# IV.B.4c Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides

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## 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) to B-H conversion.
- Leverage Rohm and Haas' expertise and experience across the entire Center: assess engineering requirements and economics, conduct life-cycle analysis.
- Provide support to DOE Chemical $H_2$ Storage Systems Analysis Sub-Group.

## Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) 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–$3/gallon gasoline equivalent

Additionally, Rohm and Haas' support of DOE's Chemical $H_2$ Storage Systems Analysis Sub-Group, and leveraging our engineering and experience across the entire Center, will assist with the identification of chemical hydrogen storage systems that meet the following DOE 2010 targets:

- $H_2$ weight density: 2 kWh/kg or 6 wt% $H_2$
- $H_2$ volume density: 1.5 kWh/L or 0.045 kg/L $H_2$
- Storage system costs: $4/kWh or $133/kg $H_2$
- Loss of useable hydrogen: 0.1 g/hour per kg $H_2$ stored

## Accomplishments

- Established performance-based metrics (options reduction matrix) for quantitatively evaluating potential regeneration routes against DOE targets.
- Identified several potential energy-efficient and cost-effective regenerations routes.
  - Metal (Al, Zn, Si, etc.) reduction of borates.
  - Electrochemical reduction (one-step and two-step routes).
  - Borane-based routes that do not rely on $NaBH_4$ as a starting material.
- Completed a baseline life-cycle inventory analysis for the current commercial Schlesinger process for producing $NaBH_4$.
- Completed preliminary cost and thermal stability assessments for ammonia borane.

## 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 Center participants, efforts will be directed towards defining and evaluating novel chemistries and processes for producing chemical hydrides, with emphasis on sodium borohydride, $NaBH_4$. 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 $NaBH_4$ 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 will therefore also be focused on supporting the efforts of the DOE Chemical $H_2$ Storage Systems Analysis Sub-Group.

## Approach

The approach toward meeting the above objectives is to use engineering-guided research. Engineering-guided research is a process that facilitates the rapid down-selection of a large number of options to a smaller, more manageable number of options having the greatest probability of success. For this project, the options represent different chemical pathways and processes for converting boron-oxygen bonds to boron-hydrogen bonds.

This overall process is illustrated in Figure 1. The various options are analyzed or screened against a variety of established technical and financial metrics. Options not meeting the criteria are eliminated, while those that do meet the criteria continue through the screening process until only those with a high probability of success remain. It should be noted that to a large extent, this is an analysis that is done "on paper" – valuable laboratory time and personnel are used only for experimental evaluation of the options that are most likely to succeed. In summary, engineering-guided research reduces both technical and economic risk.

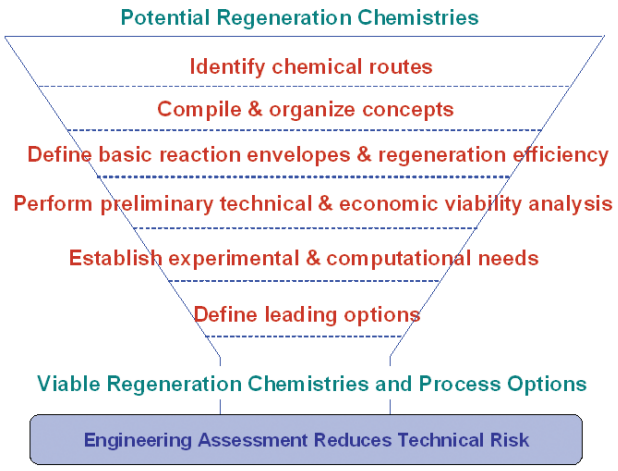


**FIGURE 1.** Engineering-Guided Research

## Results

An options reduction matrix has been established for evaluating various chemical hydrogen storage options against performance-based criteria. This tool was jointly developed with LANL, PNNL, and Millennium Cell. The tool contains approximately 15 criteria or metrics ranked in order of criticality (must-have, desirable, optional, etc.). The must-have criteria include the DOE 2010 targets, desirable criteria include DOE 2015 targets, etc. Each option is evaluated against the various metrics; the options meeting the largest number of the most critical metrics are considered to be the leading options and are subjected to more detailed technical and economic analysis, including experimental study.

Six classes of regeneration chemistries have been targeted for investigation:

- Metal reduction of borates
- Electrochemical reduction of borates
- Borane-based routes
- Elemental synthesis
- Metathesis routes
- Transfer hydrogenation

Within each class, numerous chemical reactions and variations thereof (including process variations) can be written. Each of these options is screened against a variety of metrics as part of the engineering-guided research down-selection process. The metrics include theoretical energy efficiency, reductant regeneration requirements, energy costs, raw material cost and availability.

Metal reduction of borates typically involves a two-step process: 1) reduction of borate to borohydride by an appropriate metal (or mixed metal) with concurrent formation of the corresponding metal oxide, and 2) reduction of metal oxide back to the elemental metal with a suitable reductant (i.e., $H_2$, methane, electrons, etc.). Preliminary analysis of the energetics of both reactions, and analysis of raw material availability and cost have identified three promising metal systems: Al, Si, and Zn. Detailed analysis of these systems, as well as other potential metal reductants, will continue in FY 2007, including experimental evaluations.

For electrochemical reductive routes to borohydride, Rohm and Haas is collaborating with LANL, Millennium Cell, and Pennsylvania State University (PSU). Accomplishments include the following:

- Validation of analytical methods and electrolytic cell.
- Establishment of reporting criteria and metrics for electrolytic studies.
- Previous Rohm and Haas successes shared with team and concepts suggested for improvement.
- Discussions with PSU regarding planning of experimental activities.

Previous Rohm and Haas experimental studies involved the investigation of various boron substrates, solvent systems, and cathode materials. Some of the cathode materials investigated included high hydrogen overpotential cathodes, hydrophobic composites, and gas diffusion electrodes. Positive results were obtained for both a one-step direct reduction of borate to borohydride, as well as a two-step reduction via a sodium trimethoxyborohydride intermediate. Yields were low, but these studies were not optimized, and several possibilities exist to improve upon these yields. These findings are significant, since it appears that this is the first time borohydride has been generated electrolytically with unequivocal analytical confirmation of the presence of $BH_4^-$.

Compilation and analysis/screening of options within the other four classes of chemistry are ongoing and expected to be completed in early FY 2007.

A baseline life cycle inventory (LCI) has been completed for the current commercial Schlesinger $NaBH_4$ process (Figure 2). LCI is a cradle-to-grave assessment of all the material and energy requirements for a given process. It addresses one of the two key technical barriers: lack of understanding of the environmental impacts (energy usage and emissions) of the regeneration process. A preliminary comparison of the baseline Schlesinger LCI with other chemical hydrogen storage options has also been conducted. As shown in Figure 3, the energy requirements for the current process are very high relative to compressed or liquefied hydrogen. Even with the adoption of improved sodium production routes (i.e., improved electrolytic routes), as long as the Schlesinger process is employed, the energy requirements are undesirably high. However, if one considers ideal regeneration:

$$NaBO_2 + 4\,H_2 \rightarrow NaBH_4 + 2H_2O$$

with 100% recycle of all materials, energy requirements begin to approach that of compressed or liquefied hydrogen. This project seeks to identify those options that approach most closely the ideal regeneration scenario. LCI data generated for the various regeneration options can be input into the H2A analysis tool.

Preliminary cost and thermal stability assessments of ammonia borane (AB) have also been completed in support of PNNL's work with this very promising hydrogen storage material. Currently, AB costs are very high because it is priced as a low-volume, specialty chemical. Lower cost AB is needed to meet DOE 2010 system cost targets. Initial fill AB production chemistry will likely require $NaBH_4$ as one of the starting materials, either directly by reaction with an ammonium halide salt or indirectly via diborane. Initial cost assessments indicate that AB regeneration via $NaBH_4$ may not meet the regeneration fuel cost targets.

Accelerated reaction calorimetry (ARC) data have been provided to PNNL in support of its efforts to assess the thermal stability of AB relative to DOE's storage targets. The ARC can be used to determine conditions where the exothermic AB decomposition may become self-propagating under adiabatic conditions. An example of a typical ARC plot is shown in Figure 4, which provides information on pressure buildup and self-heating with temperature. The effects of storage conditions, AB impurities, AB aging, and other parameters on thermal stability are being investigated. These data are being used, together with PNNL's thermal gravimetric analysis and differential scanning calorimetry results, to support stability modeling for AB and efforts to define AB fuel formulations that are both stable for on-board storage and sufficiently reactive to

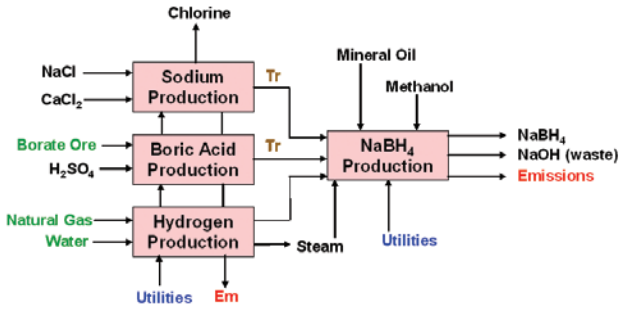


**FIGURE 2.** LCI for Current Brown-Schlesinger $NaBH_4$ Process

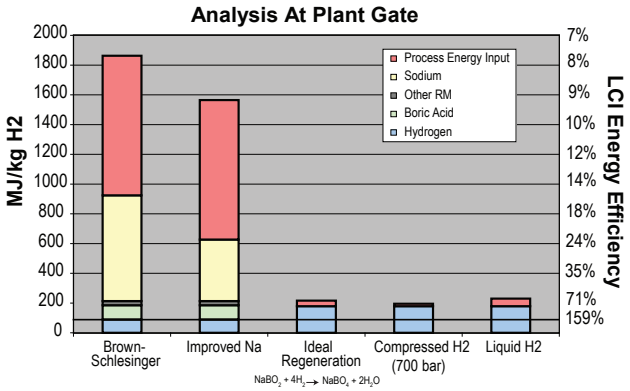


**FIGURE 3.** LCI Comparison of $H_2$ Storage Options

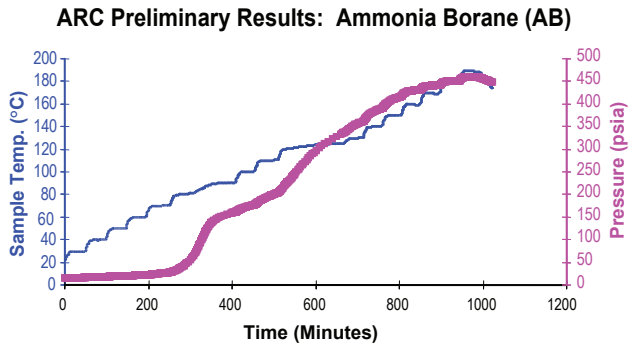


**FIGURE 4.** Ammonia Borane Thermal Stability

release $H_2$ at the rates required for fuel cell operation. Results will be presented at the 2006 Materials Research Society meeting and at the American Chemical Society Fall 2006 National Meeting (joint PNNL/Rohm and Haas papers).

## Conclusions and Future Directions

### Conclusions

- $NaBH_4$ Regeneration Routes - leading metal reduction systems with lower energy usage have been identified.
- Direct and two-step electroreduction routes to $NaBH_4$ have been identified.
- LCI methodology has been developed for the current Brown-Schlesinger process.
- LCI models can be built for regeneration alternatives and data interfaced with H2A analysis tool.
- Ammonia Borane - lower cost $NaBH_4$ is required for first fill, or regeneration routes not requiring $NaBH_4$ may be needed.
- Rohm and Haas ARC stability data for AB complement PNNL research.

### Future Directions

- Complete compilation of other $NaBH_4$ regeneration routes; conduct computational analysis to identify at least one option for laboratory demonstration. (12/31/06)
- Laboratory demonstration of at least one $NaBH_4$ regeneration process meeting regeneration efficiency criteria. (6/30/07)
- Develop conceptual design for laboratory demonstrated $NaBH_4$ regeneration process and associated on-board system. (9/30/07)
- Develop conceptual AB manufacturing process and cost estimate.
- Complete ARC studies for AB.
- Leverage Rohm and Haas competencies across Center and support DOE Chemical $H_2$ Storage Systems Analysis Sub-Group.

## FY 2006 Publications/Presentations

**1.** F. J. Lipiecki, "Sodium Borohydride Regeneration and Analysis," presentation to FreedomCAR Hydrogen Storage Tech Team, Houston, TX, Feb. 16, 2006.

**2.** S. W. Linehan, "Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides," presentation on project status at DOE Annual Merit Review, May 2006.

**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," to be presented at the Fall 2006 MRS meeting.

**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," to be presented at the Fall 2006 National ACS Meeting.