progress has also been made to define feasible pathways for the regeneration of spent ammonia borane fuel. A preliminary cost assessment of LANL's thiacatechol-based AB regeneration route, assuming AB production equivalent to 100-250 TPD $H_{2,}$ resulted in a baseline AB regen cost of \$7-8/kg H_2, indicating this route is incapable of meeting the DOE fuel cost target. Several opportunities to reduce the cost by lowering the capital and utilities requirements were noted. LANL's simpler hydrazine-based AB regen route also shows promise for meeting the DOE fuel cost target, but requires the development of a lower-cost and more energy efficient pathway to hydrazine production.

Dow's process analyses have helped to establish baseline costs and identify key areas for improvements and highlight the need for both high chemical and process efficiency for the development of cost and energy efficient processes.

2 Overview

This final report describes the objectives, activities and results of the hydrogen storage project *Low-Cost Precursors to Novel Hydrogen Storage Materials* performed by The Dow Chemical Company (Dow), formerly Rohm and Haas Company, under the Department of Energy (DOE) Chemical Hydrogen Storage Center of Excellence (CHSCOE), contract # DE-FC36-05GO15053. This effort officially began in March 2005 and performed technical research and engineering support through September 2010. The CHSCOE was a highly collaborate organization comprised of over twelve academic and industrial organizations. Dow worked closely with several of the COE partners, most notably Los Alamos National Laboratory (LANL) and Pacific Northwest National Laboratory (PNNL), co-leads for the COE; Pennsylvania State University; University of Pennsylvania; University of Alabama; Millennium Cell; University of California (Davis); and US Borax.

Background and Technical Targets

The emergence of a hydrogen fuel economy requires identification and development of viable hydrogen storage materials and systems. In 2005, when this project was initiated, sodium borohydride was a leading candidate for efficient, safe, and cost-effective hydrogen fuel storage systems. The feasibility for H_2 generation had been successfully demonstrated through the hydrolysis reaction of $NaBH_4$ (Eq. 2-1) in systems ranging from large-scale power applications including fuel-cell powered vehicles down to micro-power for portable electronic applications:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2(aq) + 4H_2 \qquad (2\text{-}1)$$

Regeneration of sodium borohydride from spent sodium borate solution in a closed cycle was recognized as highly desirable and essential for achieving the 2010/2015 DOE fuel cost target of $2-3/gal gasoline equivalent at the pump ($2-3/kg H_2) for on-board board hydrogen storage systems. In addition, an overall 60% energy efficiency target had been established by the DOE for off-board regeneration systems, defined as the energy content of the H_2 delivered to the automotive power plant relative to the total energy input to the process including the input energy of H_2 and any other fuel streams used for generating process heat and electrical energy.

When emphasis shifted from $NaBH_4$ to ammonia borane (AB) as a chemical hydrogen storage medium, Dow provided guidance to the Center in the selection of leading chemical pathways to AB, with the overall objective of meeting the DOE's storage system cost targets in addition to the fuel cost target of $2-3/kg H_2 noted above. The storage system cost targets, which include the first charge (first fill) of H_2 fuel storage medium, were established at $4/kWh net ($133/kg H_2) for 2010 and $2/kWh net ($67/kg H_2) for 2015. Assuming 2 to 2.5 moles H_2 release per mole of AB, a $10/kg price for the first fill AB medium alone would exceed the 2015 system cost target. Therefore, low cost AB manufacturing routes are essential to supply the first charge of AB and achieve the cost targets. Energy and cost efficient regeneration of spent AB fuel also need to be defined for the storage system to be viable and meet DOE's fuel cost target of $2-3/kg H_2 at the pump for on-board hydrogen storage systems. Dow conducted baseline cost estimates for various chemical pathways to both first fill AB and regenerated AB.

Phase 1 (2005 – 2007)

The Schlesinger process, commercialized in 1955, is the dominant industrial route to $NaBH_4$ and comprises sodium hydride reduction of borate esters.

$$4\ NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3\ NaOCH_3 \qquad (2\text{-}2)$$

However, this route is highly energy intensive due to its use of sodium metal and that only 25% of the sodium ends up with the borohydride; 75% of the Na metal consumed eventually downgrades to NaOH. As such, the current $NaBH_4$ route was deemed unable to meet the DOE targets.

In Phase 1 of this project, Dow's efforts in the DOE Center of Excellence for Chemical Hydrogen Storage were directed largely towards defining and evaluating low-cost, energy efficient regeneration processes for producing sodium borohydride. The methodology employed in this program was to first identify leading $NaBH_4$ regeneration pathways based on a review of the technical and patent literature and screening based on theoretical energy efficiency and other key metrics. The screening identified three top pathways to $NaBH_4$: 1) metal reduction using lower-cost, lower usage reducing metal in place of sodium, 2) carbothermal reduction which eliminates use of metals and their recovery to increase theoretical efficiencies, and 3) electrochemical routes which also do not require addition of metals and have potentially a lower carbon footprint. The feasibility of the leading pathways was then determined by laboratory demonstration of key chemical and process steps, followed by process analysis comprising flow sheet development, energy efficiency calculations, and preliminary cost estimates. The key tasks and milestones outlined in the Statement of Project Objectives for Phase 1 work are shown in Table 2.1.

Task	Milestones
1. Electrochemical Reduction of Borates	Year 1: Technical information compiled for controlled release to Center participants under NDA and IP agreements Year 2-3: Criteria and economic analysis for emerging concepts established
2. Chemical Reduction of Borates	Year 2-3: Criteria and economic analysis for emerging concepts established
3. Engineering-Guided Research	Year 2: Protocols and criteria for rigorous engineering guidance defined Year 3: Application to and analysis of emerging concepts, development of conceptual process flowsheets, reaction process engineering, life cycle analyses completed

Table 2.1. Phase 1 tasks and milestones (The Dow Chemical Company)

Electrochemical studies were conducted at Penn State University, with assistance from Dow in designing an experimental program that built off past positive results for $NaBH_4$ formation, using both a direct one-step reduction in aqueous medium and a two-step approach involving formation of an intermediate trialkoxyborohydride.

The metal reduction pathway was experimentally investigated in Dow's laboratories and was successfully demonstrated in room temperature reactive milling studies. Screening studies to assess the reactivity of various metal hydrides led to the selection of aluminum as the target metal for further studies, due to its lower cost, higher theoretical efficiency, and greater abundance relative to other metals. Literature studies have demonstrated formation of alane-amine complexes by reaction of Al, H_2 and an amine at moderate temperature and pressure. Thus, a 2-step process converting $NaBO_2$ to $NaBH_4$ via an alane amine intermediate was deemed feasible. Formation of the metal hydride followed by reduction of $NaBO_2$ in a one-pot synthesis using Al metal, hydrogen gas and borate feed, in autoclave studies capable of high temperature and high pressure operations using H_2 gas, was also investigated. The Chemical Hydrogen Storage COE lacked the experimental facilities to investigate carbothermal reduction pathways. However, Idaho National Laboratory had successfully demonstrated carbothermal reduction of $NaBO_2$ using solid carbon and methane as reductants, followed by exposure to an electric arc to produce a high temperature plasma, to drive conversion to $NaBH_4$. $NaBH_4$ yield was reported to be about 50% as confirmed by XRD and NMR. This process was far from being optimized, therefore, Dow entered into a confidentiality agreement with INL and a 3rd party to gain access to the data and received approval to provide specific information for the DOE review.

Go/No-Go Review (September 2007)

Results presented by Dow at the 2007 DOE Go/No-Go Review are summarized in Table 2.2. The scope of Dow's analysis was limited to aluminum reduction and carbothermal reduction (under plasma conditions) of $NaBO_2$. Due to low yields, the electrochemical pathway was not included in the analysis.

Pathway	Cost, \$/kg H_2 [1]	Fuel Energy Efficiency [2]	Capital [3]	Comments
DOE 2010 Target	2-3	60%		
Metal Reduction	6-12	43(19)%	\$350MM	Reduction of metal oxide back to the metal is key contributor to cost and energy efficiency.
Carbothermal Reduction	2-7	50(19)%	\$300MM	Heat integration is critical. Improvement in borate conversion could enable cost target to be met.

1 - Delivered H_2 cost to auto
2 - Energy content of H_2 delivered to auto relative to total energy to process including fuel input energy of H_2 and any other fuel streams used for generating process heat and electrical energy. Electricity from hydroelectric. () indicates efficiency based on US Electrical Grid.
3 – For 100 mt/day H_2 plant

Table 2.2. Summary of preliminary cost and energy efficiency analyses of metal reduction and carbothermal routes to $NaBH_4$ (2007 DOE Go/No-Go Review)

Dow concluded that both the metal reduction and carbothermal reduction routes represent significant improvements in energy efficiency and manufacturing costs over the current Schlesinger process to produce $NaBH_4$. However, additional improvements were needed to meet the 2010 DOE storage technical targets of <\$3/kg H_2 fuel cost and >60% energy efficiency. Development of an experimental program to advance the carbothermal pathway and identify opportunities to reduce the performance gap was therefore recommended. It was also recommended that the metal reduction pathway be progressed to address scale-up options with reactive milling and define process feasibility. This would require a tight coupling of engineering assessment, economic analysis, and process synthesis, with innovative chemical and materials research in order to identify the most feasible $NaBH_4$ pathway.

DOE decided to discontinue funding projects on $NaBH_4$ for on-board vehicular applications due to its inability to achieve high H_2 densities stemming from fuel waste management issues. However, funding continued on developing low-cost and energy efficient routes to $NaBH_4$ due to its criticality to the commercial success of other boron-based fuel, including ammonia borane (AB) and other borohydride-based materials being investigated by the Metal Hydride Center of Excellence (MHCOE). In the 2007 MHCOE Materials Go/No Go Decision report, over 60% of the materials that met H_2 density, reversibility, and H_2 release characteristics targets are borohydride based. Of the materials that have >10 wt% H_2, over 90% are borohydride-based.

Phase 2 (2008 – 2010)

$NaBH_4$ is a starting material for AB and these other boron-based fuels; hence these materials will require low cost $NaBH_4$ in for initial system fill. In Phase 2, research continued towards identifying and developing a single low-cost $NaBH_4$ synthetic route for cost-efficient AB first fill, with emphasis on metal reduction and carbothermal routes. In addition, Dow provided preliminary cost estimates for producing 1st fill AB and regenerating spent AB. The key tasks and milestones outlined in the Statement of Project Objectives for Phase 2 work are shown in Table 2.3.

Task	Milestones
1. Low Cost Production of Sodium Borohydride	Year 4: Carbothermal experimental capabilities established. Process performance of top routes defined. Conceptual process and costs to enable selection of top pathway detailed. Year 5: Experimental studies progressed on single pathway to define, develop, and optimize process; flowsheets and economics updated.
2. Ammonia Borane "First Fill" Analysis	Year 4: Metrics defined to guide selection of leading AB pathways, leading chemical pathways to AB identified. Year 5: Conceptual flowsheets and cost assessment for leading pathway completed.
3. Ammonia Borane Regeneration Support	Year 4: NDA and IP agreements to facilitate sharing of technical information developed. Metrics to guide evaluation of leading AB regen concepts developed. Conceptual flowsheets to determine preliminary costs developed. Year 5: Top AB regen pathway selected. Cost and energy efficiencies determined for optimal pathway.

Table 2.3. Phase 2 tasks and milestones (The Dow Chemical Company)

In 2008, a Cooperative Research and Development Agreement (CRADA) was executed between Dow (then Rohm and Haas) and INL, through the DOE Center of Excellence program, to progress carbothermal studies and allow a better understanding of $NaBH_4$ formation via this pathway. An important milestone was to select either the carbothermal reduction or metal-base reduction option by the end of the first year of the CRADA, and move to the next phase of development of a low cost $NaBH_4$ process with a single route selected for further development. It was agreed that INL experimental results needed to consistently demonstrate at least a 40% conversion of borate to SBH in order to move ahead in the program. Details of the collaborative effort with INL can be found in Section 3.5 of this report.

Dow continued its in-house investigation of metal reduction pathways, using aluminum as an alane complex as the reductant. Reactive milling experiments using a high-energy laboratory mill were expanded to involve optimization of both boron and aluminum starting materials, milling conditions and separation and purification schemes. The studies demonstrated the feasibility of a high yield, recyclable process, but one that was not likely to be amenable to scale-up. Attempts to identify a scalable process led to the investigation of slurry milling in a stirred media mill, using solubilized aluminum hydrides in the presence of solid borax or sodium metaborate, and eventually progressed to solution-based routes. A solution-based route would utilize conventional reactor designs and processing equipment, and would therefore be expected to be fully scalable. Details of this work can be found in Section 3.4 of this report.

For first fill applications, the synthesis of AB via the metathesis reaction of sodium borohydride with ammonium salts (Eq. 2-3) in organic solvents is readily achieved and is well known:

$$xNaBH_4 + (NH_4)_xL \xrightarrow{\text{solvent}} xNH_3BH_3 + Na_xL + xH_2 \qquad (2\text{-}3)$$

In the past five years, significant advances in AB synthesis to achieve AB yields and purities in excess of 95% have been realized. Purdue University researchers reported increased AB yields using various ammonium salt and solvent combinations. PNNL achieved high AB yields by reacting $NaBH_4$ and NH_4Cl in ammonia/THF, via the formation and subsequent decomposition of intermediate ammonium borohydride. Both pressurized and cryogenic processes were described. Additionally, Shore and researchers at Ohio State described a pathway involving the base displacement of borane complexes with ammonia.

Baseline costs for various first fill routes to AB were conducted by Dow, assuming a $NaBH_4$ starting material cost of $5/kg and a 10,000 MTA AB sized plant. A number of process characteristics such as yields, purities, solvent requirements, etc., were also taken into consideration in the analyses to determine the best overall process. Details of the first fill AB cost analysis work and implications for meeting DOE's storage system cost targets can be found in Section 4.2 of this report.

The regeneration of AB from spent fuel was also an important focus of the DOE Chemical Hydrogen Storage Center of Excellence. A variety of approaches were investigated, including the use of superacids, thiols, alcohols, and combinations of these systems to digest spent fuel to chemical intermediates that can be more readily processed and converted back to AB.

Dow supported the Center efforts by conducting baseline cost assessments of two AB regeneration pathways developed at LANL: 1) digestion of the polyborazylene spent fuel by thiacatechol, followed by reduction to AB using tin hydride compounds and 2) use of hydrazine to digest and reduce borazylene directly to AB. Additionally, preliminary examinations of PNNL's alcohol-based and UPenn's halo-superacid-based AB regeneration pathways were made. Appropriate assumptions were made to create a conceptual process, establishing the necessary material and energy balances, and scale up to a commercial plant producing AB at a rate equivalent to 100 metric ton per day of delivered H_2. Details of the AB regen cost estimate work can be found in Section 4.3 of this report.

3 Sodium Borohydride

3.1 Chemistry Survey

3.1.1 Introduction

The technical and patent literature on methods to synthesize sodium borohydride is quite extensive, ranging from proposed chemical pathways to commercial production routes. Brief surveys of these $NaBH_4$ routes have been published.[1,2] In this study, a comprehensive review of $NaBH_4$ pathways was undertaken to identify potential alternatives to the commercial Schlesinger process that can provide significant cost and energy savings in sodium borohydride manufacturing.[3] Pathways that can directly utilize the products of $NaBH_4$ hydrolysis, an aqueous alkaline borate feed stream, as raw material would be especially advantageous.

The Schlesinger process[4-6], comprising sodium hydride reduction of borate esters, was first commercialized by Metal Hydrides Inc. in 1955 and remains the primary commercial process to produce $NaBH_4$. Dow Chemical Company is the leading global producer with manufacturing facilities in the United States and Europe based on the Schlesinger process. Other processes that have also been commercialized to varying degrees of success include the reaction of boranes with sodium hydride, reduction of boron oxides with sodium in conjunction with silica or aluminum, and metathesis of sodium aluminum hydride with borate esters to produce sodium borohydride.

The literature describes over 30 different chemical pathways (and more than 100 possible routes when variations and combinations of the chemistries are considered) as potential alternatives to the current Schlesinger process for producing $NaBH_4$, Most of these pathways can be classified into six general categories: 1) metal reduction, 2) electrochemical, 3) carbothermal, 4) elemental, 5) borane-based, and 6) metathesis. Representative chemistries from each of the six categories are shown in Table 3.1. All have the potential for higher energy efficiency and lower metal usage compared to the current Schlesinger process, which is limited to a maximum of 25% utilization of Na metal in borohydride production.

Pathway	Illustrative Chemistry
Schlesinger (current)	$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$
Metal reduction	$NaBO_2 + 2x/y\ M + 2H_2 \rightarrow NaBH_4 + 2/y\ M_xO_y$
Electrochemical	$B(OH)_4^- + 4H_2O + 8e^- \rightarrow BH_4^- + 8OH^-$
Carbothermal	$NaBO_2 + 2H_2 + CH_4 + O_2 \rightarrow NaBH_4 + CO_2 + 2H_2O$
Elemental synthesis	$Na + B + 2H_2 \rightarrow NaBH_4$
Borane-based	$1/2\ B_2H_6 + NaH \rightarrow NaBH_4$ $2/3\ B_2H_6 + NaOCH_3 \rightarrow NaBH_4 + 1/3\ B(OCH_3)_3$
Metathesis	$Na + Al + 2H_2 \rightarrow NaAlH_4$ $NaAlH_4 + B(OR)_3 \rightarrow NaBH_4 + Al(OR)_3$

Table 3.1. Representative chemistries for major chemical pathways for producing $NaBH_4$

A brief description on each of these six chemical pathways is provided in the following sections.

3.1.2 Metal Reduction of Borates

Reduction of alkylborate esters with alkali metal hydrides (or alternatively alkali metals plus hydrogen) via the Schlesinger process has been the preferred route to manufacture sodium borohydride for more than 50 years.

$$4\ NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3\ NaOCH_3 \qquad (3.1\text{-}1)$$

This pathway achieves nearly quantitative yields based on the given reaction stoichiometry, operates at moderate temperatures of ca. 260°C, and employs mineral oil as a reaction medium. However, the process consumes four moles of monovalent Na metal per mole of borohydride produced, and as a result, generates substantial quantities of sodium methoxide or hydroxide byproduct, depending on the $NaBH_4$ recovery process.

Numerous attempts have been made to improve the Schlesinger process, for example, by conducting the process in organic solvents at reduced temperatures, and by the use of homogenizers or milling equipment to reduce reaction times while maintaining yield.[7-8] Alkali metal hydride reduction of boron oxides was also investigated by Schlesinger:

$$4\ NaH + 2\ B_2O_3 \rightarrow NaBH_4 + 3\ NaBO_2 \qquad (3.1\text{-}2)$$

Nevertheless, these pathways involving alkali metal reduction of borates are disadvantaged by the high metal usage and will be unable to achieve the desired manufacturing cost reduction.

Alternative metal reduction processes for boron oxides have been reported by Bayer and Ethyl using combinations of sodium plus silica and hydrogen, sodium and silicon metal plus hydrogen, or sodium and aluminum metal plus hydrogen as reductants.[9 -11]

$$Na_2B_4O_7 + 16\ Na + 7\ SiO_2 + 8\ H_2 \rightarrow 4\ NaBH_4 + 7\ Na_2SiO_3 \qquad (3.1\text{-}3)$$

$$3\ Na_2B_4O_7 + 20\ Na + 7\ Si + 24\ H_2 \rightarrow 12\ NaBH_4 + 7\ Na_2SiO_3 \qquad (3.1\text{-}4)$$

$$2\ Na_2B_4O_7 + 7\ Al + 11\ Na + 16\ H_2 \rightarrow 8\ NaBH_4 + 7\ NaAlO_2 \qquad (3.1\text{-}5)$$

Addition of the higher valence metals results in improved metal usages. However, these pathways using borax feed require even higher temperatures (350-500°C) and generate substantial silicate or aluminate byproduct.

An emerging technology that has gained much interest has been the direct reaction of borates with magnesium hydride under very mild reaction conditions via reactive milling.[12-13]

$$NaBO_2 + 2\ MgH_2 \rightarrow NaBH_4 + 2\ MgO \qquad (3.1\text{-}6)$$

Other studies had shown this reaction to proceed at elevated temperatures using alkaline earth hydrides.[14-15] Low milling energy requirements coupled with a cost-effective means of recycling the magnesium oxide byproduct to magnesium hydride would make this an attractive option. Similar pathways using other metals with more favorable metal-to-$NaBH_4$ usage ratios could also be worth investigating.

3.1.3 Electrochemical Processes

Electrolytic conversion of a borate salt or other oxidized boron species in an electrochemical cell could offer a potentially attractive route to boron hydrides by eliminating the need for reducing metals as production of Na involves a highly energy intensive electrolytic process. Thus, borohydride could be produced by the following half cell reactions:

Cathode: $B(OH)_4^- + 4\ H2O + 8\ e^- \rightarrow BH_4^- + 8\ OH^-$ (3.1-7)
Anode: $8\ OH^- \rightarrow 2\ O_2 + 4\ H_2O + 8\ e^-$ (3.1-8)
Net: $B(OH)_4^- \rightarrow BH_4^- + 2\ O_2$ $E^0 = -1.64$ V (3.1-9)

This approach would thus use electrical energy directly for reduction of B-OH to B-H bonds.

The attractiveness of an electrochemical process, especially in aqueous media, has been recognized in the patent literature[16-20], but only recently has some experimental evidence been provided to suggest that such a process might be feasible. Identification of electrochemical process conditions (boron substrate, cathode and anode compositions, solvents, electrolytes and various additives, etc.) to achieve the desired reduction remains an active area of research.

If electrochemical reduction of borates can be achieved with good current efficiency and chemical yield, and a source of inexpensive and renewable electricity is available, this process could offer perhaps the best potential alternative to the Schlesinger chemistry.

3.1.4 Elemental and Carbothermal Processes

Synthesis of sodium borohydride from elemental sodium, boron and hydrogen has been achieved in an autoclave under high temperature and pressure reaction conditions, for example, 600-800°C and 150 atm hydrogen.[21]

$$Na + B + 2\ H_2 \rightarrow NaBH_4 \qquad (3.1\text{-}10)$$

A slight excess of sodium metal, or alternatively sodium hydride, and the use of amorphous boron is claimed to improve yields. The primary benefit to the elemental synthesis route is efficient utilization of sodium, albeit at the expense of more demanding reaction conditions.

A variation of the elemental synthesis route involves carbothermal reduction of a sodium borate salt to produce elemental sodium and boron followed by reaction with hydrogen to produce sodium borohydride.[22]

$$NaBO_2 + 2\ CH_4 \rightarrow Na + B + 2\ H_2 + 2\ CO \qquad (3.1\text{-}11)$$
$$Na + B + 2\ H_2 \rightarrow NaBH_4 \qquad (3.1\text{-}12)$$

The simplicity of this process is attractive, especially the potential of utilizing aqueous alkaline borate or mined borax as raw material. An understanding of the process thermochemistry and energy requirements is necessary to pursue the elemental synthesis route. Specialized equipment such as plasma systems can be used to achieve the elevated temperatures required for conversion to sodium borohydride.[23]

3.1.5 Borane-Based Routes

If diborane (B_2H_6) or its complexes is available as a reactant, several pathways to sodium borohydride are possible that result in better alkali metal utilization. By first hydriding the boron atom (via some process other than reaction of a borate with metal hydrides) the sodium requirement is reduced to simply providing the cation for the borohydride anion. Thus, diborane can be reacted with sodium hydride (or sodium methoxide, sodium tetramethoxyborate, sodium carbonate, etc.) to produce sodium borohydride under mild conditions:

$$NaH + \tfrac{1}{2}\ B_2H_6 \rightarrow NaBH_4 \qquad (3.1\text{-}13)$$

To achieve sodium economies, this process requires a non-sodium route to produce diborane, e.g., by reduction of boron compounds such as halides (BCl_3), borate esters, boron oxide, boric acid, or boron alkyls, etc. Microwave generation of boron hydride has also been demonstrated, although the energy required for the transformation is excessive.

The difficulties in handling diborane, a flammable, pyrophoric and toxic gas can be minimized by complexation with amines, ethers, etc. For example, triethylamine borane (prepared by trapping diborane as formed with the amine) can be reacted with sodium hydride to produce sodium borohydride.[24]

$$NaH + N(Et)_3BH_3 \rightarrow NaBH_4 + N(Et)_3 \quad (3.1\text{-}14)$$

3.1.6 Metathesis Processes

Metathesis processes are defined here as those utilizing complex metal hydrides, such as sodium or lithium aluminum hydride to transfer hydride to a boron substrate, e.g.:

$$NaAlH_4 + B(OR)_3 \rightarrow NaBH_4 + Al(OR)_3 \quad (3.1\text{-}15)$$

The metathesis process is operable under moderate conditions (100-260°C) in solution or via dispersion milling techniques to afford good yields. The primary benefit is the reduction in the moles of metal required per mole of borohydride produced, from 4:1 to 2:1, compared to the Schlesinger process. However, the process requires preparation of sodium aluminum hydride from reaction of the metals with hydrogen at high pressure, and produces substantial aluminum alkoxide byproduct that must be recycled in large scale production.

Options for recycling the alkoxide product such as reacting with sulfuric acid to produce alum and recovering the alcohol could be of interest.[25]

3.1.7 Other Borohydride Processes

Other methods to prepare $NaBH_4$ have been reported in the literature. However, none of these appear sufficiently promising at this time to warrant consideration as viable alternatives to the Schlesinger process.

<u>Boron halides</u> can be reacted directly with sodium hydride to form sodium borohydride. Thus reaction of sodium hydride with boron trifluoride in ether solvents under moderate conditions or via dispersion milling at higher temperatures in the presence of various additives can afford sodium borohydride:

$$4NaH + BF_3 \rightarrow NaBH_4 + 3NaF \quad (3.1\text{-}16)$$

While incremental yield improvements have been realized by process modifications including improved mixing, use of thin film reactors, etc., the Na usage of the basic boron halide process provides no advantage over the Schlesinger process. Learnings from the boron halide process development however may be leveraged to other routes.

<u>Boron phosphate</u> reduction using sodium and hydrogen or sodium hydride at elevated temperature produces sodium borohydride in reasonable yield, but also requires high Na usage.

$$4Na + BPO_4 + 2\,H_2 \rightarrow NaBH_4 + Na_3PO_4 \quad (3.1\text{-}17)$$

Furthermore, this process replaces preparation of trimethylborate in the Schlesinger process with the more energy-demanding step of preparing boron phosphate.

<u>Hydrolysis of magnesium diboride</u> with aqueous caustic is claimed to produce sodium borohydride, probably via a borane intermediate:

$$4\ MgB_2 + 8\ NaOH + 20\ H_2O \rightarrow 3\ NaBH_4 + 5\ NaB(OH)_4 + 4\ Mg(OH)_2 + 4\ H_2 \qquad (3.1\text{-}18)$$

However, preparation of magnesium diboride requires high process temperatures and the hydrolysis process is wasteful of boron values.

3.1.8 Conclusions

A review of the patent and scientific literature indicated that there are several chemical pathways to produce sodium borohydride that warrant continued investigation. To differentiate between these alternate routes and select the leading pathway to $NaBH_4$, a comparative analysis of the pathways was conducted. This effort is described in Section 3.2.

3.2 Route Selection

Route selection is an important activity in the development of a new synthetic route to $NaBH_4$. A disciplined approach is needed to focus efforts and resources on the options that have the highest technical and commercial probability of success, especially when there are numerous alternatives to choose from. Accordingly, an engineering-guided R&D approach was used, which evaluates each of the $NaBH_4$ options against a set of established screening criteria or metrics and enables rapid down-selection to a smaller set of routes for more detailed investigation.[26] The overall technical approach utilized involves 1) identifying leading pathways, 2) establishing the feasibility of the leading pathways, 3) detailing performance to select a single, top pathway, and 4) developing the single, top pathway. As one progresses through the process, more accurate and detailed process and economic analyses are obtained.

For initial screening to identify candidate pathways for $NaBH_4$ regeneration, a 2007 milestone was set by DOE to identify at least one $NaBH_4$ regeneration process meeting interim efficiency target of 50% for laboratory demonstration and further development studies. This efficiency is based on the lower heating value LHV of hydrogen that is released on-board the vehicle relative to the primary energy consumed in regenerating the spent borate material to $NaBH_4$. Electricity consumed during regeneration had to be converted back to the primary energy on the basis of 2015 US grid.

For each pathway, complete reaction cycles were defined, Gibbs free energies (ΔG's) were determined for each reaction step to determine spontaneity under a range of conditions and eliminate disfavored routes, and reaction enthalpies (ΔH's) were calculated. A minimum reaction energy requirement is obtained based on the sum of reaction enthalpies of endothermic steps and crediting for 0-75% heat recovery of exothermic steps. The theoretical regeneration efficiency was then determined from the usable energy (LHV) value of products relative to the reactants and minimum reaction energy change.

$$\text{Regen Efficiency} = (\text{LHV of } H_2 \text{ released in product}) / (\text{LHV of reagents} + \text{Net Heat of Reaction}) \quad (3.2\text{-}1)$$

For the heating value of reactants, the lifecycle energy requirements were applied and account for the amount of energy consumed in its production (such as natural gas, electricity, coal, etc). Conversion to a primary energy basis was done by applying the following factors:

	Efficiency
Hydrogen from Central SMR	68% (FCHtool 2.0)
Natural Gas	94% (FCHtool 2.0)
Carbon	88% (Boustead 5.0)
Carbon Anode	69% (BCS)
Coal	98% (FCHtool 2.0)
Electricity - US 2015 Grid	32% (FCHtool 2.0)
Electricity - Hydro	100%

FCHTool is an Excel based application developed by Argonne National Laboratory for evaluating the fuel cycle efficiencies of different automotive on-board H_2 storage options.
Boustead 5.0 is a life cycle software package, developed by Boustead Consulting Ltd., UK
BCS report on Al production (Choate and Green, Feb 2003) contains information on the C anode consumed during electrolytic production.

Calculations were conducted assuming electricity generation efficiencies ranging from 32% (2015 US grid) to 100% (hydroelectric power), to reflect real-world scenarios where highly integrated energy sources might be used.

Representative results, summarized in Table 3.2.1, revealed several regeneration routes that appear promising (greater than 60% energy efficiency). Three key energy efficiency drivers were noted: 1) heat recovery from exothermic reactions of regeneration, 2) process used to recover metal or reductant, and 3) efficiency of energy source used for regeneration.

Pathway (metal recovery route)	Theoretical Efficiency		Primary Energy * 2015 US Grid (32%)		Primary Energy * Hydro (100%)	
	@ Heat Recovery		@ Heat Recovery		@ Heat Recovery	
	0%	75%	0%	75%	0%	75%
Metal Reduction						
Na (Downs w/Schlesinger)	45%	52%	17%	18%	41%	47%
Na (MCEL w/Schlesinger)	62%	76%	30%	33%	48%	56%
Mg (e-)	57%	70%	23%	24%	51%	61%
Al (carbon)	57%	67%	54%	62%	54%	62%
Ti (e-)	68%	74%	27%	28%	58%	63%
Si (carbon)	65%	70%	61%	65%	61%	65%
Zn (carbon)	69%	71%	60%	61%	60%	61%
Electrochemical Reduction						
1-step (B(OH)4- + 8e-)	71%	71%	24%	24%	71%	71%
2-step through NaBH(OCH3)3	69%	72%	33%	34%	63%	67%
Carbothermal Reduction	75%	75%	62%	62%	62%	62%
Carbothermal/Elemental	77%	82%	74%	78%	74%	78%
B2O3 Reduction via Mg/Elemental	55%	70%	27%	30%	53%	66%
Borane Routes						
BHCl2 disproportionation	44%	65%	38%	53%	38%	53%
BH(OR)2 disproportionation	68%	78%	51%	57%	51%	57%
B2O3 + M + H2	64%	69%	59%	64%	59%	64%
Metathesis						
B(OR)3 + NaAlH4	53%	65%	22%	23%	48%	57%

*** based on theoretical energy of metal oxide reduction back to metal**

Table 3.2.1. Summary of theoretical energy efficiency calculations for alternative $NaBH_4$ pathways

This type of analysis enabled the identification of the leading metals to screen as potential alternatives to Na in the metal-based borate reduction pathway. The results show that the process used for metal recovery (to convert the metal oxide back to the metal) can have a substantial impact on the overall regeneration energy requirements. Advances in metal production and processing can significantly improve efficiency and are considered in the analysis. Electrochemical routes will require high efficiency sources of electrical power.

The energy efficiency results are incorporated into a series of metrics to further differentiate and rank the $NaBH_4$ pathways. The metrics selected for evaluation relate to energy efficiency, chemical efficiency (yields and conversions), process simplicity (number of chemical transformations, separations, and processing steps), process severity (temperature and pressure), raw material availability and costs, byproduct and waste impacts, and EHS (environmental/health/safety) considerations. Each metric is assigned a weighting factor according to its relative impact to address the DOE targets, and each regeneration pathway was assessed and scored against each metric. An overall score for each pathway is then calculated by summing the product of the weighting factors and scores for each metric. Results of the scoring process are shown in Table 3.2.2.

Goal: Define energy efficient and cost effective process to regenerate spent borate to NaBH4 to meet DOE targets

Option Criterion	Weighting	Schlesinger	Metal Reduction					Carbothermal	Elemental *	Echem			Borane			Metathesis
			Mg	Al	Ti	Si	Zn			1-stop	2-step	HT melts	BCl3	TMB	M + B2O3	
Chemistry demonstrated	**Pref**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**No**	**No**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
Cost/per unit H2 (NaBH4)																
Energy consump (theor efficiency)	**25**	1	5	7	7	7	9	9	8	7	7	7	4	6	7	3
Raw material consump - high conv / yields	**25**	3	8	7	7	7	7	5	7	1	3	5	7	3	3	7
Low operating severity	**5**	7	8	8	8	8	8	5	3	10	10	5	5	3	5	7
Few chemical reactions	**5**	5	8	8	8	8	8	9	8	10	8	8	4	7	4	5
Few separation / processing steps	**5**	5	8	8	8	8	8	9	6	10	8	6	3	7	5	5
Capital cost, $ per unit H2 (NaBH4)																
Low complexity	**10**	6	8	8	8	8	8	8	6	9	8	6	5	7	5	5
Low technical risk	**5**	10	7	7	7	7	7	5	5	7	7	5	6	7	5	7
EHS (environmental / health / safety)																
emissions, wastes, CO2	**10**	10	8	8	8	8	8	7	8	10	9	8	7	7	7	6
toxicity, safety, flammability, H2O-reactive	**5**	8	7	6	7	7	7	7	7	10	9	7	5	6	6	6
other ecological components?																
Logistics (supply / distribution)																
abundant raw materials	**5**	10	7	10	7	8	6	10	8	10	10	10	10	10	8	10
Total Score		485	710	745	735	740	780	725	700	675	680	645	560	565	535	560

* Elemental - B by carbo, 600 if B by Mg

Rankings:

Metal reduction # 1

Carbo and elemental (B via carbo) # 2 and 3

Electrolytic # 4

Borane, metathesis # 5 and 6

Table 3.2.2. Summary of comparative analysis of potential alternative pathways to $NaBH_4$

The analysis showed that the top ranking options are 1) metal reduction, 2) carbothermal/elemental reduction, and 3) electrochemical reduction of borate. A sensitivity analysis performed on the rating system indicated that the difference in scores was significant and that this is a useful screening tool. These three leading synthesis routes allow for the possibility for direct conversion of $NaBO_2$ to $NaBH_4$ in a single step. Separation of the spent borate fuel to individual Na and B containing streams is not necessary as the Na and B are already in stoichiometric proportion. The ratings formed the basis of Dow's experimental program.

The metal reduction pathway is the most advanced, with the highest demonstrated yields, potential for low severity operations and fewest processing steps, and numerous metal candidates with satisfactory energy efficiency. The carbothermal/elemental route has the potential for high efficiency and does not require introduction of a metal reductant. The electrochemical paths are attractive but require improved yields. The borane-based paths are multi-step processes and involve multiple complex chemistries as well as a higher hazard class. The metathesis route is proven but has lower energy efficiency.

Experimental investigation of the metal-based reduction pathway was conducted in Dow's laboratories. For the carbothermal pathway, collaboration with Idaho National Laboratory was initiated to leverage the experimental capabilities of INL. Guidance was provided to COE partner Penn State University in the pursuit of electrolytic reduction routes to borohydride. These three areas of research are detailed in the following sections of this report

3.3 Electrochemical Reduction of Borate

3.3.1 Introduction

Electrolytic reduction of spent borate in aqueous or organic media is potentially the most attractive route to $NaBH_4$ as it would likely occur at low temperature and in the case of an aqueous process, there would be no need to dehydrate the feed to anhydrous $NaBO_2$ for processing. The theoretical energy efficiency is 71%, and requires efficient electricity production to achieve high primary energy efficiency.

$$B(OH)_4^- + 4H_2O + 8e^- \rightarrow BH4^- + 8OH^- \quad \text{(cathode)} \qquad (3.3\text{-}1)$$

A 2-step process could involve conventional Schlesinger chemistry to attach the first hydride to boron. This step would be followed by a six-electron electroreduction process to attach the remaining three hydrides, representing a lower energy electrochemical process. .

$$NaH + B(OCH_3)_3 \rightarrow NaBH(OCH_3)_3$$
$$NaBH(OCH_3)_3 + 6H^+ + 6e^- \rightarrow NaBH_4 + CH_3OH \quad \text{(cathode)} \qquad (3.3\text{-}2)$$

A number of patents claim successful production of sodium borohydride via electrolytic means. Cooper[16] claimed reduction of borate anions in aqueous media using hydrogenations catalyst materials as the cathode (Raney nickel, Ni_2B, cobalt). No examples were given. Two Southwestern Analytical patents[17,18] described the aqueous reduction of quaternary ammonium or alkali metal borate in aqueous media, using Ni, stainless steel, Fe or hydrogenation catalyst as the cathode and graphite or Ti, among others, as the anode. Current efficiencies 8 – 80% were claimed. No analytical confirmation of borohydride was given.

Millennium Cell[27,28] claimed aqueous or non-aqueous reduction of borate using high hydrogen overpotential cathode materials (i.e., Bi, Pb, Sn) and high surface area, low oxygen overpotential anodes (i.e., Au, Ir oxide). The use of conductivity and solubility enhancers was described. No examples were given. Another patent by Millennium Cell[29] described the reduction of borate in molten NaOH using Ni, Cu, or stainless steel as cathodes and a gas diffusion electrode, Ni or Pt/Ni as the anode. Again, no experimental data was given.

Nissan Motor Co. Ltd.[20] claimed aqueous reduction of borate in concentrated aqueous NaOH. The cathode was Ta, In, Pb, Zn or carbon, with or without H_2 (high hydrogen overpotential), and the anode was a gas diffusion electrode, Ni, with or without H_2 (low oxygen overpotential). Hydrogen was fed to the anode to reduce cell voltage. Current efficiencies 20 – 80% were claimed, but analytical confirmation of borohydride was lacking.

3.3.2 Preliminary Studies

During the period 1982 – 1992, Dow (then Morton International) funded a series of contract research studies at Electrosynthesis Company (ESC) in Lancaster, NY. The objectives were to assess the methods described in the Cooper[16] and Southwest Analytical[17,18] patents and to evaluate new potential electrochemical approaches to form boron hydride. A number of analytical methods to quantify boron hydride formation were also investigated.

ESC did not detect any reducing species when following the teachings of the Cooper or Southwestern Analytical patents, and concluded that the Cooper and Southwest patents were not operable. Interestingly, in 1998 Gyenge and Oloman[30] at the University of New Brunswick also concluded that the Cooper and Southwestern Analytical patents were inoperable.

During the course of investigating the Cooper and Southwestern patents, ESC also evaluated a number of novel aqueous as well as non-aqueous approaches for reducing borate electrolytically. Several systems appeared to produce positive results, and patents were filed for both a one-step electrolytic process in aqueous media[31], and a two-step approach involving formation of an intermediate trialkoxyborohydride[32]. Much of the work focused on the use of high activity, high hydrogen overpotential cathode materials and a variety of catholytes.

During the course of the ESC work, a number of analytical techniques for detecting borohydride were utilized. It became apparent that past positive results reported by others in the patents and literature may have in fact been false positive results due to the non-selective nature of the analytical methods used. Among the non-selective methods are iodimetry and certain tests based on the reducing capability of the samples (i.e., carbonyl reduction). Since there are species besides borohydride that will react with iodine and reduce carbonyl compounds, these tests are considered non-selective and cannot be used alone for positive identification of borohydride. ^{11}B NMR and cyclic voltammetry[33], however, are highly selective for borohydride and are preferred.

3.3.3 Electrochemical Studies at Pennsylvania State University

The ESC studies, while promising, yielded poor current efficiencies for sodium borohydride (<3%), particularly for the one-step process. There remained, however, several possibilities to improve upon these past results, and in 2005 a program was initiated with Penn State to further this work through the DOE Center of Excellence. The program pursued a two-prong approach, with objectives to investigate aqueous and non-aqueous systems, although the bulk of the work centered on aqueous systems.

For reasons described in the previous section, an initial priority for the Penn State researchers was the establishment of a reliable cyclic voltammetric (CV) method for confirming the presence of borohydride in situ. The method, which detected borohydride accurately down to 0.65 mM, was used early on in the Penn State work.[34] Figure 3.3.1a shows a CV scan for a 20mM $NaBH_4$ solution in 2M NaOH, and Figure 3.3.1b illustrates the effect of catholyte composition on linearity, and hence on quantitation and detection limits.[35]

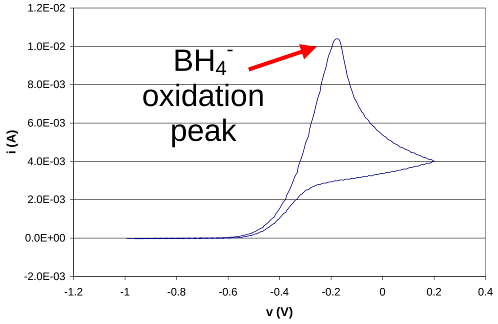


Figure 3.3.1a. Cyclic voltammetry of a 20mM BH_4^- solution in 2M NaOH

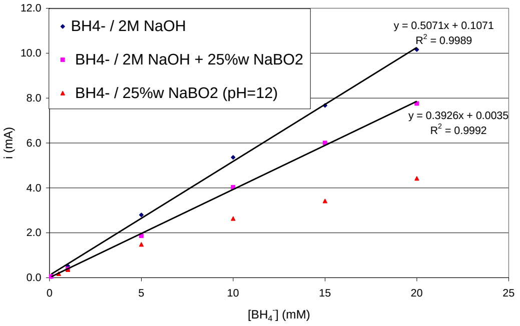


Figure 3.3.1b. Calibration curves in different electrolytes

An assessment of the reporting criteria for evaluating electrolytic routes to sodium borohydride was also provided by Dow. This included an extrapolation of experimental results to the electrical energy requirements for commercial electrochemical cell systems. It is important to note the role that current efficiency plays in determining the economics of commercial processes:

- Electric power consumption, K_P (kWh/kg = kilowatt hours/kilogram of product) is defined as

$$K_{\underline{P}} = (100\ n\ F\ V) / (M_p\ E_c) \qquad (3.3\text{-}3)$$

where n = number of electrons taking part in the reaction
F = Faraday = 26.8 amp-hours/mole of electrons

V = volts = cell voltage
M_P = grams/mole = molecular weight of product
E_C = current efficiency (percent)

- Low current efficiencies translate to high electric power consumption, which in turn means high power costs. Electrochemical cell power cost (C_P = dollars/kg = cost of electricity for production of 1kg of product) can be calculated as:

$$C_P = L_C K_P \qquad (3.3\text{-}4)$$

where L_C = dollars/kWh = local electrical cost
K_P = kWh/kg = kilowatt hours/kilogram of product

For electrolytic borate reduction to $NaBH_4$, n=8 electrons, and V=1.64 volts as the theoretical cell voltage. Thus, electric power needed is 12.4 kWhr/kg $NaBH_4$ at 75% current efficiency. For electricity at \$0.055/kWh, the electricity costs would be \$0.7/kg $NaBH_4$ or \$3.2/kg H_2. If a cell voltage of 4V is used to take into account the added voltage due to electrode overvoltage and the effects of solution and membrane resistance at higher current density, electricity cost increases to \$1.7/ kg $NaBH_4$ or \$7.8/kg H_2. The importance for high current efficiency and low cell voltages are illustrated in Figure 3.3.2.

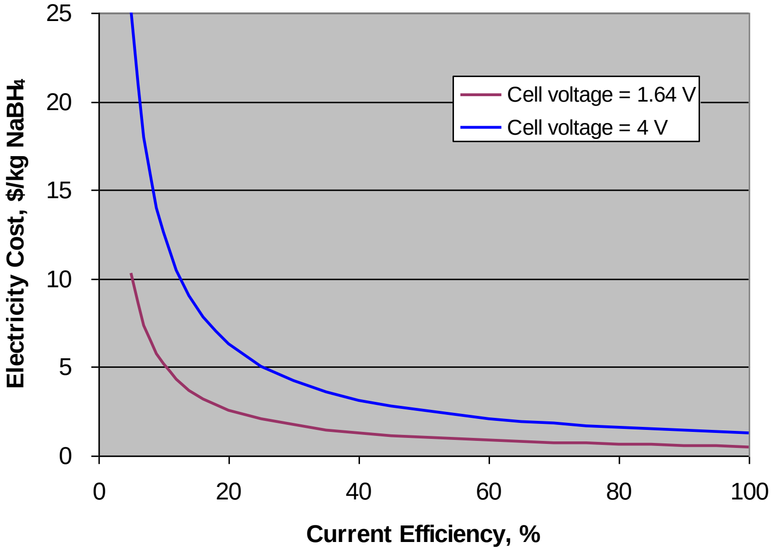


Figure 3.3.2. Impact of current efficiency on electricity cost

- Low current efficiencies also mean high cell costs, because a high electrode surface area is required. The electrode area required (A = m^2 = active electrode area required: anode or cathode) is determined by:

$$A = (1.12 \times 105 \text{ n P}) / (M_p \text{ i } E_c) \qquad (3.3\text{-}5)$$

where n = number of electrons taking part in the reaction
P = kg/day = production rate of product
M_P = grams/mole = molecular weight of product
I = amps/ m^2 = current density
E_C = current efficiency (percent)

Again, the influence of low current efficiency on electrode area is evident. At a current efficiency of 75% and current density of 3000 A/m^2, an electrode surface area of 105 m^2 per 1000 kg/day $NaBH_4$ production would be needed. Thus, the large electrical requirement for the process provides a large impetus to explore low cost cell designs that provide significant economies of scale.

Penn State began by investigating the various high hydrogen overpotential cathode materials identified by Dow for the direct, one-step reduction of borate to borohydride in aqueous media. The following variables were identified for study:

- Cathode compositions
  - High surface area, high hydrogen overpotential
  - Combinatorial approaches
- Influence of additives on hydrogen overpotential
- Membrane separator
- Process conditions
  - Process temperature, reactant, electrolyte concentrations
- H_2 feed to cathode and/or anode

Several high hydrogen overpotential cathode materials were recommended by Dow, based on past results, for initial studies. Penn State investigations showed positive formation of $NaBH_4$ using a Hg pool cathode, despite some hydrolysis of $NaBH_4$ at this cathode. Tentative positive results were also obtained with the Ni/PTFE cathode material. Results using graphite felt as the cathode were generally negative. Other cathode materials investigated included Ti, Au, Pb, and Hg plated Cu, with the majority of the experiments failing to produce any borohydride.

Although borohydride appeared to have been produced under aqueous borate electrochemical operations in some of the experiments, yields and current efficiencies were relatively low. The Penn State researchers developed an explanation for the lack of electrochemical activity: an electrostatic barrier to adsorption of metaborate onto the electrode surface. Various strategies were devised to overcome this barrier, including the use of tetraalkylammonium cations, pulsed current or potential, and modified electrodes, to try to overcome electrostatic repulsion of borate anion from the cathode and concentrate metaborate ion at the interface. The first experiment where there was indication of borohydride formation involved the use of tetraethylammonium hydroxide (TEAH) in a symmetrical electrolyte (2M TEAH + 0.2M boric acid, $B(OH)_3$). Using a Hg pool electrode, CV scans indicated possible formation of borohydride after electrolysis at 10 mA for five days (Figure 3.3.3).[35]

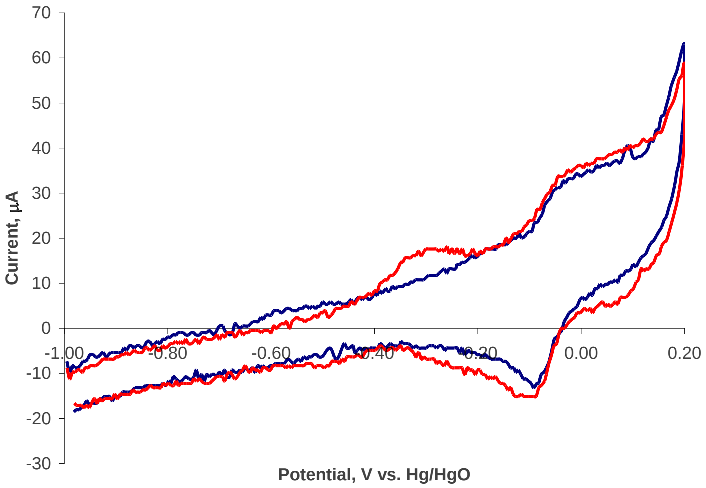


Figure 3.3.3. Cyclic voltammetry scans showing possible formation of borohydride (Hg pool electrode, 2M TEAH + 0.2M H_3BO_3, 10 mA for 5 days)

There was also indication of borohydride production in a subsequent experiment utilizing a Ni/PFTE electrode and a symmetrical electrolyte system (1M TEAH + 0.5M H_3BO_3). This was similar to one of the systems that gave positive $NaBH_4$ results during the ESC studies.[31]

Attempts to improve upon these results were generally not met with success. Problems were encountered when attempting to reproduce experiments, and rapid decomposition of any borohydride that might have been formed was suspected. Because yields were so poor, it was not deemed worthwhile to conduct conceptual process development and more detailed energy efficiency analysis on electrolytic routes until higher reaction performance could be demonstrated.

In DOE's 2007 Go/No Go report for sodium borohydride for on-board vehicular storage[36], Penn State received praise for implementing and validating the cyclic voltammetric analytical procedure for detecting borohydride, and for conducting interesting science and elegant experimental work. However, it was concluded that the work was generally preliminary and inconclusive, and that challenges associated with the 8-electron reduction process in aqueous media were not likely to be overcome. Thus, in the latter part of 2007, research in this area ceased.

Electrolytic reduction of B-O to B-H remains elusive but is still being pursued on a number of fronts today. As recently as 2010, Sanli *et al.*[37] reported on the development of a silver catalyst to reduce metaborate to borohydride for a rechargeable direct borohydride fuel cell. Using cyclic voltammetry and iodimetric titration as analytical tools, the researchers reported 10% conversion of metaborate to borohydride after 24 hours. Researchers at the University of Illinois[38] have also recently reported on the electrolysis of borate in a regenerative fuel cell. In a comprehensive review of electrolytic routes to sodium borohydride, Santos and Sequeira[39] recommended that, in spite of challenges associated with this approach, research in this area should continue.

Details of the experiments conducted at Penn State can be found in the final report of D. Macdonald *et al.*

3.4 Metal Reduction

3.4.1 Chemistry Principles

From the alternative pathways discussed above for the synthesis of sodium borohydride, the reduction of sodium borate by metal hydrides / metals emerged as a leading general pathway. Further work in this area focused on the solid-solid reaction of sodium borate salts with various metal hydrides to produce $NaBH_4$. The generalized reaction scheme is given below for both one (Eq. 3.4-1) and two (Eqs. 3.4-2, 3.4-3) step processes to produce $NaBH_4$:

$$2x/y\ M(s) + 2H_2(g) + NaBO_2(s) \rightarrow NaBH_4(s) + 2/y\ M_xO_y(s) \qquad (3.4\text{-}1)$$

$$2x/y\ M + 2H_2 \rightarrow 2x/y\ MH_{2y/x} \qquad (3.4\text{-}2)$$
$$NaBO_2(s) + 2x/y\ MH_{2y/x}(s) \rightarrow NaBH_4(s) + 2/y\ M_xO_y(s) \qquad (3.4\text{-}3)$$

In the one-step process (Eq. 3.4-1), a solid metal is reacted with sodium metaborate in the presence of hydrogen to give sodium borohydride and metal oxide directly. Presumably, this interaction takes place through the intermediate formation of the corresponding metal hydride. For the two-step process, the metal is allowed to react with hydrogen at pressure to give a metal hydride (Eq. 3.4-2) that is isolated and combined with sodium metaborate in a solid-solid reaction to form $NaBH_4$ and the metal hydride (Eq. 3.4-3).

Although metal reduction of borates is, in fact, the underlying chemistry in the current Schlesinger process, which uses sodium as the reducing metal, the improved pathway considers lower cost, lower usage metals in place of sodium. For example, the conversion of the metal oxide byproduct (Eqs. 3.4-1, 3.4-3) back to the metal in a highly efficient reaction cycle is a key enabler (Eq. 3.4-4), and can be as important as the $NaBH_4$ formation step.

$$M_xO_y + R \rightarrow xM + R\text{ [oxidized]} \qquad (3.4\text{-}4)$$
$$R = H_2, C, e^-, \text{etc; } R[ox] = H_2O, CO, CO_2\ ...$$

Theoretical energy efficiency calculations, defined as the heating value of the H_2 produced from $NaBH_4$, divided by the sum of the heating value of the feeds and the enthalpy change for each of the reactions, were made as an initial screen to identify candidate metals (Table 3.4.1). Complete reaction cycles were defined, ΔG was determined for each reaction step to determine spontaneity under a range of conditions and eliminate disfavored routes, and $\Delta H_{25°C}$ was calculated to obtain the theoretical minimum energy. The results showed that theoretical efficiencies of 60-69% are possible for Al, Si, Ti, and Zn systems with no heat recovery of exothermic reactions and over 70% efficiency when 75% of the heat from exothermic reactions is recovered (Table 3.4.1). The process selected for metal recovery can have a substantial impact on the results.

When the energy to produce the fuel feed streams used in the reactions is considered, the primary energy efficiencies are determined and show values in the 60-65% range when hydroelectric power sources are available. These efficiencies fall to the 40-50% range when the actual efficiency of the respective metal reduction process is applied. Development of advanced and next generation metal reduction technologies with lower energy usage is an active area of research, and could provide significant improvements to the borate regeneration efficiency.

Past metal reduction studies of sodium metaborate to $NaBH_4$ have been conducted primarily with Mg as the reducing metal system, where yields in excess of 90% have been achieved using high intensity milling with MgH_2 at low temperatures using excess hydride[13] or using Mg and H_2 at higher temperatures (>400°C).[40] Conversion improves with increasing temperature or with excess MgH_2. $NaBO_2$ reduction using Al and H_2 has also been demonstrated but at lower yields, [41,42] although 70% yield has been achieved when Na_2O is fed with Al to produce $NaAlO_2$.[41,43]

Metal	**Reaction 1**		**M_xO_y Reductant R**	**Theoretical Efficiency**	
	(kcal/mol $NaBH_4$)			**@ Heat Recovery**	
	ΔG, 25C	**ΔH, 25C**		**0%**	**75%**
Mg	-82.8	-100.2	2C (Cl_2) / 4e- 4e- *	46% 57%	63% 70%
Al	-62.7	-79.7	4e- / C 2C *	60% 57%	72% 67%
Ti	-23.2	-38.5	2C (Cl_2) / 2Mg / 4e- 4e- *	46% 68%	63% 74%
Si	-15.3	-30.4	2C	65%	70%
Zn (in H_2O)	-3.6	-11.1	4C decomposition *	69% 69%	71% 71%

* technology under development

Table 3.4.1. Theoretical energy efficiency for candidate metal reduction systems

The goal of this experimental program was to demonstrate high $NaBH_4$ yields for borate reduction using metals other than Mg, especially metals with higher theoretical energy efficiency such as Al, Zn, Ti, and Si. Hydriding metals with hydrogen at moderate pressures and temperatures is used in the commercial pathway to produce NaH, TiH_2, and ZrH_2, and has been demonstrated at high yields for MgH_2.[40] However, very high pressures are required to form alane from its elements. Because of these unfavorable thermodynamics, research on developing alternate routes to ligated alane ($LAlH_3$) is being conducted in the DOE Metal Hydride Center of Excellence. Synthesis of alane ligand complexes as hydrogen fuel sources is being evaluated through organometallic approaches[44], electrochemical routes[45], and use of supercritical conditions. As a result of these studies, alane ligand complexes have been found to be a convenient low pressure alternative to the parent, unstabilized AlH_3.

The work described below will first focus on the hydride transfer reaction (Eq. 3.4-3) using the two-step methodology because of the ability to more independently vary reaction parameters and optimize performance in a two-step process. This approach facilitates a more focused evaluation of chemistry feasibility and scalability. The one-step (Eq. 3.4-1) methodology will then be described once the viability of hydride transfer-based metal reduction as an approach to $NaBH_4$ synthesis has been established. Following the discussion of these laboratory-scale studies of solid-solid milling will be an evaluation of scalable processing technologies in solid-solid and slurry milling, as well as solution-based approaches.

3.4.2 Solid-Solid Milling

Planetary Ball Mill

In the early stages of experimentation, hydride transfer studies were conducted at ambient temperature in a planetary ball mill feeding $NaBO_2$ powder and a solid metal hydride. A planetary ball mill is a device designed to grind solids in a spinning and rotating jar that contains freely moving balls among the solids (Figure 3.4.1). The motion of the jar imparts a motion to the balls and solids that cause collisions which supply the grinding energy. Its function in the reaction is to force the solid reactant particles together while supplying the energy needed for the reaction to proceed. There may be a surface activation and size reduction phenomenon, as well as abrasion of the reaction products as they form on the reactants, allowing fresh surfaces to become available for continued reaction. Use of this type of mill for MgH_2 reduction of $NaBO_2$ to form $NaBH_4$ has been described in the literature.[46,47]

Figure 3.4.1. (a) Jar shown mounted on disc with counter weight (b) Representation of motion within the jar (c) Planetary ball mill jar (reactor) mounted on sun disc (d) Motion of balls and powder in the moving jar.

The planetary mill jar serves as the reaction vessel (Figure 3.4.1b and c). During operation, the jar or 'planet' spins in a horizontal plane while orbiting the 'sun' on a rotating disc in the opposite direction in the ratio 1:-2 (disc revolutions: jar revolutions). The superimposition of the spinning and rotating centrifugal forces produces grinding ball movements with high pulverization energy.

The experiments were carried out in the above-described ball mill in batch mode. Reagent grade ingredients were used. Anhydrous $NaBO_2$ was prepared by dehydrating to ~1.5 wt% moisture as determined by TGA. Typical solids charge was at stoichiometric ratios according to the metal hydride or metal used. Milling conditions were varied according to mixing severity and run duration. Sample workup was carried out by adding a solvent to extract the $NaBH_4$ formed, filtering undissolved solids, and measuring borate conversion by analysis with ^{11}B nuclear magnetic resonance (NMR) spectroscopy using appropriate standards. X-ray diffraction (XRD) analysis of the solid reaction products was also made.

In the hydride transfer studies, efforts were focused on optimizing reaction yields and gaining an understanding of the key drivers behind the reactions. Figure 3.4.2 shows positive identification of $NaBH_4$ using ^{11}B NMR. The spectrum shows few, if any, boron-containing by-products for this one-step reaction.

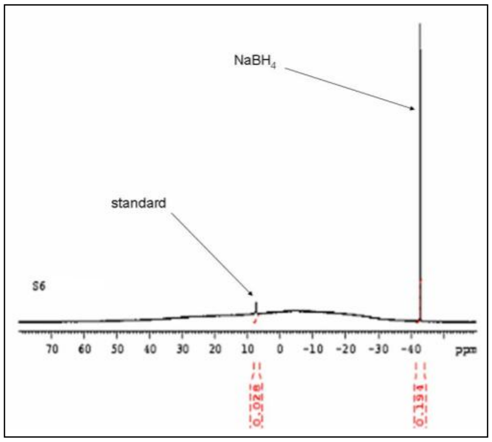


Figure 3.4.2. Proton-decoupled ^{11}B NMR spectrum of $NaBH_4$ produced from MgH_2

Further evidence of $NaBO_2$ reduction by a metal hydride to produce $NaBH_4$ and the corresponding metal oxide is given in the XRD results (Figure 3.4.3) showing formation of MgO after reaction with MgH_2.

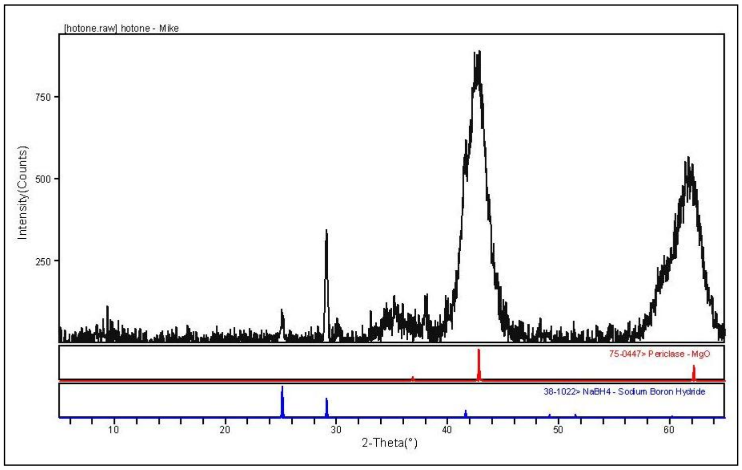


Figure 3.4.3. XRD of powder produced from the reaction of sodium metaborate with magnesium hydride

The effects of parameters such as reaction time and reaction severity were evaluated. Figure 3.4.4 illustrates the effect of reaction time and reaction severity on $NaBH_4$ yield for four of the metals studied.

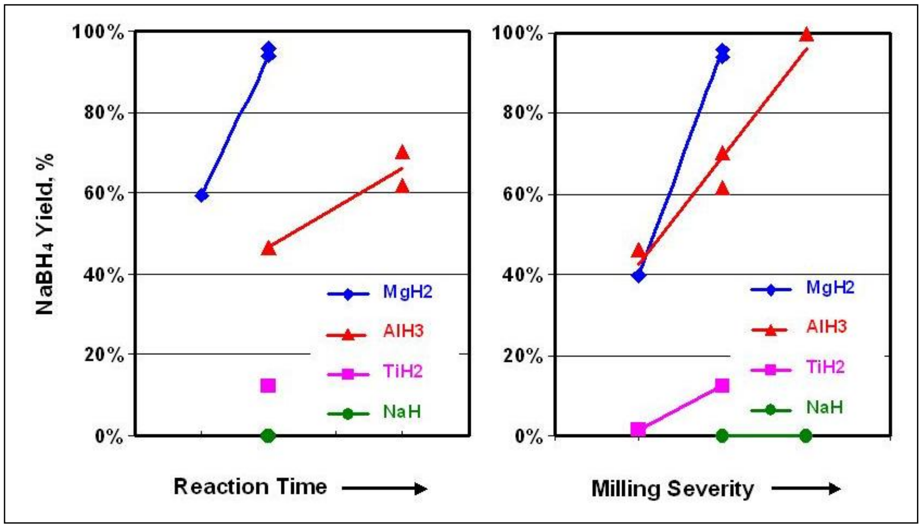


Figure 3.4.4. Comparison of the effect of reaction time (left) and milling severity (right) on the $NaBH_4$ yield for four of the metals tested

The results indicate that the order of reactivity proceeds as $MgH_2 > AlH_3 > TiH_2 > NaH$, which correlates roughly with the Gibbs Free Energy of reaction, with more thermodynamically favored reactions exhibiting a higher $NaBH_4$ yield. Yields in excess of 95% were obtained using MgH_2 and AlH_3. These results indicate that upon formation of the metal hydride, the Mg and Al systems will proceed to reduce

$NaBO_2$ readily. Experiments with ZnH_2 and SiH_x were also attempted but resulted in 0% conversion in each case

High yields in these initial screening studies were demonstrated with both magnesium and aluminum-based systems; however, aluminum-hydrides were selected for further development because they were found to be the preferred reductant based on supply logistics and costs. Thus, the continuation of the solid-solid milling studies focused on evaluating the chemistry and process variables of the aluminum-hydride reduction of sodium borate salts for the production of $NaBH_4$ (Eq. 3.4-5), where L represents a ligand that assists in the stabilization of the alane.

$$3\ NaBO_2 + 4\ AlH_3\text{-}L \rightarrow 3\ NaBH_4 + 2\ Al_2O_3 + 4\ L \tag{3.4-5}$$

The goal of this next phase of research was to build on the learnings described above and understand which variables affect overall $NaBH_4$ yield and purity. Particular attention was paid to the determination of the fate and mass balance for each of the component reagents and elements. Table 3.4.2 and Table 3.4.3 list the chemical and process variables that were tested, respectively, and their effect on $NaBH_4$ yield. When present, boron-containing byproducts are indicated in italics.

Chemical Variables

Borate (w/ 1.1 eq. $LAlH_3$)	• $NaBO_2$: **77% $NaBH_4$**, *1% "B-H"* • $Na_2B_4O_7$ + NaX : **78% $NaBH_4$,** *<1% "B-H"*
Alane adduct $LAlH_3$ (1.1 eq. w/ $NaBO_2$)	• L_1 : **89% $NaBH_4$**, *1% "B-H"* • L_2 : **1% $NaBH_4$**, *29% "B-H"* • L_3 : **0% $NaBH_4$** • L_4 : **2% $NaBH_4$** • L_5 : **67% $NaBH_4$**
Reductant Stoichiometry (w/ $NaBO_2$)	• 1.1 eq. $LAlH_3$: **60% $NaBH_4$**, *1% "B-H"* • 2.0 eq. $LAlH_3$: **77% $NaBH_4$**, *1% "B-H"*

Table 3.4.2. Chemistry variables tested in solid-solid milling of borate salts with aluminum hydrides.

Borate Source

As noted in Table 3.4.2, the use of either $NaBO_2$ or $Na_2B_4O_7$ plus an additive to maintain the sodium balance gave good and almost identical $NaBH_4$ yields (77% vs. 78%). In addition, the formation of borohydride side products was slightly reduced in the case of borax. It should be noted that while anhydrous $Na_2B_4O_7$ was commercially available for this study, anhydrous $NaBO_2$ was not and thus was prepared in the lab prior to use. The equivalence of $NaBH_4$ yield when using either $NaBO_2$ or $Na_2B_4O_7$ (with an additive) as a borate source allows for reagent options for scale up.

Alane Adduct

A selection of five alane adducts were chosen for testing on the basis of their relative expected reactivity and ease of formation through hydrogenation routes. While the ligand choice can result in a more facile alane synthesis, stability is also a concern in this reaction system given that research[48] is being carried out within the DOE Metal Hydride Center of Excellence on the thermal dehydrogenation of alane as an approach to hydrogen storage (Eq. 3.4-6).

$$AlH_3 + \text{Energy} \rightarrow Al^0 + 3/2\ H_2 \tag{3.4-6}$$

Based on the results shown in Table 3.4.2, certain alanes have been identified resulting in moderate to excellent $NaBH_4$ yields. Furthermore, while one of the ligand systems tested gave relatively low $NaBH_4$ yields but moderate “B-H” conversions, a second system resulted in high $NaBH_4$ yields without the formation of any “B-H” products in the reaction mixture. The remaining two alane systems resulted in minimal conversion.

Reductant Stoichiometry

All reactions were run using the borate source as the limiting reagent. The amount of alane was varied from 10-100% excess of that required for stoichiometric conversion. All other conditions being equal, the increase from 1.1 to 2.0 equivalents resulted in increased yield from 60% to 77%. One possibility is that the presence of excess alane allows for an increase in the frequency of borate and hydride interactions. As the reaction proceeds, the alane powder may become coated with alumina which is not removed by the ball collisions, thus preventing reaction. Excess aluminum hydride prevents this type of coating from limiting reaction progress.

Another possible explanation for the observed yield enhancement is that the presence of a large excess of reductant allows any intermediate species formed in the reaction process to be driven toward products. Furthermore, any residual moisture present in the starting borate would react irreversibly with the alane and effectively reduce the number of alane equivalents.

Process Variables

Table 3.4.3 is a summary of results obtained from the testing of the various milling parameters described below.

Bead:Powder Ratio	• Low : **48% $NaBH_4$**, *1% “B-H”* • Mid : **64% $NaBH_4$**, *1% “B-H”* • High : **42% $NaBH_4$**, *2% “B-H”*
Bead Material	• Bead$_1$: **77% $NaBH_4$**, *1% “B-H”* • Bead$_2$: **80% $NaBH_4$**
Milling Duration	• x : **34% $NaBH_4$**, *<1% “B-H”* • 2x : **83% $NaBH_4$**, *5% “B-H”* • 3x : **89% $NaBH_4$**, *8% “B-H”*
Milling Severity	• Low : **5% $NaBH_4$** • Mid : **77% $NaBH_4$** • High : **66% $NaBH_4$**, *23% “B-H”*

Table 3.4.3. Milling parameters tested in planetary milling of borate salts with aluminum hydrides

Bead to Powder Ratio

For the purposes of this study, the bead to powder ratio (B/P) is defined as the weight ratio of beads to all other reagents in the system. The current study identified an optimal bead to powder ratio. For the case where B/P is either low or high, the $NaBH_4$ yield was 48% and 42%, respectively. However, when the B/P was maintained at an intermediate value, the yield increased to 64%. The amount of borohydride byproduct present in the system remained roughly constant between the three conditions. It should be noted that this variable was not able to be tested independently; varying B/P also varies the occupied volume of the milling jar.

The proposed reasoning behind this optimum B/P value is the balancing of the kinetic energy ($\frac{1}{2} mv^2$) in the system. As the B/P (# of beads) is reduced, the number of collisions decreases thus decreasing the number of opportunities for proper orientation and energy of collision. As long as the number and energy of collisions is sufficient to provide a certain minimum energy for reaction to occur, this increase in energy should increase the rate of reaction. However, there is a balance that must be struck. Increasing the number of collisions per mass of powder will allow more energy to go into the system; however, if this energy input is too high, decomposition of the alane starting material could occur to give aluminum metal, hydrogen and free ligand (Eq. 3.4-6).

Bead Material

Two different materials (and densities) of bead construction were tested. When the conditions were varied utilizing the second bead material, the $NaBH_4$ yield slightly increased from 77% to 80%. In addition, in all experiments where the second bead type was used, no borohydride byproducts were noted.

Milling Duration

As expected, increasing the milling time increases the yield of $NaBH_4$. Yield increased from 34% to 83% following an initial doubling of reaction time, and increased further to 89% at three times the base reaction time. Furthermore, the amount of "B-H" present as a byproduct also increased with time going from <1% to 5% then 8% after x, 2x and 3x hours of milling, respectively. At a constant milling speed and therefore constant collision frequency the yield would be expected to increase according to kinetics associated with the chemistry system. The initial sharp yield increase from x to 2x hours may be due to specific surface activation provided by the collisions and/or temperature buildup. Later on a contributing factor to the reaction slow down is that the surfaces of the reactant powders may be sufficiently coated with $NaBH_4$ and alumina byproduct that the colliding balls are unable to expose fresh reactant surface as rapidly, thus limiting the reaction rate.

Milling Speed

As with many of the variables tested, an optimum milling speed was noted for these reactions. When run at low speed, only 5% $NaBH_4$ was formed. When increased further to a mid point the yield increased to 77%. However, when the speed was pushed to high values, the $NaBH_4$ yield dropped to 66%, but with 23% borohydride byproduct formation, giving the total B-H yield as 89%. The increase in yield on going from low to mid speed can be explained by the increase of kinetic energy in the system. However, when the speed is increased further, the kinetic energy may be sufficient to decompose the alane starting material. Based on the previously observed data, this decomposition of starting alane should result in lower yields, but the "B-H" yield actually increases. One possibility is that at higher severities, the initial rate of B-H formation is very high giving the overall increase in "B-H" conversion; however, the rate of alane decomposition is also high resulting in insufficient alane to fully convert the borohydride byproducts to $NaBH_4$.

Mass Balance

Two important goals of the solid-solid reactive milling research were to determine the mass balance of the reagents/products and to identify a suitable workup scheme for $NaBH_4$ isolation. In the first step of the workup scheme, excess unreacted alane and free ligand are separated from the reaction mixture. In general, the ligand recovery was very good and in most cases quantitative.

The remainder of the reaction mixture was pumped into the drybox following evacuation and the resulting solid residue slurried with a solvent and filtered. The filtrate was treated with a crystallization solvent (e.g., a solvent in which $NaBH_4$ is insoluble) and the crystallized $NaBH_4$ was filtered. The isolated $NaBH_4$ purity was found to be 99% by ^{11}B NMR and H_2 evolution analysis.

The insoluble material was washed, dried and weighed. Boron and aluminum analyses were performed by ICP or XRF on the recovered solids. The percentages obtained from these studies were used in combination with the recovered $NaBH_4$ and alane, to obtain the recovered boron and aluminum percentages, respectively. The overall gravimetric mass accountability for the process was 90% including a quantitative recovery of the ligand, an 86% recovery of aluminum and a 100% recovery of boron from all sources. This is illustrated in Figure 3.4.5.

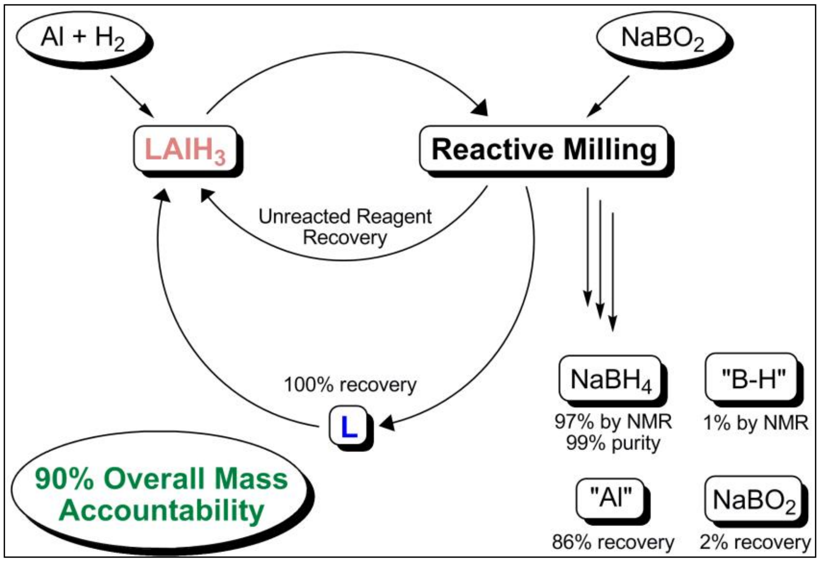


Figure 3.4.5. Recycle loop illustrating mass accountability for all reaction components

Autoclave Reactor

As an alternative to the two-step chemistry described above for the planetary ball mill studies, the one-step approach (Eq. 3.4-1) was evaluated using an agitated batch autoclave reactor (Figure 3.4.6). This reactor is capable of operating at elevated temperatures (up to 650°C) and pressures (150 atm) with a hydrogen feed in order to evaluate the reaction of sodium metaborate and a metal at higher operating severity.

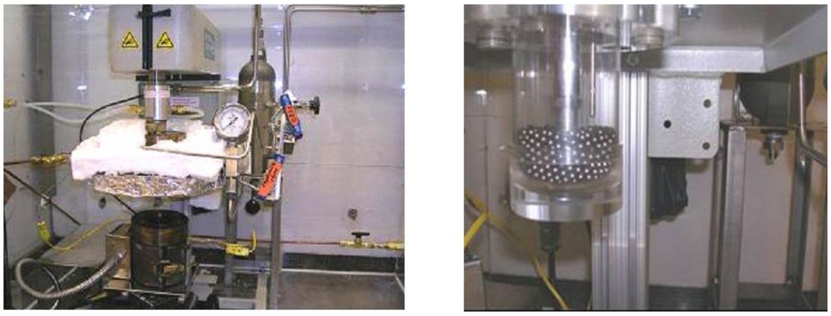


Figure 3.4.6. (Left) Autoclave reactor assembly (Right) Clear jar replica of autoclave reactor vessel showing un-agitated milling balls, pin at bottom of agitator shaft not visible. Visualization experiments were used to design the pin and determine the rpm for good ball movement

An in-house fabricated pin agitator and commercially available grinding balls were used to provide a mixing mechanism for the small quantity of powder reactants. Provisions were made for nitrogen inertion during charging and discharging the reactor solid contents, batch-wise feeding of hydrogen, pressure let-down through a caustic scrubber, and over-pressure relief through a rupture disc.

Initial runs in the autoclave reactor indeed confirmed successful reduction of $NaBO_2$ to $NaBH_4$ at 15% yield using aluminum powder (Figure 3.4.7).

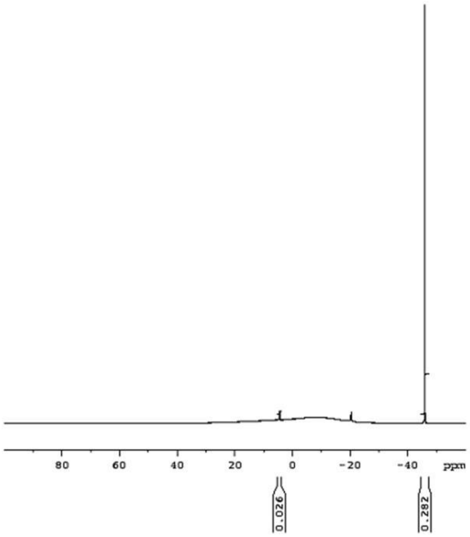


Figure 3.4.7. Proton-decoupled ^{11}B NMR spectrum of $NaBH_4$ produced from the reaction of aluminum, hydrogen and sodium metaborate in the autoclave reactor.

However, attempts at increasing the yields in these reactions through the addition of ligands, additives and catalysts were unsuccessful. Interestingly, addition of an aluminum-binding ligand to the system resulted in the formation of a borohydride byproduct that is estimated to account for a 4% $NaBH_4$ yield loss. Attempts at increasing the reaction severity alone led to $NaBH_4$ conversion falling to 0%, suggesting an upper limit for this reaction system. The typically low observed yields are in contrast to those reported in comparable reaction systems where yields are significantly higher.[40,43] Due to the lower yields in these screening studies of the one-step approach, the two-step approach of metal-hydride synthesis followed by hydride transfer (Eqs. 3.4-2, 3.4-3) was utilized for further development work.

Alternative Ball Mill: Scalable Solid-solid Milling Exploration

While the planetary ball mill served its purpose as being an excellent tool for evaluating the chemical feasibility of the solid-solid reactive pathway to SBH, this type of ball mill is not currently scalable to commercial size. As scale-up is the eventual goal, an alternative ball mill geometry with good scale-up potential was selected for evaluation.

A series of experiments was set up to test key variables identified in the initial planetary solid-solid milling work. For all experiments, the alane source, borate and B/P were held constant. The variables tested during the exploration were:

- Milling speed
- Bead material
- Bulk fill percent
- Barrel size

The basic principle behind the selection of these variables was to understand how they influenced energy input into the reaction, as described above for the laboratory scale milling work.

In all cases, the SBH yield in the alternative ball mill was minimal and the reaction mixture contained unreacted starting reagents. One possible explanation for the lower yields is that the milling energy intensity could have been below that available in the planetary mill and also below that required for significant activation and/or adequate surface renewal of the reactants. This hypothesis is especially viable when considering the lower yields seen at lower severities in the initial planetary ball milling work. As such, the low yields observed for these reactions prevent a meaningful comparison of the tested variables.

DEM modeling of the ball mills

DEM, or discrete element method, is a numerical method for computing the motion of a large number of particles in complex system.[49] As applied to the ball mills, the ‘particles’ which are modeled are the milling balls themselves. The powder particles are not part of the model other than their estimated influence on assumed parameters such as coefficient of restitution.

In conjunction with the experimental programs, DEM modeling of the ball motion in the planetary and alternative ball mill was initiated. The goal of the work was to provide an understanding of ball motions and the energy distribution resulting from the ball-ball collisions. This would allow for the correlation of milling operating parameters with performance data (reaction conversion, byproducts, etc.) and it would help guide further experimentation. Ultimately the model would allow for an estimation of process performance upon scale-up by providing an estimate of the available energy profile in both small and large scale ball mills.

The model output provided a visual representation of the ball movement within the mill chamber. The calculated ball movement pattern for the planetary mill was consistent with expectations based on literature[50,51], though the calculated motion and velocity for the actual conditions modeled could not be confirmed by observation due to the inability to configure the moving jar for viewing. The general ball movement pattern for the alternative mill was validated by observation using a sight glass. Thus the model for the alternative could be considered representative of the true motion and energy distribution.

Besides a visual representation of the ball movement, the DEM model output allows for the calculation of the frequency distribution of a number of parameters that describe the activity of the balls. By way of example, Figure 3.4.8 illustrates the stress energy distribution caused by ball-ball and ball-wall collisions for a particular set of mill operating conditions.

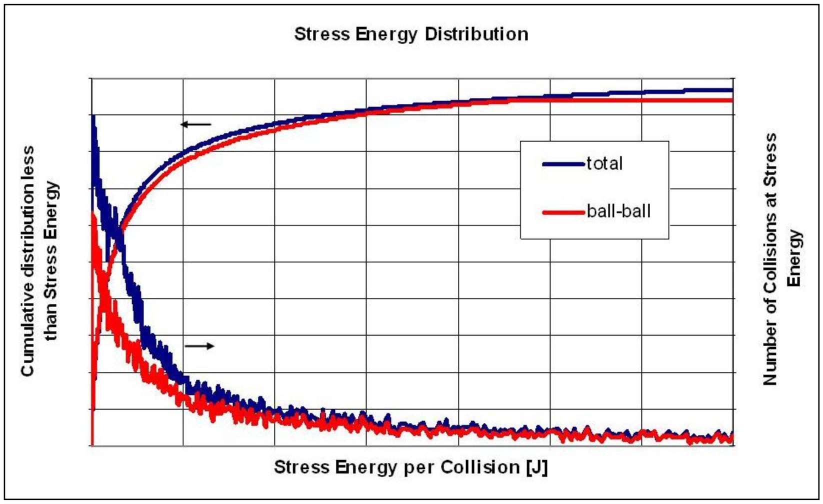


Figure 3.4.8. Example of stress energy profile in a planetary ball mill

3.4.3 *Slurry Milling*

In a continuing effort to identify a scalable milling process for the borate reduction reaction, slurry milling in a stirred media mill was identified as a scalable processing technique that might be capable of driving the reaction using solubilized aluminum hydrides in the presence of solid borax or sodium metaborate. Stirred media mills acting on slurries are capable of reducing particles to a smaller size than dry milling machines such as ball mills acting on powder. In theory, this further particle size reduction would allow for higher reaction surface area as well as more surface renewal through abrasion. The concept of slurry milling was first explored in the planetary milling system described above to demonstrate feasibility. It was found that the use of solubilized aluminum hydride with a borate salt resulted in 29% conversion to $NaBH_4$, thus further exploration of slurry milling was warranted.

A stirred media mill is a size reduction machine that works by imparting the mechanical energy of highly agitated beads to solids contained in a slurry. The slurry is pumped multiple times through a chamber that contains the grinding beads. In addition to size reduction there may be a surface activation role as well as abrasion of the reaction products as they form on the reactants, allowing fresh surfaces to become available for continued reaction.

The stirred media mill was set up in circulation mode so that the slurry would pass through the chamber containing the grinding beads multiple times for the duration of the reaction. Experiments were also conducted in batch mode where the circulation loop was closed off and the entire slurry was contained in the milling chamber for the extent of the reaction time. Cooling was provided on the chamber wall to remove heat generated by friction.

Below is a list of variables that were tested during the course of this study. It should be noted that the variables could not be studied independently of each other due to the scouting nature of the program.

- Borate Source
- Borate Feed Size
- Alane
- Stoichiometry
- Slurry Percentage
- Bead Material
- Milling Speed
- Milling Time
- % Fill; Residence time
- Milling Temperature

The work described previously using a solid-solid milling approach in the planetary mill had identified a number of these variables as critical to obtaining high product yields. Among those that were tested in the solid-solid milling approach - milling time, stoichiometry, bead to reagent ratio, bead material and milling speed were all found to have a significant effect on SBH yield.

In addition to the above variables, other considerations must be made in the case of slurry-based systems. One such variable is the percentage slurry solids, defined as the ratio of the mass of undissolved solids to the mass of the solids + solution. This percentage plays a role in defining the frequency of particle hits and the slurry viscosity which can affect milling efficiency. Another variable that was not able to be tested in the solid-solid milling approaches but was deemed important and controllable in slurry milling is the bulk process temperature.

Unfortunately, while a range of ten variables were tested, the SBH yield for all experiments was insufficient to continue development with this milling option. Attempts at both increasing the energy input into the system by raising the agitator speed and extending the slurry residence time in the milling chamber were not successful. Other routes toward increasing energy input, such as externally heating the milling chamber above 55°C were considered but not attempted due to the operating constraints of the system. Given the low conversions, slurry milling was determined to be unsuitable for the low-cost formation of sodium borohydride and exploration of this technique was terminated.

3.4.4 Solution Route

The solution route centers on the reaction of a novel soluble alane (CompoundA-Alane) in an organic solvent reacted with a soluble boron-containing material (Compound1). The economic benefit of a solution route is that the scale up uses conventional chemical plant processes leading to predictable cost and development. The development of the route optimized the production and composition of CompoundA, Compound1, and the solvent to meet economic and safety goals.

Compound1 is a boron-containing compound generated from common commercially available boron starting materials. The production of Compound1 was researched and reaction conditions optimized to maximize boron concentration resulting in a 250% increase in boron concentration, greatly reducing the mass of material in the process. The starting materials are also environmentally friendly and minimally toxic, reducing the hazards of the process. The non-boron material is completely recycled into starting materials or captured as waste.

The alane starting material is produced from the reaction of CompoundA with aluminum metal and hydrogen gas in a solvent to produce the active alane. The reactions were conducted in 300 mL Parr® Reactors, capable of holding 340 atm of hydrogen pressure. Initial scouting runs found the reaction to proceed rapidly at 80-100 atm, with further refinement this requirement was reduced to below 70 atm. The product purity was found to be acceptable for the production of sodium borohydride, and the yield was optimized to be 95%+ at larger scales.

The reaction of the CompoundA-Alane with the Compound1 in a solvent with limited sodium borohydride solubility gives a mixture of insoluble sodium borohydride and aluminum by product. The product is then filtered off and dried, giving >98% pure material. Analytical testing of the product revealed only trace impurities from the filtration. The purity of sodium borohydride increased with a slight stoichiometric excess of CompoundA-Alane relative to Compound1, as shown in Figure 3.4.9.

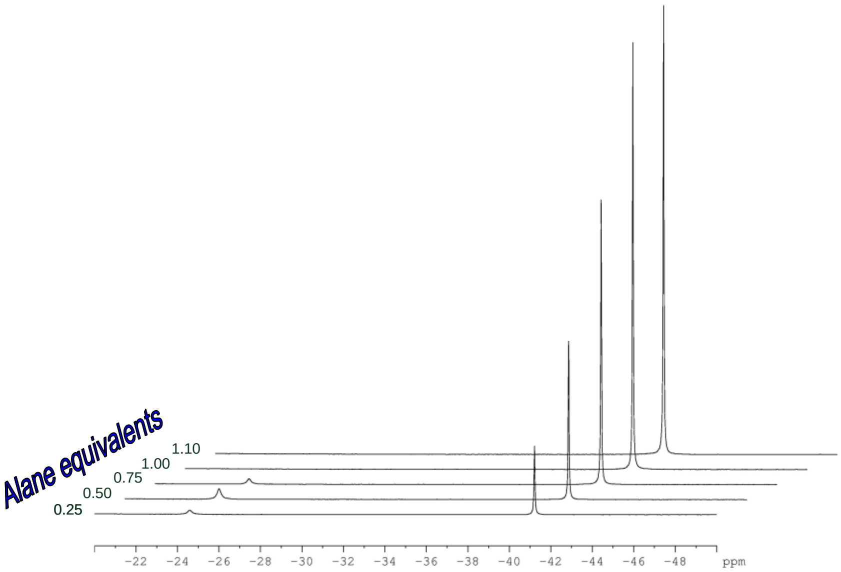


Figure 3.4.9. ^{11}Boron NMR of experimental SBH synthesis

The by-product is then recycled to recover CompoundA and the starting materials for Compound1 for reuse and solvent recovery, as illustrated in Figure 3.4.10. The CompoundA and Compound1 recovery was found to be 98%+ at laboratory scale, and is expected to be higher in a closed loop system at scale. The solvent recovery was a key concern for the process economics, and investigations with several solvents eventually gave acceptable results for the performance, recovery and cost.

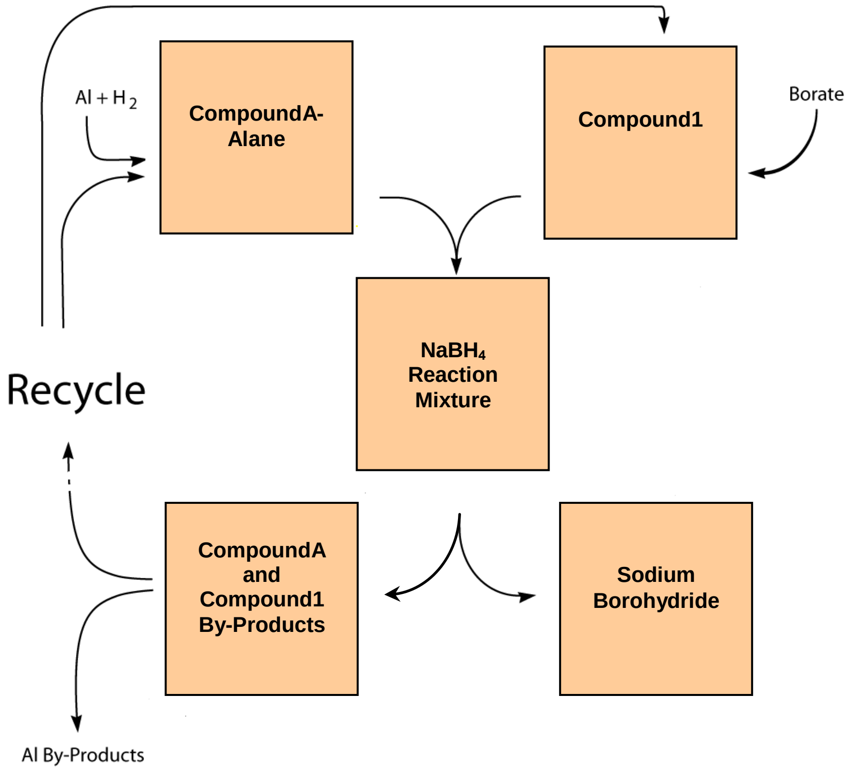
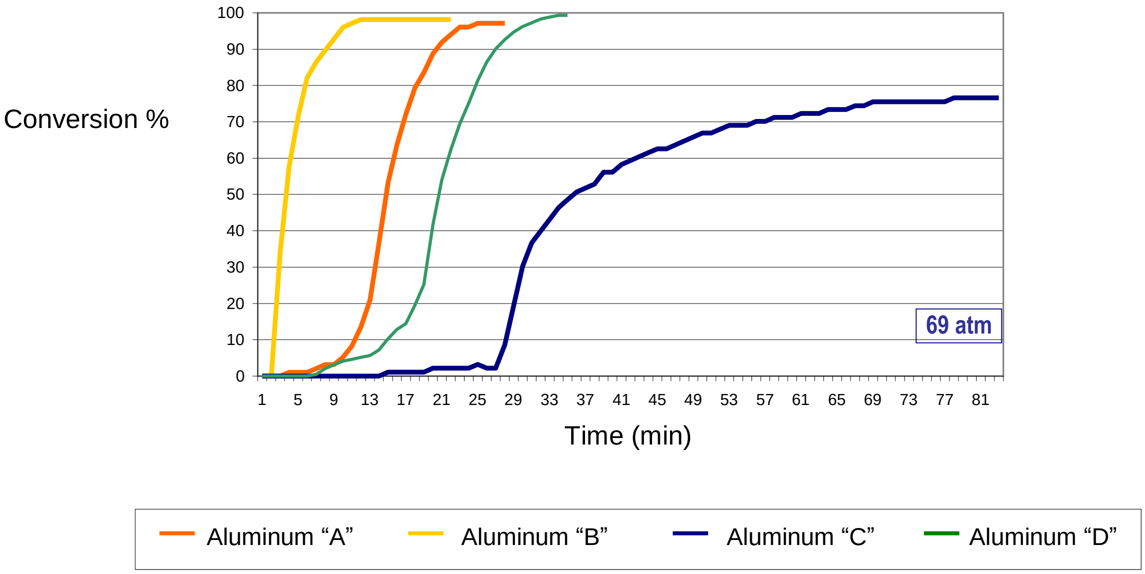


Figure 3.4.10. Recycle loop for solution-based process

A primary research goal of the project was to optimize the synthesis of CompoundA-Alane to run under economical pressure and temperature conditions in a feasible time frame. Extensive research on parameters revealed a novel reaction mechanism, knowledge of which was used to further optimize the reaction pathway.

Initial reactions found a long incubation period before the reaction started, and incomplete reaction. Modification of the reaction conditions and reagent preparation resulted in a reduction of the incubation period and an increase in the yield, eventually resulting in the complete elimination of the incubation period with good yields. Figure 3.4.11 shows the improvements achieved with different aluminum feed systems. These results compare very favorably to reports in the literature which require 12-24 hours and up to 340 atm to accomplish complete conversion.[52]

Figure 3.4.11. Optimization of Alane Synthesis



3.5 Carbothermal Routes to Sodium Borohydride

3.5.1 Introduction

Direct reduction of $NaBO_2$ using a reducing gas such as hydrogen or methane represents a very attractive 1-step reaction that does not involve the use of reducing metals and could permit reversible regeneration of borates. However, both reactions:

$$NaBO_2 + 4H_2 \rightarrow NaBH_4 + 2H_2O \text{ and} \qquad (3.5\text{-}1)$$
$$NaBO_2 + CH_4 \rightarrow NaBH_4 + CO_2 \qquad (3.5\text{-}2)$$

are highly disfavored thermodynamically at all reaction temperatures.[2] Recently, a number of investigators have proposed carbothermal pathways coupled with combustion to provide an overall favorable reaction ΔG.

Suda of Kogakuin University[53] claims reacting metaborate with a reducing gas in the presence of a hydrogenation catalyst to produce $NaBH_4$ according to the reactions:

$$NaBO_2 + H_2 + CH_4 + CO + O_2 \rightarrow NaBH_4 + 2\,CO_2 + H_2O \qquad (3.5\text{-}3)$$
$$NaBO_2 + 2H_2 + CH_4 + O_2 \rightarrow NaBH_4 + CO_2 + 2\,H_2O \qquad (3.5\text{-}4)$$

Process conditions of 500-700°C and up to 300 atm H_2 are proposed to achieve up to 70% at 5 hrs reaction time.

Idaho National Lab (INL) researchers claim a process for $NaBO_2$ reduction using a source of carbon to produce combustion gases followed by exposure to an electric arc to produce high temperature plasma which facilitates conversion to $NaBH_4$.[54]

$$NaBO_2 + 2CH_4 \rightarrow NaBH_4 + 2CO + 2H_2 \qquad (3.5\text{-}5)$$

The process is claimed to be thermodynamically favorable above 2000°C.

Rohm and Haas proposed the direct reduction of $NaBO_2$ or $Na_2B_4O_7$ occurring through a 2-step mechanism involving formation of elemental Na and B at high temperature (>1000°C) under net reducing conditions followed by reaction of the elements at milder temperatures (<600°C) to produce $NaBH_4$.[22]

$$NaBO_2 + 2CH_4 \rightarrow Na + B + 4H_2 + 2CO \qquad (3.5\text{-}6)$$

$$Na_2B_4O_7 + 7CH_4 \rightarrow 2Na + 4B + 14H_2 + 7CO \qquad (3.5\text{-}7)$$

$$Na + B + 2\,H_2 \rightarrow NaBH_4 \qquad (3.5\text{-}8)$$

Note that Equation 3.5-6 and Equation 3.5-8 combine to give Equation 3.5-5. The borate reductant can be C or a C_1-C_4 hydrocarbon. Borax can also be converted to $NaBO_2$ first by reaction with NaOH to obtain the desired Na:B molar ratio for the $NaBH_4$ synthesis step.

$$Na_2B_4O_7 + 2NaOH \rightarrow 4NaBO_2 + 14H_2O \qquad (3.5\text{-}9)$$

Elemental synthesis (Eq. 3.5-8) has been demonstrated at high yield (81%) as reported in a 1960 German patent.[21] Reaction conditions generally involved heating the mixture of solid reactants at temperatures in the 600-650°C range and hydrogen pressures of ~150 atm for several hours to affect conversion to the borohydride. Formation of $NaBH_4$ at lower temperatures would seem to be more favorable considering the thermal stability characteristics of $NaBH_4$.

3.5.2 Preliminary Assessments

Calculations of reaction energetics indicate a 75% theoretical energy efficiency, which is higher than the metal reduction routes. The 3 carbothermal reaction pathways are endothermic (Figure 3.5.1) and are thermodynamically favored at specific temperature regimes (Figure 3.5.2).[55] INL's reaction is thermodynamically favored at >1900°C which is in agreement with their claims. Rohm and Haas' route is favored at >1300°C and the elemental synthesis of $NaBH_4$ favored at <600°C, suggesting that a cooling step is required. The borate reduction reactions proposed by Suda are not thermodynamically favored at the 500-700°C conditions specified. In addition, the stability of $NaBH_4$ in the presence of a hydrogenation catalyst is questionable. Nevertheless, these routes have a high degree of uncertainty due to the lack of experimental data.

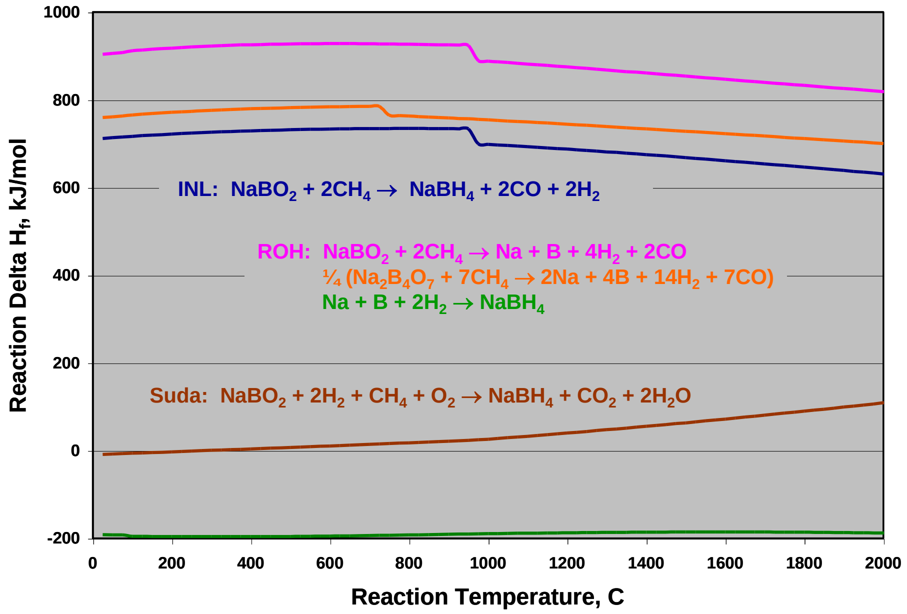


Figure 3.5.1. Heat of reaction for carbothermal routes

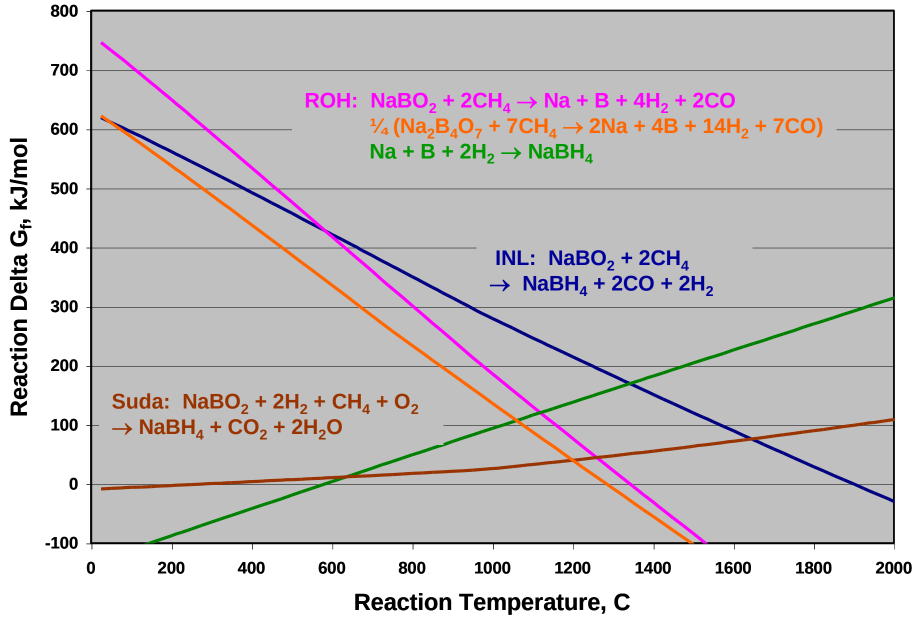


Figure 3.5.2. Gibbs free energy of reaction for carbothermal routes

In 2006, studies conducted at INL by a team led by Peter Kong indicated formation of $NaBH_4$ by carbothermal reduction of sodium borates based on a combustion flame and plasma hybrid concept. A combustion flame provides initial heating of borate and CH_4 reactants followed by application of an arc discharge on the combustion flame to superheat the gas into the plasma state (Figure 3.5.3).[54]

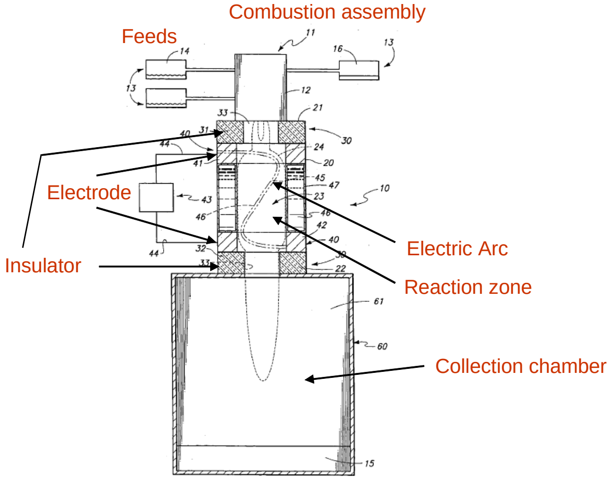


Figure 3.5.3. INL flame-plasma reactor configuration

INL proposed that the conversion of borate to borohydride occurs through a sequence of reactions:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{3.5-10}$$

$$3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2 \tag{3.5-11}$$

$$NaBO_2 + 2CH_4 \rightarrow NaBH_4 + 2CO + 2H_2 \tag{3.5-12}$$
$$NaBO_2 \bullet 4H_2O + 6CH_4 \rightarrow NaBH_4 + 6CO + 14H_2 \tag{3.5-12a}$$

The partial combustion of CH_4 produces CO and H_2 and provides a net reducing gas environment for the carbothermal reaction to take place as well as to serve as the plasma gas. Temperatures in excess of 2000°C are readily achieved in the plasma state. Flow rates are very high through the reaction zone and so the high temperatures are experienced for very short durations (~10 msec) before the products are quenched. These reactions all take place at atmospheric pressure.

Both XRD and ^{11}B NMR analyses of the product solids confirmed the presence of $NaBH_4$. Nearly 50% $NaBO_2$ conversion to $NaBH_4$ was reported to be achieved using this flame-plasma concept based on NMR.

3.5.3 Dow/INL Research Program

Idaho National Lab's preliminary studies on carbothermal reduction of $NaBO_2$ were encouraging in that they demonstrated initial viability and proof-of-concept. However, a number of knowledge gaps were identified and need to be addressed in order to translate these concepts into viable and scalable systems and operations. Some of the gaps included:

- <u>Reaction mechanism</u> – The mechanism for carbothermal reduction of borate to produce $NaBH_4$ is not well understood. It is not clear if the reaction takes place as a single reaction as proposed by INL or via a series of reactions such as reduction to some reduced intermediate at high temperatures, followed by $NaBH_4$ synthesis (e.g., by elemental synthesis) at some lower temperature. Clearly a route that permits lower temperatures is preferred. The extent of undesirable reaction byproduct formation such as boron carbide B_4C also needs to be established and minimized.

- Operating window – Definition of the process window that achieves maximum yields while minimizing capital and operating costs is necessary. A basic understanding of process parametric effects is needed. Determining the extent of reaction occurring with just the combustion flame versus with the plasma arc operating in addition will define the need for plasma operations.

- High temperature experience – Special consideration will be needed in equipment design, maintenance and reliability monitoring, and EHS reviews.

- Reaction quench – Means to rapidly cool the carbothermal reduction products to minimize $NaBH_4$ decomposition need to be identified and evaluated.

The Chemical Hydrogen Storage Center of Excellence partners lack high temperature experimental capabilities (>1200°C), thus collaboration with an external group to conduct high temperatures (>1000°C) experimental studies was deemed necessary. To pursue a plasma-based route, INL was selected for collaborative studies.

In 2008, a collaborative research program was established between Rohm and Haas and INL and funded through the DOE Center of Excellence program to further understanding of $NaBH_4$ formation via the carbothermal reduction pathway. DOE established a Go/No Go milestone after Year 1 of the program to select either the carbothermal reduction or metal-base reduction option and move to the next phase of development of a low cost $NaBH_4$ process. A decision criterion was agreed to that the INL experimental studies needed to consistently demonstrate at least a 40% conversion of borate to SBH in order to move into Year 2 of the program.

Experimental. The reactor used for this work is shown in Figure 3.5.4. Figure 3.5.5 shows the partially reducing combustion flame with reactants injected into the plasma jet.

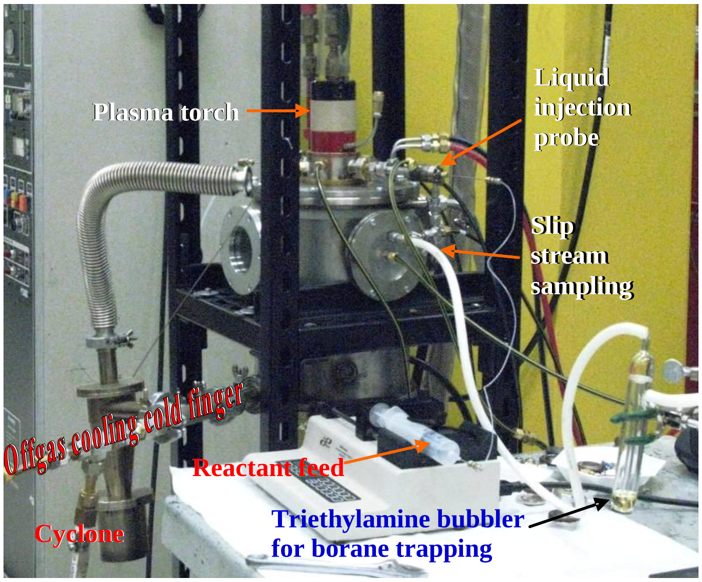


Figure 3.5.4. Plasma reactor for $NaBH_4$ synthesis

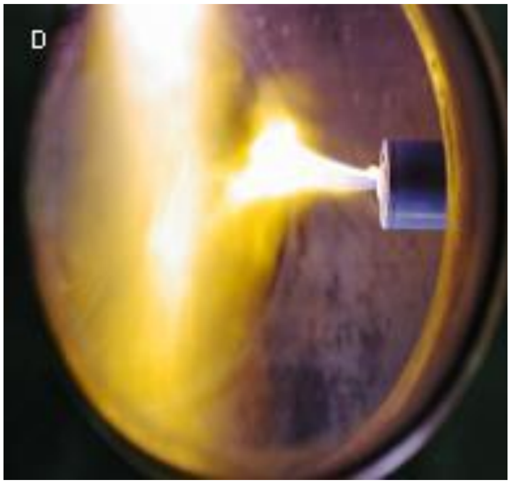


Figure 3.5.5. Combustion flame – plasma hybrid operations

Methane was the principal reducing agent; additional CO and H_2 were used to mimic the byproduct gases to keep the reactor under net reducing conditions. $NaBO_2$ was added in aqueous solution as was done in the initial INL studies where $NaBH_4$ was produced. In the experiments, CH_4 and the $NaBO_2$ feed rates were generally kept constant while the CO and H_2 compositions were varied to assess the effect of the reducing gases on the formation of SBH. Other experimental variables included plasma power (to simulate different high temperature reaction environments), and the length of the graphite reaction tubes (used to assess the effect of residence time for reactants in the plasma). Hydrogen was added downstream to serve as a reaction quench.

An online residual gas mass spectrometer was used to monitor the exhaust gas compositions to assess the extent of reaction in the reactor. In some experiments, a slip stream of the process gas was bubbled through triethylamine to capture any boranes that might form in the reaction.

Following each reaction run, any solid material that was produced was carefully collected, with attempts to exclude air/moisture during the collection process. In some experimental runs, a portion of the collected product was visually tested for reactivity towards dilute mineral acid (a positive test indicated positive formation of B-H species). The material was then either extracted with tetraglyme (dried over molecular sieves), or dissolved in 8% aqueous NaOH, and analyzed using liquid phase ^{11}B NMR. For quantitative ^{11}B NMR work, an internal reference standard was used to quantify the $NaBH_4$ and sodium metaborate. Other analytical techniques used included solid phase Fourier Transform Infrared (FTIR) spectroscopy and x-ray diffraction (XRD).

Prior to initiating the studies, a review of INL's past work was conducted to identify the experimental conditions under which sodium borohydride had been produced, including the boron:sodium ratio in the aqueous borate feed solution. After some initial difficulties obtaining a suitable borate feed, experiments were commenced.

After more than 60 plasma carbothermic runs, it appears that it was not possible to exactly reproduce the set of conditions which had previously yielded $NaBH_4$. No evidence of $NaBH_4$ formation was seen in any of the runs, although some runs did produce an unidentified water-reactive material. At the end of Year 1, with the Go/No Go criteria not met, the project at INL was terminated. Several factors likely contributed to the lack of success of the INL work:

- The reactor itself was several years old and required frequent maintenance and repair of water and air leaks.

- The original injector had to be replaced. It was difficult to reproduce exactly the geometry of the injector.
- The size and configuration of the reactor made it difficult to maintain an inert atmosphere during sample collection and manipulation.
- Problems with monitoring instruments (power meters, mass flow meters) made it difficult to reproduce any particular set of conditions, and to determine cause-and-effect relationships.
- Malfunction of the online mass spectrometer made it impossible to monitor reactor exhaust gases, making mass balance determination impossible and also making it difficult to determine if the reactor was leaking or not.
- Some material may also have been lost to the ventilation system, also making mass balance determinations difficult.

One fairly consistent observation throughout the course of the studies was the presence of higher levels of water vapor in the reactor exhaust compared to earlier studies. In fact, very large amounts of water were even visible in the sample collection tube at the bottom of the reactor. It was theorized that the H_2O may originate from the aqueous $NaBO_2$ feed, however, attempts to reduce the H_2O or even feeding dry $NaBO_2$ did not produce $NaBH_4$.

Researchers at INL concluded that construction of a new, smaller reactor, and use of more robust monitoring equipment and analytical instruments, would overcome the above difficulties and enable the establishment of the reducing environment necessary to reduce borate to borohydride.

3.6 Cost and Energy Efficiency Analysis

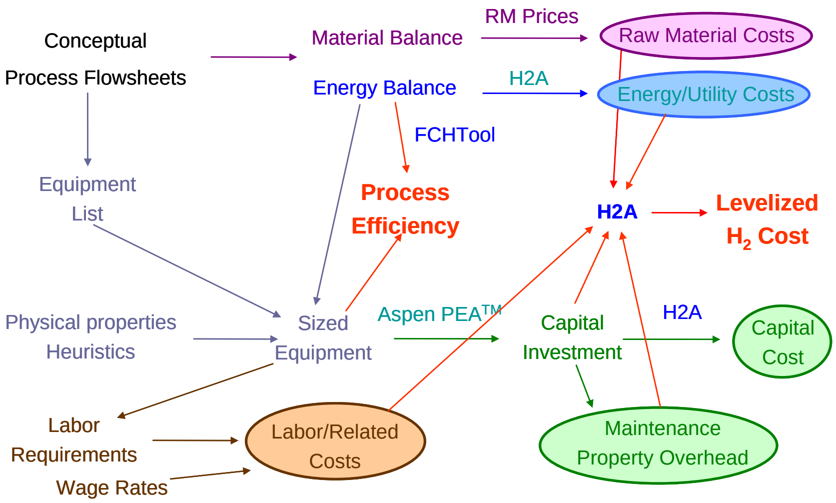
3.6.1 Methodology

Reliable methods for providing early stage estimates of cost and capital are important for economic evaluation and R&D planning purposes. These methods range from factored approaches based on correlations of capital costs requiring only information on process complexity and capacity to more detailed analyses requiring process flows, mass and energy balances and detailed equipment lists.[56]

Figure 3.6.1 shows the methodology and tools that were employed for estimating the levelized cost for producing hydrogen from chemical hydrides. In a typical conceptual cost estimate there are four types of costs that need to be estimated: raw material costs, energy and utility costs, labor related costs and capital related costs. The process begins by developing conceptual process flowsheets for the reaction and separation processes based upon the chemistry and physical properties of the materials. Complete material and energy balances are then estimated based upon laboratory data and process simulation runs. Raw material prices and usages based on the material balance give an estimate of the raw material costs. Likewise, energy costs are estimated from energy prices and usages based on the energy balance. Energy prices are obtained from the H2A analysis model[57] developed by the DOE, which is essentially a financial template with a database of energy costs. Use of this software ensures that all options will be compared using a consistent set of energy costs and financial assumptions.

Next, an equipment list is assembled from the process flowsheets. This equipment is sized based on the material and energy balances as well as physical properties of the materials, simulations and rules of thumb. Based on the equipment, a labor complement is estimated and multiplied by wage rates to estimate the direct labor cost. Typically labor related charges such as quality control, supplies and overhead are factored from the direct labor cost. In producing hydrogen, energy efficiency is very important and has specific targets established by DOE.[58] The efficiency of the process is based upon the energy balance and electricity used by the operating equipment. FCHTool[59] is a Microsoft Excel-based application developed by Argonne National Laboratory for evaluating the fuel cycle efficiencies of different automotive on-board hydrogen storage options. This was used for estimating process efficiency based on primary energy usage similar to calculations found in life cycle tools. The capital investment is estimated using Aspen Process Economics Analyzer (PEA^{TM}) software, which uses the sized equipment list, materials of construction and temperature and pressure conditions as input. Maintenance and property overhead costs are typically factored from the capital investment, and the capital cost can be estimated based on discount rate, depreciation schedule, tax rate and term of analysis. All of these costs are rolled into the H2A model for consistency to estimate the levelized cost of hydrogen over the life of the installation.

Figure 3.6.1. Cost and efficiency analysis methodology



Phase 1 of the DOE Chemical Hydrogen Center of Excellence program emphasized the evaluation of sodium borohydride for on-board vehicular hydrogen storage. Dow's efforts were focused on assessing the feasibility of leading borate reduction pathways to regenerate spent fuel back to $NaBH_4$. Accordingly, the cost and energy usage analyses described in this report are limited to the regeneration plant only and exclude logistics involving delivery (terminal and freight) and forecourt costs. Studies of the latter were made by Argonne National Lab and TIAX.[60,61]

3.6.2 Results

As described in Section 3.2, the top borate reduction routes identified are 1) metal reduction using lower-cost, lower usage reducing metal in place of sodium, 2) carbothermal reduction which eliminates use of metals and their recovery to increase theoretical efficiencies, and 3) electrochemical routes which also do not require addition of metals and have potentially a lower carbon footprint. Details of the experimental studies are summarized in Sections 3.4, 3.5, and 3.3, respectively.

The results summarized herein are directed to the aluminum-based and carbothermal reduction of $NaBO_2$. Aluminum was selected for this analysis due to the high demonstrated yields for borate reduction and its higher theoretical energy efficiency compared to Mg. Carbothermal reduction under plasma conditions was demonstrated in early studies conducted at Idaho National Labs and served as the basis for the analysis. Although these results were not able to be reproduced in subsequent studies at INL under the DOE project, the analysis reflects the potential benefits of a carbothermal route if proven. The electrolytic reduction pathway requires substantial yield improvements, and some general cost guidelines are provided in Section 3.3.3.

Appropriate assumptions and heuristics are employed to translate the key chemistry steps demonstrating $NaBO_2$ reduction to $NaBH_4$ to a conceptual large scale industrial plant corresponding to 100 mt/day delivered H_2 and establishing the necessary material and energy balances needed to determine energy efficiency and manufacturing costs. DOE has established technical targets for energy and cost efficient fuel regeneration. For systems regenerated off-board the energy content of the hydrogen delivered to the automotive power plant must be >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.[58]

Metal-based Reduction of Borate

A simplified block diagram of the metal reduction pathway is shown in Figure 3.6.2.

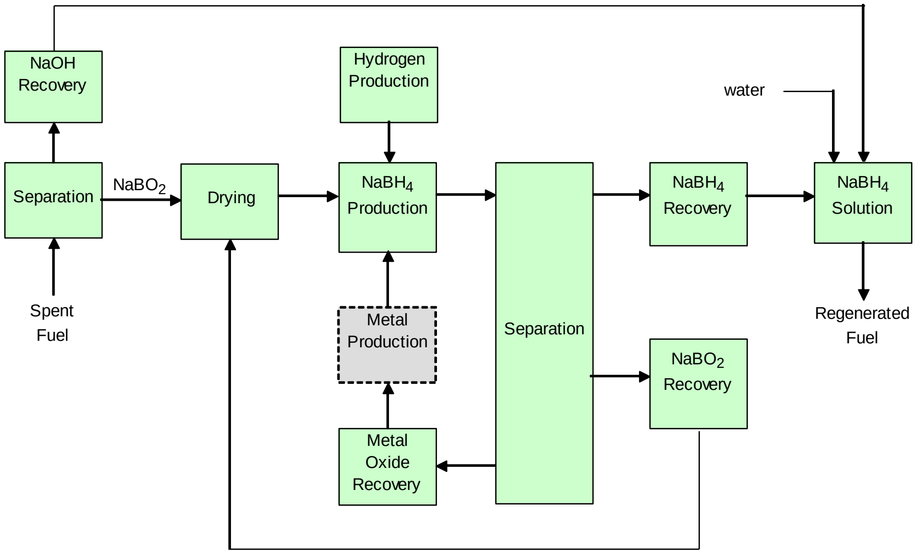


Figure 3.6.2. Metal-based $NaBO_2$ reduction process scheme

Spent fuel from automotive application containing an aqueous solution of $NaBO_2$ and NaOH is fed to a separation unit to preferentially remove borate crystals from the caustic solution. A number of schemes can be applied to minimize the energy used to concentrate $NaBO_2$. The $NaBO_2$ is next dried to an anhydrous powder, and fed to the $NaBH_4$ production unit along with metal and H_2 gas, where it is converted to $NaBH_4$ at 95% yield. The metal hydride and $NaBH_4$ can be produced directly in a 1-pot synthesis or in a 2-step process where the hydride is produced prior to contact with $NaBO_2$. The exothermic heat of reaction as well as heat input by motors is captured and used for downstream processing. Product recovery and purification are achieved in several separation steps that involve solvent extraction of $NaBH_4$, solvent removal and recovery, followed by extraction of any unreacted borate, and finally recovery of the metal oxide for conversion back to the metal. The metal production step can take place at another facility or at the same location for improved process integration. The $NaBH_4$ product is recombined with the NaOH removed from the spent solution to form a target fuel composition of 20-30%. $NaBH_4$.

The analysis indicates that the metal oxide reduction step back to the metal is the dominant contributor to the overall regeneration energy requirements. Therefore, conversion back to the metal in a highly efficient reaction cycle is a key enabler, and is as important as the $NaBH_4$ formation step. Selection of the optimal metal recovery process will significantly improve the energy efficiency of a metal-based reduction process. Moreover, it is important to consider not only the current metal reduction pathway but also any important technological advances being made in the metal industry.

For aluminum production, the current Hall-Héroult process is a mature technology, dating back to 1886, and is based on a somewhat inefficient electrolytic process using carbon anodes.[62,63]

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \qquad (3.6\text{-}1)$$

An overall borate regeneration efficiency of 29% on a primary energy basis was calculated. About 70% of the energy usage is related to the conversion of Al_2O_3 back to Al. Therefore, improvements in the Al manufacturing technology will have a profound impact on the overall energy efficiency for borate regeneration to borohydride. Efforts to improve the process have led to numerous advanced technologies, including a carbothermal process piloted by Alcoa that is estimated to provide >30% reductions in both energy and manufacturing cost compared to the Hall Héroult pathway.[64]

$$2Al_2O_3 + 6C \rightarrow 4Al + 6CO \qquad (3.6\text{-}2)$$

CO produced as a byproduct in the carbothermal process can be shifted to H_2 for the borate reduction step. These improvements combine to increase energy efficiency to 43%. Improvements to the Hall-Héroult cell technology are also being made, such as using wetted cathodes to reduce voltage drop and inert anodes to eliminate the need for carbon anode replacement, and provide intermediate levels of efficiency improvement.[62] Additional advancements should be expected to evolve over time and raise efficiencies higher. These efficiency results are somewhat lower than values shown in Section 3.4.1, and can be attributed to the energy used for $NaBH_4$ processing and product separation.

Electricity is assumed to be derived from hydroelectric power as large-scale plants will require high efficiency sources rather than the grid mix. In fact, 68% of North American plants are hydro-based and the majority of green-field aluminum plants for the next decade will be based on hydroelectric power.[62] Primary energy efficiency would drop from 43% to 19% if electricity is based on the US 2015 electrical grid (32% efficiency to produce electricity).

An evaluation of the process costs was conducted. The carbothermal process for aluminum production is assumed to have advanced to the point where the technology is commercially feasible. On this basis, regenerated $NaBH_4$ cost exiting the plant is estimated to be in the range of \$8.6 - \$9.8/kg H_2, The upper bound is based on an average cost for grid electricity while the lower bound is based upon purchase of lower cost hydroelectric power at 3¢//kWh. TIAX estimates of terminal, transportation, and forecourt costs sum to about \$0.9/kg H_2[61], so overall fuel cost at the “pump” would be in the range of

$9.5-10.7/kg H_2. Figure 3.6.3 provides a breakdown of $NaBH_4$ cost and shows the dominant effect of Al, similar to its impact on energy consumption. A cost sensitivity analysis of the metal reduction process to determine various parametric effects indicated that delivered hydrogen cost to be in the $6-12/kg H_2 range.

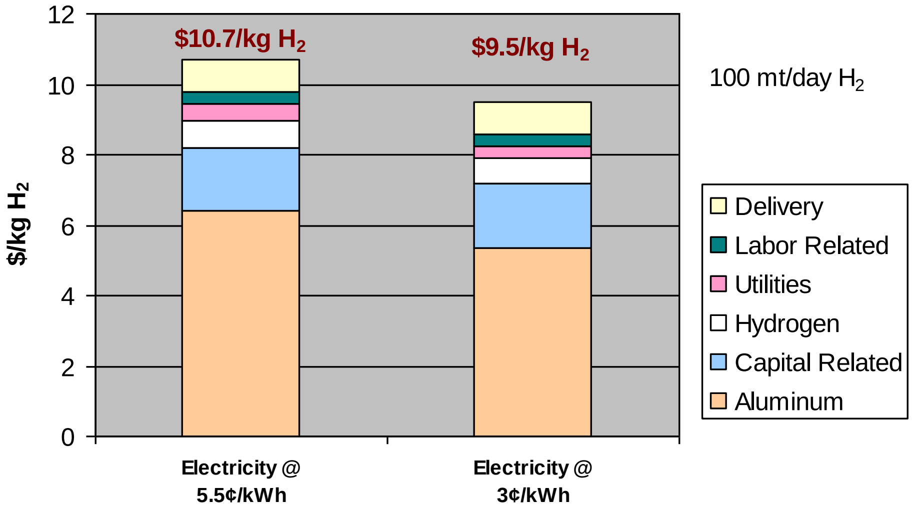


Figure 3.6.3. H_2 cost breakdown via Al-based reduction of borate to $NaBH_4$

Use of the current Hall-Héroult technology for aluminum recovery would have increased the cost by about $2/kg H_2. Thus, additional improvements in Al technology should result in considerable savings. A levelized cost of aluminum of $1.2-1.4/kg Al is shown in Figure 3.6.4, based on a $1.5B capital investment for a 400,000 mt/yr world scale aluminum plant, and represents a 30% reduction in construction cost compared to an aluminum smelter. In addition, the labor requirement for carbothermal Al technology is estimated to be 20% of the current technology.[64] An annual capital recovery cost of 13.8% of the investment based on 20 year analysis, 20 year plant life, 10% rate of return, 38.9% tax rate, 10 year MACRS for tax depreciation was applied, similar to all the other studies.

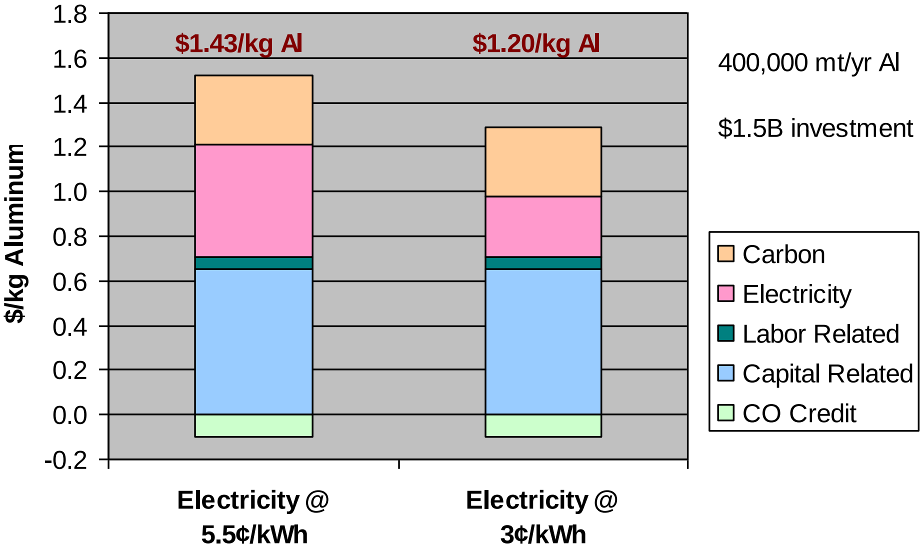


Figure 3.6.4. Carbothermal aluminum production cost

The continual improvement in aluminum manufacturing technology is in fact being borne out. A new carbothermal process being developed by the Australian company Calsmelt Pty. Ltd. was recently announced in 2010 and is claimed to reduce capital cost by up to 80% and operational cost and power consumption by 40% compared to the Hall Héroult pathway,[65] Named the Thermcial™ concept, it operates at 500°C below the Alcoa process and has simpler gas collection requirements. Proof of concept has been demonstrated and the company is seeking to move to a semi-works scale.

Carbothermal Reduction of Borate

A simplified block diagram of the carbothermal-based reduction pathway is shown in Figure 3.6.5.

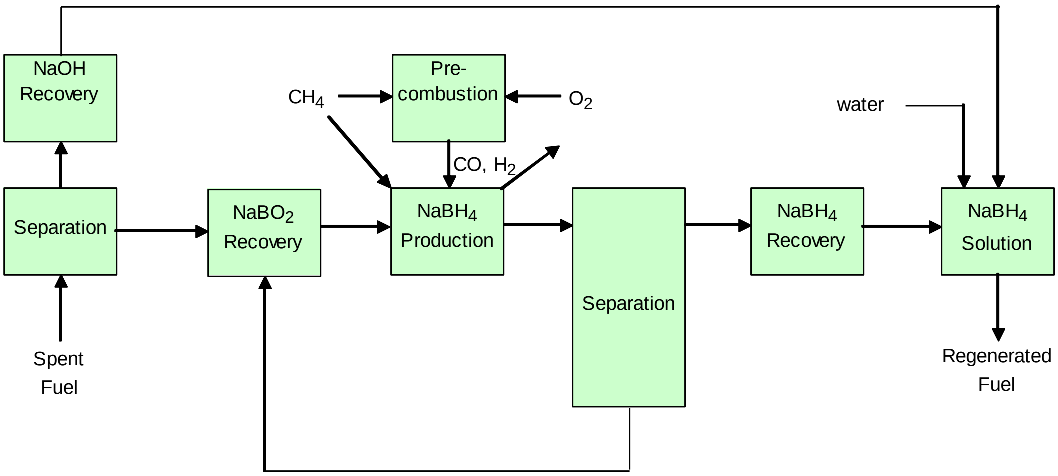


Figure 3.6.5. Carbothermal-based reduction pathway to $NaBH_4$

The borate feed preparation steps are similar to that described for the aluminum-based reduction process. Methane is converted to CO and H_2O in a partial combustion zone and produces a combustion flame that preheats the $NaBO_2$ and CH_4 feedstocks to high temperature. Additional CH_4 is added to produce H_2 and CO and maintain net reducing conditions. $NaBO_2$ and the effluent gases are then fed to the electric arc reactor to superheat the feed into the plasma state. Rapid quenching and separation of the borohydride containing product from the off gas are important to prevent the occurrence of secondary reactions. The hot gas exiting the reactor enters a cooling zone and the solids are removed. $NaBH_4$ product is recovered, purified and recombined with the NaOH removed from the spent solution to produce the target $NaBH_4$ fuel composition. Effective heat recovery during cooling is important for achieving high energy efficiency and low manufacturing costs.

The commercial viability of plasma arc technology is well established, and is used in a number of industrial applications including the manufacture of acetylene from natural gas, in metallurgical processing, and for waste treatment.[66,67] In acetylene operations, the thermal efficiency of the reactor is about 90% and about 50% of the electrical energy is used to supply the heat of reaction for the endothermic conversion process.[66] The largest installation is the 150 MW heater in the ISP acetylene plant located in Marl, Germany and has been in operation since 1940. INL's flame-plasma reactor concept to superimpose an electric arc onto a combustion flame and use the combustion products as the plasma gas has not been demonstrated in a large-scale manufacturing environment. Additional development will be required for use in industrial applications. However, INL also claimed to demonstrate $NaBH_4$ formation in other reactor configurations, including flame combustion and plasma-only operations.

Therefore, successful development of INL's flame-plasma concept is not requisite for commercialization of the carbothermal reduction pathway.

Energy efficiency for carbothermal reduction of borate was determined for a number of process configurations to preheat the feed to reaction temperatures, ranging from combustion flame-plasma arc hybrid options to a thermal plasma-only operation. All of these options can achieve higher efficiencies than the Al-based reduction pathway described above. The plasma-only option, which represents minimum gas flows, provided the highest efficiency of 50% on a primary energy basis when electricity is supplied by hydroelectric power. If electricity is based on the US 2015 electric grid, primary energy efficiency drops to 19%, similar to the Al-based reduction option. Again, these values are lower than the theoretical values due to the additional energy used for borate processing and $NaBH_4$ product separation steps.

Capital investment and manufacturing costs were estimated for the carbothermal reduction process. The reactor section is the largest component of capital costs, based on the ISP acetylene plant installation. For the arc discharge-only reactor configuration, regenerated $NaBH_4$ cost exiting the plant is estimated to be in the range of \$3.7–5.1/kg H_2, again depending on the cost of electricity. Total cost at the pump would be in the range of \$4.6-6.0/kg H_2, after accounting for terminal, transportation, and forecourt costs. Figure 3.6.6 provides a general breakdown of costs.

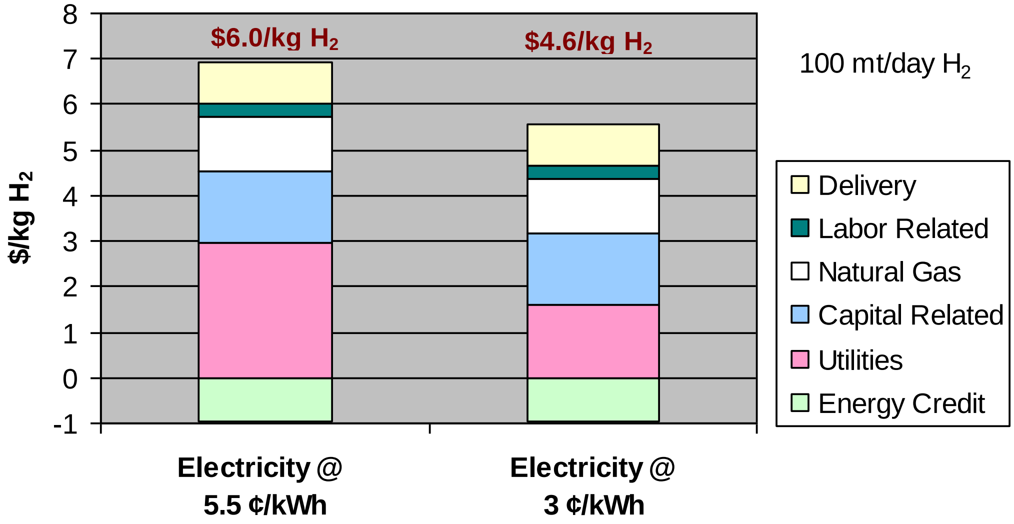


Figure 3.6.6. H_2 cost breakdown via carbothermal reduction of borate to $NaBH_4$

If the product offgas (1:1 H_2:CO) can be valued as synthesis gas and command a chemical feedstock value, the manufacturing costs can be reduced by \$1.3/kg H_2. Thus, the combination of favorable electricity pricing from hydroelectric power and credit for syngas production leads to a substantial improvement in delivered hydrogen costs. A cost sensitivity analysis for the carbothermal process to determine various parametric effects indicated that delivered hydrogen cost to be in the \$2-7/kg H_2 range. In fact, the cumulative effects of lower investment, higher borate conversion, and other favorable cost factors could allow the carbothermal reduction route to achieve the \$3/kg H_2 DOE cost target (Figure 3.6.7).

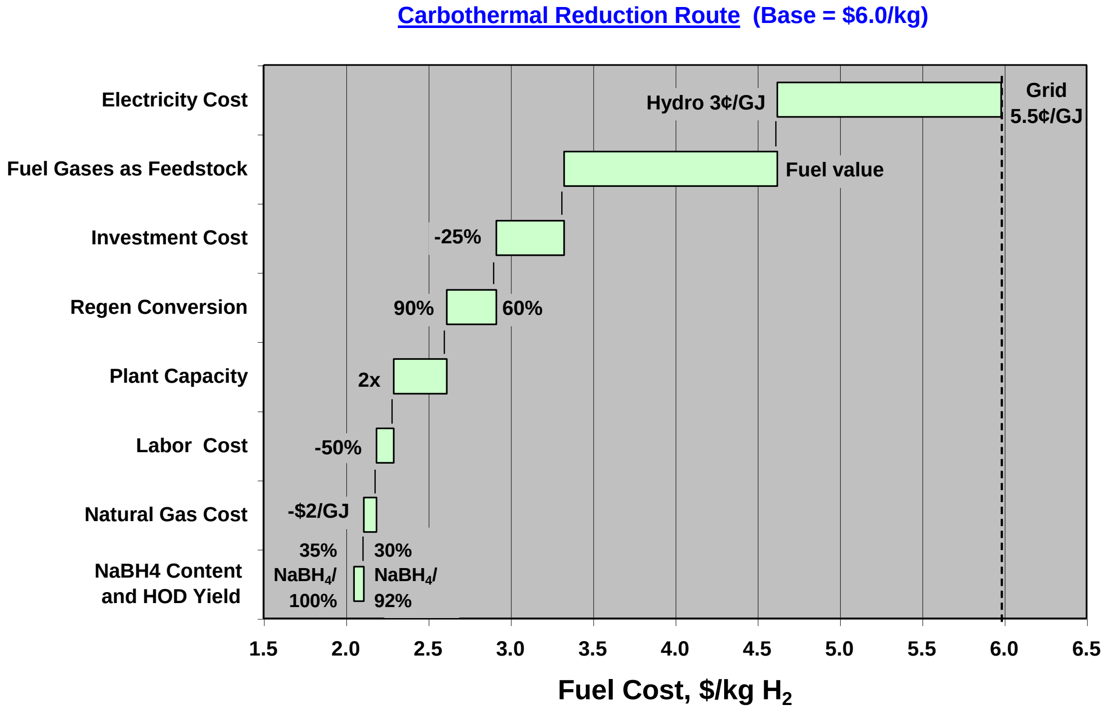


Figure 3.6.7. Sensitivity Analysis for Delivered Hydrogen Cost via Carbothermal $NaBH_4$ Production

Analysis

The metal reduction and carbothermal reduction routes represent potential pathways for significant improvements in energy efficiency and manufacturing costs over the current Schlesinger process to produce $NaBH_4$. Both processes enable facile regeneration of spent fuel after $NaBH_4$ hydrolysis to release H_2. However, additional improvements are needed to meet the DOE storage technical targets of <$3/kg H_2 fuel cost and >60% energy efficiency for regeneration, as shown in Table 2.2.

Despite good progress made toward achieving the fuel cost target, a DOE-commissioned independent review panel issued a No-Go decision for sodium borohydride for on-board hydrogen storage for vehicular application in November 2007.[36] Their decision was made principally due to difficulties achieving the hydrogen capacity performance targets because of solubility issues associated with the spent fuel, and in part because of the inability to meet the 60% efficiency target. However, the review panel recognized the importance of continuing efforts to develop low-cost $NaBH_4$ routes. $NaBH_4$ is a key starting material for production of ammonia borane and other borane- and boron-based H_2 storage systems still under consideration.[14] In fact, $NaBH_4$ is the dominant factor for ammonia borane system costs as described in Section 4.2.

Overall, significant advances have been made on the metal reduction pathway to define scalable options and determine process feasibility. Although the carbothermal borate reduction route can potentially achieve higher efficiencies and lower costs, more work will be needed to advance the concept, demonstrate the earlier claims for $NaBH_4$ production, and identify opportunities to reduce the performance gap. In all cases, a close coupling of engineering assessment, economic analysis, and innovative chemical and materials research is required to identify and develop the most feasible $NaBH_4$ pathway.

3.7 References

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4 Ammonia Borane Analysis

Ammonia borane (NH_3BH_3, AB) is widely regarded as one of the leading hydrogen carriers in fuel cell systems for automotive applications due to its high hydrogen density (19.6 wt%), favorable hydrogen release characteristics, and excellent thermal stability at ambient conditions.[1,2] The U.S Department of Energy (DOE) has established technical targets for on-board hydrogen storage systems including the storage system cost, fuel cost, and durability/operability.[3,4] Dow's contributions to the Chemical Hydrogen Storage Center of Excellence projects to address these targets for AB are described in this section.

4.1 AB Thermal Stability

4.1.1 Introduction

The thermal stability of ammonia borane is an important criterion for determining its feasibility for vehicular application. DOE targets for on-board hydrogen storage systems provide a requirement for operating temperatures in full-sun exposure as high as 60°C (50°C by 2010), and specify no allowable performance degradation to 40°C.[3] Studies were made in collaboration with Pacific Northwest National Laboratory (PNNL) to investigate the thermal stability of solid AB during storage at 40 to 60°C.[5,6] Although the optimum product form of ammonia borane has yet to be determined, an option under consideration is to use AB in granule form that would be contained on-board the vehicle in a storage tank and transported on demand to a heated reaction zone where it would decompose and release H_2 gas to the fuel cell. Of particular interest is to evaluate potential safety issues associated with the premature release of hydrogen gas within the storage tank when the fuel is stored on-board at relatively high temperatures (e.g., 50 to 60°C). Such conditions might be experienced when parking a vehicle in full-sun exposure in a desert climate.

Ammonia borane thermal decomposition occurs in steps. Prior calorimetric studies have shown that the first equivalent of H_2 gas is released exothermically ($\Delta H \sim -22$ kJ/mol) by AB thermolysis when heated to ≤125°C:

$$NH_3BH_3 \rightarrow NH_2BH_2 + H_2(g) \qquad (4.1\text{-}1)$$

with an onset temperature as low as 70°C depending on heating rate, and another 1.2 equivalents of H_2 being released between 125°C and 200°C.[7,8] Less information is available on H_2 release rates at below 70°C.

4.1.2 Experimental

Calorimeter measurements were made at Dow to support development of PNNL's computational models to estimate AB thermal stability and H_2 release kinetics under isothermal and adiabatic storage conditions as a function of storage time, temperature, and AB purity. The ARC® (Accelerated Rate Calorimeter) was used to determine the thermal characteristics of AB decomposition (Figure 4.1.1), and whether the exothermic 1st release step becomes self-sustaining under adiabatic storage conditions. AB samples were loaded into Hastelloy test cells rated to >10,000 psi gas pressure, with a total sealed vessel volume of ~11 mL. Reaction progress was monitored through thermocouples affixed to the cell surface and heater zones and a pressure transducer. Sample size was varied according to the test conditions and to safely maintain pressure within the system component specifications.

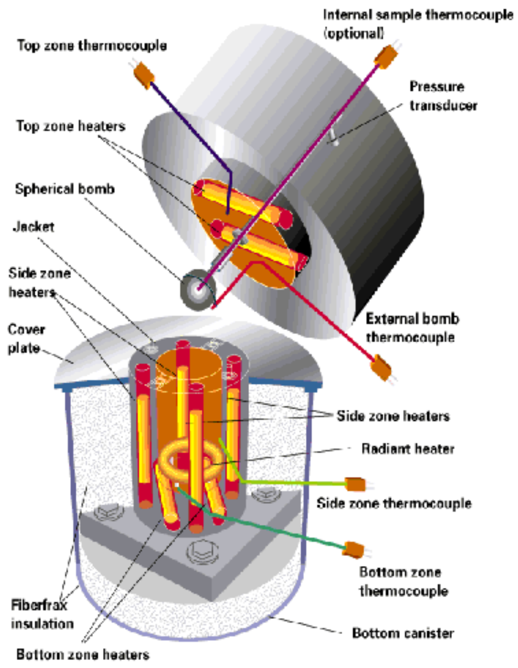


Figure 4.1.1.
Schematic of ARC®
from Arthur D. Little

Two testing modes were investigated: (i) In the heat-wait-search (HWS) mode, the temperature is increased in a step (e.g., by 5 or 10°C), followed by a defined hold period at the temperature to determine if the reaction self-heating rate exceeds a threshold criterion (e.g., 0.02 °C/min), and in cases where self-heating is detected, a search phase is completed until the threshold heating rate is no longer satisfied. The HWS process is continued step-wise to a predefined end point. (ii) The second method is a variation on the HWS mode in which the temperature is stepped relatively quickly up to a storage temperature of interest, say 60°C, and a long duration wait period is established to evaluate the potentially delayed self-propagating reaction. The extent of H_2 release from AB in the sealed ARC vessel is determined by pressure change.

4.1.3. Results and Conclusions

ARC testing was completed in the HWS mode to evaluate experimental factors such as temperature step size, sample source and size, and initial headspace gas composition. Results of a typical screening experiment for AB heated in 5°C increments are shown in Figure 4.1.2 below.

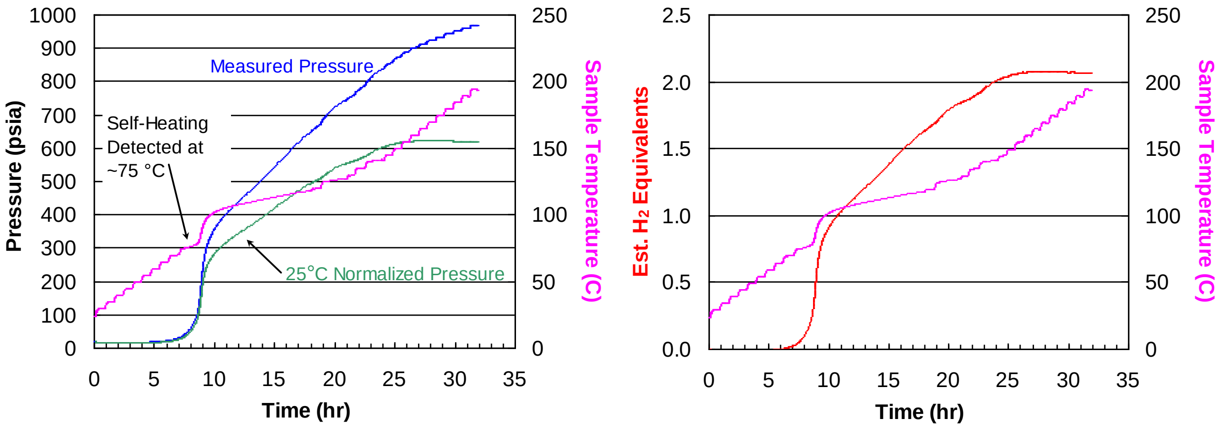


Figure 4.1.2. Typical ARC screening for ammonia borane

The results show appreciable self-heating starting at ~75°C associated with the release of the 1st H_2 equivalent and again at ~120°C associated with the release of the 2nd H_2. The two-step evolution of hydrogen gas is observed in the time varying cell pressure when corrected for cell temperature. The data are consistent with results reported for temperature-programmed thermolysis of AB.[8]

As shown in Figure 4.1.3, runs with different AB sample sources indicate an impact on self-heating, with onset temperature increasing to 90°C for samples of higher AB purity as confirmed by ^{11}B NMR analysis.

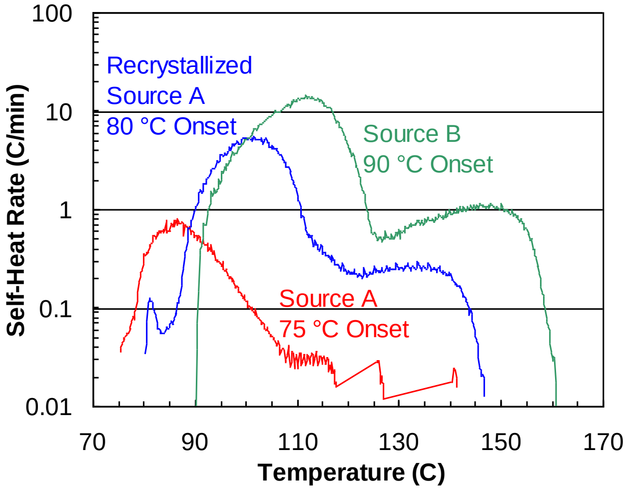


Figure 4.1.3. ARC runs for different sources of ammonia borane

The effect of air or nitrogen heating did not have a significant impact on stability.

In the longer duration thermal stability studies, storage temperature and AB purity are primary factors. A slow increase in pressure corresponding to 0.1 H_2 equivalents/day for the lowest purity AB samples is observed and reduces to <0.01 H_2 equivalents/day with increasing AB purity in 4-10-day adiabatic holds carried out at 60°C. However, there is no evidence for a runaway exothermic reaction taking place. Increased thermal stability is found at 50°C compared to 60°C tests, with decomposition dropping to 0.006 H_2 equivalents/day for the least stable AB sample. Purer AB samples would be expected to exhibit even greater stability.

These results were used by PNNL to develop kinetic models (modified Avrami form) describing AB thermal decomposition. Both initial calculations and experiments indicate that the stability of ammonia borane is a function of its purity and that it can remain stable for many days or longer in a high temperature environment. Heat management, including engineered controls such as auxiliary cooling, remains an option to minimize the inadvertent release of hydrogen in the storage tank.

4.2 Analysis of AB 1st Fill Processes

4.2.1. Introduction

DOE hydrogen storage system cost targets, which include the first charge of hydrogen fuel storage media, were initially established at \$4/kWhr net (\$133/kg H_2) for 2010 and \$2/kWhr net (\$67/kg H_2) in 2015.[3] Assuming 2 to 2.5 mol H_2 release per mol of ammonia borane, a \$10/kg price for the AB media alone would essentially exceed the 2015 system cost target. Although DOE's revised system cost targets are expected to be less stringent than the original cost targets established in 2005[4], low cost ammonia borane manufacturing routes will still be essential to supply the first charge (1st-fill) of AB and achieve the cost targets. Numerous advances in AB synthesis have been made in recent years to improve AB yields and purities.[9-13] This section summarizes Dow's studies to evaluate the manufacturing cost of leading 1st-fill AB production routes. Regeneration of spent fuel back to AB after hydrogen release would occur through a different chemical pathway and is described in Section 4.3.

4.2.2. Ammonia Borane Pathways

Ammonia borane can be conveniently produced through the metathesis reaction of sodium borohydride with an ammonium salt in an organic solvent:

$$xNaBH_4 + (NH_4)_xL \xrightarrow{\text{solvent}} xNH_3BH_3 + Na_xL + xH_2 \qquad (4.2\text{-}1)$$

Just 5 years ago, the leading route was based on $(NH_4)_2CO_3$, where isolated yields of 80% AB were obtained.[14] The new AB pathways all achieve >95% AB yields and purities in laboratory systems. Ramachandran and Gagare at Purdue reported higher yields using specific ammonium salt and solvent combinations.[9,10] Pacific Northwest National Laboratory (PNNL) demonstrated improved AB yields by reaction of $NaBH_4$ and NH_4Cl in ammonia/THF via the formation and decomposition of intermediate ammonium borohydride.[11,12] In addition, Shore at Ohio State described a pathway involving the base displacement of borane complexes with ammonia.[13] These are discussed in greater detail below.

4.2.3 Purdue AB Process

The Purdue group demonstrated successful AB formation from $NaBH_4$ and various ammonium salts (ammonium chloride, ammonium carbonate, ammonium fluoride, ammonium sulfate, ammonium nitrate, and ammonium formate) at moderate pressures and temperatures with moderate to high yields.[9,10] However, many of the reactions required long reaction times to achieve moderate to high yields, and would not be desirable for commercial production. Their published data indicate that the reaction of $NaBH_4$ with $(NH_4)_2SO_4$ in THF or NH_4HCO_2 in dioxane is optimal and generated 95% $NaBH_4$ yields in a 2 hr reaction time. Dow's analysis showed that the formate based scheme is more attractive and would require less energy, generate less byproduct waste, and have a lower overall manufacturing cost than the $(NH_4)_2SO_4$ based process.

A conceptual process of the Purdue AB route was developed and shown in Figure 4.2.1. Fresh $NaBH_4$ powder and NH_4HCO_2 powder are fed to an agitated reactor containing dioxane, where the metathesis reaction takes place to produce AB:

$$NaBH_4 + NH_4HCO_2 \rightarrow NH_3BH_3 + NaHCO_2 + H_2 \qquad (4.2\text{-}2)$$

The hydrogen byproduct is captured as waste heat and used to generate energy for downstream processing. The reactor effluent is fed to a separation unit to remove the unconverted reactants and the insoluble $NaHCO_2$ product. The byproducts formed are treated in a 2nd separation unit to recover and recycle NH_4HCO_2 back to the reactor. High purity $NaHCO_2$ is recovered as a solid and sold at market price. Some of the aqueous NH_4HCO_2 is not recoverable and is sent out of the facility for further waste processing. The AB product solution is fed to an evaporator to recover most of the dioxane. The remaining wet product is fed to a rotary dryer to recover the remaining solvent and to produce a dry ammonia borane product.

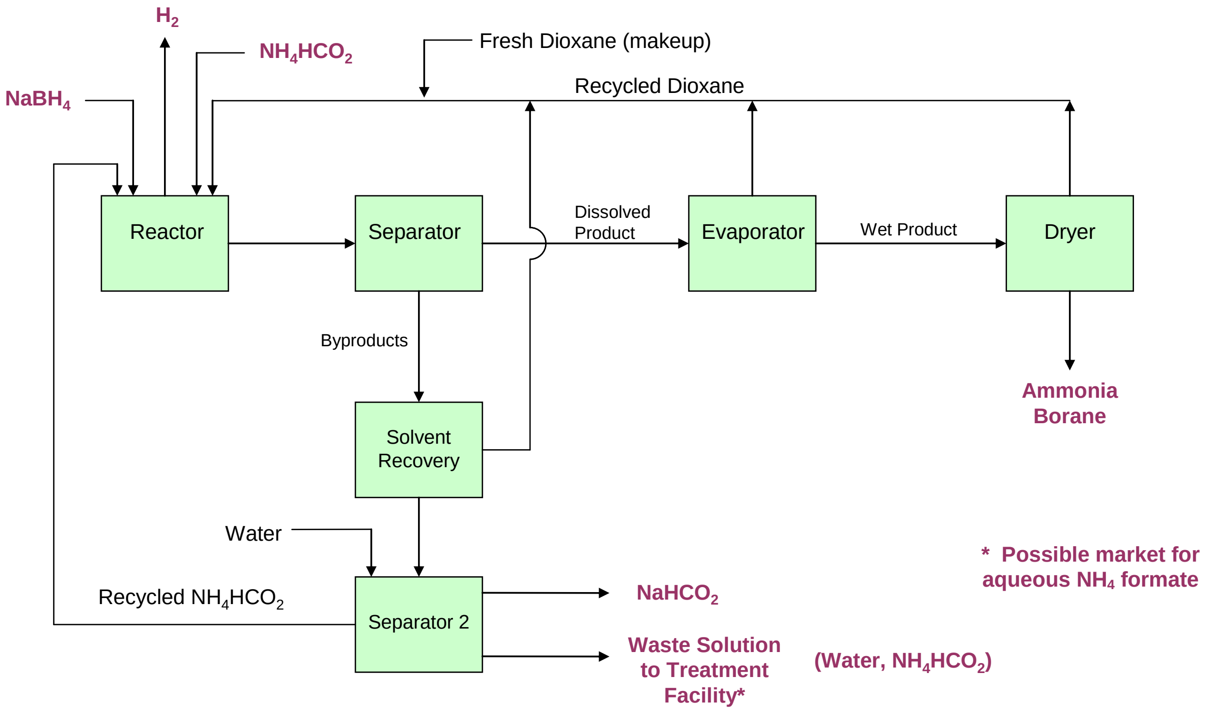


Figure 4.2.1. Simplified block diagram for Purdue ammonia borane process

The major differences between the sulfate and formate based pathways are solvent requirements and waste generation. Ramachandran and Gagare found that in order to obtain high yields and maintain a short reaction time, the $NaBH_4$ concentration in THF solvent should be kept below 0.165 M for the $(NH_4)_2SO_4$ system. In contrast, high yields and short reaction times were also obtained for the NH_4HCO_2 system with a 1 M NaBH4 in dioxane solution. For commercial application, the higher concentration NH_4HCO_2 route is preferred, since it would require less capital equipment and use less energy during solvent recovery. However, Shaw et al. reported that at >2M AB concentrations, AB decomposes in a few hours when held at 50˚C.[15] Therefore, a balance must be made between reactant concentration and process temperature to optimize operations. In the conceptual process developed by Dow, temperatures were kept below 40˚C to minimize AB decomposition.

Both pathways described by Ramachandran and Gagare use excess ammonium salt to drive the metathesis reaction. Recycle of the excess salt is necessary to minimize waste, and requires separation of the excess ammonium salt from the sodium salt byproduct. The solid NH_4HCO_2 and $NaHCO_2$ mixture can be separated using the solubility difference between NH_4HCO_2 and $NaHCO_2$ in water at different temperatures. This separation allows for approximately 75% of the excess NH_4HCO_2 to be recycled back to the reactor vessel, and generates a relatively pure solid $NaHCO_2$ stream which could be sold at market price. For the work described herein, the remaining aqueous stream of NH_4HCO_2 was assumed to be treated at an off-site wastewater treatment facility. However, a 50% aqueous ammonium formate solution is sold commercially, indicating the possibility of recovering and selling the remaining waste salt solution from the AB production process. Further investigation into the potential markets for this salt solution would be necessary to confirm this option. In contrast, $(NH_4)_2SO_4$ and Na_2SO_4 have similar solubilities in most solvents, making a simple solubility separation unlikely. Until further investigation into a $(NH_4)_2SO_4$

and Na_2SO_4 separation is completed, it is assumed that none of the excess $(NH_4)_2SO_4$ would be recovered or recycled, and all of the solid byproduct mixture generated in this method would be landfilled.

Cost estimates for AB production using Purdue's ammonium formate route for a 10,000 MT/yr plant are given in Table 4.2.1, based on cost assumptions detailed in Appendix 1. Raw material usage, particularly sodium borohydride, dominates the AB manufacturing cost. Assuming \$5/kg $NaBH_4$ is achieved through the successful development and implementation of a lower cost $NaBH_4$ technology, an AB manufacturing cost of approximately \$9/kg is obtained. Still, $NaBH_4$ would account for 75% of the AB cost. Based on current sodium borohydride costs of \$40-60/kg[18] ,the manufacturing cost of AB would be \$55-85/kg.

Figure 4.2.2 illustrates the capital cost breakdown at different solvent usage levels, expressed as product sodium borohydride concentration in the solvent. In all cases, the largest components to capital cost relate to equipment for solvent recovery, separation of insoluble byproducts, and utilities. Thus, changes in solution concentration would have a direct impact on capital costs related to solvent recovery and utilities, confirming that the lower $NaBH_4$ concentration for the $(NH_4)_2SO_4$ method would result in substantially higher capital requirements.

A cost sensitivity analysis is given in Figure 4.2.3, showing that changes in the cost of sodium borohydride would make the greatest impact on AB manufacturing cost, and that options for lowering the $NaBH_4$ cost need to be pursued. The analysis also indicates that the cost of NH_4HCO_2, selling price of $NaHCO_2$, and AB production rate have minor impacts on AB manufacturing cost.

Table 4.2.1. Manufacturing cost of AB via Purdue route ($NaBH_4$ + NH_4HCO_2/dioxane)

Volume:	10,000 MT AB per year
Capital Investment:	$47 million

Item	Unit Cost		Usage (per kg AB)		Cost ($ / kg AB)
Raw Materials					
Sodium Borohydride	$5.00	per kg	1.36	kg	$6.79
Ammonium Formate	$0.42	per kg	2.44	kg	$1.02
Dioxane	$3.31	per kg	0.005	kg	$0.02
Water	$0.00044	per kg	0.27	kg	$0.00
Sodium Formate Recovery	$(0.30)	per kg	2.41	kg	$(0.72)
Total Raw Material Cost					**$7.11**
Utilities					
Natural Gas	$6.00	per GJ	0.014	GJ	$0.09
Steam	$0.025	per kg	0.66	kg	$0.02
Electricity	$0.0555	per kWh	1.10	kWh	$0.06
Chilled Water	$0.0555	per kWh	2.19	kWh	$0.12
Waste Treatment	$0.50	per kg BOD	0.07	kg	$0.04
	$1.75	per kg NH3-N	0.08	kg	$0.14
Hydrogen Credit	$6.00	per GJ	0.007	GJ	$(0.04)
Total Utility Cost					**$0.41**
Labor					
Direct Labor	$40.50 per hour	24 operators			$0.20
Supplies	10% of direct labor cost				$0.02
QC	20% of direct labor cost				$0.04
Overhead	80% of labor cost				$0.25
Total Labor Cost					**$0.51**
Capital					
Capital Recovery	13.8% of project investment				$0.64
Maintenance	3% of project investment				$0.14
Property Overhead	2% of project investment				$0.09
Total Capital Cost					**$0.87**
Royalty Cost	$1,500,000 annually				**$0.15**
Total AB Manufacturing Cost					**$9.06**

Figure 4.2.2. Capital cost breakdown for Purdue AB production via metathesis of $NaBH_4$ with NH_4HCO_2 : Effect of sodium borohydride concentrations

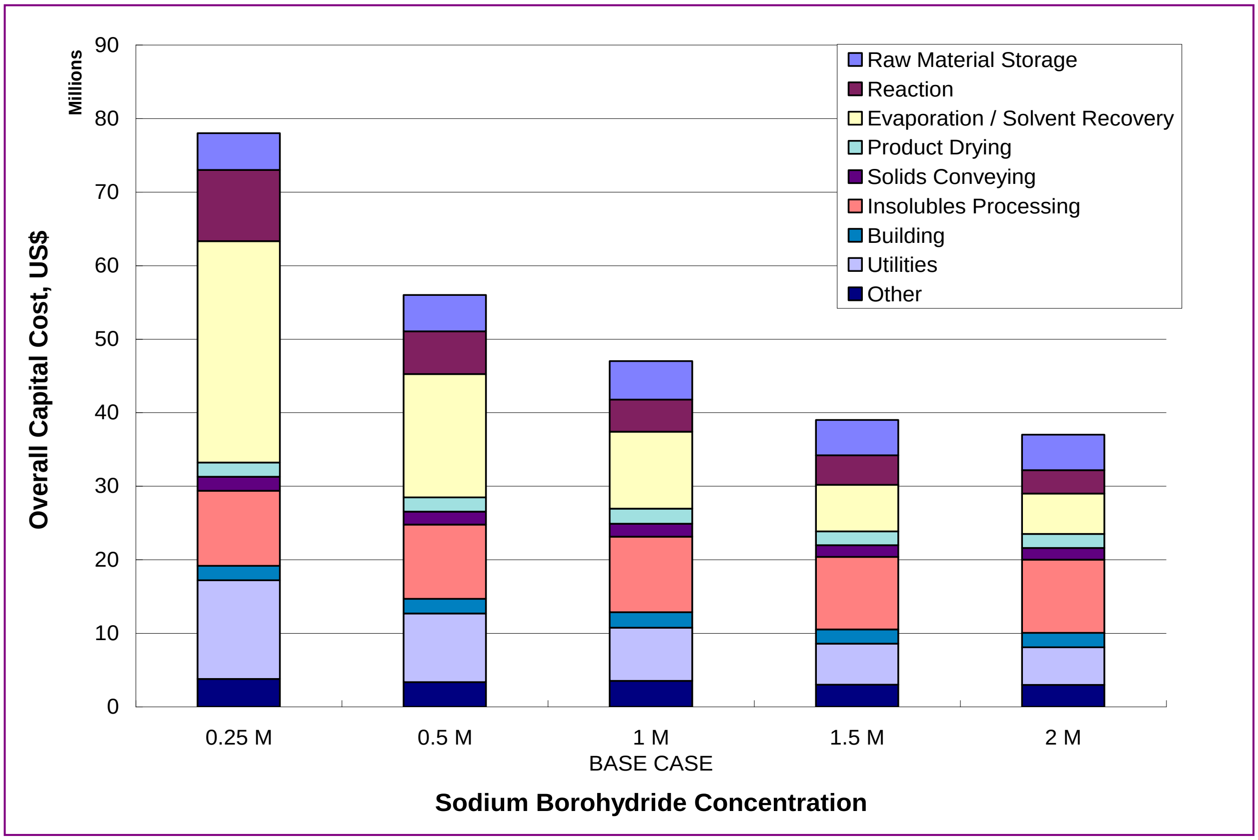
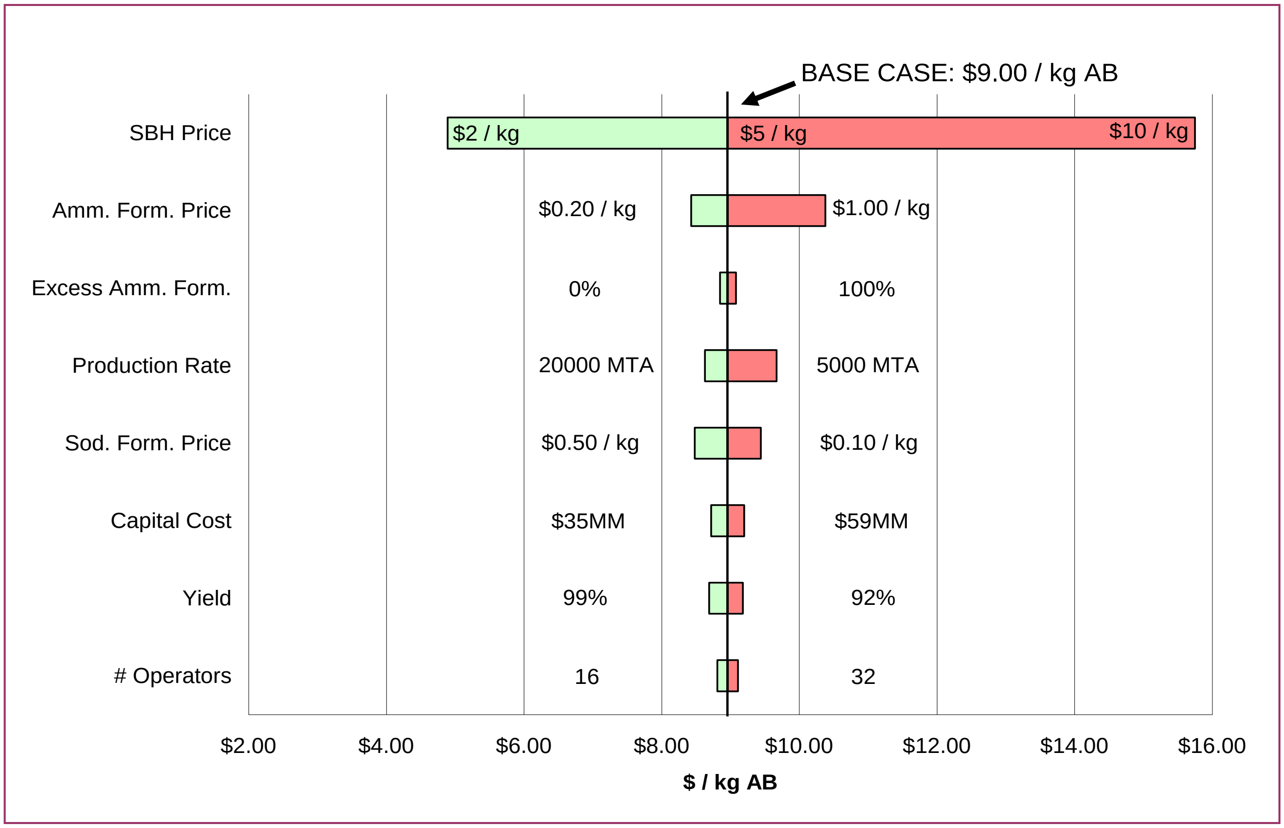


Figure 4.2.3. Cost sensitivity of Purdue AB manufacturing formate route



Note: The “Base Case” Criteria is:

- Sodium borohydride price of $5/kg
- Ammonium formate price of $0.42/kg
- 50 mol% excess ammonium formate
- 10000 MTA production rate
- Sodium formate selling price of $0.30/kg
- Capital cost of $47MM
- 95% yield
- 24 operators

4.2.4 *PNNL AB Process*

Laboratory studies performed by PNNL demonstrate near-quantitative AB production (>99% yield and 99% purity) from $NaBH_4$ and NH_4Cl in near-cryogenic conditions (-78˚C) with a NH_3-ether solvent.[11,12] In this reaction scheme, ammonium borohydride and byproduct sodium chloride are formed in a liquid mixture of NH_3 and THF. The presence of NH_3 provides stability to NH_4BH_4 and suppresses undesirable side reactions.

$$NaBH_4 + NH_4Cl \overset{NH_3/THF}{\longrightarrow} NH_4BH_4 + NaCl \tag{4.2-3}$$

The mixture is then warmed to room temperature, causing NH_3 to evaporate, and results in ammonium borohydride decomposition to form AB and H_2.

$$NH_4BH_4 \overset{THF}{\longrightarrow} NH_3BH_3 + H_2 \tag{4.2-4}$$

The AB produced is soluble in THF, whereas the byproduct NaCl is essentially insoluble[14], therefore, the NaCl can be readily separated from the AB-THF solution. The THF solvent is subsequently evaporated from the remaining solution, resulting in a high purity AB solid product.

The high yield and purity of AB produced by the PNNL scheme make this pathway very attractive for commercial AB production. However, the near-cryogenic conditions may place a high energy demand on refrigeration and impact the cost and viability of large-scale AB production. PNNL has also investigated a moderate pressure (200-300 psia), ambient temperature variation of the process that maintains the NH_3 in liquid phase prior to NH_3 release.[12] Preliminary lab results also indicate AB purity of 99% and yields as high as 98%, which make the moderate pressure route a viable option to AB production on a commercial scale.

Analysis of both these PNNL alternatives was conducted to better understand the relative cost impacts of operating at near-cryogenic (or 'cryogenic') conditions versus moderate pressure (or 'pressure') operations. A conceptual process of the PNNL AB route was developed and is shown in Figure 4.2.4.

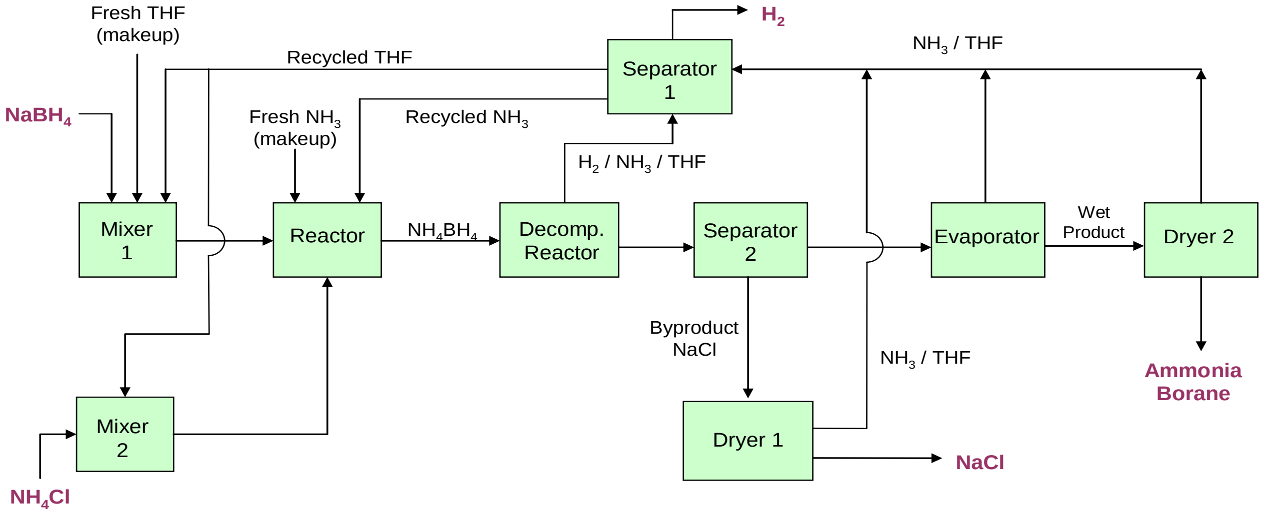


Figure 4.2.4. Simplified block diagram for PNNL ammonia borane process

Fresh $NaBH_4$ powder and NH_4Cl powder are fed to separate mixing vessels to form slurries with THF solvent. These slurries are then metered continuously to a first reactor, along with liquid NH_3, to produce ammonium borohydride. In the pressure route, the reactor conditions are 25˚C and 20 atm. In the cryogenic route, the reactor conditions are -70˚C and 1 atm. The product solution is then fed to a second reactor that brings the solution to 25˚C and 1 atm pressure. As the solution returns to ambient conditions, NH_3 evaporates, resulting in the decomposition of ammonium borohydride to produce AB and the release of hydrogen gas.

The remaining solution is fed to a solid/liquid separation unit to remove unconverted ammonium chloride and the insoluble NaCl product. The solvent in this byproduct stream is recovered for subsequent reactions, and the recovered NaCl byproduct is sold at 50% of market price. Next, the AB product solution is transferred to an evaporator to recover the NH_3 and THF solvent. The resulting wet product is fed to a dryer to recover any remaining solvent and to produce a solid ammonia borane powder. All processing steps containing AB in solution are limited to a maximum of 40°C to minimize AB decomposition.[15] The recovered solvents are fed to a distillation unit to separate the H_2, NH_3, and THF. The hydrogen generated is captured as waste heat and used to produce steam for downstream processing. The THF and NH_3 streams are recycled back to the mixers and to the reactor, respectively.

Cost estimates for AB production using the PNNL cryogenic and pressure routes for a 10,000 MT/yr plant are given in Table 4.2.2 and 4.2.3, respectively, based on cost assumptions detailed in Appendix 1. As in the analysis of Purdue's reaction pathway, sodium borohydride remains the principal component of raw materials and overall manufacturing cost for both of the PNNL schemes. The analysis assumes a base sodium borohydride cost of $5/kg to be consistent with the Purdue study, and results in a manufacturing cost of approximately $9/kg AB for the pressure route and $9.5/kg AB for the cryogenic route. About $0.40/kg AB of the cost difference comes from an increase in coolant usage ($0.30/kg) and capital cost ($0.10/kg) for the cryogenic scheme as compared to the pressure scheme. Accordingly, the capital cost of the cryogenic scheme ($51 MM) is greater than that of the pressure route ($46 MM). Thus, the pressure option would appear to be the leading route, although arguably the difference in cost between the 2 process options is within the accuracy of the analysis.

Figure 4.2.5 provides a capital cost breakdown for the PNNL pressure and cryogenic process routes at 10,000 MTA AB production. In both cases, the largest components to capital are the equipment for solvent recovery and utilities, accounting for up to 60% of the total cost. The refrigeration requirements of the cryogenic scheme result in a relatively costly coolant system.

Figure 4.2.6 shows a sensitivity analysis on the pressure scheme and confirms that a change in the cost of sodium borohydride has the greatest impact on AB manufacturing cost, and that a lower-cost $NaBH_4$ process would be desired to decrease this cost. The analysis also indicates that production rate has minor impacts on AB manufacturing cost, but other factors such as cost of ammonium chloride, capital cost, yield, and labor have lesser effects on AB manufacturing cost.

Table 4.2.2. Manufacturing cost of AB via PNNL cryogenic route

Volume:	10,000 MT AB per year
Capital Investment:	$51 million

Item	Unit Cost		Usage (per kg AB)		Cost ($ / kg AB)
Raw Materials					
Sodium Borohydride	$5.00	per kg	1.30	kg	$6.52
Ammonium Chloride	$0.15	per kg	1.93	kg	$0.29
THF	$2.36	per kg	0.02	kg	$0.04
NH_3	$0.32	per kg	0.002	kg	$0.00
Sodium Chloride Recovery	$(0.02)	per kg	2.11	kg	$(0.04)
Total Raw Material Cost					**$6.81**
Utilities					
Natural Gas	$6.00	per GJ	0.012	GJ	$0.07
Steam	$0.025	per kg	4.61	kg	$0.11
Electricity	$0.0555	per kWh	2.72	kWh	$0.15
Coolant	$0.0555	per kWh	11.76		$0.65
Chilled Water	$0.0555	per kWh	1.77	kWh	$0.10
Waste Treatment	$0.50	per kg BOD	0.04	kg	$0.02
	$1.75	per kg NH3-N	0.001	kg	$0.00
Hydrogen Credit	$(6.00)	per GJ	0.008	GJ	$(0.05)
Total Utility Cost					**$1.06**
Labor					
Direct Labor	$40.50 per hour	24 operators			$0.20
Supplies	10% of direct labor cost				$0.02
QC	20% of direct labor cost				$0.04
Overhead	80% of labor cost				$0.26
Total Labor Cost					**$0.52**
Capital					
Capital Recovery	13.8% of project investment				$0.69
Maintenance	3% of project investment				$0.15
Property Overhead	2% of project investment				$0.10
Total Capital Cost					**$0.95**
Royalty Cost	$1,500,000 annually				**$0.15**
Total AB Manufacturing Cost					**$9.48**

Table 4.2.3. Manufacturing cost of AB via PNNL pressure route

Volume:	10,000 MT AB per year
Capital Investment:	$46 million

Item	Unit Cost		Usage (per kg AB)		Cost ($ / kg AB)
Raw Materials					
Sodium Borohydride	$5.00	per kg	1.30	kg	$6.52
Ammonium Chloride	$0.15	per kg	1.93	kg	$0.29
THF	$2.36	per kg	0.02	kg	$0.04
NH_3	$0.32	per kg	0.002	kg	$0.00
Sodium Chloride Recovery	$(0.02)	per kg	2.11	kg	$(0.04)
Total Raw Material Cost					**$6.81**
Utilities					
Natural Gas	$6.00	per GJ	0.010	GJ	$0.06
Steam	$0.025	per kg	4.62	kg	$0.11
Electricity	$0.0555	per kWh	2.72	kWh	$0.15
Coolant	$0.0555	per kWh	6.53		$0.36
Chilled Water	$0.0555	per kWh	2.15	kWh	$0.12
Waste Treatment	$0.50	per kg BOD	0.04	kg	$0.02
	$1.75	per kg NH3-N	0.001	kg	$0.00
Hydrogen Credit	$(6.00)	per GJ	0.008	GJ	$(0.05)
Total Utility Cost					**$0.77**
Labor					
Direct Labor	$40.50 per hour	24 operators			$0.20
Supplies	10% of direct labor cost				$0.02
QC	20% of direct labor cost				$0.04
Overhead	80% of labor cost				$0.25
Total Labor Cost					**$0.51**
Capital					
Capital Recovery	13.8% of project investment				$0.63
Maintenance	3% of project investment				$0.14
Property Overhead	2% of project investment				$0.09
Total Capital Cost					**$0.86**
Royalty Cost	$1,500,000 annually				**$0.15**
Total AB Manufacturing Cost					**$9.10**

Figure 4.2.5. Capital cost breakdown for AB production via PNNL process (10,000 MTA production rate)

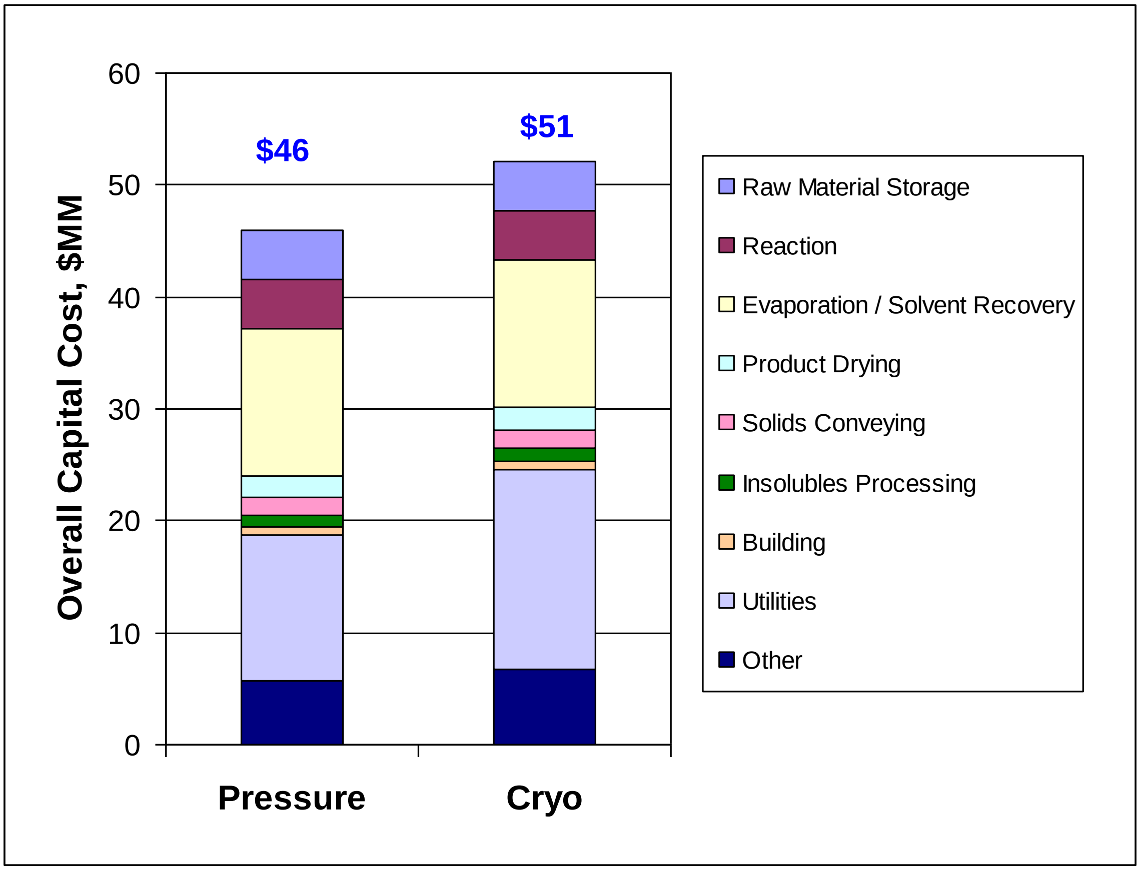
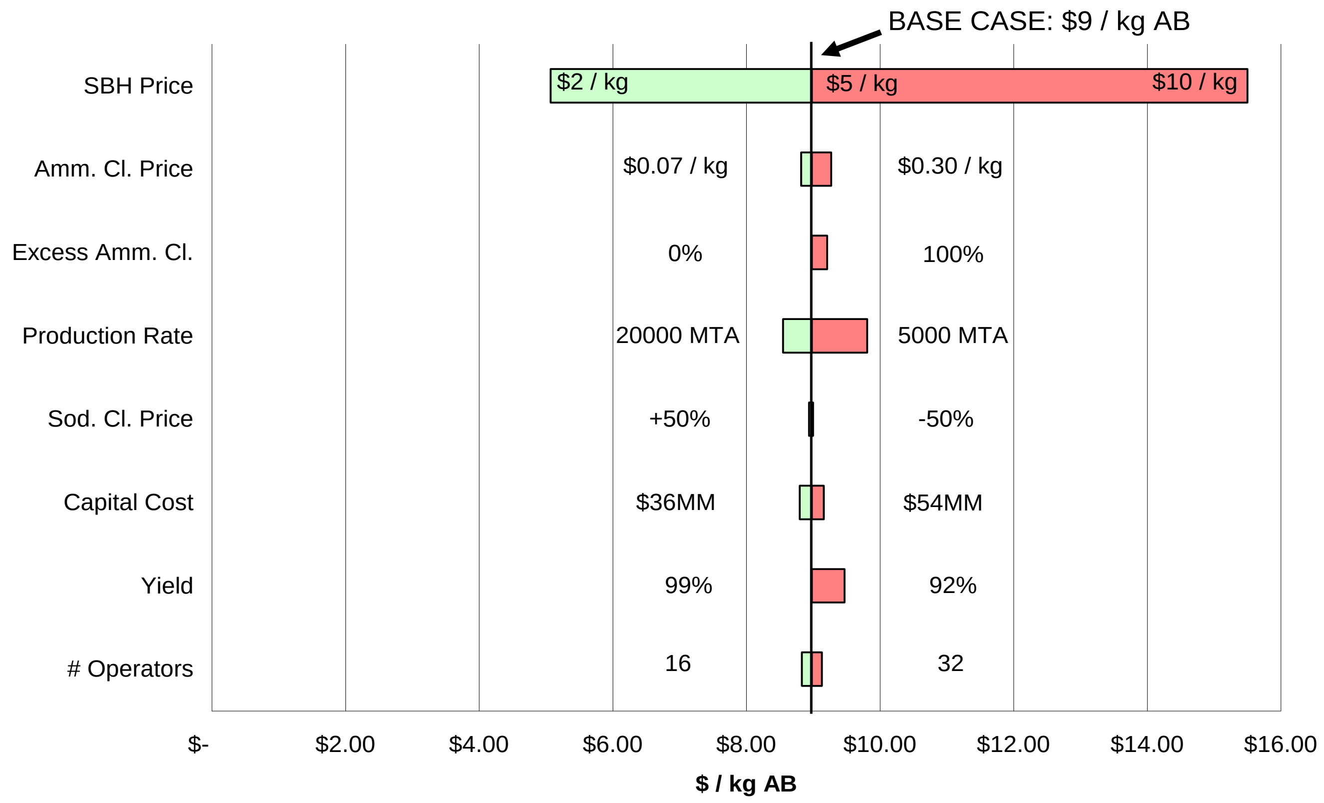


Figure 4.2.6. Sensitivity of AB manufacturing cost (PNNL pressure route)



Note: The “Base Case” Conditions are:

- Sodium borohydride price of $5/kg
- Ammonium chloride price of $0.15/kg
- 5 mol% excess ammonium chloride
- 10000 MTA production rate
- Sodium chloride selling price of $0.02/kg
- Capital cost of $45MM
- 99% yield
- 24 operators

4.2.5 Comparison of AB Manufacturing Schemes

Purdue's AB synthesis route by the reaction of sodium borohydride and ammonium formate in dioxane showed a manufacturing cost of \$9/kg, which is equivalent to the cost obtained for the PNNL pressure route.

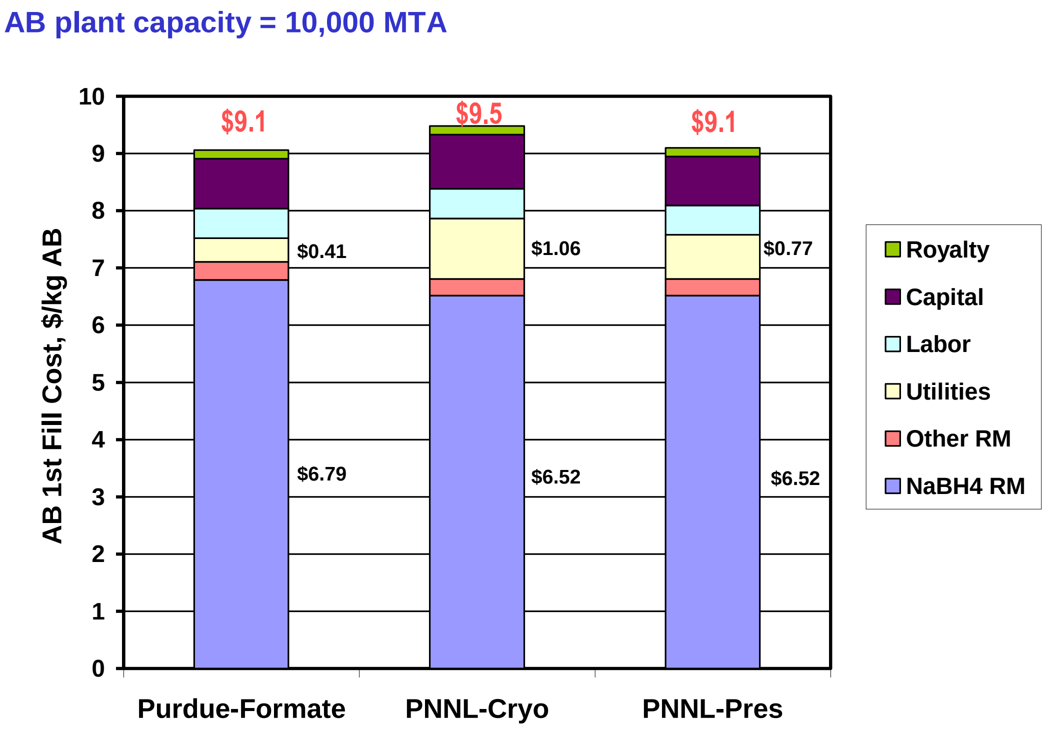


Figure 4.2.7. Comparison of AB manufacturing costs (10,000 MTA production rate)

While cost is an important driver for selection of an optimal chemical pathway for implementation, other factors may also have key role in the determination including process operability and robustness, technical risk, environmental, health, and safety impacts, product quality, and raw material availability and logistics. Therefore, it was desirable to compare these two pathways on these criteria. A comparison of the PNNL and Purdue pathways is summarized in Table 4.2.4.

On this basis, the PNNL pathway is better defined, provides a higher purity product required for hydrogen storage, and is overall a more robust technology than the Purdue route.

Figure 4.2.8 illustrates the relationship between AB manufacturing cost and on-board hydrogen storage system cost. At a sodium borohydride cost of \$5/kg, the AB media cost contributes less than 50% of the DOE 2010 hydrogen storage system cost target of \$133/kg H_2.[3] However, AB manufacturing cost becomes a significant component to the DOE target system cost of \$67/kg H_2 in 2015.[3] Based on this analysis, it is clear that sodium borohydride cost would need to be less than \$5/kg in order to achieve the DOE 2015 hydrogen storage system cost target. Therefore, investigations into reducing sodium borohydride cost are critical to meeting the future DOE goals for hydrogen storage system cost.

Other methods of ammonia borane production such as the base displacement of borane complexes with ammonia have also been reported:

$$L\text{-}BH_3 + NH_3 \rightarrow NH_3BH_3 + L \qquad (4.2\text{-}5)$$

	PNNL	Purdue
Chemistry	NH_4BH_4 decomposition	Metathesis
Boron source	Sodium Borohydride	
Nitrogen source	Ammonium Chloride	Ammonium Formate / Sulfate
Solvent	THF and NH_3	Dioxane or THF
AB yield	99%	95%
AB purity	99%	98%
Reactor conditions	-70˚C /1 atm or 25˚C /20 atm.	40˚C /1 atm
Feed stoichiometry	Near-stoichiometric	50% excess NH_4 formate
Raw material costs	$NaBH_4$ principal component of costs	
	NH_4Cl pricing well defined.	Low NH_4HCO_2 pricing requires high volume
Solvent requirements	>2M $NaBH_4$ in solvent	1M $NaBH_4$ in solvent
Solvent separation	Distillation column required to separate THF and NH_3 solvents	Single solvent – no solvent separation required.
Na byproduct recovery	Relatively easy separations via solubility differences.	Separation of Na and NH_4 salts requires more complex processing
Waste generation	Minimal waste – only losses are small solvent losses.	Moderate liquid waste generated from insolubles processing step.

Table 4.2.4. Comparison of PNNL and Purdue AB synthesis routes

Shore describes achieving high AB yields and purities though the formation of an amine borane intermediate such as dimethylaniline borane.[13] However, the production of the borane requires additional reaction steps such as the conversion of $NaBH_4$ to produce diborane and its condensation in dimethylaniline to form the borane complex. The multi-step synthesis coupled with the safety systems needed for the handling of diborane will almost certainly lead to a higher cost to produce AB.

Alternative synthesis routes to produce borane adducts (L-BH_3) without the direct conversion to diborane such as reaction of an amine hydrochloride with $NaBH_4$ are possible but would still require multiple reactions and process steps.

$$\text{L} + \text{HCl} \rightarrow \text{L-HCl} \qquad (4.2\text{-}6)$$

$$\text{L-HCl} + \text{NaBH}_4 \rightarrow \text{L-BH}_3 + \text{NaCl} + \text{H}_2 \qquad (4.2\text{-}7)$$

4.2.6 Conclusions

Dow's results indicate that the ammonium formate scheme developed by Purdue as well as the moderate pressure scheme developed by PNNL can be used to produce AB on a commercial scale at a cost of about $9/kg AB, depending on the cost of $NaBH_4$. At this cost, both pathways have the potential to meet the DOE hydrogen storage system cost targets for 2010. The PNNL route holds additional advantages of achieving higher AB purity, utilizes more abundant raw materials (with well-defined costs) and generates less waste. Decreases in sodium borohydride cost and further investigation into process technology could result in a lower AB manufacturing cost. It is important to recognize that the manufacturing cost analysis discussed in this report provides a baseline cost, and should be updated as additional information becomes available to better define equipment and operating requirements.

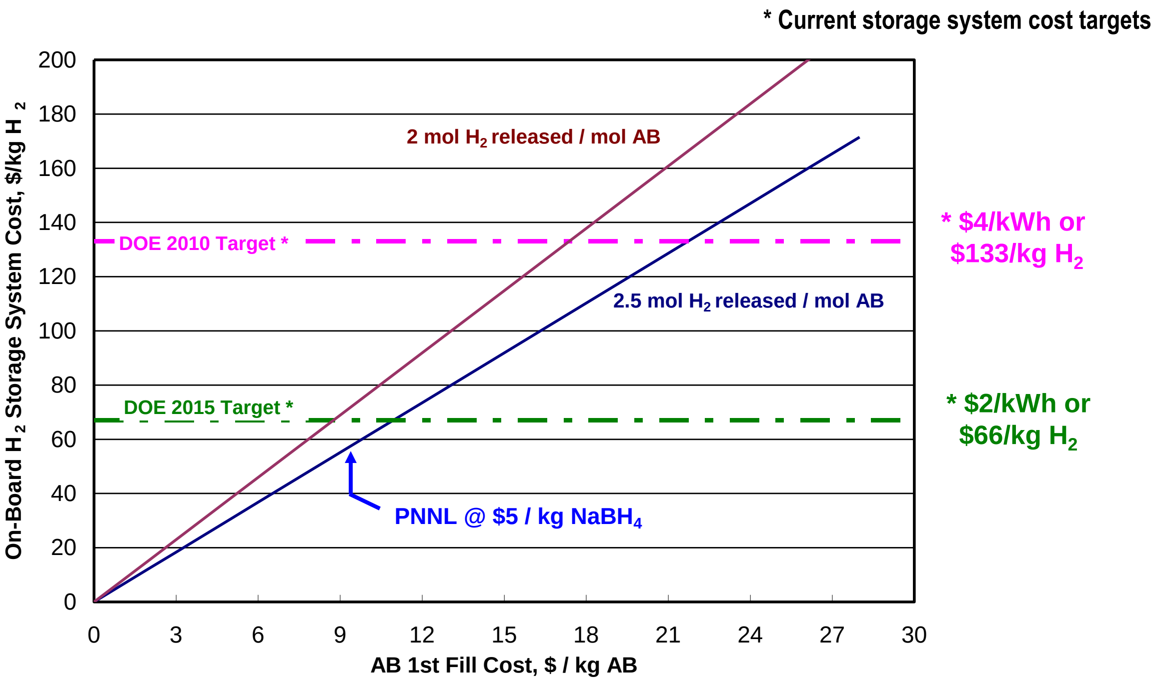


Figure 4.2.8. Relationship between AB manufacturing cost and on-board hydrogen storage system cost

Note: This analysis only includes AB manufacturing cost. Additional on-board system costs and logistics costs (distribution and forecourt costs) should be added to the AB manufacturing cost to determine the overall effect of AB cost on total system cost.

Appendix 1. Ammonia Borane 1st Fill Cost Estimate Assumptions

Process

Purdue

1. Reaction occurs at 40˚C, 95% $NaBH_4$ conversion to AB. NH_4HCO_2 usage is stoichiometric based on $NaBH_4$ reacted.

2. 50% excess NH_4HCO_2 is used in the process; the reactor contents are 1 M in $NaBH_4$.[9]

3. Solid AB product is produced. Purity of the AB product is 98%; the 2% impurity is assumed to be unreacted $NaBH_4$ or other soluble byproduct, and would correspond to a calculated solubility of $NaBH_4$ in dioxane of 0.06 g/100 g solvent.

4. The solubility of AB in dioxane is assumed to be equal to the solubility of AB in THF (25 g/100 g). NH_4HCO_2 and $NaHCO_2$ are assumed to be insoluble in dioxane, based on the solubilities of the salts in THF.

5. Dioxane losses in the process were assumed to be a value equal to 0.5 wt% of the final AB product.

6. After separation, the byproduct stream containing unreacted NH_4HCO_2 and $NaHCO_2$ also contains 20% dioxane that requires recovery.

PNNL

1. The Parallel Reaction Sequence as described by PNNL is used where NH_4BH_4 is produced in the presence of NH_3 and THF.[11]

2. For the cryogenic scheme, the reaction occurs at -70˚C and 1 atm. For the pressure scheme, the reaction occurs at 25˚C and 20 atm. $NaBH_4$ conversion to AB is 99%[12] ; NH_4Cl usage is stoichiometric based on $NaBH_4$ usage. A 4 hr residence time is used to provide continuous operations.

3. 5 mol% excess NH_4Cl is used in the process. Feed ratios: 4.9M $NaBH_4$ in THF; 3.9M NH_4BH_4 in NH_3; 2.2M $NaBH_4$ in overall THF-NH_3 feed used for both pressure and cryogenic schemes. Although these concentrations are higher than the 2.6M $NaBH_4$ in THF and 3.1M NH_4BH_4 in NH_3, provided in PNNL's recent patent application,[12] Dow's previous study indicates that the capital and operating cost sensitivity to concentration effects starts to plateau at above 2M concentrations. The level of THF used in this study is also above the AB solubility requirements for effective separations.

4. Solid AB product is produced. Purity of the AB product is 99%[11] ; the 1% impurity is assumed to be unreacted $NaBH_4$ or other soluble byproduct, and would correspond to a calculated solubility of $NaBH_4$ in THF of 0.22 g/100 g solvent (solubility of 0.1 in literature). .

5. The solubility of AB in THF is 25 g/100 g. NH_4Cl and NaCl are assumed to be insoluble in THF.

6. The separation of NH_3 and THF results in a THF recycle stream of ~100 wt% THF and a NH_3-rich recycle stream comprising 99 wt% NH_3, 1 wt% THF.

7. Solvent losses in the process were assumed to be equal to 0.5 wt% of the final AB product.

8. After separation, the byproduct stream containing unreacted NH_4Cl and NaCl also contains 20 wt% solvent that requires recovery.

Capital Costs

1. The plant is sized to produce 10,000 metric tons annually (MTA) AB. The rate is based on the DOE's projected demand for FCVs by the year 2025, assuming the lowest projection of FCV deployment in the 2018-2023 period[16] (deployment of 50,000 new hydrogen fuel cell vehicles per year). If this rate of market penetration is achieved, a new 10,000 MTA 1st-fill AB plant would be required every two years to meet demand. A larger plant capacity, corresponding to a more rapid market growth, is considered as a sensitivity case.

2. All capital, raw material, utility and labor costs are on a 2005 basis.[3]

3. Plant capital investment includes all process equipment, process building, utilities, and storage tanks for a one month inventory of raw materials and product. Investment includes a 25% contingency factor.

4. Capital cost is estimated for the nth plant. Therefore engineering costs have been estimated at 10% of the total direct cost and startup costs are assumed to be minimal. Land cost is minimal compared with total capital investment.

5. Annual capital recovery cost is 13.8% of the total capital investment based on a 20 year analysis, 20 year plant life, 10% rate of return, 38.9% total tax rate and a 10 year MACRS depreciation schedule. These costs are the same as for the DOE H2A Model.[17]

Raw Material Cost

1. Cost of ammonium formate is assumed to be \$0.42/kg or 4x the price of ammonium sulfate as obtained from the SRI.[18] Market selling price of sodium formate is assumed to be \$0.30/kg.[18]

2. Cost of water is assumed to be \$0.00044/L. This is consistent with the DOE H2A model.[17]

3. Costs of THF, NH_3, and ammonium chloride were obtained from the SRI Consulting PEP 2006 Yearbook.[18]

4. Cost of sodium borohydride is assumed to be \$5/kg (note: the current cost of sodium borohydride is \$40-60/kg [18]).

5. Market selling price of the NaCl byproduct is assumed to be 50% of the cost of NaCl obtained from the SRI Consulting PEP 2006 Yearbook,[18] due to the excess ammonium chloride impurity.

Utility Cost

1. Natural gas cost is \$6/GJ.[17]

2. Fully allocated steam cost is \$0.025/kg. This cost is based on a fuel cost of \$6/GJ and assumes a 75% efficiency factor for the boiler and that fuel costs are approximately 75% of the fully allocated steam cost.

3. Cost for industrial electricity is \$0.0555/kWh.[17]

4. Coolant electricity requirement is based on the estimated coolant system motor power requirements operating continuously. Electricity requirement is based on the estimated total motor power requirements (minus the coolant motor power requirements) operating continuously.

5. Waste treatment costs are $0.50 per kg of BOD waste and $1.75 per kg Nitrogen waste, based on typical publicly owned treatment works (POTW) costs.[19]

6. 80% of the hydrogen generated is captured and used to supply process heating requirements.

Other Costs

1. Total operating labor requirement is 24 operators. Operating labor wage rate is $40.50/hr.[18] Operating supplies are 10% of operating labor; quality control is 20% of operating labor. Plant overhead is estimated at 80% of total labor requirement.

2. A charge of $0.15/kg AB (or $1.5 million annually) was added to the manufacturing cost to account for licensing and royalty fees. This charge is within the typical royalty fee of 1-2% of the selling price of a commodity material.[18]

4.3 Analysis of AB Regeneration Processes

4.3.1. Introduction

Energy and cost efficient regeneration of spent fuel resulting from the dehydrogenation of AB need to be defined for the storage system to be viable and meet DOE's fuel cost target of \$2-3/gal gge at the pump (\$2-3/kg H_2) for on-board hydrogen storage systems.[3,4] Indeed, regeneration of ammonia borane is one of the focus activities of the DOE Chemical Hydrogen Storage Center of Excellence. A variety of approaches have been investigated including the use of superacids, thiols, alcohols, and combinations of these systems to digest spent fuel to chemical intermediates that can be more readily processed and converted back to AB.[20]

Dow supported the Center efforts by preparing baseline cost evaluations for two AB regeneration pathways developed at Los Alamos National Laboratory (LANL).[20-21] The first involves digestion of the polyborazylene spent fuel by thiacatechol followed by reduction to AB using tin hydride compounds. The second route uses hydrazine to digest and reduce borazylene directly to AB. In addition, preliminary examinations of PNNL's alcohol-based and UPenn's halo-superacid-based AB regeneration pathways were made. Appropriate assumptions were made to create a conceptual process, establishing the necessary material and energy balances, and scale up to a commercial plant producing AB at a rate equivalent to 100 metric ton per day of delivered H_2.

4.3.2. LANL Thiacatechol-Based Process

LANL's work in spent fuel regeneration has identified thiacatechol (benzenedithiol or BDT) as an effective digestion agent that quantitatively reacts with the polyborazylene spent fuel (BNH_x with x=1 corresponding to 2.5 mol H_2 release per mol AB) to generate products that can undergo further chemical transformations to produce ammonia borane. Tin hydride compounds can reduce this thiacatechol-digested material to form B-H bonds, and under appropriate conditions, ammonia can be re-added to this mixture to generate ammonia borane.[22] Recycling of the tin reagents back to tin hydride is proposed via the direct catalytic hydrogenation of the tin thiacatecholates with hydrogen. Argonne engineering studies have shown that the alternative reaction of tin thiol byproducts with formic acid to generate tin formate, and its subsequent recycle to tin hydride and formic acid, is very energy intensive due to gas compression and distillation steps necessary in formic acid production.[23]

A simplified process flowsheet is provided in Figure 4.3.1 based on the underlying reactions and information supplied by LANL.[21,22,24] In the digestion step, solid spent AB and BDT react to form two digestion products. The reactor is run under BDT-limiting conditions to minimize its reaction with $HSnBu_3$ in the subsequent reactor. Excess spent fuel is filtered and returned to the reactor. THF is added as a carrying agent for the products. LANL has demonstrated 90%+ yields for this reaction step using borazine feed. In the 2nd reactor, the metal reduction reactions of the digested products and amine exchange with Et_2NH (DEA) are combined to produce Et_2NHBH_3 (DEAB). This step has also been demonstrated by LANL to give 70% yield in a one-pot synthesis. Ammoniation of DEAB occurs in the 3rd reactor; this step has been demonstrated at 80% AB yield in studies at LANL for NH_3 exchange of TEAB. In the schematic shown in Figure 4.3.1, toluene or some other light hydrocarbon is added to assist precipitation of ammonia borane, which is subsequently fed to a rotary dryer to produce a pure dry AB powder. In the final step, the tin thiacatecholates $C_6H_4(SH)(SSnBu_3)$ and $C_6H_4(SSnBu_3)_2$ undergo direct hydrogenolysis to recover BDT and $HSnBu_3$. Hydrogen gas arising from secondary reactions in prior steps is recovered and fed to this metal recovery step along with fresh H_2 from SMR.

This program was in the early stages of development, with laboratory studies still in progress to demonstrate and improve upon the key chemistry steps, during the period when this analysis was completed.

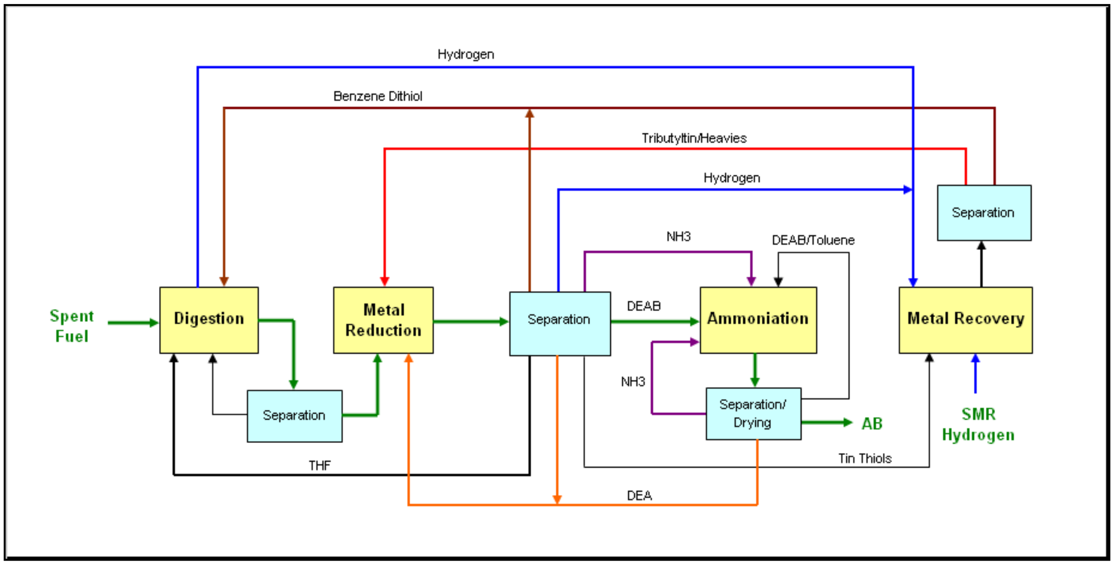


Figure 4.3.1. Process flowsheet for LANL thiacatechol-based spent fuel regeneration

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

In addition to the chemistry steps outlined above, effective intermediate and product separations will be a key element to demonstrating process feasibility due to the large number of components and recycle streams involved as illustrated in Figure 4.3.1. Distillation was chosen as the means for separation for this process analysis. Because of thermal instability above 110-120°C, vacuum distillation is necessary to separate components that have higher boiling points, such as BDT and DEAB. LANL DSC studies showed that $HB(C_6H_4S_2)NHEt_2$ and $HB(C_6H_4S_2)NH_3$ decompose in this range while the tin thiacatecholates start to decompose at 160-175°C. However, with a broad mixture of high and low boiling compounds, vacuum operations will require very cold condenser conditions and result in considerable refrigeration costs.

Process assumptions and cost bases used for the analysis are summarized in Appendix 1. The overall regenerated, solid AB manufacturing cost at the plant gate is estimated to be \$7.90/kg H_2. Capital recovery and utilities are the largest components of costs. Overall capital cost is \$520M, and includes about \$60M of raw materials to fill the reactors (with Sn metal being the largest component). Cost details are provided in Table 4.3.1. It should also be noted that hydrogen alone contributes \$1.50/kg H_2 to the AB cost while the target material cost is \$2-\$3/kg H_2.

Figure 4.3.2 provides the capital cost breakdown and shows that the metal reduction section and utilities have the largest contribution and account for nearly 60% of the installed cost. This can be attributed to the large streams flows in the metal reduction section as shown in Appendix 1 relative to the amount of AB produced. Separation of product intermediates between reactors has a significant cost impact on each reaction section. About 75% of the utilities cost is used to supply refrigeration to satisfy separation requirements. Altogether, over 50% of the capital is related to product separations.

Figure 4.3.3 illustrates the components of energy usage. Energy efficiency (H_2 produced from AB divided by H_2 + process energy used in AB regen process) is 23% and only 15% on a primary energy basis. The results clearly reflect a very high penalty associated with separations, especially related to the large-flow metal reduction/amine exchange effluent where both low and high boilers are present. Numerous distillation columns and flashes with very large reboiler and condenser duties are required to produce high purity recycle streams. This is required due to the different dispositions for each of the product components as illustrated in Figure 4.3.1 (H_2 to metal recovery, NH_3 to ammoniation, DEA to metal reduction, THF and BDT to digestion, DEAB to ammoniation and all heavier components to metal recovery). Condenser temperatures below 0°C are required to separate light components such as DEA and THF from higher boiling BDT and DEAB when run under vacuum conditions. Similarly, high pressure and very low temperatures are needed to generate a pure H_2 stream, free of NH_3.

High reaction yields are essential to minimize reactor and separation costs. Table 4.3.1 illustrates this effect by showing the required reactor volumes as a function of yields and feed usage. From a base of 90% conversion in each reactor, dropping to 70% yields results in a 70% larger reactor for the critical metal reduction and metal recovery sections. Improving yields to 100% yield reduces reactor flows by more than 30%. High conversion in the metal recovery section is especially important since it has a direct impact on the magnitude of the BDT recycle stream back to the metal reduction/amine exchange reactor. Excess reactant usage has a lesser impact as long as conversions remain high.

As a sensitivity case, costs were determined for a larger AB regen plant corresponding to 250 mt/day H_2 delivery and with a 95% on-stream factor. Overall investment cost is \$1000 million and regen AB costs drops to \$7/kg H_2 due to some economies of scale, as shown in Figure 4.3.4.

Dow’s analysis served to establish an initial baseline cost for the AB regen process using the LANL thiol-based route. Although the costs and energy usage are high, numerous opportunities and approaches to lowering costs were identified by reducing the high mass flows (dilute streams and heavy tin reductant) and separation requirements. These include:

a) Confirm thermal stability requirements of reaction products and basis for setting constraints on distillation operations. Relaxing these will significantly reduce capital costs and energy usage.

b) Determine if separation of reaction product intermediates can be eliminated, such that mixed streams can be fed to downstream reaction steps without impacting yields.

c) Drive conversions to eliminate feed components from product streams and simplify separation requirements. For instance, complete reaction of BDT in the digestion will reduce undesired side reactions downstream.

d) Consider less stringent separation targets (e.g., 99% vs. 99.9% separation). Further optimize column operations, such as reflux and optimal feed locations.

e) Ammoniation – use lower boiling solvent than toluene to reduce energy.

f) Metal reduction – use lower molecular weight reducing agent to reduce material processing needs.

g) Implement heat integration.

h) Consider alternatives to energy intensive distillation. Consider precipitation, adsorption, and membrane-based separations as options.

Additional engineering analysis guided by results of laboratory experimentation addressing the above concepts should be able to define alternate separation schemes and targets. Substantial reduction in costs and energy use should be expected.

Table 4.3.1. AB manufacturing cost for LANL thiol-based regen process

Volume:	**100 mt/day H_2 or 223,500 MTA ammonia borane**	
Capital Investment:	**$460 million**	
1st Time Raw Material Purchases	**60**	**($HSnBu_3$ = 72%, BDT = 21%)**
Total Investment	**$520 million**	

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**

Figure 4.3.2. Capital cost breakdown for spent AB regeneration via LANL thiol-based digestion process

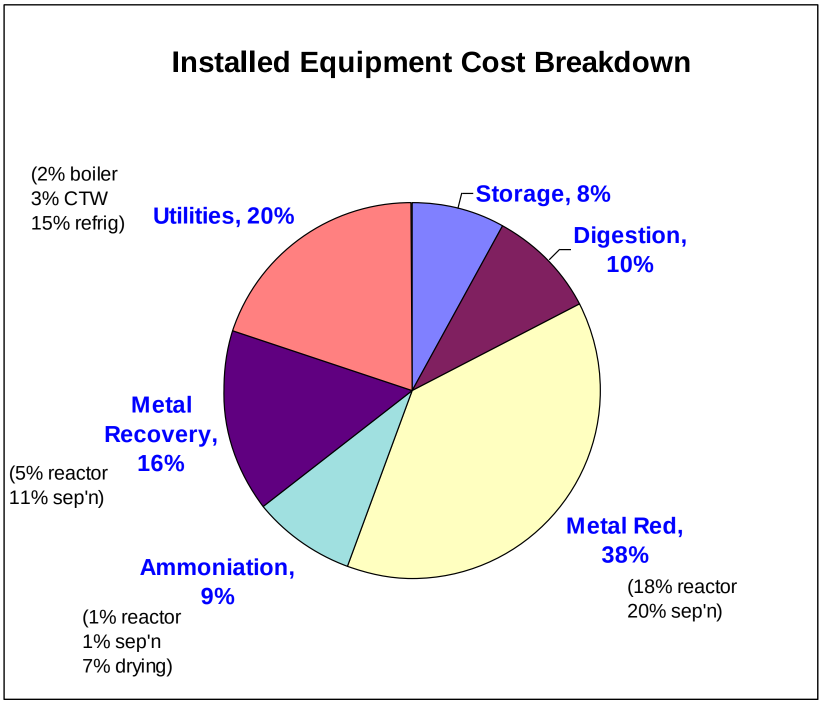


Figure 4.3.3. Energy usage breakdown

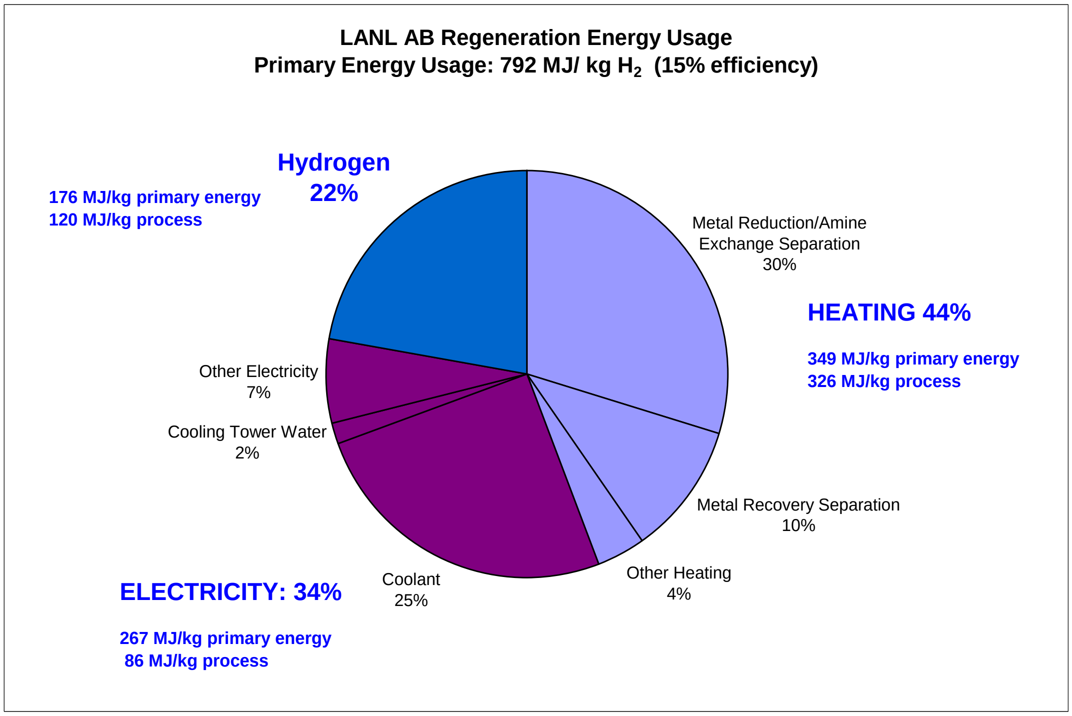
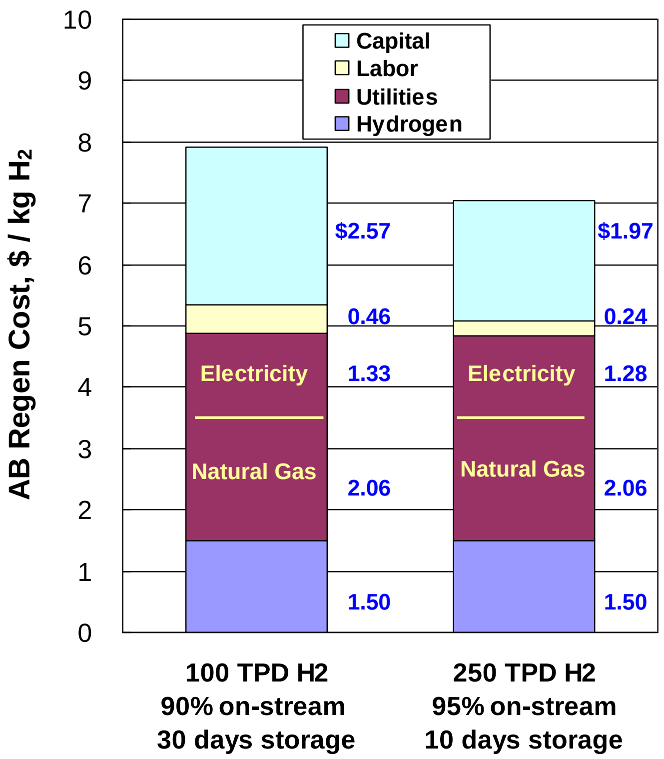


Table 4.3.2. Impact of reaction yields and conditions on reactor requirements

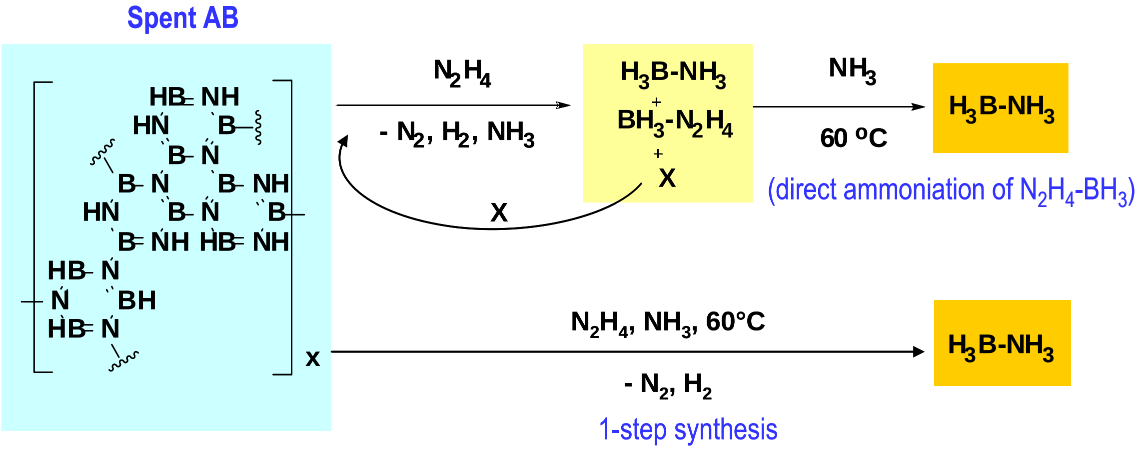
	Ideal (100% Yields)	Base (90% Yield)	70% Conversion	10% Conversion metal recovery	50% Excess Feed Usage
Digester Reactor Volume (l)	1,800,000	2,100,000	2,700,000	2,100,000	2,400,000
Residence time (hr)	4.0	4.0	4.0	4.0	4.0
Excess Spent Fuel	0%	10%	10%	10%	50%
Digestion Conversion	100%	90%	70%	90%	90%
THF Usage (on fuel)	300%	300%	300%	300%	300%
Metal Reduction Reactor Volume (l)	3,300,000	4,800,000	8,200,000	35,900,000	6,100,000
Residence time (hr)	1.0	1.0	1.0	1.0	1.0
Excess Tributyl tin	0%	10%	10%	10%	50%
Excess Amine	0%	10%	10%	10%	50%
(NH4)B(C6H4S2)2 Conversion	100%	90%	70%	90%	90%
Amine Exchange Conversion	100%	90%	70%	90%	90%
HB(C6H4S2)NH(Et)2 Conversion	100%	90%	70%	90%	90%
Ammoniation Reactor Volume (l)	250,000	280,000	350,000	280,000	290,000
Residence time (hr)	1.0	1.0	1.0	1.0	1.0
Excess Ammonia	0%	10%	10%	10%	50%
Conversion	100%	90%	70%	90%	90%
Toluene/Et2NHBH3 ratio:	1.0	1.0	1.0	1.0	1.0
Metal Recovery Reactor Volume (l)	1,000,000	1,400,000	2,500,000	11,800,000	1,700,000
Residence time (hr)	1.0	1.0	1.0	1.0	1.0
Conversion	100%	90%	70%	10%	90%

Figure 4.3.4. Effect of larger AB plant capacity (LANL thiol-based route)



4.3.3. *LANL Hydrazine-Based Process*

Dow's analysis of the thiol-based AB regen route and recommendations to lower costs by reducing stream flows and separation requirements led LANL to seek alternate chemistry routes. A new pathway based on using hydrazine as both the digestion and reducing agent for spent AB has been reported by LANL, and is substantially simpler than the thiol/tin based regeneration route.[25] Two options have been described and demonstrated that hold promise for commercial application. In the first, hydrazine is used to digest and reduce spent AB fuel to produce hydrazine borane, followed by direct ammoniation to form AB. In the 2nd route, direct addition of hydrazine and ammonia takes place to produce AB in a single step.



Progress is being made to optimize reaction conditions for maximum AB yield and selectivity, define reaction stoichiometry, and obtain a mechanistic understanding of the underlying chemistry. The hydrazine-based path is effective for regenerating both polyborazylene and borazine spent fuel types. In discussions with the LANL staff, it was decided to focus Dow's analysis on the 1-step synthesis using borazine, which allows a more simple treatment of the process chemistry.

$$BNH_2 + N_2H_4 \xrightarrow{NH_3} H_3NBH_3 + N_2 \qquad \Delta H_{rxn,\,25C} = -6.95 \text{ kcal/mol} \qquad (4.3\text{-}1)$$

$$\Delta G_{rxn,\,25C} = -22.88 \text{ kcal/mol}$$

Reaction energies calculated by Dave Dixon (University of Alabama) indicate that the reaction is slightly exothermic and thermodynamically favored.[26] LANL studies show that high AB yields and selectivity are obtained when hydrazine is the limiting reagent when the reaction is carried out in liquid NH_3. At a 2:1 BNH_2: N_2H_4 molar feed ratio, 99.5% yield of AB was obtained after 1 hr at 60°C, without formation of any byproducts. Selectivity falls in the presence of higher amounts of hydrazine. Product recovery is fairly straightforward as AB has high solubility in NH_3.[27] The unreacted spent AB can be separated from the ammonia product solution by decanting, followed by evaporation of the ammonia to give high purity AB. The unreacted spent fuel can be recycled to the same reactor without any ill effects.

A simplified block diagram of the conceptual process is shown in Figure 4.3.5.

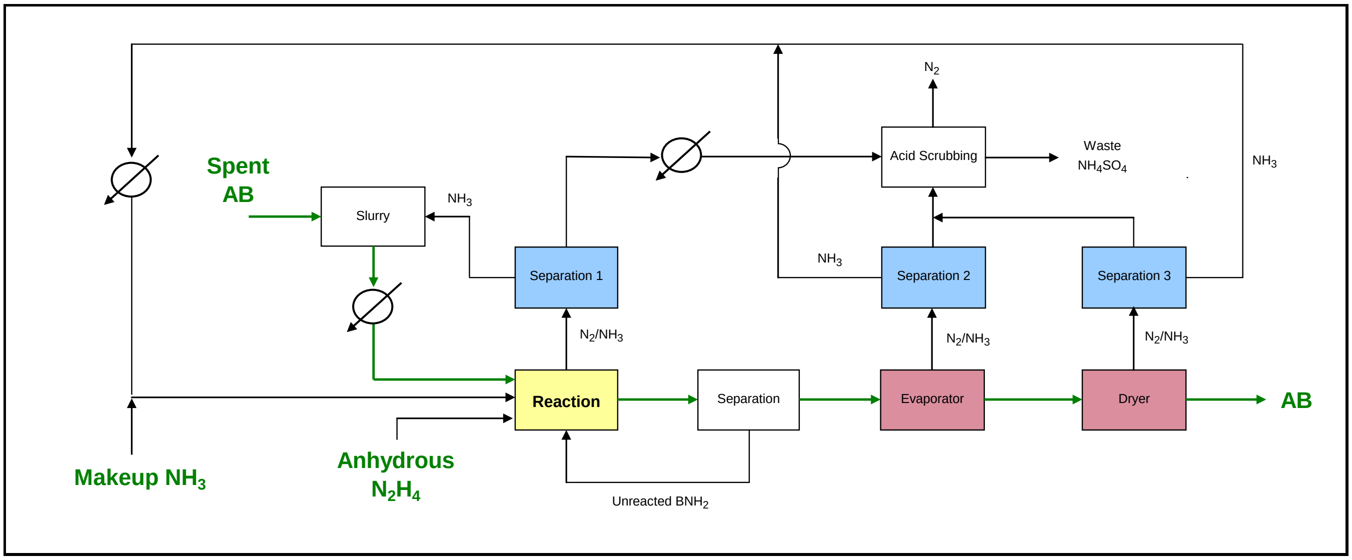


Figure 4.3.5. Block diagram for LANL hydrazine-based AB regen process

Spent AB powder is mixed with cold liquid NH$_3$ to form a slurry that can be metered continuously to the reactor along with anhydrous N$_2$H$_4$. Nitrogen, produced in the reaction, is purged from the system along with potentially a high concentration of NH$_3$ depending on the reactor temperature and pressure. Downstream of the reactor, the excess unconverted spent AB solids are filtered off and returned to the reactor while the solution product is transferred to an evaporator to drive off most of the ammonia. The resulting wet AB product is fed to a dryer to recover any remaining NH$_3$ and produce a dry ammonia borane product. All processing steps containing concentrated AB in solution are limited to a maximum temperature of 40°C to minimize AB decomposition.[15]

Ammonia is recovered from the N$_2$-containing gas mixtures using refrigerated condensation, similar to the large scale NH$_3$ separation found in the recycle loop of an ammonia synthesis plant, and recycled to the spent AB mixer and reactor. NH$_3$ solvent requirements will need to be established, balancing reaction needs against separation costs. The amount of NH$_3$ used in initial LANL studies corresponds to a 0.3M AB concentration in NH$_3$. However, it should be possible to take advantage of the much higher AB solubility limit in NH$_3$ of 50M (260 g AB per 100 g NH$_3$).[27] In this analysis, NH$_3$ usage is set at 10M, with sensitivity cases run at 5M and 20M AB.

Details of the process assumptions and cost bases used for the analysis are summarized in the Appendix 2. Overall regenerated AB manufacturing cost at the plant gate is dominated by the price of hydrazine, as shown in Table 4.3.4. Using the current raw material price of hydrazine hydrate expressed on a 100% hydrazine basis ($5.51/kg), the cost is estimated to be over $45/kg H$_2$, with hydrazine accounting for over 95% of the cost. Excluding hydrazine costs, manufacturing cost would be less than $2/kg. Over 50% of these operating costs are related to utilities. Clearly, costs can be higher if the hydrazine conversion is not 100% selective to AB production.

Total capital cost is $130 million. Figure 4.3.6 provides a breakdown of the capital cost components for a 279,000 MT/yr AB plant which corresponds to 100 MT/day H$_2$. In contrast to the thiacatechol route, where over 50% of the capital is related to product separations, costs are more evenly distributed between reactor, product storage, and product separation equipment. This difference can be attributed in part to the reduced usage of NH$_3$ solvent, the lower mass flow of reaction intermediates, the lack of need for product distillation, and the fewer number of components to separate.

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Figure 4.3.7 shows the effect of NH$_3$ concentration used in the reactor on AB manufacturing cost. At the higher hydrazine prices, the costs associated with NH$_3$ use and recovery have a negligible impact on AB costs. However, as hydrazine pricing falls below $1/kg, the effect becomes more appreciable as a percentage of cost. The difference between the 5M and 20M cases is about $1/kg H_2. Hydrazine costs need to be below $0.20/kg to meet a $3/kg H_2 DOE target.

Hydrazine Costs

Since hydrazine plays such a prominent role in determining the overall cost of regenerating ammonia borane in the LANL regen process, it is worthwhile to consider the various industrial methods to manufacture hydrazine and their associated costs. Hydrazine is produced and sold predominantly as an aqueous solution, which is substantially safer to store, transport and handle than the less stable anhydrous liquid. It is highly toxic and the anhydrous liquid must be stored under N_2 blanketing to be below the 100% LEL (self-detonating) value of hydrazine gas. The hydrate is used in a wide range of commercial applications including as a blowing agent for plastic foams, as a polymerization initiator, and in agricultural pesticides, pharmaceuticals, and dyes. As a strong reducing agent, hydrazine is also used as an oxygen scavenger for corrosion and scale control in boiler water treatment. Anhydrous hydrazine is used primarily as a propellant in rocket propulsion systems.

Each AB regen plant producing the equivalent of 100 mt/day H_2 will require on the order of 300,000 mt/yr hydrazine. 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.[28] Arch Chemicals is currently the only US producer of hydrazine with its plant in Lake Charles, LA.[31] Thus, construction of new facilities will be required to support a hydrazine-based AB regeneration process. The hydrazine plant will likely be co-located with the regen plant to minimize shipping and storage of hydrazine.

The direct synthesis of hydrazine from N_2 and H_2 to produce hydrazine would be ideal for an AB regen cycle; however this reaction is highly unlikely due to the unfavorable thermodynamics at modest temperature and pressures (free energy of formation of +158.5 kJ/mol at 25°C).[29] Indirect oxidation of ammonia or urea remains the only industrial means of producing hydrazine, using chlorine, hypochlorite, or H_2O_2 as the oxidant in aqueous solution.[28-30] Anhydrous hydrazine is produced by dehydration of the hydrate via azeotropic distillation with aniline. The oxidation of ammonia with sodium hypochlorite to produce hydrazine was the first industrial process, demonstrated by Raschig in 1907. These pathways are summarized in Table 4.3.3.

Most production routes today are based on a variation of the Raschig process or the peroxide based process. Hydrazine hydrate price in 2009 is given as $3.53/kg N_2H_4-H_2O or 5.51/kg on a 100% hydrazine basis.[18] The small volume and limited applications of anhydrous hydrazine makes current pricing less relevant, especially since the cost of specially designed safety containers for its transport is factored into the cost. More indicative may be the 20% higher price for the anhydrous product compared to the 85% hydrate on a contained N_2H_4 basis provided in a 1953 report on the Olin Raschig process touting the expanding uses of hydrazine.[30]

Process	Chemistry	Comments
Raschig	$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$ $NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4\text{-}H_2O + NaCl$ **Net: $2NH_3 + NaOCl \rightarrow N_2H_4\text{-}H_2O + NaCl$**	Original process demonstrated in 1907. Ammonia oxidation by Na hypochlorite, via formation of chloramine. Large excess ammonia used to minimize side reactions.
Olin Raschig	**Net: $2NH_3 + 2NaOH + Cl_2 \rightarrow N_2H_4.H_2O + 2NaCl + H_2O$**	Raschig process coupled with continuous hypochlorite formation from Cl2 and dilute NaOH. Anhydrous hydrazine production uses aniline to break hydrazine-H2O azeotrope. (Arch)
Bayer Ketazine	$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$ $2NH_3 + NaOCl + (CH_3)_2CO \rightarrow (CH_3)_2C{=}N\text{-}NH_2 + NaCl + 2H_2O$ $(CH_3)_2C{=}N\text{-}NH_2 + (CH_3)_2CO \rightarrow (CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + H_2O$ $(CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + 3H_2O \rightarrow N_2H_4\text{-}H_2O + 2(CH_3)_2CO$ **Net: $2NH_3 + 2NaOH + Cl_2 \rightarrow N_2H_4\text{-}H_2O + 2NaCl + H_2O$**	Variation of Rachig process used today. Chloramine reaction in presence of acetone produces ketazine, which is hydrolyzed to form hydrazine.
Urea	**Net: $(NH_2)_2CO + 2NaOH + NaOCl \rightarrow N_2H_4\text{-}H_2O + NaCl + Na_2CO_3$**	Urea used in place of ammonia. No longer used commercially. Had been economical at low production levels.
Peroxide (PCUK)	$NH_3 + H_2O_2 + (CH_3)(C_2H_5)CO \rightarrow (CH_3)(C_2H_5)CONH + 2H_2O$ $NH_3 + (CH_3)(C_2H_5)CONH \rightarrow (CH_3)(C_2H_5)CNNH_2 + H2O$ $(CH_3)(C_2H_5)CNNH_2 + (CH_3)(C_2H_5)2CO \rightarrow 2CH_3(C_2H_5)C{=}NN{=}C(C_2H_5)CH_3 + H_2O$ $(CH_3)(C_2H_5)C{=}N\text{-}N{=}C(C_2H_5)(CH_3) + 3H_2O \rightarrow N_2H_4\text{-}H_2O + 2(CH_3)(C_2H_5)CO$ **Net: $2NH_3 + H_2O_2 \rightarrow N_2H_4.H_2O + H_2O$**	Latest of commercial processes. Peroxide reaction carried out in MEK produces methyl ethyl ketazine via oxaziridine intermediate, which is hydrolyzed to form hydrazine. Activation by acetamide Na phosphate needed. Lower processing costs: high yields, concentrated feeds, and easier product separations

Table 4.3.3. Comparison of chemical pathways to hydrazine

While an analysis of these different routes is beyond the scope of this study, a lower bound on hydrazine price can be established by reviewing raw material requirements and costs of the hypochlorite-ketazine and the peroxide process.

	Theoretical Usage wt/wt	**RM Unit Cost $/kg**	**Cost $/kg hydrazine**
	Bayer Ketazine		
Raw Materials			
NH_3	1.063	0.264	0.28
NaOH (50%)	2.496	0.193	0.48
Cl_2	2.213	0.194	0.43
Total			**1.19**
	Peroxide-Based		
Raw Materials			
NH_3	1.063	0.264	0.28
H_2O_2 (70%)	1.061	0.995	1.06
Total			**1.34**

The results shown above indicate that raw material requirements, assuming theoretical yields and ideal recoveries, would have over a $1/kg effect on hydrazine cost based on 2009 prices.[18]

A new 12,000 mt/yr hydrazine hydrate plant in China (Yaxing Chemical) based on the Bayer ketazine technology was constructed in 2005 for $23 million.[32] The corresponding capital-related costs would be $0.36/kg hydrazine hydrate or $0.56/kg contained hydrazine. If plant investment can be scaled using the typical 0.6 exponential factor, capital charges would drop to $0.13/kg contained hydrazine.

Combining hydrazine raw material and capital costs would result in a minimum impact of over $10/kg H_2. Thus alternative ammonia oxidation pathways to produce hydrazine need to be identified for a hydrazine-based AB regeneration technology to be viable. Ideally, the pathway would not necessitate multiple reactions and process steps, or formation of the hydrate to produce anhydrous hydrazine. Possible pathways may include improvements to the direct oxidation of ammonia using oxygen or air.[33] Raw material costs would fall by over 75% to $2.2/kg H_2 if ammonia becomes the only raw material. Similar findings are expected to achieve high energy efficiency.

Table 4.3.4. AB manufacturing cost for LANL hydrazine-based regen process

Volume:	100 MT hydrogen per day equivalent
Capital Investment:	$130 million

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**

or $1.94 + 7.95x

where x = unit price of anhydrous hydrazine
($/kg hydrazine)

Figure 4.3.6. Capital cost breakdown for AB regeneration via LANL hydrazine-based process (100 mt/day H_2)

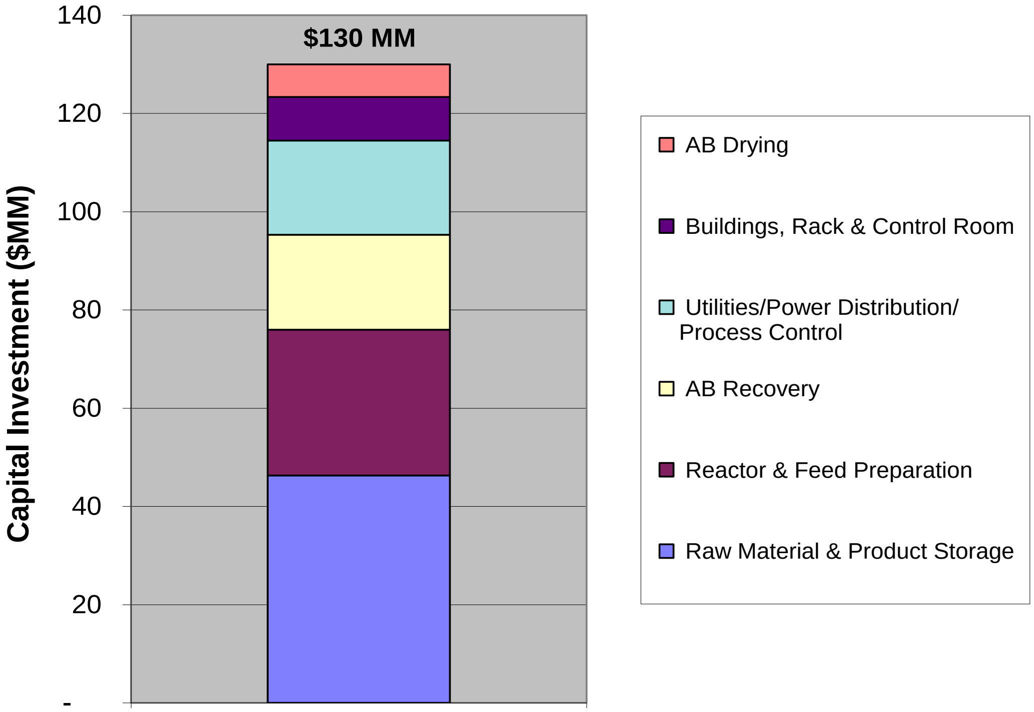
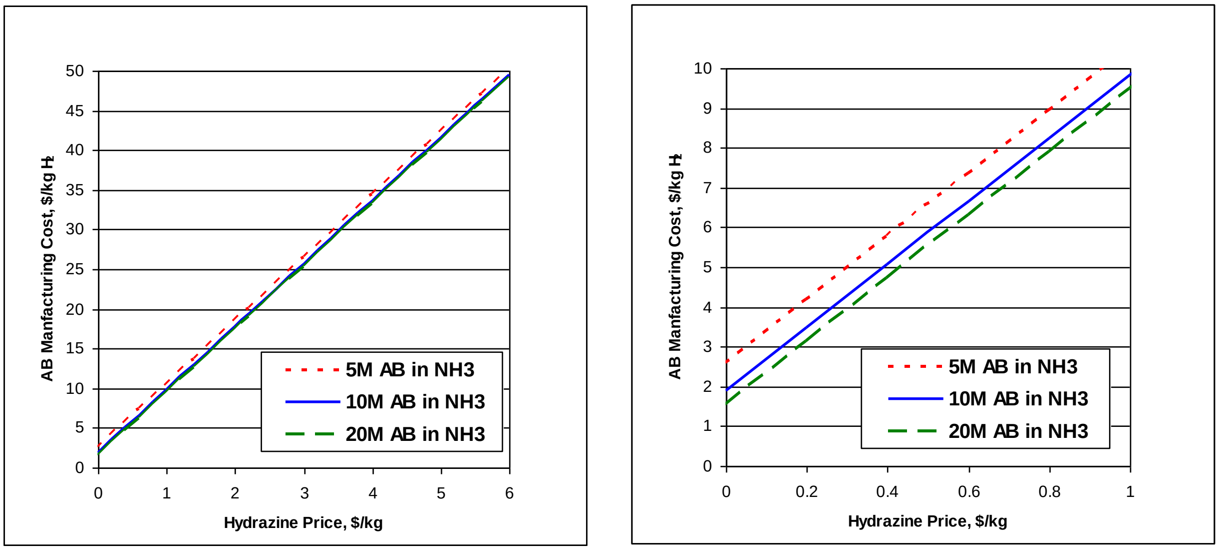


Figure 4.3.7. Sensitivity of H_2 production cost to hydrazine price and NH_3 concentration



4.3.4 PNNL Process

PNNL has been investigating regeneration pathways based on alcohol digestion of the AB spent fuel. Like the LANL thiacatechol-based route, a multi-step scheme is employed involving digestion of spent fuel, reduction with transition metal hydrides followed by disproportionation to produce BH_3, ammoniation of BH_3 to produce AB, and recycle of metal and other intermediates.[34]

Digestion

$BNH_n + 3\ ROH \rightarrow B(OR)_3 + {}^{n}/_{2}\ H_2 + NH_3$ (4.3-2)

$B(OR)_3 + 3\ PhOH \rightarrow B(OPh)_3 + 3\ ROH$ (4.3-3)

Transition Metal Hydride Formation

$3\ M^+ + 3\ H_2 \rightarrow 3\ MH_2 + [+\ 3\ base] \rightarrow 3\ MH + 3\ H^+base$ (4.3-4)

Hydride Transfer/Ligand Redistribution

$3\ MH + 3\ B(OPh)_3 \rightarrow 3\ M^+ + 3\ HB(OPh)_3^-$ (4.3-5)

$3\ HB(OPh)_3^- + B(OPh)_3 + Et_3N \rightarrow 3\ B(OPh)_4^- + Et_3NBH_3$ (4.3-6)

Recycle

$3\ B(OPh)_4^- + 3\ H^+base \rightarrow 3\ PhOH + 3\ base + 3\ B(OPh)_3$ (4.3-7)

Ammoniation

$Et_3NBH_3 + NH_3 \rightarrow BH_3NH_3 + Et_3N$ (4.3-8)

Net: $BNH_n + (3 - {}^{n}/_{2})\ H_2 \rightarrow BH_3NH_3$ (4.3-9)

However, work continues at PNNL to fully define the complete regeneration cycle, so that the digestion agent and reducing agent are optimally paired to allow for facile digestion and hydride formation and transfer. Tranesterification of the digested spent fuel to form the more easily reduced $B(OPh)_3$ opens up additional options for the selection of agents. A system using $HRh(dmpe)_2$ as the metal hydride has been demonstrated[35] but would be cost prohibitive. Although the price of Rh has dropped from ~$10,000/troy oz in mid-2008 to the present price of ~$2500/troy oz, the metal contribution alone to cost would still be on the order of $ billions, even when assuming reaction times on the order of 10 minutes for the metal hydride formation and transfer steps. Shifting to a less expensive metal such as cobalt and nickel is necessary and has been a focus of PNNL's research efforts.

A detailed analysis of PNNL's regen cycle has not been carried out since the regen systems are still being defined. However, some parallels can be drawn from the analysis of LANL's thiol-based regen system. The mass flows in the process and recycle streams of the PNNL process are very large relative to the amount of AB produced. Again, the use of high molecular weight digestion and reducing agents is a disadvantage. The amount of t-BuOH and PhOH used for digestion would be greater than the amount of BDT used for digestion in the LANL thiol-based process. In addition, the stream flows for $HCo(dmpe)_2$ as reducing agent is almost 50% greater than the amount of Bu_3SnH used in the thiol-based case. These impacts need to be considered when screening for potential lower cost AB options.

4.3.5. U. Penn Pathway

Prof. Larry Sneddon's approach at University of Pennsylvania to AB regeneration is based on the digestion of spent fuel by super acidic halo-acids to produce boron halide, followed by conversion of the halide to AB. The latter is accomplished via a sequence of steps comprising base coordination of BX_3, reduction of the halide using silanes or stannanes to form the base-coordinated borane, and NH_3 displacement of the base to form AB.[36]

$BNH_x + 4\ HX \xrightarrow{AlX_3} BX_3 + NH_4X \quad (X{=}Cl, Br)$ (4.3-10)
$BX_3 + Base \rightarrow BaseBX_3 \quad (Base = R_2S)$ (4.3-11)
$BaseBX_3 + 3HMR3 \rightarrow BaseBH_3 + 3XMR \quad (M{=}Sn, Si)$ (4.3-12)
$BaseBH_3 + NH_3 \rightarrow H_3NBH_3 + Base$ (4.3-13)

The boron halide reduction steps have been demonstrated at high yields (96-100%) and high purity AB is produced using conventional product separations based on volatility differences. A simplified flowsheet of the halide conversion to AB is shown in Figure 4.3.8 and should be readily scalable. Details of the Bu_3SnX hydrogenolysis step, however, need to be defined.

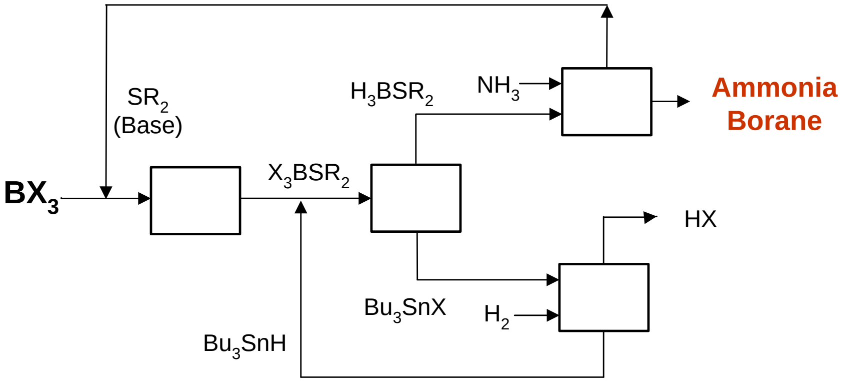


Figure 4.3.8. Block diagram for UPenn AB regen process

Nevertheless, this pathway was only able to show effective digestion of spent AB fuel corresponding to 1 mol equivalent H_2 release per mol AB. Digestion of more highly dehydrogenated spent AB fuel represented by borazine or polyborazylene (corresponding to 2+ equivalents of H_2 release) was not achieved. A similar method reported by Mertens[37] for digesting spent AB using superacid $HCl/AlCl_3$ could not be reproduced by the UPenn researchers.[36] Hence, a more detailed analysis of the regen cycle was not carried out.

4.3.6. Conclusions

Substantial progress has been made by the DOE Chemical Hydrogen Storage Center of Excellence to define feasible pathways for the regeneration of spent ammonia borane fuel. Numerous regen cycles have now been defined and demonstrated in the lab, from complex multi-step reaction processes to LANL's one-pot regen process using hydrazine. Although these options do not currently meet the DOE fuel cost targets of \$2-3/kg H_2, Dow's process analyses have helped to determine baseline costs and identify key areas for improvements and highlight the need for both high chemical and process efficiency for the development of cost and energy efficient processes. Thus, in addition to seeking pathways to digest spent AB material without wasting remaining BH bonds, identifying thermoneutral or reversible steps to maintain high theoretical energy efficiency, and using low cost components where possible, the potential impacts of reaction complexity and separation requirements also need to be taken into consideration,

Although cost is a significant driver for selection of an optimal chemical pathway for commercialization, other factors also play an important role in the determination including process operability and robustness, technical risk, environmental, health, and safety impacts, product quality, and raw material availability and logistics. These elements will also need to be reviewed as processes become better defined.

Appendix 2. Cost Estimate Assumptions for AB Regen Processes

Design Scope

1. Manufacturing cost is based on a solid spent AB fuel delivered to the plant and a regenerated AB bulk powder leaving the plant. Logistics costs including terminal, transportation, and forecourt costs are not considered. These depend on the final design of the AB fuel which has yet to be determined.

2. The AB regen plant is sized to produce 100 metric tons per day hydrogen. At a 90% plant on-stream factor, the H_2 design basis would be 111 mt/day hydrogen. Losses during delivery and storage are negligible. AB stability studies have found no detectable fuel decomposition over 30 days at 50°C, as described in Section 4.1. Therefore no provisions for sizing the AB regeneration plant beyond 100 mt/day were made.

   For the thiol-based digestion path. the H_2 production corresponds to 681 mt/day AB at the targeted hydrogen release of 2.5 mol H_2 per mol AB, and results in a spent fuel with composition $B_3N_3H_3$, or for simplification BNH.

   For the hydrazine-based digestion path. the H_2 production corresponds to 851 mt/day AB at the targeted hydrogen release of 2 mol H_2 per mol AB, and results in a spent fuel with composition of BNH_2.

3. A small amount of heat is expected for on-board hydrogen release from the AB fuel. The exact level will be determined by the Engineering Storage Center. No provisions for generating that heat from AB fuel have been made in sizing the AB regeneration plant.

4. Spent AB fuel is received as a bulk dry solid requiring only crushing prior to regeneration. Solid dry AB powder is produced at 100% purity.

Process

Thiol-Based Route

1. Reactor conditions are set as follows:
   a) Digestion : 60°C, 1 atm, 4 hrs batch reactor
      benzenedithiol (BDT) limited feed (10% excess spent fuel)
      90% digestion of spent fuel based on BDT (Rxn 1a)
      3:1 (wt/wt) THF:spent fuel
      10% of $HB(C_6H_4S_2)NH_3$ reacts further with BDT to produce NH_4 salt and H_2 (Rxn 1b)

   b) Metal Reduction/Amine Exchange: 60°C, 2 atm, 1 hr, single batch reactor
      10% excess DEA and $HSnBu_3$
      90% conversion of $(NH_4)B(C_6H_4S_2)_2$ salt (Rxn 2a – metal reduction 1)
      90% conversion of $HBC_6H_4S_2)NH_3$ (Rxn 2b – amine exchange)
      90% conversion of $HB(C_6H_4S_2)NHEt_2$ (Rxn 2c – metal reduction 2)
      90% conversion of BDT by Bu_3SnH to $C_6H_4(SH)(SSnBu_3)$ (Rxn 2d)
      10% of $C_6H_4(SH)(SSnBu_3)$ reacts further with Bu_3SnH to $C_6H_4(SSnBu_3)_2$ (Rxn 2e)

   c) Ammoniation: 25°C, 8 atm, 1 hr reaction time
      10% excess NH_3 feed
      1:1 (wt/wt) Toluene:DEAB
      90% conversion of DEAB to AB (Rxn 3)

   d) Metal Recovery: 60°C, 8 atm, 1 hr residence time
      10% excess H_2

90% reduction of $C_6H_4(SH)(SSnBu_3)$ to BDT and Bu_3SnH (Rxn 4a)
90% reduction of $C_6H_4(SSnBu_3)$ to BDT and Bu_3SnH (Rxn 4b)

2. Separation is set to provide >99.9% recovery of the feed component into the targeted stream. Recycle of benzenedithiol, tributyltin hydride, diethyamine, and any unreacted reaction intermediates is complete, with no replacement requirements to offset losses.

3. Maximum temperature of ~120°C is set due to thermal stability considerations and requires vacuum distillation to accomplish separations.

4. Hydrogen generated in the digestion and metal reduction reactors is captured, compressed and used to offset H_2 requirements in the metal recovery reactor.

5. Product streams exiting each reactor are given below:

Reactor Product, kg/hr	**Digestion**	**Metal Reduction / Amine Exchange**	**Ammoniation**	**Metal Recovery**
H_2	93	431		1,145
NH_3		15,645	3,303	
$(Et)_2NH$		14,930	67,187	
THF	86,989	86,989		
Toluene			88,773	
BNH	5,272			
$C_6H_4(SH)_2$	22,505	2,250		222,795
$(Et)_2NHBH_3$		79,896	8,877	
Bu_3SnH		162,797		906,777
$HB(C_6H_4S_2)NH_3$	69,895	17,258		17,258
$(NH_4)B(C_6H_4S_2)_2$	156,278	17,364		17,364
$HB(C_6H_4S_2)NH(Et)_2$		22,985		22,985
$(C_6H_4)(SH)(SSnBu_3)$		276,252		27,625
$C_6H_4(SSnBu_3)_2$		792,217		79,222
NH_3BH_3			**28,354**	
Total, kg/hr	**341,031**	**1,489,015**	**196,494**	**1,295,171**

Hydrazine-Based Route

6. Continuous reactor is used and operated at 45˚C, 35 atm and 2 hr reaction time. These conditions help to reduce the amount of NH_3 losses that would exit with the N_2 purge from the reactor. BNH_2 to N_2H_4 molar feed ratio is 2:1. Conversion to AB is 100% based on hydrazine. Unreacted spent fuel is recovered and recycled back to the reactor.

7. Design concentration of AB in NH_3 is 10 molar (52 g AB/100 g NH_3) to take advantage of the very high solubility of AB (260 g AB in 100 g NH_3).[27] Sensitivity cases were also examined at 20 molar and 5 molar conditions.

8. NH_3 losses in the nitrogen stream are minimized through the use of refrigerated condensers. NH_3 losses amount to less than 0.2% of the NH_3 used. NH_3 losses to N_2 are scrubbed with sulfuric acid and sent to waste treatment.

9. Solid AB product is recovered using evaporative crystallization and an atmospheric pressure dryer. Purity of the AB product is assumed to be 100%. NH_3 is recovered and recycled to the reactor without the need for purges.

10. Anhydrous hydrazine is prepared on site and as needed to minimize inventory. A four hour surge is provided.

Capital Cost

1. All capital, raw material, utility and labor costs are on a 2005 basis. [3]

2. Plant capital investment includes all process equipment, process building, utilities, and storage tanks for a one month inventory of raw materials and product. Investment includes a 25% contingency factor.

3. Capital cost is estimated for the nth plant. Therefore engineering costs have been estimated at 10% of the total direct cost and startup costs are assumed to be minimal.[18] Land cost is minimal compared with total capital investment.

4. Annual capital recovery cost is 13.8% of the total capital investment based on a 20 year analysis, 20 year plant life, 10% rate of return, 38.9% total tax rate and a 10 year MACRS depreciation schedule. These costs are the same as for the DOE H2A Model.[17] First fill raw material costs are capitalized for the thiol-based process due to the high cost of Sn. .

5. Depreciation and property overhead are estimated at 3% and 2%, respectively, of the capital investment excluding first fill raw material costs.

Raw Material Cost

Thiol-Based Route

1. Tributyltin hydride cost is estimated by considering the stepwise synthesis of BuCl, BuMgCl, SnCl, Bu_4Sn, and Bu_3SnCl for its production, and applying a 1.5 factor over the raw material costs, resulting in a value of $8.50/kg Bu_3SnH. About 60% of the raw material cost is due to tin metal. Tributyltin hydride may also need to be additized with a stabilizer such as 50 ppm BHT. No adjustments have been made to this estimate at this time.

2. Cost of benzenedithiol is assumed to be $5/kg based on similar costs for catechol and sulfolane.[18]

3. Cost for hydrogen generated in a central SMR plant is $1.50/kg.

Hydrazine-Based Route

4. Cost of other solvents and chemicals were taken from the SRI Consulting PEP 2006-2008 Yearbooks.[18]

5. Cost for 100% hydrazine hydrate was obtained from the SRI Consulting PEP Yearbook[18], and corrected to an anhydrous basis on raw material cost only.

Utility Cost

1. Natural gas cost is $6/GJ and industrial electricity cost is $0.0555/kWh.[17]

2. Fully allocated steam cost is $0.025/kg. This cost is based on a fuel cost of $6/GJ and assumes a 75% efficiency factor for the boiler and that fuel costs are approximately 75% of the fully allocated steam cost.

3. Cost for Electricity requirement is based on the estimated total motor power requirements operating continuously.

4. Fully allocated cooling water cost is 2.7¢/Mliter.[18]

6. Waste treatment costs based on typical publicly owned treatment works (POTW) costs.[19]
7. Cost estimate does not include any allowance for heat recovery.

Other Costs

1. Total operating labor requirement is 60 operators for the thiol-based process and 40 operators for the hydrazine-based process.. Operating labor wage rate is $40.50/hr.[18] Operating supplies are 10% of operating labor; quality control is 20% of operating labor. Plant overhead is estimated at 80% of total labor requirement.

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5 Conclusions

Dow's research conducted within the DOE Chemical Hydrogen Storage Center of Excellence was highly interactive and collaborative in nature. As such, the research program evolved dynamically, based not only upon Dow's results, but also on the efforts of the other Center partners, as well as feedback from DOE and other stakeholders in the Hydrogen Storage Program. Nonetheless, throughout the project, Dow was singularly focused on the identification and development of viable hydrogen storage systems and materials to meet the DOE targets of \$2-3/kg H_2 fuel cost, 60% energy efficiency for regeneration, and 2010 and 2015 storage system cost targets of \$4/kWh and \$2/kWh, respectively.

When this project was initiated, investigation into sodium borohydride ($NaBH_4$) for on-board H_2 storage and release was already well underway, and Dow's efforts were directed towards defining and evaluating low-cost, energy efficient regeneration processes for regenerating $NaBH_4$ from spent fuel. This was done systematically using an engineering-guided research approach, beginning with an analysis of the patents and literature. Three promising borate reduction pathways emerged: metal-based reduction, reduction by carbothermal means, and electrolytic reduction of borate, and experimental programs ensued at Dow, Idaho National Laboratory, and Penn State University (respectively). Research on electrochemical processes was eventually stopped when experiments failed to yield any appreciable amount of $NaBH_4$. The research on carbothermal approaches was plagued by equipment and analytical problems and was likewise stopped because of the lack of positive results. Although large-scale, commercial carbothermal processes exist, the difficulties encountered called into question the robustness of a large-scale, plasma carbothermal process to produce $NaBH_4$.

The metal reduction approach, however, was progressed throughout the life of this project. Significant advances were made on aluminum-based chemistries to define scalable options and determine process feasibility. Currently this approach represents important progress in energy efficiency and manufacturing costs over the commercial Schlesinger process to produce $NaBH_4$, however, additional improvements are still needed to meet the DOE storage technical targets of <\$3/kg H_2 fuel cost and 60% energy efficiency.

In 2007 a DOE-commissioned independent review panel issued a No-Go decision for $NaBH_4$ for on-board H_2 storage for vehicular applications primarily because of difficulties in achieving the H_2 capacity performance targets due to solubility characteristics of the spent fuel, but also in part because of the inability to meet the 60% efficiency target. Despite this, the review panel recommended that Dow continue its research into developing low-cost routes to $NaBH_4$ because of this material's importance in the cost of ammonia borane (AB) and other boron-based systems.

In Phase 2 of the project, Dow's efforts were therefore directed primarily at supporting the Center's ammonia borane initiative. Dow provided baseline cost estimates for AB regeneration routes proposed by LANL and PNNL, as well as for AB prepared from low cost $NaBH_4$ for first system charge (first fill AB). Further research on low cost routes to $NaBH_4$ confirmed the technical feasibility of solution-phase aluminum reduction route, based on conventional process unit operations, and should be amenable to scale-up. Dow's analysis work clearly demonstrated the dominant role that $NaBH_4$ starting material plays in first fill AB manufacturing cost. Significant reduction in $NaBH_4$ cost will be necessary if AB is to meet the DOE storage system cost targets; therefore, continued research to further lower the cost to produce $NaBH_4$ would be beneficial.

The substantial progress made by Dow's Center partners to define and demonstrate feasible and simpler chemical pathways for the regeneration of spent ammonia borane fuel, as well as first fill synthesis of AB, is very encouraging. Although the regen options do not currently meet the DOE fuel cost targets of \$2-3/kg H_2, Dow's process analyses have helped to determine baseline costs, identify key areas for improvements, and highlight the need for both high chemical and process efficiency for the development of cost and energy efficient processes.

Dow’s approach, which involved a tight coupling of engineering assessment, economic analysis, and process synthesis with innovative chemical and materials research, established a foundation for the Center’s identification of viable hydrogen storage materials and systems, and may find application in future evaluation of H_2 storage systems and other R&D programs

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