

# ***Ammonia borane regeneration and market analysis of hydrogen storage materials***

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U.S. Borax Inc.

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Project ID # ST\_21\_Schubert



# Overview

## Timeline

- Start date: Oct 1, 2008
- End date: Sep 30, 2010
- Percent complete: 25%

## Budget

- Total project funding
  - DOE: \$600K
  - Contractor share: \$347K
- Funding received in FY09: \$75K
- Funding for FY10: \$225K

## Barriers

- Cost
- Efficiency
- System Life Cycle Assessment
- Regeneration

## Partners

- Pacific Northwest National Lab
- Los Alamos National Lab
- Rohm & Haas Co.



# Relevance

## Objectives

### *New Project*

- **Regeneration:** Need to maximize efficiency of off-board regeneration of ammonia borane fuel
  - Need recyclable thermodynamically favorable intermediates
  - Collaborate with PNNL and other Center partners to maximize efficiency of spent fuel regeneration
  - Tune chemistry of borate esters as hydride acceptors in PNNL's cycle
- **Boron Resources:** Understanding of global supplies of boron ore resources required for hydrogen storage
  - Develop better understanding of global supplies of boron ore resources required for hydrogen storage
  - In addition to boron, resource model developed will be applicable to other materials of interest for hydrogen storage, e.g., Li, Mg

## Impact

- Results of collaboration expected to enable practical regeneration of ammonia borane fuel to meet needs of large automotive fleet
- Borate resource analysis is critically important to feasibility of chemical hydrogen storage as well as many proposed metal hydride systems

## Milestones

- Q109-Q309: Synthesis of selected set of borate esters and borate resource analysis
- Q309-forward: Digestion studies, regen cycle fine tuning and market impact analyses

## Deliverables

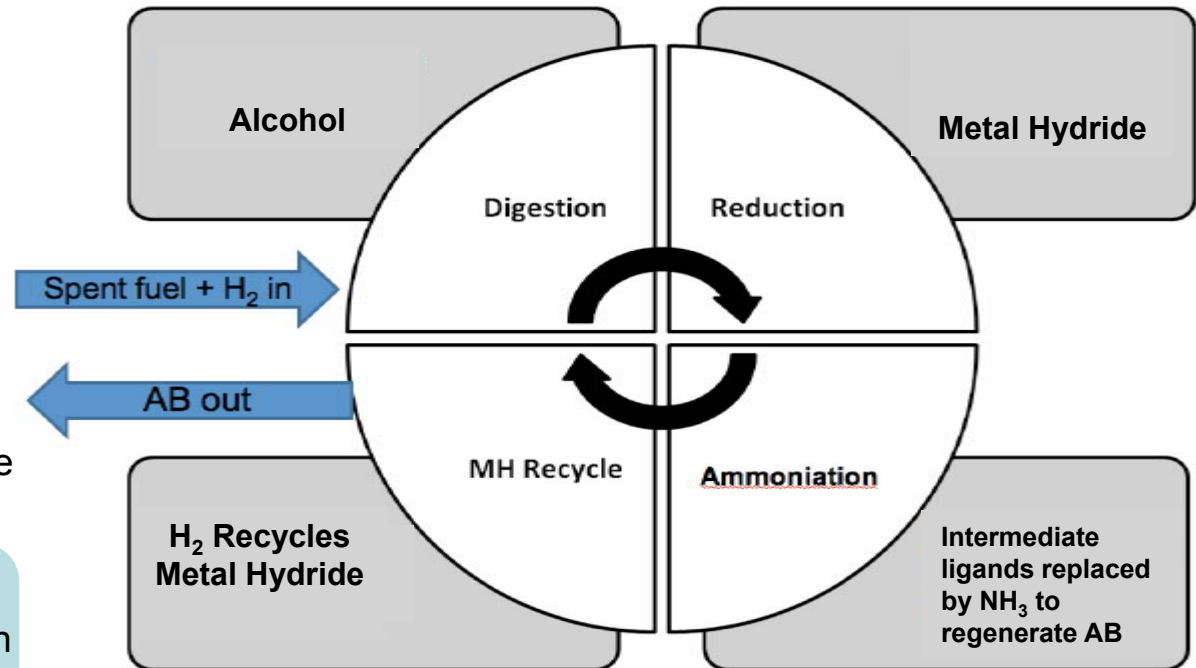
- Analysis of global borate reserves and impacts of hydrogen storage technology deployment on market parameters, including competing uses and borate prices
- Synthesis of supply to PNNL of selected borate esters compounds and spent fuel digestion studies

# Technical Approach

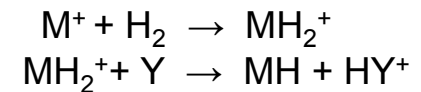
## Regeneration of ammonia borane (AB) spent fuel

- PNNL's proposed regen cycle has high theoretical efficiency
- Use of 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

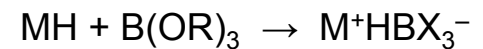
Approach focuses on tuning the chemistry of the critical digestion and reduction steps of the regen cycle



Metal hydride formation

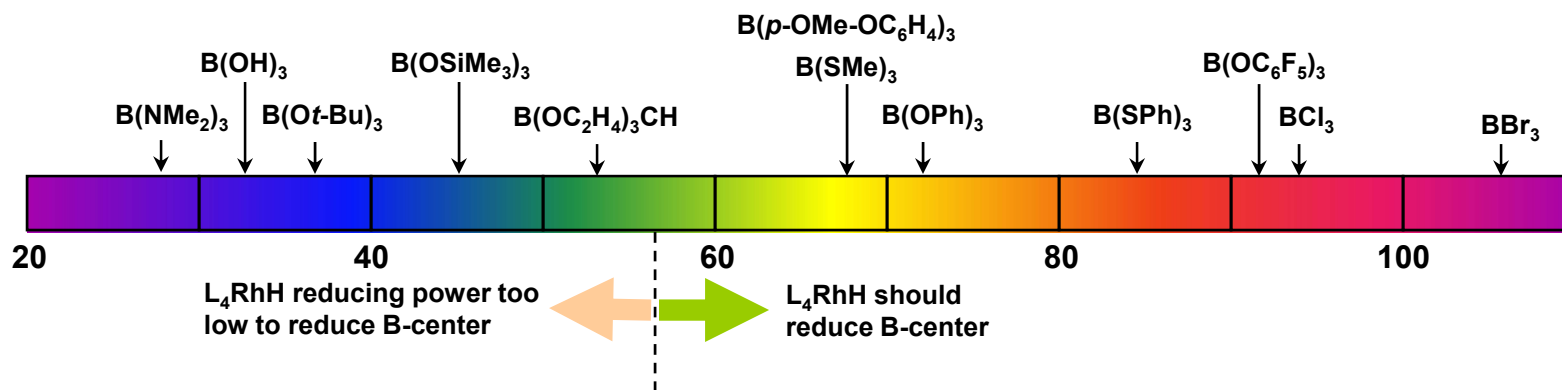


Hydride transfer



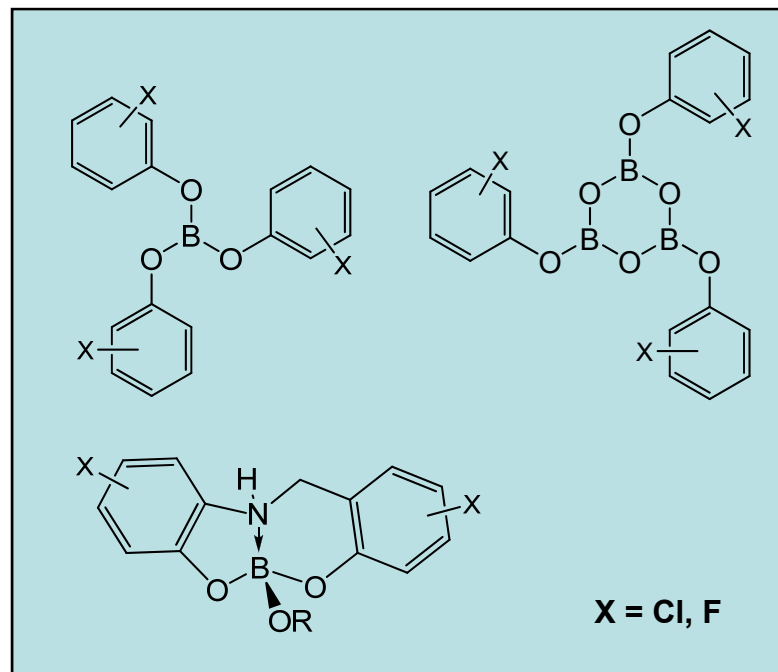
# Technical Approach

## Absolute hydride affinities of $BX_3$ compounds based on gas phase calculations



- AB regeneration pathway requires spent fuel digestion intermediate having sufficient hydride affinity for reduction by metal hydride
- U.S. Borax 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

**Approach will validate theory and practical process**



# Approach: Borate Reserves and Chemical Hydrogen Storage

## 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*
- Published estimates from U.S. Geological Survey are much lower than other reports
  - *80 Mmt B<sub>2</sub>O<sub>3</sub> globally compared with approximately 1,000 Mmt B<sub>2</sub>O<sub>3</sub>.*
  - *Significantly underestimates both U.S. and Turkish reserves*
- Anticipated consumption of reserves from competing uses through projected initial fill timeframe (2009 → 2050) should be included in estimates

### Model for Boron Demand

360 million FCVs  
57.5 miles/kg H<sub>2</sub>\*  
400 mile range per tank  
12,000 miles per year per vehicle\*  
1 month supply in infrastructure  
15% H<sub>2</sub> storage in AB  
No losses (100% recycle)

\* from H2A model

### Sources:

*Borates: A Handbook of Deposits, Processing, Properties, and Use*  
D.E Garret, Academic Press  
*The Economics of Boron – 11<sup>th</sup> Edition*  
Roskill



# U.S. Borax Inc. borate mine at Boron, California



## Important borate minerals



**Tincal**  
 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$



**Kernite**  
 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$

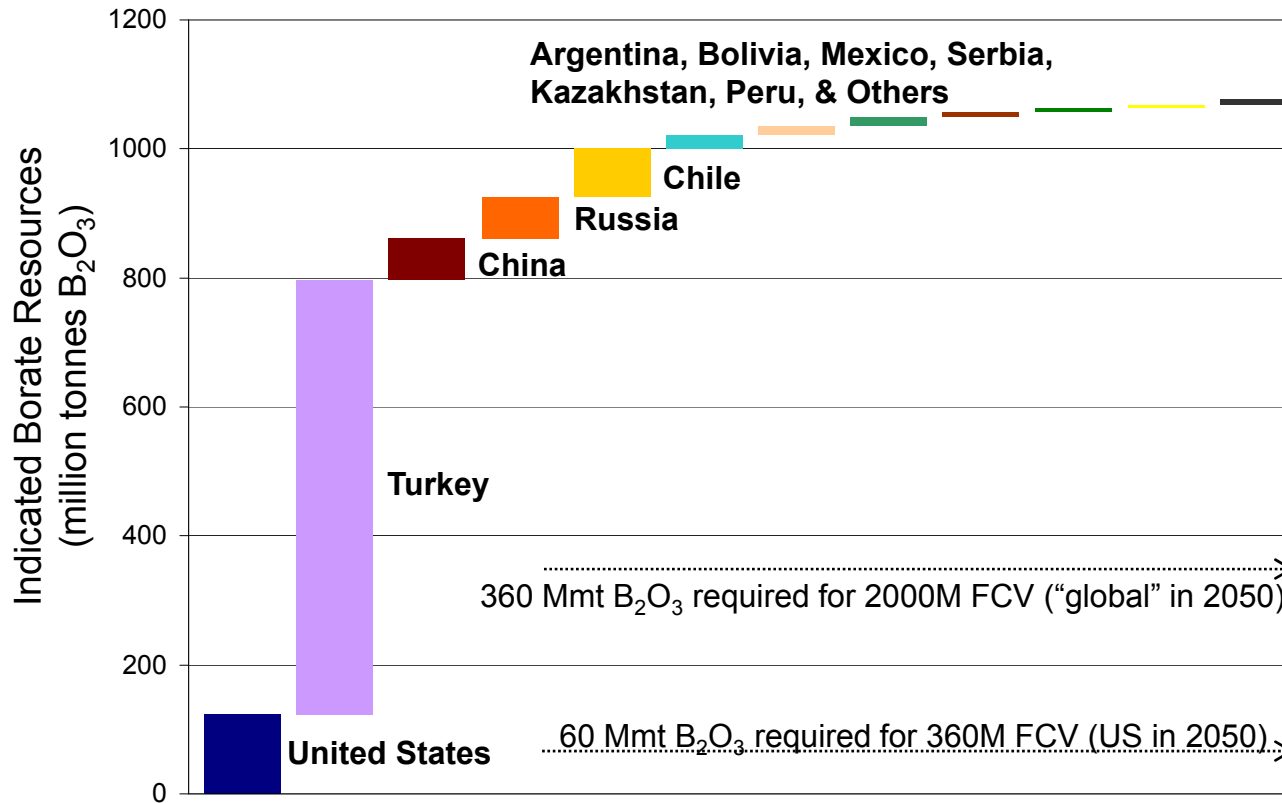


**Ulexite**  
 $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$



**Colemanite**  
 $\text{Ca}_2\text{B}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$

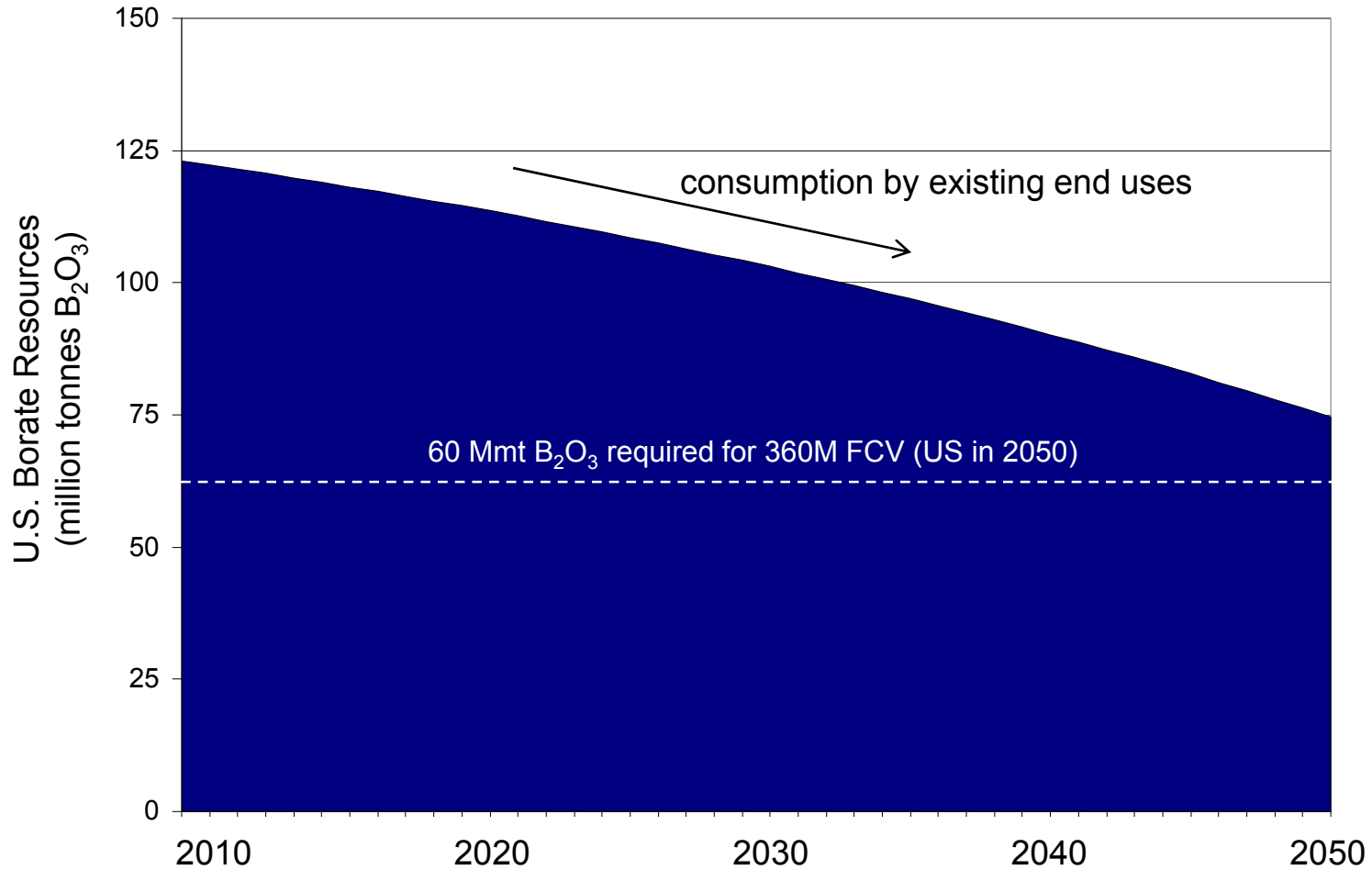
# Progress: Borate Reserves and Chemical Hydrogen Storage



*Present day known global borate resources are sufficient for U.S. and global hydrogen storage needs*



# Progress: Borate Reserves and Chemical Hydrogen Storage



*Even with some reserves consumed by existing end uses it is possible to meet US hydrogen demand solely with US borate reserves*

# Accomplishments

## Resource Analysis

- Review and analysis of published data sources on known borate world deposits completed
- Initial assessment of global borate resources completed (>1 billion B<sub>2</sub>O<sub>3</sub> tonnes available)
- Assessment of projected depletion of borate reserves by non-hydrogen storage demands completed
- Estimate of global borate ore reserves are determined to be sufficient for hydrogen storage needs, as well as and other projected industrial demands

## Regen Studies

- New laboratory program initiated
- General laboratory methods for borate ester synthesis developed
- Initial set of borate esters for regen testing supplied to PNNL

### Examples

#### *Orthoborate esters:*

- Tri-(2-halophenyl)borate
- Tri-(3,5-dihalophenyl)borate
- Tri-(4-halophenyl)borate
- Tri-(3,4,5-trihalophenyl)borate
- Analogous boroxine esters
- Chelated borate esters in progress

# Collaborations

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## Pacific Northwest National Lab (PNNL)

U.S. Borax is working closely with PNNL

- Synthetic work on borate esters is guided by computations done at PNNL
- Spectroscopy and hydride transfer experiments using compounds supplied by U.S. Borax are being carried out at PNNL

## Los Alamos National Lab (LANL)

LANL is coordinating efforts on AB regeneration. U.S. Borax participates in regular conference calls and technical discussions organized by LANL

## Rohm & Haas Company

Boron resource and market data generated by this project will be used in on-going cost, efficiency, and life cycle analyses conducted by Rohm & Haas

*This is a highly collaborative project integrated into the overall Chemical Hydrogen Storage program*



# Future Work

## Resource Analysis

- 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

## Regen Studies

- Synthesis of larger set of borate esters of several categories for regen studies at PNNL
- Spent fuel digestion studies
- Regen cycle validation in collaboration with PNNL

## Other Activities

- Analytical Support
- Safety Analysis and Consultation

# Project Summary

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- Relevance:**
- (1) Collaborate with partners to optimize practical regeneration pathways for ammonia borane (AB) hydrogen storage fuel
  - (2) Quantify boron raw material resources required for hydrogen storage

- Approach:**
- (1) Synthesis of large set of borate esters of several types to serve as prototypes AB regen intermediates to validate theory. Done in collaboration with PNNL

- Progress:**
- (1) U.S. Borax has begun supplying borate esters to PNNL for testing
  - (2) First order estimation of U.S. and global borate reserves completed, taking into account consumption by competing applications through initial fill timeframe

**Technology Collaborations:** PNNL, LANL, and Rohm & Haas Co.

## Proposed Future Research:

- (1) Synthesis of larger set of borate esters for regen studies at PNNL, spent fuel digestion studies, and regen cycle validation
- (2) Further refinement of boron reserve data and analysis of impacts of hydrogen storage on competing uses and prices

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