IV.B.1g Ammonia Borane Regeneration and Market Analysis of Hydrogen Storage Materials

David Schubert (Primary Contact),
Jonathan Owen, Duane Wilson
U.S. Borax Inc.
8051 E. Maplewood Avenue
Glenwood Village, CO 80111
Phone: (303) 713-5226; Fax: (303) 713-5788
E-mail: david.schubert@borax.com

DOE Technology Development Manager:
Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: James Alkire
Phone: (303) 275-4795; Fax: (303) 275-4753
E-mail: Jim.Alkire@go.doe.gov

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Objectives

- Synthesize target borate ester expected to have enhanced hydride affinity for use in demonstrating a practical ammonia borane regeneration cycle.
- Supply selected borate esters to project collaborators at the Pacific Northwest National Laboratory (PNNL).
- Assess U.S. and global borate resources and reserves available for large-scale implementation of ammonia borane as a transportation fuel.
- Estimate U.S. and global borate reserves available in 2050, adjusted for consumption by competing industrial uses.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) System Cost
(C) Efficiency
(K) System Life Cycle Assessments
(R) Regeneration Processes

Technical Targets

Regeneration There is a need to maximize efficiency of off-board regeneration of ammonia borane:

- Recyclable thermodynamically favorable intermediates are required.
- We are collaborating with PNNL and other Chemical Hydrogen Storage Center of Excellence (CHSCoE) partners to maximize efficiency of spent fuel regeneration.
- Our work involves tuning the chemistry of borate esters as hydride acceptors in PNNL's cycle.

Boron Resources An understanding of the global supplies of boron ore resources is required for hydrogen storage:

- A key objective is to develop a better understanding of global supplies of boron ore reserves required for hydrogen storage.
- In addition to boron, a resource model developed as part of this work will be applicable to other materials of interest for hydrogen storage, e.g., Li, Mg.

Accomplishments

- Prepared a series of target borate ester compounds and supplied these to collaborators at PNNL for testing as hydride acceptors in a practical ammonia borane regeneration cycle.
- Completed assessment of global borate reserves, including estimated reserve base in 2050 adjusted for consumption by existing industrial applications.

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Introduction

A major emphasis of the CHSCoE) is the regeneration of ammonia borane (AB) spent fuel. This has created needs in areas in which U.S. Borax Inc. (USB) has strong capabilities. USB is collaborating with the CHSCoE to assist in solving important problems relating to the use and regeneration of ammonia borane as an off-board reversible hydrogen storage material, with activities in the following areas critical to key goals: 1) synthesis of borate esters related to AB fuel regeneration intermediates, and 2) analysis of boron resources and impacts on supplier and end-use industries. As strategies for AB fuel regeneration have progressed, more attention has focused on borate ester chemistry. Given its considerable experience with the synthesis and process development of borate esters, USB is collaborating with members of the CHSCoE to identify a set of borate esters that can be prepared from digested AB spent fuel (BNH_x), and can be converted back to AB in an efficient process.

In addition, the impacts on boron resources associated with the initial fill requirements of a large AB-fueled automotive fleet require further analysis. USB is undertaking a study to address frequently asked questions regarding the adequacy of key boron resources, production capacities needed to meet a steeply rising demand curve followed by a return to baseline, and impacts upon prices and competing end-uses.

Approach

Activity 1. Regeneration of AB Spent Fuel

- PNNL's proposed regen cycle has high theoretical efficiency.
- Use alcohols for digestion of spent AB leads to borate ester intermediates.
- Tuning the properties of aryl borates esters will lead to thermodynamically favorable regen intermediates and validate computations.
- AB regeneration pathway requires spent fuel digestion intermediate having sufficient hydride affinity for reduction by metal hydride.
- USB is undertaking synthesis of a large set of borate esters of several types to be supplied to PNNL for experimental validation of theory and regen process.
- Approach will impact likelihood of success of PNNL's regen system and validate theory.

Activity 2. Establish Global Reserve Estimates

- Review and analyze publicly available information sources to quantify borate resources.
- Other published numbers have poorly attributed data sources.
- Our work is aimed at establishing most reliable publicly available reserves data.
- Anticipated consumption of reserves from competing uses through projected initial fill timeframe (2009 → 2050) should be included in estimates.

Results

Activity 1. Regeneration of AB Spent Fuel

A major activity of this project is the preparation of borate esters that can be reduced to borane as part of a practical regeneration cycle, returning BNH_x (spent fuel) to AB fuel. This requires esters that have enhanced hydride affinities. Calculations done at PNNL and elsewhere indicate that phenolic esters possessing electrophilic substituents may have suitable hydride affinities. In order to validate these calculations, we have set out to prepare a series of orthoborate esters of the type shown in Figure 1, where X is fluorine or chlorine and n = 1-5.

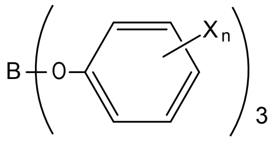

FIGURE 1. Halogenated Orthoborate Esters

At this point we have evaluated various laboratory methods that can be applied to the systematic synthesis of a complete series of borate esters that are substantially free of hydroxyl group-containing contaminates (R-OH, =B-OH, H_2O). While still experimenting with these methods, we have prepared a number of target borate esters, which were supplied to our collaborators at PNNL for nuclear magnetic resonance (NMR) spectral analysis and further testing in connection with ammonia borane regeneration.

- Another approach to controlling the hydride affinities of borate esters involves the use of chelated esters. To this end, we have prepared several borate esters of the type shown in Equation 1, where X is chlorine in our initial experiments. In each of the chlorine-containing ligands, the halogen substituents were at ortho positions relative to the phenolic -OH groups. Because the presence of the imine functionality is undesirable in hydride transfer reactions, we have reduced these imine precursors to amines and also formed borate ester from these reduced ligands. We accomplished these objectives in a one-step reaction using sodium borohydride as both reductant and boron source, as shown in Equation 1. The products were characterized by gas chromatograph mass spectroscopy and NMR spectroscopy. Borate ester compounds prepared in our laboratory and supplied to PNNL collaborators so far during 2009 include those listed in Table 1.

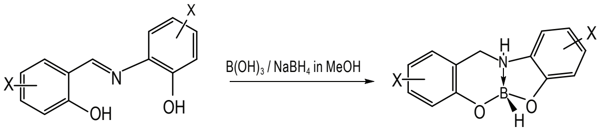 (1)

TABLE 1. Borate Ester Compounds Prepared and Supplied to PNNL in 2009

Chlorophenylborate esters	
Tri(2-chlorophenyl)orthoborate	$B(O\text{-}o\text{-}ClC_6H_4)_3$
Tri(3-chlorophenyl)orthoborate	$B(O\text{-}m\text{-}ClC_6H_4)_3$
Tri(4-chlorophenyl)orthoborate	$B(O\text{-}p\text{-}ClC_6H_4)_3$
Tri(2,4-dichlorophenyl)orthoborate	$B(O\text{-}2,4\text{-}Cl_2C_6H_3)_3$
Tri(2,6-dichlorophenyl)orthoborate	$B(O\text{-}2,6\text{-}Cl_2C_6H_3)_3$
Tri(3,4-dichlorophenyl)orthoborate	$B(O\text{-}3,4\text{-}Cl_2C_6H_3)_3$
Tri(3,5-dichlorophenyl)orthoborate	$B(O\text{-}3,5\text{-}Cl_2C_6H_3)_3$
Tri(2,4,6-trichlorophenyl)orthoborate	$B(O\text{-}2,4,6\text{-}Cl_3C_6H_2)_3$
Fluorophenylborate esters	
Tri(2-fluorophenyl)orthoborate	$B(O\text{-}o\text{-}FC_6H_4)_3$
Tri(3-fluorophenyl)orthoborate	$B(O\text{-}m\text{-}FC_6H_4)_3$
Tri(4-fluorophenyl)orthoborate	$B(O\text{-}p\text{-}FC_6H_4)_3$
Tri(3,4-difluorophenyl)orthoborate	$B(O\text{-}3,4\text{-}F_2C_6H_3)_3$
Tri(3,5-difluorophenyl)orthoborate	$B(O\text{-}3,5\text{-}F_2C_6H_3)_3$
Tri(3,4,5-trifluorophenyl)orthoborate	$B(O\text{-}3,4,5\text{-}F_3C_6H_2)_3$
Mixed halophenylborate esters	
Tri(2-fluoro-4-chlorophenyl)orthoborate	$B(O\text{-}2\text{-}F\text{-}4\text{-}Cl\text{-}C_6H_3)_3$
Tri(2-fluoro-4-bromophenyl)orthoborate	$B(O\text{-}2\text{-}F\text{-}4\text{-}Br\text{-}C_6H_3)_3$

Activity 2. Establish Global Reserve Estimates

A second major activity of this project is the analysis of the impacts on boron resources associated with the initial fill requirements of a boron-based fuel for a large automotive fleet. Initially, this requires an assessment of world boron resources in terms of known borate minerals reserves. This involves analysis and reconciliation of publicly available information on borate reserves in various parts of the world. To date, we have compiled and analyzed key public sources of information and refined the combined borate resource estimates. These estimates were projected out to 2050 using estimates of boron demands from other competing industrial applications, to produce an adjusted assessment of boron resources over the time frame relevant to hydrogen fuel cell vehicle (FCV) deployment. These data were then compared with estimates of boron requirements for hydrogen storage in FCVs.

The first priority of our work was to establish the most credible estimates of boron reserves. It can be noted that publicly available reports and discussions of borate reserves differ markedly. For example, the U.S. Geological Survey figures are the lowest in the literature [1]. Furthermore, the variance is greatest for the two nations with the largest reserves, the United States and Turkey. We determined that other sources of information are more realistic [2,3]. This analysis, based upon publicly available data sources deemed to be reliable, indicates that available boron from known reserves exceeds 1 billion metric tonnes of boric oxide (B_2O_3).

The model we used for boron demand resulting from FCV deployment employed the assumptions listed in Table 2. Boron demand associated with automotive use of ammonia borane hydrogen storage material was based on the known chemistry of the AB storage system and the number of FCVs to be deployed, as projected in the Department of Energy publication, *Analysis of the Transition to Hydrogen Fuel Cell Vehicles & Potential Hydrogen Energy Infrastructure Requirements* (ORNL/TM-2008/30), and the VISION model. Using these methods, we calculated the cumulative boron demand associated 360 million FCVs deployed by 2050 as 60 million metric tonnes B_2O_3.

TABLE 2. Assumptions Used in Boron Demand Model

No. FCVs deployed in USA by 2050	60 million
No. FCVs deployed worldwide by 2050	360 million
Miles per kg H_2	57.5*
Miles range per tank	400
Miles per year per FCV	12,000*
Months supply in infrastructure	1
% H_2 stored in ammonia borane	15
% Recycle	100 (insignificant losses)
	* from H2A model

Our assessment of global borate resources, summarized in Figure 2, indicates that more than 1 billion B_2O_3 tonnes are available from known borate reserves. Figure 2 also shows the cumulative amounts of B_2O_3 estimated to be required for both a U.S. and a global fleet of FCVs fueled with ammonia borane.

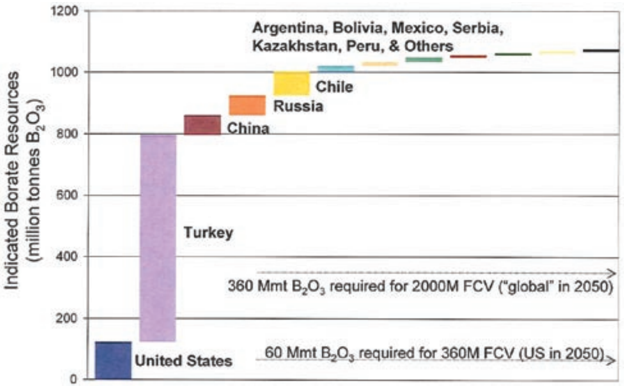

FIGURE 2. Estimated global borate resources showing the cumulative amounts of B_2O_3 estimated to be required for both a U.S. and a global fleet of FCVs fueled with ammonia borane.

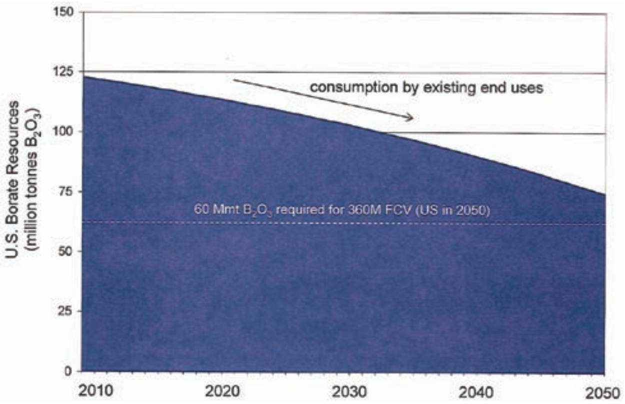

FIGURE 3. Comparison of boron reserves in the U.S., showing estimated depletion by existing non–hydrogen storage applications, with the projected demand from a U.S. fleet of FCVs.

Figure 3 shows the known U.S. borate reserves, with a projection of how these reserves might be depleted over time by the demands of existing non-hydrogen storage applications, compared with the requirements of a U.S. fleet of 360 million FCVs, 60 million B_2O_3 tonnes. The conclusions drawn from these data is that, even when other competing applications are factored in, there is sufficient borate reserves within the United States to satisfy the B_2O_3 requirements for initial fill of a U.S. FCV fleet.

Our conclusion from this initial work is that global borate ore reserves are sufficient for hydrogen storage needs, as well as the other industrial demands projected over the relevant time period. In addition, we further conclude that borate reserves within the U.S. are sufficient to supply a U.S. fleet of 360 million FCVs. Further refinements to these estimates, and sensitivity analyses, will be done during subsequent performance periods of this project, but these refinements are not expected to alter our basic conclusion that sufficient borate reserves are available for automotive hydrogen storage needs.

Conclusions and Future Directions

Future Directions

- Further refinement of boron global reserve data.
- Analysis of important questions regarding industry impacts of hydrogen storage technologies and market parameters, including:
  - Impacts on competing uses.
  - Impacts on borate prices.
- Prepare larger set of borate esters of several categories for regen studies at PNNL.
- Conduct spent fuel digestion studies.
- Regen cycle validation in collaboration with PNNL.

FY 2009 Publications/Presentations

1. Two quarterly reports were submitted to the DOE.

2. This project was presented for peer review at the DOE Annual Review Meeting in Washington, D.C. in May, 2009.

References

1. *Mineral Commodities Summaries*, U.S. Geological Survey, U.S. Gov. Printing Office, Washington, D.C. 2009, p 34-35.

2. *Borates: A Handbook of Deposits, Processing, Properties, and Use*, D.E Garret, Academic Press, San Diego, CA, 1998, p 442.

3. *The Economics of Boron – 11th Edition*, Roskill Information Services: London, England, 2006, Chapters 1 & 2.