

## IV.B.5b Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides

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### Subcontractors:

- Innochem, Inc., Boxford, MA
- Electrolytica, Inc., Amherst, NY

Project Start Date: March 1, 2005  
Project End Date: February 28, 2010

### Objectives

- Define and evaluate novel chemistries and processes to produce chemical hydrogen storage materials that meet DOE 2010 targets and that have the potential to meet 2015 targets.
- Focus primarily on energy efficient and cost-effective options for B-OH (borate) B-H conversion.
- Leverage Rohm and Haas' expertise and experience across the entire Chemical Hydrogen Storage Center of Excellence (CHSCoE) to assess engineering requirements and economics and to conduct life cycle analysis.
- Provide support to DOE Chemical H<sub>2</sub> Storage Systems Analysis Sub-Group.

### Technical Barriers

This project addresses the following technical barrier from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(R) Regeneration Processes

### Technical Targets

This project involves conducting fundamental studies to identify energy-efficient and cost-effective regeneration routes for boron hydride compounds from borates (spent fuel). Insights gained from these studies will be applied toward the identification of chemical hydrogen storage materials that meet the following DOE target:

- Fuel cost: \$2 to 3/gallon gasoline equivalent

Additionally, Rohm and Haas's support of DOE's Chemical Hydrogen Storage Systems Analysis Sub-Group, and leveraging our engineering and experience across the entire CHSCoE will help identify chemical hydrogen storage systems that meet the following DOE 2010 targets:

- H<sub>2</sub> weight density: 2 kWh/kg or 6 wt% H<sub>2</sub>
- H<sub>2</sub> volume density: 1.5 kWh/L or 0.045 kg/L H<sub>2</sub>
- Storage system costs: \$4/kWh or \$133/kg H<sub>2</sub>
- Loss of useable hydrogen: 0.1 g/hour per kg H<sub>2</sub> stored

### Accomplishments

#### Chemical reduction of borates:

- Compiled a comprehensive list of possible regeneration pathways (report issued).
- Developed a system of weighted metrics for analyzing the various pathways.
- Selected leading systems for experimental work and initiated experimental program.
- Experimentally confirmed NaBH<sub>4</sub> production.

#### Electrochemical reduction of borates:

- Initiated investigation of aqueous and non-aqueous systems with Penn State.
- Recent studies suggest successful production of NaBH<sub>4</sub>.

**Ammonia borane stability:** Collaborated with Pacific Northwest National Laboratory (PNNL) on adiabatic calorimetry studies.

**Analysis:** Received and applied H<sub>2</sub>A model, developed conceptual regeneration process.



## Introduction

This project focuses on identifying and developing viable hydrogen storage technologies using chemical hydrides that have the potential to achieve DOE 2010 and 2015 performance targets for transportation applications. In collaboration with the other CHSCoE participants, efforts are directed towards defining and evaluating novel chemistries and processes for producing chemical hydrides, with emphasis on sodium borohydride,  $\text{NaBH}_4$ . Sodium borohydride is a strong candidate for hydrogen storage because of its hydrogen storage capacity, chemistry, safety, and functionality. The ability to recycle the spent fuel (borates) back to borohydride in an energy-efficient, cost-effective, and environmentally sound manner is critical to the commercial success not only of  $\text{NaBH}_4$ , but of other irreversible chemical hydrogen storage materials.

Another important aspect of this project is the consistent and accurate analysis and comparison of various hydrogen storage options against DOE targets. Efforts are therefore also focused on supporting the work of the DOE Chemical  $\text{H}_2$  Storage Systems Analysis Sub-Group.

## Approach

The overall approach used is engineering-guided research. This involved identifying all possible  $\text{NaBH}_4$  regeneration pathways via comprehensive reviews of the literature and patents. A series of weighted criteria was used to evaluate the pathways, with emphasis on theoretical energy requirements. This identified the leading candidates and narrowed the possibilities to a manageable number of options for experimentation to demonstrate the key chemical reactions in the regeneration scheme. From this, conceptual process flowsheets are developed. Further experimentation, including optimization of yields, enables refinement of the flowsheets and eventual cost estimates for the entire regeneration process, including raw materials, capital, utilities, and labor.

## Results

A comprehensive review of the literature and patents (1950s–present) identified over 30 pathways for producing  $\text{NaBH}_4$ , and more than 100 possible routes when variations and combinations of the chemistries are considered. The pathways can be generally classified into six categories: 1) metal reduction, 2) electrochemical, 3) borane-based, 4) carbothermal, 5) elemental, and 6) metathesis. All have the potential for greater energy efficiency and metal utilization compared with the current Schlesinger process.

Theoretical energy efficiencies were calculated (primary energy basis) for each regeneration pathway, assuming 0–75% heat recovery from exothermic reactions. For analysis purposes, calculations were conducted assuming electricity generation efficiencies ranging from 32% (2015 U.S. grid) to 100% (hydroelectric power), to reflect real-world scenarios where highly integrated energy sources might be used. The calculations revealed several regeneration routes that appear promising (greater than 60% energy efficiency). Three key energy efficiency drivers were noted: 1) recovery of heat from exothermic reactions, 2) overall process for regeneration (including reductant cycle), and 3) efficiency of energy source.

To further the analysis, several additional metrics pertaining to manufacturing, capital, environmental, logistics, health, and safety aspects were identified. These included reaction yields, raw material abundance, number of processing steps, emissions/toxicity, etc. Each metric was assigned a weighting factor, and each regeneration pathway was assessed and scored against each metric. This enabled the determination of an overall score for each pathway equal to the sum of the product of the weighting factors and scores for each metric. Overall, metal reduction routes scored the highest, followed by carbothermal/elemental routes and then electrolytic routes. Borane-based and metathesis routes scored the lowest. A sensitivity analysis performed on this rating system indicated that the difference in scores was significant and that this is a useful screening tool. The ratings formed the basis of the experimental program.

Metal reduction routes were selected first for in-house study because they are highly favored (potential high yields, few processing steps, low severity operations, several possible metals, large-scale industry for metal recycle). Reactive milling capabilities were established and several metals (Mg, Al, Ti, Si, and Zn) are undergoing evaluation. A variety of metal-containing starting materials are being investigated, including hydrogen-terminated Si nanoparticles produced by Prof. Kauzlarich's group (UC Davis). Nuclear magnetic resonance (NMR) analysis has confirmed that  $\text{NaBH}_4$  has been produced (Figure 1). Operating parameters to achieve the highest yields are being identified (Figure 2). Conceptual process flowsheets such as the one shown in Figure 3 have been developed. Results from the laboratory studies are being used to refine the flowsheets. This enables the determination of material and energy balances, operational requirements, equipment sizing, and capital cost, which in turn leads to an estimation of the regeneration plant cost breakdown (Figure 4). This data can be interfaced with H2A and FCHTool to further define the overall energy efficiency and cost for the regeneration process.

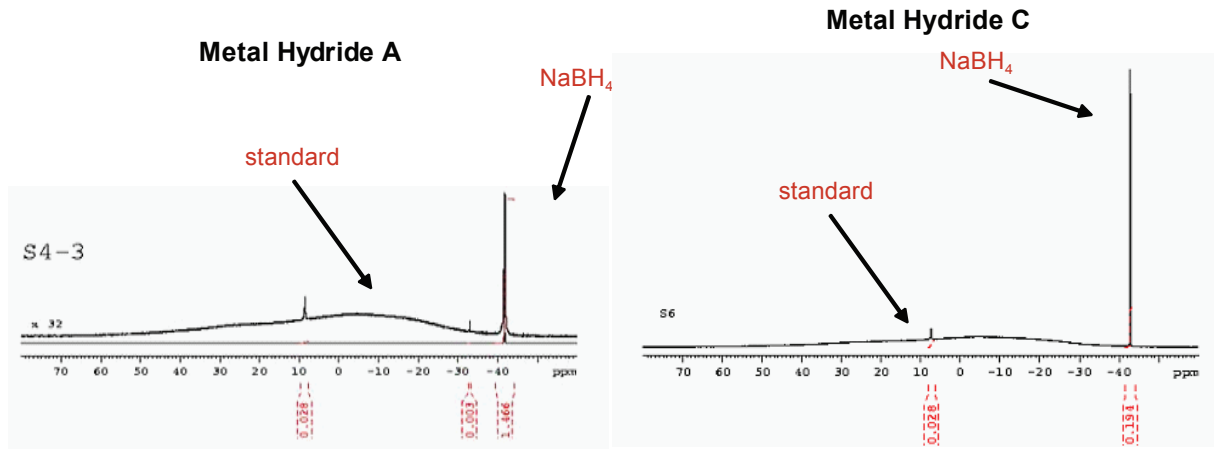


FIGURE 1. <sup>11</sup>B NMR Spectra of NaBH<sub>4</sub> Produced via Metal Reduction Pathways

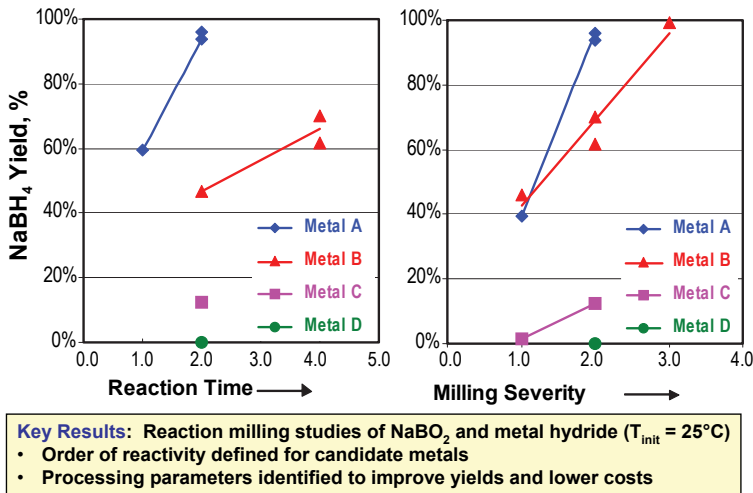


FIGURE 2. Effect of Reaction Time and Operating Severity on NaBH<sub>4</sub> Yields via Metal Reduction

Electrochemical studies were initiated at Penn State and have focused on both one-step reductions in aqueous media and reductions in non-aqueous systems, using high hydrogen potential cathode materials. NaBH<sub>4</sub> production has been demonstrated but, to date, yields have been low. Details of this work can be found in Penn State’s annual report.

Carbothermal/elemental routes offer potential for high energy efficiencies and yields, as well as for simple processes. Currently, options are being explored to address the lack of experimental capabilities within the CHSCoE.

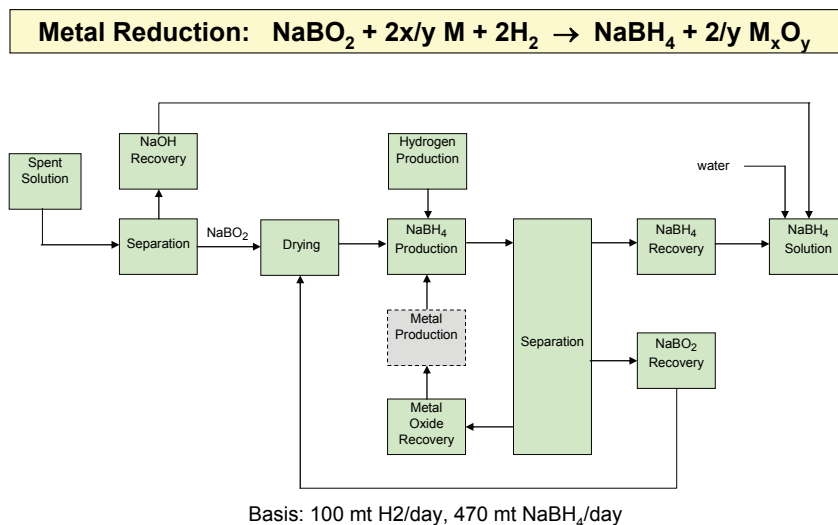


FIGURE 3. Conceptual Process Flowsheet for Metal Reduction of Borate

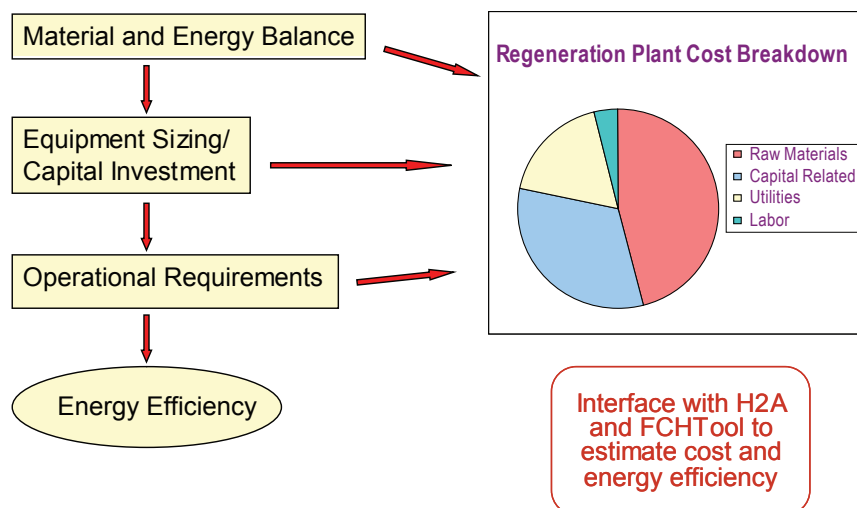


FIGURE 4.  $\text{NaBH}_4$  Regeneration Plant Cost Breakdown Schematic

Details of ammonia borane stability studies can be found in PNNL's annual report.

## Conclusions and Future Directions

### Conclusions

- Preliminary analysis has identified a series of chemistry paths with the potential to achieve high energy efficiency in  $\text{NaBH}_4$  regeneration (metal reduction, electrolytic, carbothermal/elemental).
- Work is underway to estimate potential cost and energy requirements to support the September 2007 go/no-go decision process.

### Future Directions

- Determine if laboratory demonstration of all non-commercial or unproven  $\text{NaBH}_4$  formation steps is possible and estimate the efficiency of the overall process.
- Demonstrate key chemistries to validate process flowsheets and build conceptual processes to estimate cost and energy efficiency (June 2007).
- Prepare preliminary  $\text{NaBH}_4$  production/regeneration cost estimate that contains a sensitivity analysis and qualifies it in terms of degree of confidence (July 2007).
- Determine feasibility based on laboratory-scale experimental demonstration of energy-efficient regeneration off-board. Provide results to go/no-go review panel (September 2007).
- Pending outcome of go/no-go decision, define top options, develop and optimize process, and detail selected pathways (Phase 2).

## FY 2007 Publications/Presentations

1. S. W. Linehan, F. J. Lipiecki, and A. A. Chin, "Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides," DOE Annual Merit Review Meeting, May, 2007.
2. S. W. Linehan, F. J. Lipiecki, and A. A. Chin, "Sodium Borohydride Regeneration," presentation to FreedomCAR Hydrogen Storage Tech Team, PNNL, March 22, 2007.
3. S. D. Rassat, C. L. Aardahl, R. S. Smith, S. T. Autrey, and A. Karkamkar (PNNL) and A. A. Chin, J. W. Magee, G. R. VanSciver, and F. J. Lipiecki (Rohm and Haas Company), "Impact of Solid Ammonia Borane Fuel Formulation on an On-Board Storage and Hydrogen Release System," MRS Meeting, Boston, MA, November, 2006.
4. S. D. Rassat, R. S. Smith, S. T. Autry, and C. L. Aardahl (PNNL) and A. A. Chin, J. W. Magee, G. R. VanSciver, and F. J. Lipiecki (Rohm and Haas Company), "Thermal Stability and Hydrogen Release Kinetics of Ammonia Borane Under Vehicle Storage Conditions," National ACS Meeting, San Francisco, CA, September, 2006.
5. F. J. Lipiecki and A. A. Chin, "Sodium Borohydride Regeneration," Clean Energy Research Center at University of South Florida, September 12, 2006.