PNNL Progress as Part of the Chemical Hydrogen Storage Center of Excellence

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Overview

Timeline
• Start 3/2005
• End 9/2010
• 95% Complete

Budget
• FY09: $2350K
• FY10: $1910K

Barriers Addressed
• Volumetric Density
• Gravimetric Density
• Hydrogen Release Rate
• Fuel Cost
• Fuel Cycle Energy Efficiency
• Hydrogen Purity

Collaborations

[Logos of collaborating organizations]
Objectives

- Develop materials & methods for low temperature release of pure hydrogen from chemical hydrides with potential to achieve DOE targets
  - Develop hydrogen release mechanism from MAB
  - Focus on quantitative measurements of impurities in $H_2$.
- Demonstrate high efficiency methods for large scale synthesis of chemical hydrogen storage materials
  - Fabricate reactor to prepare bench scale quantities of ammonia borane.
- Develop high efficiency off-board methods for chemical hydride regeneration with potential to achieve DOE targets
- Support collaborators through expertise in chemistry & characterization to determine the kinetics & thermodynamics of hydrogen release and regeneration of H-storage materials
  - Work with Center partners to characterize materials and novel approaches to store and release hydrogen.

Impact

- Increased assessment of materials and approaches designed to specifically address DOE barriers (volumetric & gravimetric density, H-release rates at low temperatures, $H_2$ purity, fuel cost and fuel cycle energy efficiency)
Approach

• Solid State Chemical Hydrogen Storage
  – Combine experimental & computational approaches with process engineering to develop a mechanistic understanding of H-release from amine boranes, their regeneration from spent fuels, and an understanding of costs.
  – Kinetics and thermodynamic property measurements for hydrogen release and regeneration of spent fuels
  – **Experimental**: NMR and Raman Spectroscopy, XRD, TG/DSC/MS, PCI, Volumetric analysis. Mass spec, NMR, IR, and titration to determine and quantify impurities
  – **Computational**: Electronic structure theory (DFT, MP2 & G3) to understand structural relationships and continuum solvation models to understand solvation effects
  – **Process Engineering**: Engage engineers early to understand costs.

Solid phase chemical hydrogen storage materials studied

\[
\begin{align*}
\text{NH}_4\text{BH}_4 & \Leftrightarrow \text{BNH}_x + \text{H}_2 & (240 \text{ g H}_2/\text{kg}, 130 \text{ g H}_2/\text{l}) \\
\text{NH}_3\text{BH}_3 & \Leftrightarrow \text{BNH}_x + \text{H}_2 & (195 \text{ g H}_2/\text{kg}, 140 \text{ g H}_2/\text{l}) \\
[\text{NH}_3\text{BH}_2\text{NH}_3]\text{[BH}_4\text{]} & \Leftrightarrow \text{BNH}_x + \text{H}_2 & (195 \text{ g H}_2/\text{kg}, 140 \text{ g H}_2/\text{l}) \\
\text{LiNH}_2\text{BH}_3 & \Leftrightarrow \text{LiBNH}_x + \text{H}_2 & (109 \text{ g H}_2/\text{kg}, 52 \text{ g H}_2/\text{l}) \\
\text{NaNH}_2\text{BH}_3 & \Leftrightarrow \text{NaBNH}_x + \text{H}_2 & (76 \text{ g H}_2/\text{kg}, 43 \text{ g H}_2/\text{l})
\end{align*}
\]
PNNL’s path of progress through the AB Forest

- Started with AB
  - $\text{H}_2$, non toxic, low T release
  - **BUT**- borazine (Bz) release and foam, SO…

- Scaffolds – **discontinue**
  - MCM – **discontinue**
  - ↓ Bz, ↓ foaming, ↓ T release and ↓ $\text{H}_2$ content
  - ↑ AB loading ↓ stability
  - Carbon and MOF (with Channing) ↓ stability **discontinue**
  - BN ↑ stability, ↑ Bz **discontinue** (with UC Davis)

- Additives- **continue**
  - AB release mechanism studies- found additives to improve kinetics
  - AB/MH (with Graetz, Ronnebro) – **continue**
  - AB/CoCl$_2$ (with Chen- IPHE) - ↓ Bz by 10x! - **continue**
  - AB/cellulose – tested >50 mixtures, eliminated foaming - **continue**

- PNNL started metal amidoborane work and recruited IPHE partners and LANL

- $\text{H}_2$ release mechanisms (with Craig Jensen)
  - AB, DADB, AB+$\text{H}_2$ and MAB **completed**, still working on Bz formation mechanism.

- 1$^{\text{st}}$ Fill – single pot AB production developed, studies indicate can be continuous.

- Regeneration - **continue**
  - AB in concentrated solutions for regen- decomposes by 2$^{\text{nd}}$ order mechanism
  - Demonstrated steps with Rh – Rh too expensive- **discontinue**
  - Searching for non-precious metal catalyst system – **continue**

- Increased expert staffing- Abhi Karakamkar, Ewa Ronnebro (IEA), Mark Bowden (IPHE)
Solid Ammonia Borane Key Findings

- **16 H₂ wt%** (material) *usable* gravimetric capacity (system target= 9 wt%)
- **120 gH₂/L** (material) *usable* volumetric capacity (system target= 80 gH₂/L)
- **1.3 gH₂/sec/kg AB** release rate (system target = 0.022 gH₂/sec/kg)
- **Stability**
  - 50°C for over 90 days with no loss observed
  - Stable in air and water
- **Exothermic release 5 kcal/mol H₂** (first equivalent)
- **Release temperature – stepwise 90 – 160°C**
- **Additives- improve performance**
  - CoCl₂ (IPHE collaboration)
    - <1 wt% borazine
    - 60°C for release on-set – accelerated release
  - Anti-foaming additives demonstrated
- **Off-board regeneration steps demonstrated**
  - Center demonstrated multiple routes

**Recommendation – Continue Development**
# Accomplishments: Milestones FY10

<table>
<thead>
<tr>
<th>Q3</th>
<th>Complete quantitative analysis of hydrogen purity and kinetics from neat AB</th>
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</thead>
<tbody>
<tr>
<td>Q3</td>
<td>Complete quantitative analysis of hydrogen purity and kinetics from AB in nano-scaffold materials</td>
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<tr>
<td>Q3</td>
<td>First fill AB production in continuous reactor(s) scheme</td>
</tr>
<tr>
<td>Q3</td>
<td>Go/No-go recommendation on chlorinated phenols compatible with Co-H complexes for AB regeneration</td>
</tr>
<tr>
<td>Q3</td>
<td>Go/No-go recommendation on fluorinated phenols compatible with Co-H complexes for AB regeneration</td>
</tr>
<tr>
<td>Q2</td>
<td>Update flow sheets with regeneration process for Dow to perform high level cost analysis</td>
</tr>
<tr>
<td>Q3</td>
<td>Complete Go/No-go recommendation on transition metal amidoboranes, without solvents, composed of TiH$_2$ mixed with alkali and alkali earth binary hydrides</td>
</tr>
<tr>
<td>Q3</td>
<td>Determine feasibility for LiAB regeneration</td>
</tr>
<tr>
<td>Q4</td>
<td>Report on hydrogen purity from larger scale (10-100 gram) pellet reactor</td>
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</tbody>
</table>
Significant PNNL Accomplishments FY10

- Ammonia borane (AB) first fill reactor capable of 100 gram batch
  - Provided high purity AB to Center Partners
- Metal amidoborane (MAB) release mechanism identified
- Quantified impurities in H₂ from AB and demonstrated approaches to mitigate and control
- AB + metal hydride mixtures showed different features compared to AB; decreased impurities, less foaming, less exothermic release
- Demonstrated >99% boron recovery from digestion of real spent fuels
- Identified potential new ammonia synthesis route which may be able to combine first fill and regeneration with potential for lower costs and higher efficiency
- Fully characterized spent ammonia borane
- 13 peer-reviewed publications
- Over 45 peer reviewed publications in life of the project
Accomplishments: Scale-up First Fill Ammonia Borane

- **One-pot batch reactor**
  - Quantitative (isolated yields ~98%)
  - Purity ($^{11}$B NMR ~99%)
  - 100 gram batch reactor
  - Demonstrated 20 gram production
  - Provided partners with high purity AB
  - Parametric study indicated semi-flow reactor system possible and provided data for design

*Demonstrated 20 gram batch reactor with 100 gram design capacity*

*Dow’s analysis indicated that high purity and yield make PNNL’s synthesis superior to State of Art, projected cost $9.1/kg AB*
Accomplishment: Metal Amidoborane rate trend for H₂ release from MAB is exact opposite rate trend for H₂ release from Metal borohydrides

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (°C)</th>
<th>time to 0.5 equiv. H₂ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNH₂BH₃</td>
<td>LAB</td>
<td>80.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>85.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90.2</td>
</tr>
<tr>
<td>NaNH₂BH₃</td>
<td>SAB</td>
<td>70.0</td>
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<td></td>
<td></td>
<td>75.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80.2</td>
</tr>
<tr>
<td>NaNH(Me)BH₃</td>
<td>SMAB</td>
<td>95.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.2</td>
</tr>
<tr>
<td>KNH(Me)BH₃</td>
<td>PMAB</td>
<td>85.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90.2</td>
</tr>
<tr>
<td>KNH(tBu)BH₃</td>
<td>PBAB</td>
<td>130</td>
</tr>
</tbody>
</table>

The rate trend for release is K > Na > Li
Mechanism is metal assisted hydride transfer
M-N and B-H bond breakage is rate limiting step.

*International Partnership for Hydrogen Economy Project: PNNL, Dalian, RAL, Oxford, IRL, LANL
Accomplishment: Metal Amidoborane

- H₂ release from MAB *completely different mechanism* than AB
  - No “DADB”, no induction period, steep temperature dependence
  - No borazine impurity, but slightly higher ammonia.

- Regeneration
  - Using AB regen cycle
    - Need to separate the metal from the B-N
  - Other regeneration cycles not investigated yet

- XAB - new material
  - <6 wt% H₂ (doesn’t meet DOE targets)
  - Endothermic release! – shows possibilities

*MAB produces no borazine*

*Endothermic release demonstrated*

*LiAB, NaAB, and KAB discontinued*

*Work should continue with possibility of better thermodynamics in as yet unknown materials*
Accomplishment: Quantitative Direct Impurity Measurement

Our approach

- Use multiple analysis tools to quantify Borazine (Bz): NMR, FTIR, Mass spec etc.
- Develop mechanistic understanding of Bz formation
- Study effect of H\textsubscript{2} release conditions on concentration
- Use theory to understand barriers involved

Experimental set up

- Use a trap (THF/Glyme) to trap volatile impurities. Use solution NMR to measure.
- Compare as a function of heating profile
- FTIR
- TG-Mass spec/ RGA

Parametric study performed to provide detailed understanding of borazine yields
Accomplishment: Ammonia and Borazine Impurity

- **Solid AB**
  - **Ammonia:** 100-250 ppm
  - **Borazine:** 0.8 wt% - 12 wt%

- **MAB**
  - **Borazine:** 0 wt%
  - **Ammonia:** 0.2 wt%

- **Remaining work**
  - High pressure
  - No sweep
  - Filters

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**Catalysts, additives and temperature can control borazine. Ammonia is low**

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![Borazine Release at Atmospheric Pressure](image_url)
Regeneration Approach: Transition Metal Hydrides to Regenerate AB

- Hydrogen in ammonia borane is polarized ... NH₃BH₃
  - Regen spent fuel by addition of H⁺ and H⁻
- Use transition metal to catalyze heterolysis of H₂
  \[ \text{H}_2 + \text{base} + \text{BX}_3 \xrightarrow{\text{LnM}^+} \text{HBX}_3^- + \text{H}^+\text{base} \]
- Metal complex activates H₂
  \[ \text{LnM}^+ + \text{H}_2 \rightarrow \text{LnMH}_2^+ \]
- Base promotes formation of hydride donor, LnMH
  \[ \text{LnMH}_2^+ + \text{base} \rightarrow \text{LnMH} + \text{H}^+\text{base} \]
- LnMH transfers H⁻ to boron
  \[ \text{LnMH} + \text{BX}_3 \rightarrow \text{LnM}^+ + \text{HBX}_3^- \]
Accomplishment: Regeneration Scheme Steps Demonstrated with Rh

1) **Digestion**
   \[ \text{BNH}_n + 3 \text{ROH} \rightarrow \frac{n}{2} \text{H}_2↑ + \text{NH}_3↑ + \text{B(OR)}_3 \]
   \[ \text{B(OR)}_3 + 3 \text{PhOH} \rightleftharpoons \text{B(OPh)}_3 + 3 \text{ROH}↑ \]

2) **Transition Metal Hydride Formation**
   \[ 3 \text{M}^+ + 3 \text{H}_2 \rightarrow 3 \text{MH}_2^+ [+ \text{3 base}] \rightarrow 3 \text{MH} + 3 \text{H}^+\text{base} \]

3) **Hydride Transfer/Ligand Redistribution**
   \[ 3 \text{MH} + \text{B(OPh)}_3 \rightarrow 3 \text{M}^+ + \text{HB(OPh)}_3^- \]
   \[ 3 \text{HB(OPh)}_3^- + \text{B(OPh)}_3 + \text{Et}_3\text{N} \rightarrow 3 \text{B(OPh)}_4^- + \text{Et}_3\text{NBH}_3 \]

4) **Recycle**
   \[ \text{B(OPh)}_4^- + 3 \text{H}^+\text{base} \rightarrow 3 \text{PhOH}↑ + 3 \text{base} + 3 \text{B(OPh)}_3 \]

5) **Ammoniation**
   \[ \text{Et}_3\text{NBH}_3 + \text{NH}_3 \rightarrow \text{BH}_3\text{NH}_3↓ + \text{Et}_3\text{N} \]

*Demonstrated with Rh(dmpe)$_2^+$ and Verkade’s super base*

...Efforts directed to systems using non-precious metals.

*ANL analysis: 22-37% efficiency*
Accomplishment: Digestion of spent fuel achieving high B recovery

- Boron recovered:
  - 85% as B(OEt)_3 ... still optimizing.
  - white solid bi-product ...
    - all convertible to B(OAr)_3.
  - >99% B recovery possible

- New digestion reagent, NH₄BF₄.

  \[
  \text{BNH}_x \xrightarrow{\text{NH}_4\text{BF}_4, \text{THF}} \text{NH}_3\text{BF}_3
  \]

  - “HF” transfer
  - Et₃NBF₃ reduced with RhH
  - potentially lower processing cost

  \[
  4 \text{Et}_3\text{NBF}_3 + 3 \text{(dmpe)}_2\text{RhH} \xrightarrow{50^\circ, 1h} \text{Et}_3\text{NBH}_3 + 3 \text{(dmpe)}_2\text{RhBF}_4
  \]

\text{B recovered in high yield}

\text{Novel digestion by NH}_4\text{BF}_4, \text{ potential to lower cost}
Accomplishment: Co and Ni Catalysts

FY08-FY09 developed and validated tools

Predicts hydride formation (Step 2)

Accomplishment: Co and Ni Catalysts

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

Substitution at Both 2 and 6 Positions:
Cl: hinders Et₃PO coordination as observed for 2,6-Cl and 2,4,6-Cl
F: effect not as obvious based on data from per-F ester

Various Et₃PO-B(OAr)₃ Adducts:
Top Axis: Δδ ³¹P ppm
Middle Axis: Gutmann’s Acceptor Numbers
Bottom Axis: Gas Phase Calculations of Hydride Affinity (-ΔH): BX₄ + H⁺ → HBX₄⁻

Predicts hydride formation (Step 2)

H⁺base ↔ H⁺ + base

Predicts hydride transfer (Step 2,3)

FY10: Using the tools, identified halogenated phenyl borates for testing with CoH and NiH⁺

Co de-chlorinates chlorophenyl borates – discontinue

Fluorinated phenyl borates do work with Co - continue

Nickel being evaluated for both Cl and F compounds

Accomplishment: Co and Ni Catalysts
Accomplishment: New 1st Fill Route, Potential new Regen Route

- PNNL 1\textsuperscript{st} fill route produces H\textsubscript{2} as byproduct.

\[
\text{NH}_4\text{Cl} + \text{NaBH}_4 \xrightarrow{\text{NH}_3/\text{THF}} \text{NH}_3\text{BH}_3 + \text{NaCl} + \text{H}_2
\]

- 25 \% efficiency hit.

Direct synthesis of R\textsubscript{3}NBH\textsubscript{3}

- Avoids inefficiency of using NaBH\textsubscript{4}
- Uses Al\textsuperscript{°} more efficiently

Potential to reduce 1\textsuperscript{st} Fill Cost
Recommend- Direct conversion of Al-OPh to Al-H – we have ideas
Potentially applicable to both Regen and 1\textsuperscript{st} Fill
Summary

Release
- Metal Amidoborane
  - Mechanism determined
  - XAB- endothermic release demonstrated
- Quantified Borazine and Ammonia Impurity
  - Borazine impurity is dependent on temperature
  - Temperature above 160°C increase borazine from <2wt% to 12wt%
  - Additives can decrease borazine at T>160°C (<1wt%)
  - AB ammonia 100-250ppm
  - MAB – 0wt% borazine, 2000ppm ammonia

First fill Ammonia Borane scale up
- 20 g scale demonstrated with potential for 100 g scale
- Parametric studies to understand engineering scale up
- Semi-continuous flow reactor being designed.

Regeneration
- Characterized spent fuel
- Demonstrated regeneration steps
- High boron recovery from real spent fuel digestion
- Novel digestion with NH₄BH₄ - potential to lower cost
- With US Borax, identified possibilities to regen with Co and Ni.
- Identified potential First Fill Route
  - Uses Al° more efficiently and Avoids inefficiency of using NaBH₄
  - Less expensive First Fill
- Can we directly go from Al-OPh to Al-H?
  - Potential to combine Regen with First Fill into 1 plant
## Accomplishments: Summary Table H₂ Release

<table>
<thead>
<tr>
<th>compound</th>
<th>gravimetric g H₂/kg</th>
<th>volumetric g H₂/l</th>
<th>additive</th>
<th>enthalpy kJ/mol</th>
<th>peak rate g/s/kg</th>
<th>temperature C</th>
<th>NH₃ ppm</th>
<th>Bz</th>
<th>notes</th>
<th>Continue?</th>
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</thead>
<tbody>
<tr>
<td>NH₃BH₃</td>
<td>194 (160)</td>
<td>146 (120)</td>
<td>none</td>
<td>-23</td>
<td>1.3</td>
<td>160</td>
<td>100-250</td>
<td>4-12</td>
<td>foams</td>
<td>C</td>
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<tr>
<td>NH₃BH₃</td>
<td></td>
<td></td>
<td>none</td>
<td>-23</td>
<td>0.93</td>
<td>145</td>
<td>100-250</td>
<td>2-4</td>
<td>foams</td>
<td></td>
</tr>
<tr>
<td>NH₃BH₃</td>
<td></td>
<td></td>
<td>none</td>
<td>-23</td>
<td>0.43</td>
<td>130</td>
<td>100-250</td>
<td>2-4</td>
<td>foams</td>
<td></td>
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<tr>
<td>NH₃BH₃ + AF</td>
<td>155 (136)</td>
<td>117 (102)</td>
<td>anti foaming</td>
<td>-23</td>
<td>0.43</td>
<td>130</td>
<td>100-250</td>
<td>2-4</td>
<td>no foam</td>
<td>C</td>
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<tr>
<td>NH₃BH₃</td>
<td>155</td>
<td>117</td>
<td>CoCl₂</td>
<td>?</td>
<td>?</td>
<td>60</td>
<td>?</td>
<td>0.8</td>
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<td>scaffold (1:1)</td>
<td>-1 (-22)</td>
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<td>130</td>
<td>100-250</td>
<td>&lt;1</td>
<td>no foam</td>
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<td>?</td>
<td>130</td>
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<td>&lt;1</td>
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<td>1.8</td>
<td>145</td>
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<td>52</td>
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<td>?</td>
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<td>130</td>
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<td>2000</td>
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<td>2000</td>
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<td>43</td>
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<td>?</td>
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<td>80</td>
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<td>0</td>
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<tr>
<td>KNH(‘Bu)BH₃</td>
<td>15</td>
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<td>none</td>
<td>?</td>
<td>?</td>
<td>130</td>
<td>?</td>
<td>0</td>
<td>no foam</td>
<td>D</td>
</tr>
</tbody>
</table>

Summary of rates, enthalpies and purity of hydrogen. theoretical density (measured density). Bz = borazine. ? = not yet measured, will be determined in future work. All compositions tested are not shown. C= Continue, D = Discontinue for on or off board transportation systems, still may be applicable for stationary or portable applications.
## Collaborative Activities

### Chemical Hydrogen Storage Center of Excellence
- UCD - study AB on nanoBN
- Penn - NMR and calorimetry support to Penn
- UW - measure $\Delta H$ for catalytic AB
- UO - measure $\Delta H$ for CBN compounds
- Dow - develop cost est. for 1st fill & regen
- Alabama - develop solvation models & benchmarking thermochemistry
- USB - characterize novel BX$_3$ esters

### IPHE
- Dalian Institute of Chemical Physics (China), Industrial Research Limited (New Zealand), Rutherford Appleton Laboratory (UK), Oxford (UK), LANL - study properties of metal amido boranes

### Independent Projects
- H2 Tech - best practices for chemical hydrides

### Materials ‘Reactivity’ Program
- Dedrick (SNL) and Anton (SRNL) - understand reactivity properties of AB
- Dedrick - study impurities in H$_2$

### Independent Analysis
- Dow and Alabama with ANL and TIAX - provide parameters for regen cost and efficiency analysis
Future Work – Center Ends FY10
Remaining issues / recommendations

▶ AB 1st fill
  ● Batch to continuous reactor approaches

▶ Solid forms
  ■ Enhance H₂ purity
    ● Reduce or avoid borazine formation (preliminary results for additives promising)
    ● Impact of increased pressure
    ● Spent fuel as a borazine filter
  ■ Fuel blends (AB mixed with other H-storage materials)
  ■ Heat/mass transfer effects in pellets (exothermic kinetic benefit)

▶ Regeneration
  ■ Complete transition metal regeneration candidate screening
  ■ Optimize the process steps
  ■ New first fill cycle evaluation
    ● Direct conversion of Al-OPh to Al-H: enable Regen and 1st Fill
  ■ Regeneration of MAB, and AB+Metal hydride mixtures
Abhi Karkamkar, Avery Luedtke, John Linehan, Wendy Shaw, Richard Zheng, Daiwon Choi, Chris Sorensen, Tricia Smurthwaite, David Heldebrant, Scot Rassat, Chris Aardahl, Don Camaioni, Michael Mock, Robert Potter, Dan Dubois, Jun Li, Jerry Birnbaum, Richard Zheng, John Linehan, Suh-Jane Lee, Ken Rappè, David Rector, Tom Autrey, Dean Matson, Ewa Rönnebro, Jamie Holladay, Mark Bowden, Doinita Neiner
Extra Slides

• Post project transition
• Publications
• Presentations
• Response to reviewer comments
• Lessons learned, a partial list
• Preliminary regen efficiency analysis (ANL)
• Characterization of spent fuel
• Summary of PNNL’s accomplishments FY06 to FY09
Post Project Transition

• Project due to end March 2010
• Final report will be submitted to DOE with recommendations for future research in chemical hydrogen storage materials
  – Materials
  – Regeneration schemes
• Hand off of properties information to Engineering CoE and other relevant DOE projects
Lesson’s Learned*

• **Pro’s to Center Concept and Structure**
  – Common platform for interactions
    • Need to have solid IP agreements and NDA’s
    • Need respectful, but frank discussions.
  – Facilitated the creative process through open discussions workshops
  – Faster progress through spreading the work around and having access to more resources
  – 5 yr funding provides stability for academic partners to attract the best students and national laboratories to attract and retain the best scientists and post docs.
  – Center partnership instilled high performance standards

• **Cons**
  – Very difficult to add new partners
  – Very difficult to remove underperforming partners
  – Very difficult to look at new ideas that are on the edge of the Center’s area
  – Certain partners take things very seriously and are responsive....others not so much. This may be the same for a collection of separate projects.

*This is just a brief summary. More in depth lesson’s learned will be in the final report.
Lesson’s Learned*

• Must haves
  – TRUST- all Center partners must respect the other partners and not “stab them in the back”. For example, before negative information about one Partner’s research or area is communicated, all partners should discuss with that partner what is being communicated and how to give them a chance to respond.
  – IP rights must be respected. Even the appearance of “stealing of ideas” will destroys trust which is a key for Center success.
  – Diverse team- theorists, experimentalists, and industry ALL giving input
  – Engage engineers/industry early and often, and use their input.
  – Strong Center Lead(s)
    • Must ensure communication between the labs
    • Must be able to keep the participants focused on the ultimate goals. It is easy to get parochial and/or side tracked.
    • Must be able to keep a level head and smooth things over when “bumps” occur
    • Must be able to kill off technologies that won’t work. It helps to be able to redirect the investigators to other areas.
  – Strong support from DOE TDM’s, who work with the Center leads and partners in directing the work.

*This is just a brief summary. More in depth lesson’s learned will be in the final report.
ANL performed energy and efficiency analysis

- Two approaches for digesting spent fuel to B(OPh)$_3$ and NH$_3$ were considered.
  - Convert residual B-H to H$_2$.
  - Preserve residual B-H bonds in (BHNH)$_n$.
- Preliminary estimate of well-to-tank efficiency is 25-47%.
  - Base and transition metal complex undefined.
  - Energy for separations in recycle of B(OPh)$_4^-$ not included.
- Approach that preserves residual B-H is ~10% more efficient.
- Analysis will be performed to determine dependence of efficiency on residual H in spent fuel, i.e., “n” in BNH$_n$. 
Process efficiency sensitive to stoichiometries, separations and heat integration

FCHtool Analysis: Well-To-Tank Efficiency

Reflex ratio

Stoichiometry

Reflex ratio

Stoichiometry

30% distillation savings

SR = 2

R = 1 0.5 0.3

SR = 3 2 1

R = 0.5

0% distillation savings

Analysis for scheme that preserves B-H in spent fuel

Hua and Ahluwalia
Characterization of spent fuel

- Prepared from gram quantities of AB
  - Heated in Parr reactor for 3 hours at 150 °C (>200 psi); cooled to 25° and flu gas vented.
  - Heated in burette system 150 °C till >2 equiv. of H₂ evolved.
- Elemental analysis and hydridic hydrogen content of spent fuel determined by US Borax.
  - Nitrogen is present in excess of boron
  - More NH than BH
- Boron content (~39 %) used to calculated yield of digestion yields.
Ammonia borane (AB) and metal hydrides - new combinations at PNNL

Candidates

- AB + Mg
- AB + CaH₂
- AB + TiH₂
- AB + MgH₂ + TiH₂
- AB + Mg(BH₄)₂
- AB + Ca(BH₄)₂

MBH₄+AB detailed analysis underway

- Isothermal
- Enthalpies / activation energy
- Molar ratio effect on properties

AB + 50 mole% MgH₂ + 10mol% TiH₂

- 7.3 H₂ wt%
- Thermal features similar to AB ‘as is’
- Release T = 88°C
- Almost no borazine or ammonia
- Much less foaming
- Less exothermic H-release observed

New features were observed – decreased borazine and foaming
Regeneration using current schemes would require separation of the metals

Work should continue with possibility of better thermodynamics in as yet unknown additives
Summary of Major Achievements in FY 05 and 06

► FY05- beginning of project
  ■ Ammonia borane studies begun
  ■ Computations show potentially high storage capacity
  ■ Synthesis of scaffolds of varying pore diameters
  ■ Flowsheets and completed for “model” systems

► FY06
  ■ Multi-scale models developed
  ■ Increased thermochemistry understanding
  ■ “Seeding” of ammonia with partially spent AB to accelerate release demonstrated
  ■ AB on scaffolds demonstrated
Summary of Major Achievements in FY 07

- **Release**
  - Developed understanding of mechanism for $\text{H}_2$ release from AB
  - Identified additives that accelerate release
  - Shown AB stability at 50/60°C and that impurities have a large impact on release
  - Explored higher loading in silica MCM-41 scaffolds

- **Regeneration**
  - Demonstrated complete digestion of solid spent fuel
  - Theory used to identify better digestion approaches
  - Theory used to build case for reduction approaches

- **Engineering Assessment**
  - Used bench scale kinetics to understand impact of 2010 rate requirements on reactor dimensions
  - Preliminary consideration of fuel morphology indicates capacity targets likely within reach
Summary of Major Achievements in FY 08

► Release
  ■ Developed Li-NH$_2$–BH$_3$ under IPHE collaboration: increased H$_2$ release kinetics by order of magnitude
  ■ Discovered additives that suppressed foaming

► Regeneration
  ■ Demonstrated hydride transfer Chemistry from activated H$_2$ to spent fuel.
  ■ Theoretical calculations now point to energy efficient regeneration approach with non-PGM reduction pathway: reduced fuel cycle costs
  ■ Preliminary flow sheets for regeneration enables identification of process knowledge gaps.
Summary Accomplishments FY09

Release …focus on stability, solid fuel forms and H₂ purity

- Stability of AB and NH₄BH₄ … short shelf life AB in solution. NH₄BH₄ stable at room temperature
- Additives… fibrous compounds preserve solid fuel morphology
- Purity of H₂ … ammonia (100-200 ppm) and borazine (~4wt%) independent of heating rate
- Metal amido boranes (LiAB) … high rates at low temperatures but stable at moderate temperatures

First fill AB Scale up

- Batch reactor to prepare AB (98/99). Minimize separations
- 10 g scale demonstrated, 100 g scale reactor next
Summary Accomplishments FY09

Regeneration ... *developed a process for regenerating AB from H₂ and demonstrated individual steps.*

- Demonstrated H₂ activation with cobalt complex and conversion to (diphos)₂CoH with base
- Demonstrated H⁻ transfer to digested fuel targets (BX₃) from (diphos)₂CoH ... readily generated with H₂ and base

- Collaborated with ANL to obtain preliminary estimate of energy efficiency for approaches that digest spent fuel to B(OPh)₃ and NH₃.
  - Convert residual B-H to H₂.
  - Preserve residual B-H bonds in (BHNH)ₙ.
  - Preliminary estimate of well-to-tank efficiency is 25-47%.
  - Base and transition metal complex undefined.
  - Energy for separations in recycle of B(OPh)₄⁻ not included.
  - Approach that preserves residual B-H is ~10% more efficient.