Ammonia borane regeneration and market analysis of hydrogen storage materials

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U.S. Borax Inc.

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Project ID #ST043 Schubert

Overview

Timeline

- Start date: Oct 1, 2008
- End date: Sep 30, 2010
- Percent complete: 80%

Budget

- Total project funding
  - DOE: $600K
  - Contractor share: $347K
- Funding received in FY09: $346K
- Funding for FY10: $254K

Barriers

- Cost
- Efficiency
- System Life Cycle Assessment
- Regeneration

Partners

- Pacific Northwest National Lab
- Los Alamos National Lab

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Relevance

Objectives

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
- Analyze impacts on borate industry, competing uses, and borate prices

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-Q310: Digestion studies, regen cycle fine tuning and market impact analyses

Deliverables

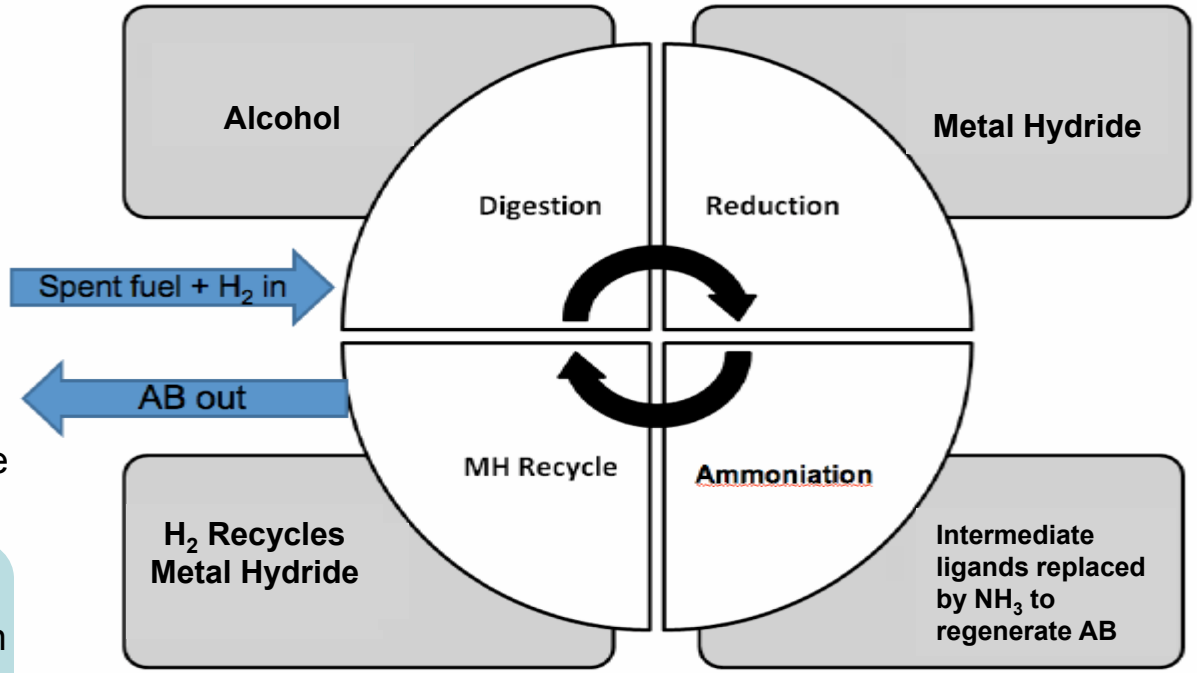
- Analysis of global borate reserves and impacts of hydrogen storage technology deployment on market parameters, including competing uses and borate prices
- Synthesis of supply to PNNL of selected borate esters compounds and spent fuel digestion studies

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

$$M^+ + H_2 \rightarrow MH_2^+$$
$$MH_2^+ + Y \rightarrow MH + HY^+$$

Hydride transfer

$$MH + B(OR)_3 \rightarrow M^+HBX_3^-$$

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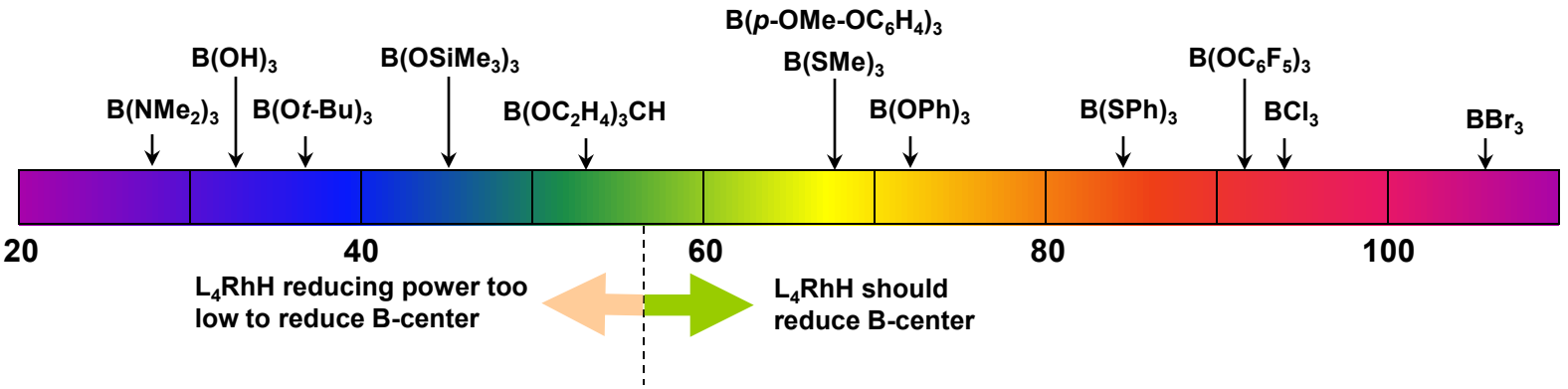
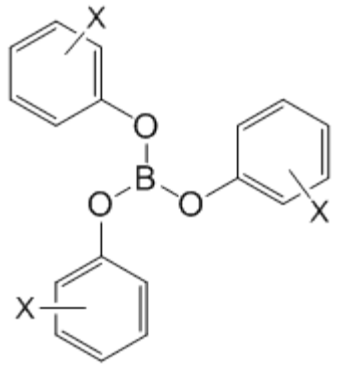
Approach

PNNL Gas Phase Calculations of Hydride Affinity (-Δ*H*): $BX_3 + H^- \rightarrow HBX_3^-$



- AB regeneration pathway requires spent fuel digestion intermediate having sufficient hydride affinity for reduction by metal hydride
- U.S. Borax targeted a large set of borate esters to supply to PNNL for experimental validation of theory and regen process
- Approach impacts likelihood of success of PNNL's regen system and validate theory



X = F, Cl, Br, I

Approach validates theory and practical process

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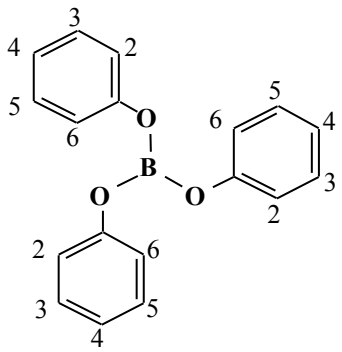
Technical Accomplishments – Regen Studies

$3\ PhOH + B(OH)_3 \rightleftharpoons B(OPh)_3 + 3\ H_2O$



- Aryl borate esters were synthesized and their purity verified by NMR spectroscopy
- Analysis of these borate esters in collaboration with PNNL complimented and aided PNNL's computational work on regen models

Fluoro	**Chloro**	**Bromo**	**Iodo**
2-F	2-Cl	4-Br	4-I
3-F	3-Cl		
4-F	4-Cl	**Mixed**	
2,3-F	2,3-Cl	2-F,4-Br	
2,4-F	2,4-Cl	2-F,4-Cl	
2,6-F	2,6-Cl	2-F,6-Cl	
3,4-F	3,4-Cl	3-F,4-Cl	
3,5-F	3,5-Cl		
3,4,5-F	2,4,5-Cl		
2,3,4,5,6-F	2,4,6-Cl		

A library of 25 high purity borate esters have been synthesized to enable a more thorough understanding of substituent effects on ester properties

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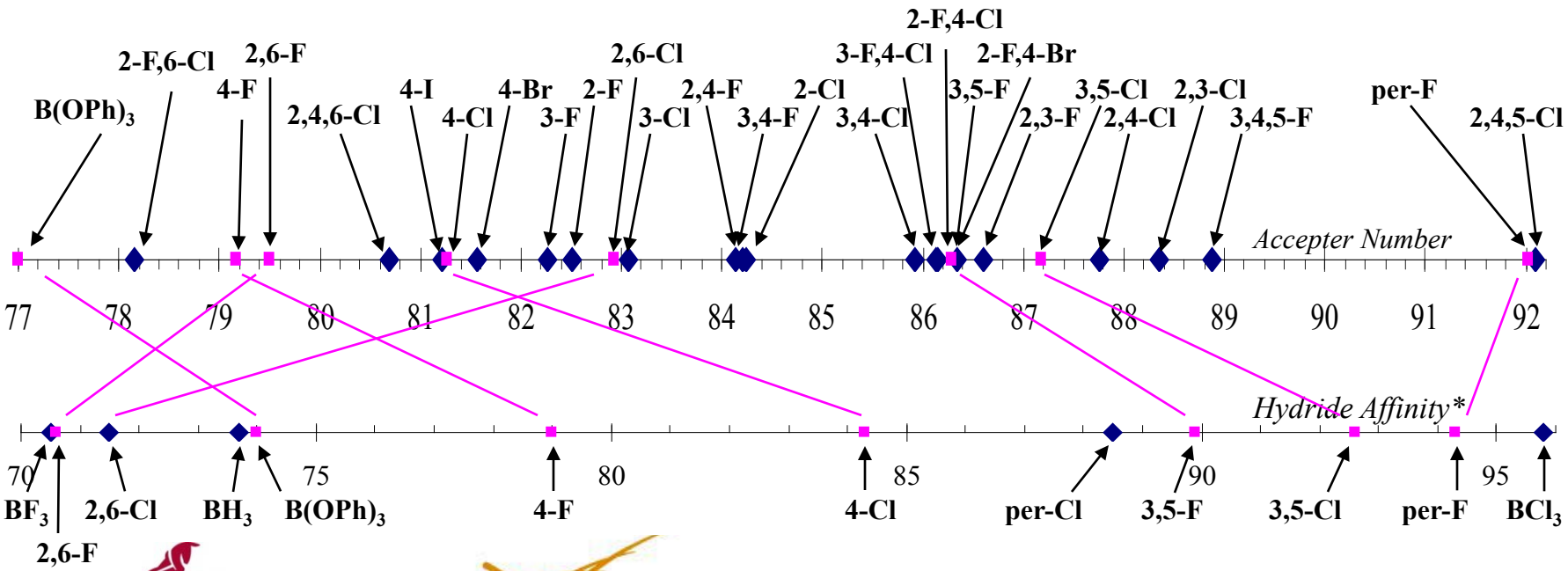
Technical Accomplishments – Regen Studies

$Et_3PO + B(OPh)_3 \rightleftharpoons Et_3PO–B(OPh)_3$

Phosphine oxide – ester adducts were synthesized to measure acceptor numbers

- *Acceptor numbers* were measured from NMR data ($\Delta\delta$ ^{31}P) of each adduct
- An *acceptor number* is a measure of *Lewis acidity* – an indicator of *hydride affinity*



*PNNL Gas Phase Calculations of Hydride Affinity ($-\Delta H$): $BX_3 + H^- \rightarrow HBX_3^-$

Technical Accomplishments – Regen Studies

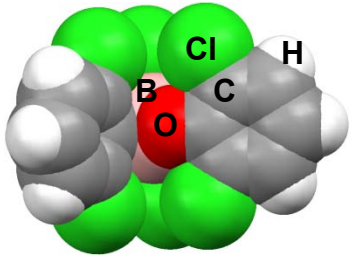
- Three effects of halogen substitution on the Lewis acidity of aryl borate esters were elucidated

Lewis Acidity by Substituent:

Identity: Br > Cl ≥ I > F > H
Quantity: 5 > 3 > 2 > 1 > 0
Position: 2 > 3 > 4

- These factors are in agreement with and validate PNNL computational models

- An additional effect on the measured Lewis acidity is the steric effect



- With substituents in both 2 and 6 positions, the measured Lewis Acidity is much greater than PNNL computational models predict

- Substitution at both the 2 and 6 positions was found to hinder adduct formation, while substitution at only the 2 position did not

These effects are key to tailoring aryl borate esters with desired properties to optimize the metal hydride reduction step of PNNL's proposed regen cycle

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Technical Progress – Regen Studies

- Recent efforts have shifted to producing borate esters from spent fuel (SF), requiring a large, well characterized batches of SF
- U.S. Borax has safely produced SF (>5 g) from 10-g amounts of ammonia borane
- Through direct methods of analysis two types of SF have been characterized:

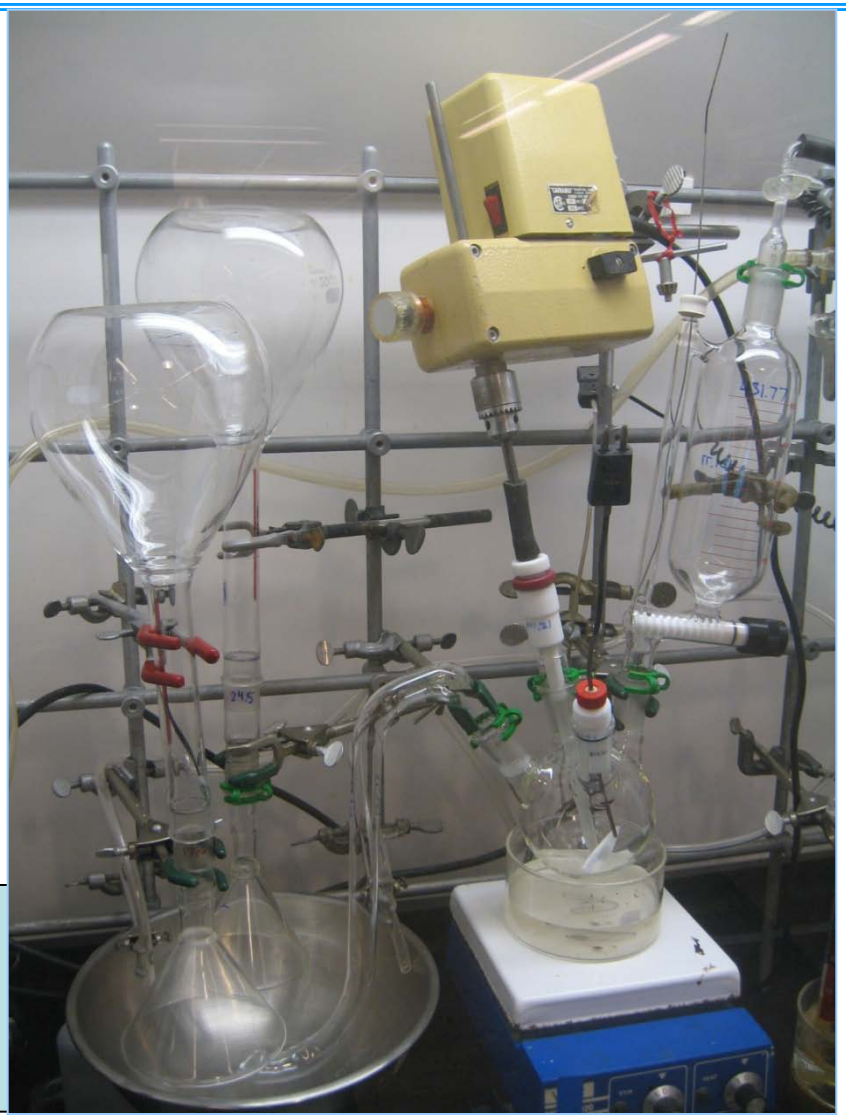
<u>SF produced in absence of oxygen</u>

$N_{0.97}H_{1.20}BH_{0.56}O_{0.23}$
$N_{1.07}H_{0.84}BH_{0.43}O_{0.19}$

<u>SF produced in absence of oxygen and water</u>

$N_{1.09}H_{0.87}BH_{0.41}O_{0.10}$
$N_{1.12}H_{0.84}BH_{0.46}O_{0.092}$

Batches of spent fuel have been made and characterized with Analytic Support provided to PNNL



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

Important borate minerals

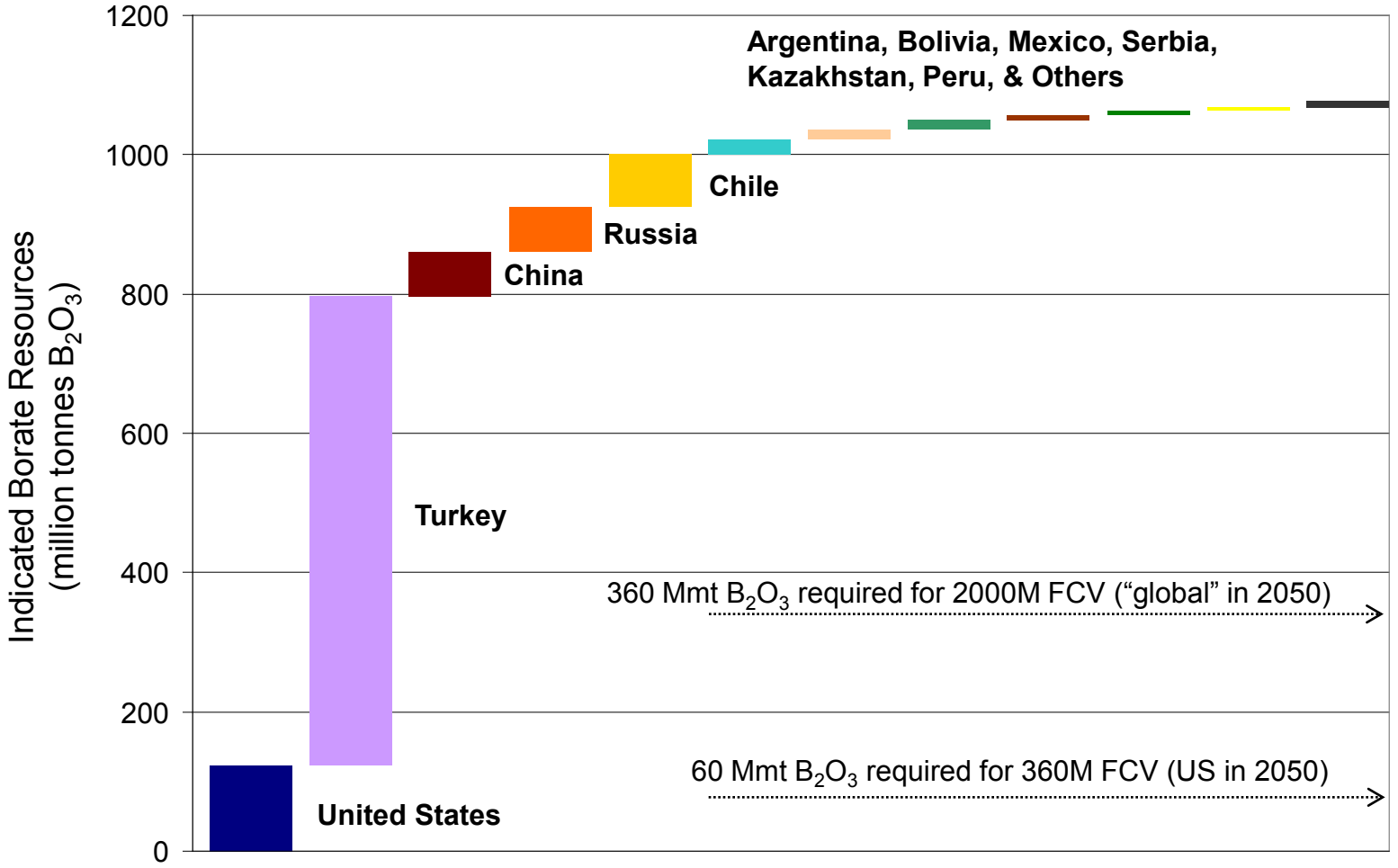
Tincal
$Na_2B_4O_7 \cdot 10H_2O$

Kernite
$Na_2B_4O_7 \cdot 4H_2O$

Ulexite
$NaCaB_5O_9 \cdot 8H_2O$

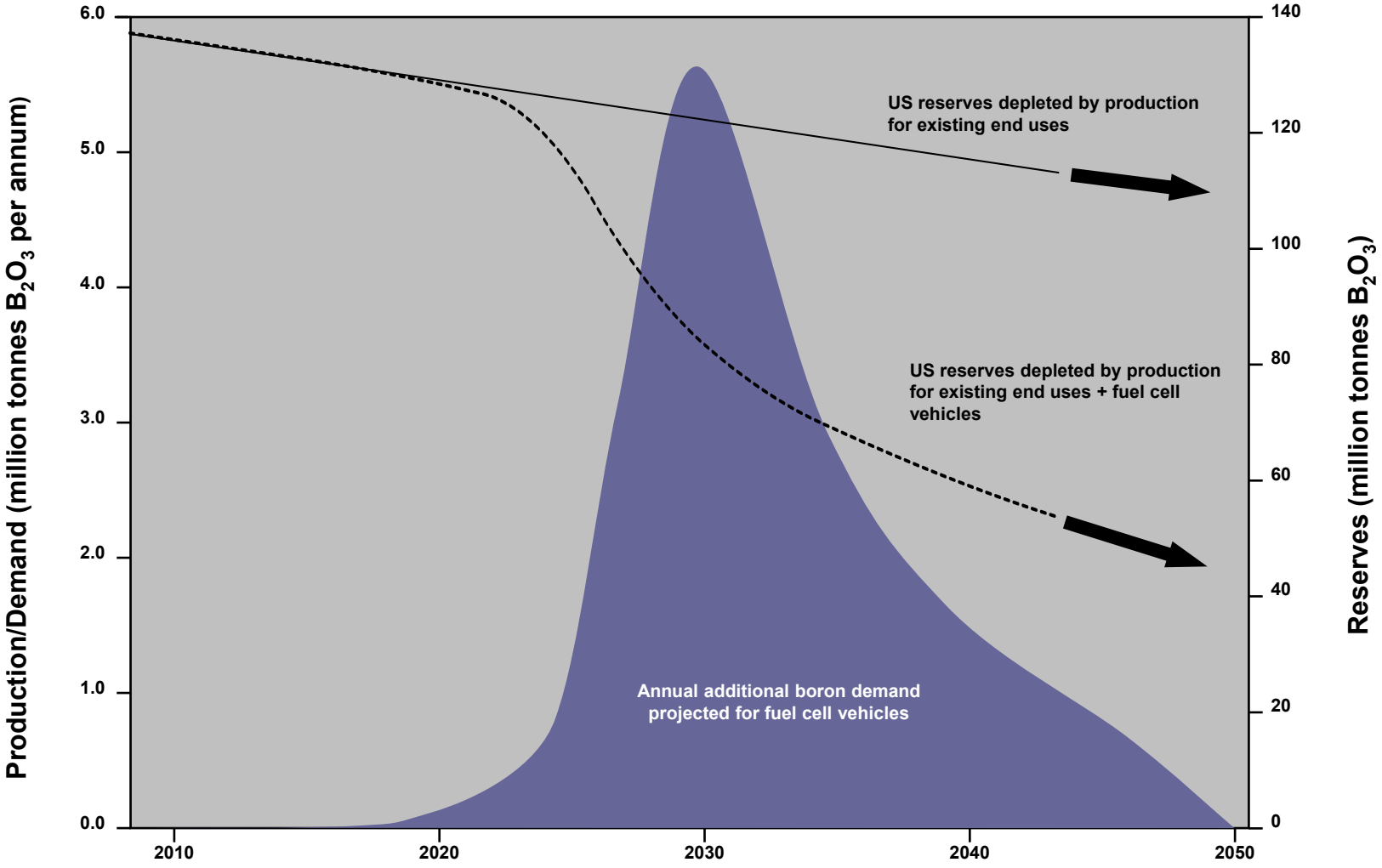
Colemanite
$Ca_2B_5O_8 \cdot 5H_2O$

Progress: Borate Reserves and Chemical Hydrogen Storage



Further refinement of present day known global borate resources are sufficient for U.S. and global hydrogen storage needs

Technical Progress – Resource Analysis



Collaborations

- **Pacific Northwest National Laboratory (PNNL)**

  The project has involved extensive collaboration with PNNL:

  – Experimental samples prepared at U.S. Borax were supplied to PNNL for further testing

  – U.S. Borax personnel spent time working at PNNL during 2009 to carry out project critical experiments

  – Regular technical discussions have been held between U.S. Borax and PNNL staff members throughout the course of this project

- **Los Alamos National Laboratory (LANL)**

  This project also involved consultation with LANL staff members

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Proposed Future Work

Resource Analysis

- Further refinement of boron global reserve data
- Further analysis of important questions regarding industry impacts of hydrogen storage technologies and market parameters, including:
  - Impacts on borate manufacturers
  - Impacts on competing uses
  - Impacts on borate prices

Regen Studies

- Spent fuel digestion studies
- Regen cycle validation in collaboration with PNNL

Other Activities

- Analytical Support
- Safety Consultation

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Project Summary

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

Approach: (1) Synthesized extensive set of borate esters to serve as prototype AB regen intermediates to validate theory. Done in collaboration with PNNL

Progress: (1) U.S. Borax has supplied a large set of pure borate esters to PNNL for testing
(2) Large batches of spent fuel have been made and characterized
(3) Analytic support provided to PNNL for spent fuel characterization
(4) Digestion studies have been initiated
(5) 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

Proposed Future Research:
(1) 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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