Low-Cost Precursors to Novel Hydrogen Storage Materials

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The Dow Chemical Company

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Project Overview

Timeline

Start: March 1, 2005

End: September 30, 2010

Percent complete: 90 %

Barriers

System cost

Regeneration processes

- Cost
- Energy efficiency
- Environmental impacts

Budget

	Total Funding	FY09 Actual	FY10 Budget*
DOE	$3,473K	$945K	$1,232K
Dow	$1,489K	$405K	$528K

Phase 2 DOE:Dow Split 70:30

Does not include DOE funding to INL ($700K) in Phase 2

Partners

Los Alamos National Laboratory

Pacific Northwest National Laboratory

INL Idaho National Laboratory

The University of Alabama

Objectives/Relevance

Provide engineering support to guide Center's development of cost effective ammonia borane (AB) processes

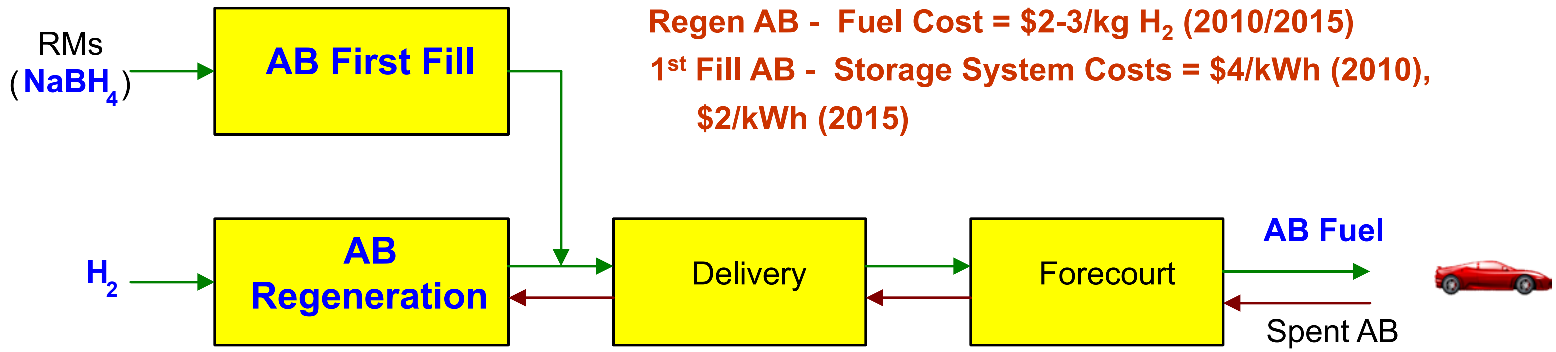
- Identify key parameters impacting cost and energy usage
- Define opportunities for improvement

Reduce cost of $NaBH_4$ to enable lower cost ammonia borane

DOE Targets (current):

Regen AB - Fuel Cost = $2-3/kg H_2 (2010/2015)

1st Fill AB - Storage System Costs = $4/kWh (2010), $2/kWh (2015)



Approach/Milestones – Low Cost $NaBH_4$ for 1st Fill AB

Identify Leading Pathways

- Develop screening and evaluation criteria specific to $NaBH_4$ regeneration cycles
- Review prior technical and patent literature
- Select leading $NaBH_4$ regeneration pathways based on theoretical energy efficiencies from reaction energetics and relevant metrics

Determine Feasibility of Leading Pathways

- Demonstrate key chemical and process steps in laboratory studies
- Develop flow sheets and preliminary energy requirements and cost estimates for leading systems

◆ Sept 2007: No Go decision for $NaBH_4$ as a storage material. Investigate low cost $NaBH_4$ for 1st fill AB.

Detail Performance to Select Single Pathway

- Establish complete material balance to determine intermediates and purification requirements
- Demonstrate all chemical and process steps
- Investigate scalability

◆ July 2009: Metal reduction selected over carbothermal for development

Develop Single Pathway

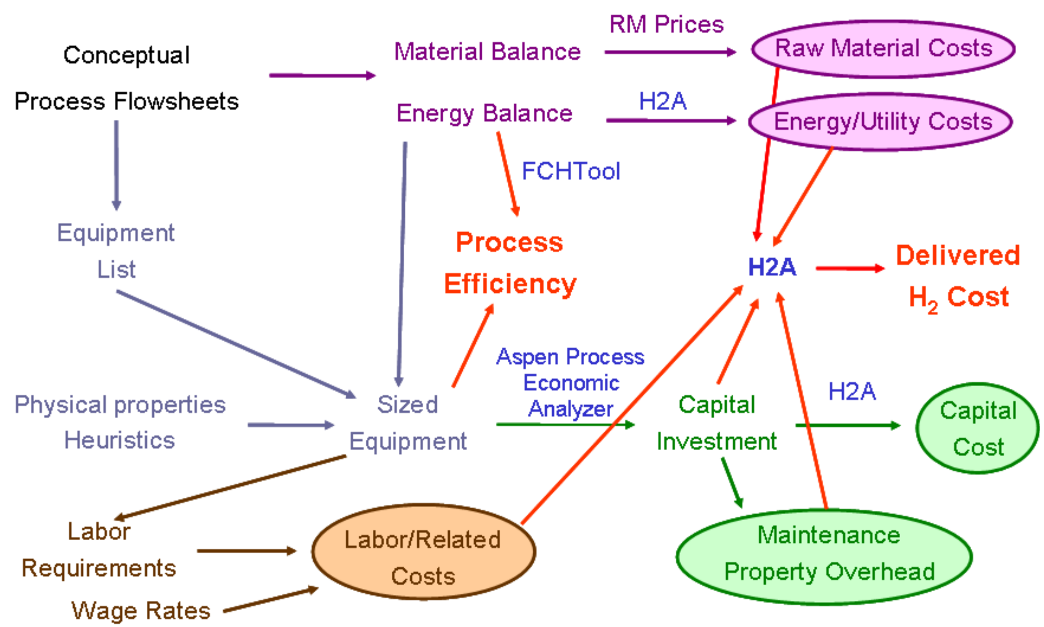
- Develop single $NaBH_4$ process
- Confirm scalability
- Update process flowsheets and economics

↑ Current focus

Phase 2 (Detail Performance to Select Single Pathway; Develop Single Pathway)

Approach/Milestones – Engineering Analysis Methodology

- **Methodology developed for determining energy efficiency and delivered costs**
- **H2A model used to develop economics**
- **Results reviewed with TIAX; feedback incorporated**



Accomplishments:
First Fill Ammonia Borane

Leading First Fill AB Pathways Being Evaluated

Metathesis of ammonium salt and MBH_4 in organic solvents

$$nNaBH_4 + (NH_4)_nX \rightarrow nNH_3BH_3 + Na_nX + nH_2$$

Purdue: Ramachandran et al, *Inorg. Chem*, 2007, 46, 7810-7817

$$NaBH_4 + \tfrac{1}{2}(NH_4)_2SO_4 \xrightarrow{THF} NH_3BH_3 + \tfrac{1}{2}Na_2SO_4 + H_2 \quad (>95\%)$$

$$NaBH_4 + (NH_4)HCO_2 \xrightarrow{dioxane} NH_3BH_3 + NaHCO_2 + H_2 \quad (>95\%)$$

Current analysis → PNNL: Heldebrant et al., *Energy & Envir. Science*, 2008, 1, 156-16

$$NH_4Cl + NaBH_4 \xrightarrow[-NaCl]{NH_3} NH_4BH_4 \xrightarrow[-H_2]{THF} NH_3BH_3 \quad \text{(up to 99\% yield)}$$

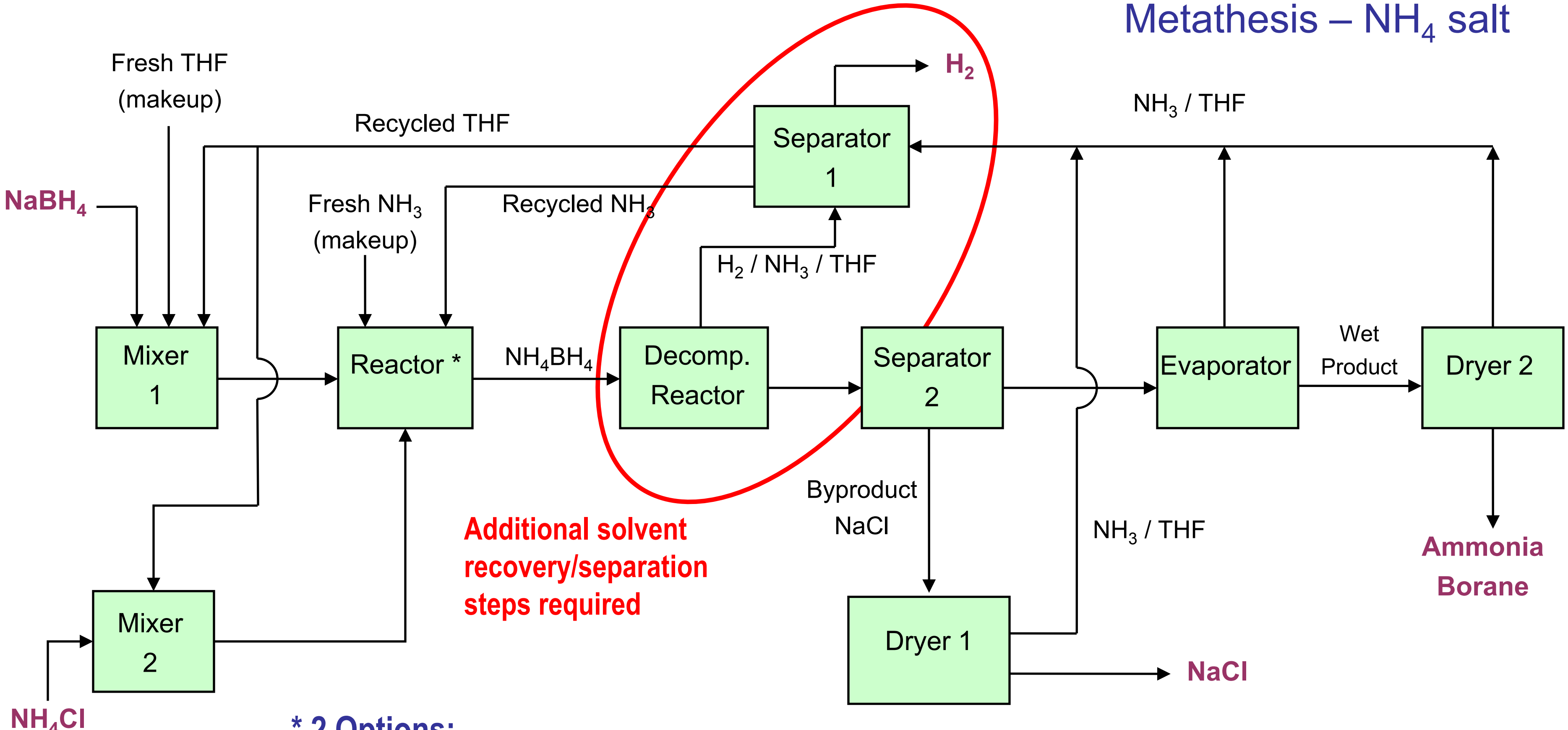
Base displacement of borane complexes with ammonia

$$L\text{-}BH_3 + NH_3 \rightarrow NH_3BH_3 + L$$

Shore: WO2007/120511 A2

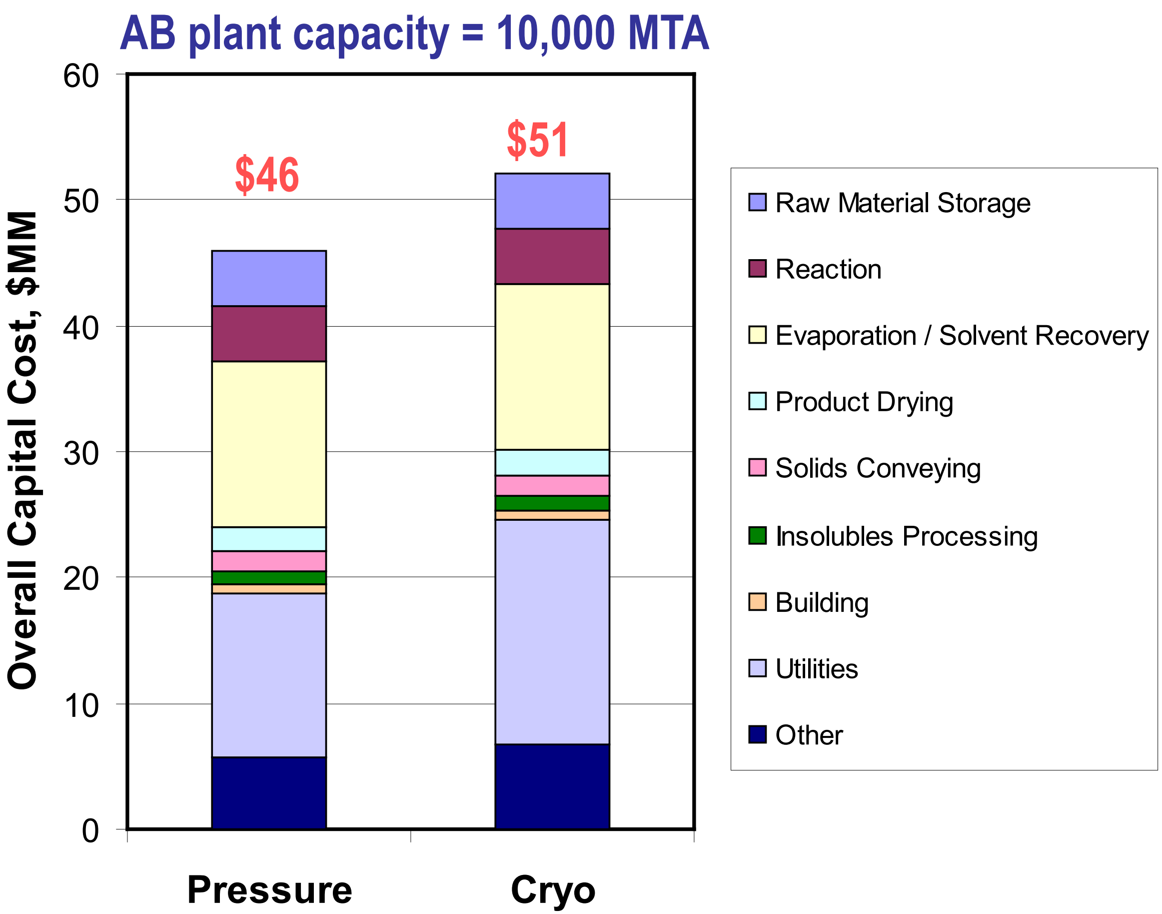
1st Fill AB: PNNL Route

Metathesis – NH_4 salt



* 2 Options:
Pressurized: 25 C, 20 atm
Cryogenic: -70 C, 1 atm

PNNL Pressurized Route is Lower Capital than Low Temperature Option



Separations and solvent recovery dominate capital cost

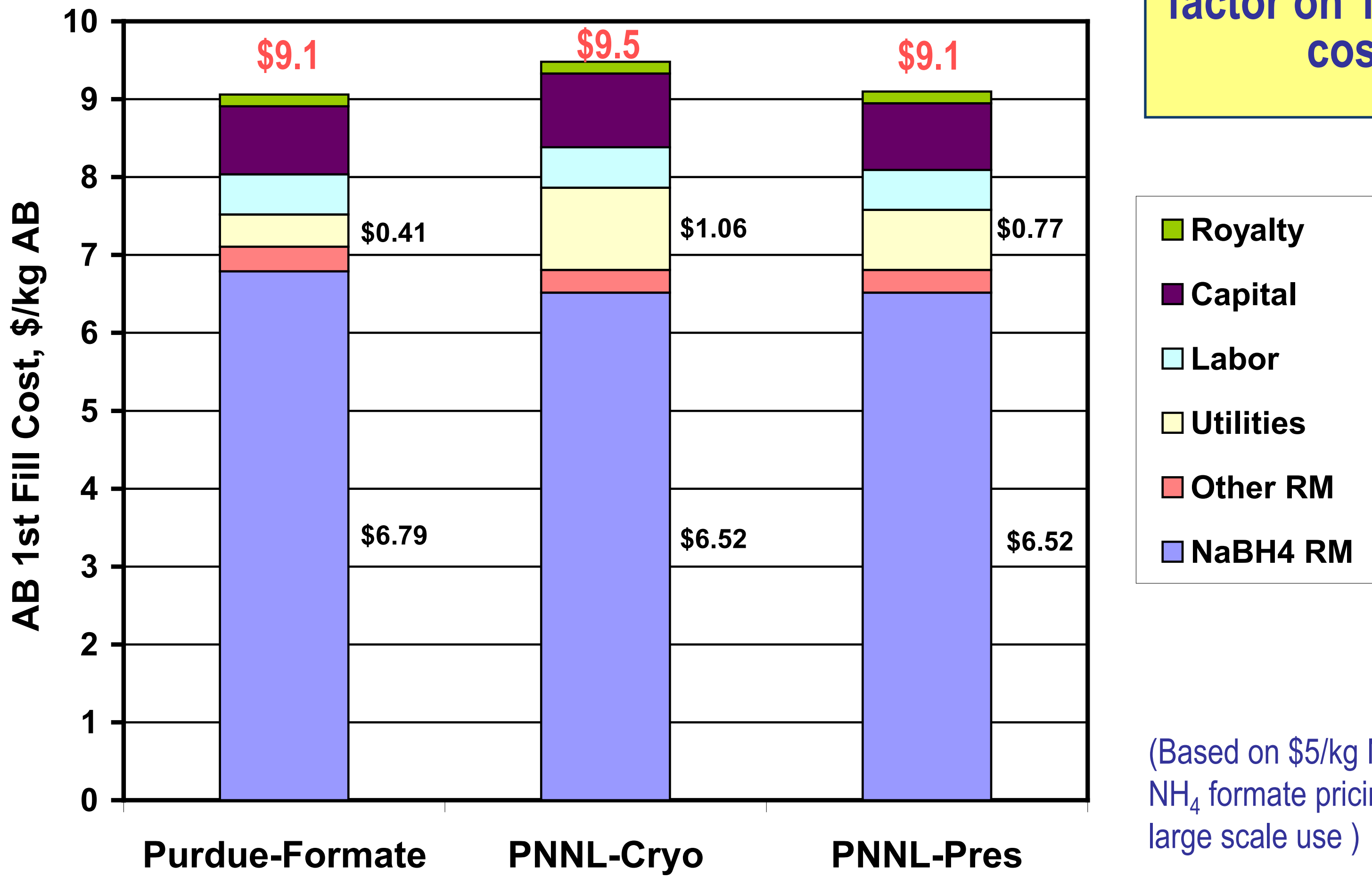
Lower refrigeration demands favor moderate pressure option

PNNL Route Provides Numerous Benefits

	PNNL	Purdue
Chemistry	NH_4BH_4 decomposition	Metathesis
Boron source	Sodium Borohydride	
Nitrogen source	Ammonium Chloride	Ammonium Formate / Sulfate
Solvent	THF and NH_3	Dioxane or THF
AB yield	99%	95%
AB purity	99%	98%
Reactor conditions	-70˚C /1 atm or 25˚C /20 atm.	40˚C /1 atm
Feed stoichiometry	Near-stoichiometric	50% excess NH_4 formate
Raw material costs	$NaBH_4$ principal component of costs	
	NH_4Cl pricing well defined.	Low NH_4HCO_2 pricing requires high volume
Solvent requirements	>2M $NaBH_4$ in solvent	1M $NaBH_4$ in solvent
Solvent separation	Distillation column required to separate THF and NH_3 solvents	Single solvent – no solvent separation required.
Na byproduct recovery	Relatively easy separations via solubility differences.	Separation of Na and NH_4 salts requires more complex processing
Waste generation	Minimal waste – only losses are small solvent losses.	Moderate liquid waste generated from insolubles processing step.

Pressurized PNNL AB Process Provides Best Overall Cost and Performance

AB plant capacity = 10,000 MTA



$NaBH_4$ is dominant factor on 1st fill AB cost

(Based on \$5/kg $NaBH_4$. NH_4 formate pricing assumes large scale use)

Other AB Synthesis Routes

Base displacement of borane complexes with ammonia

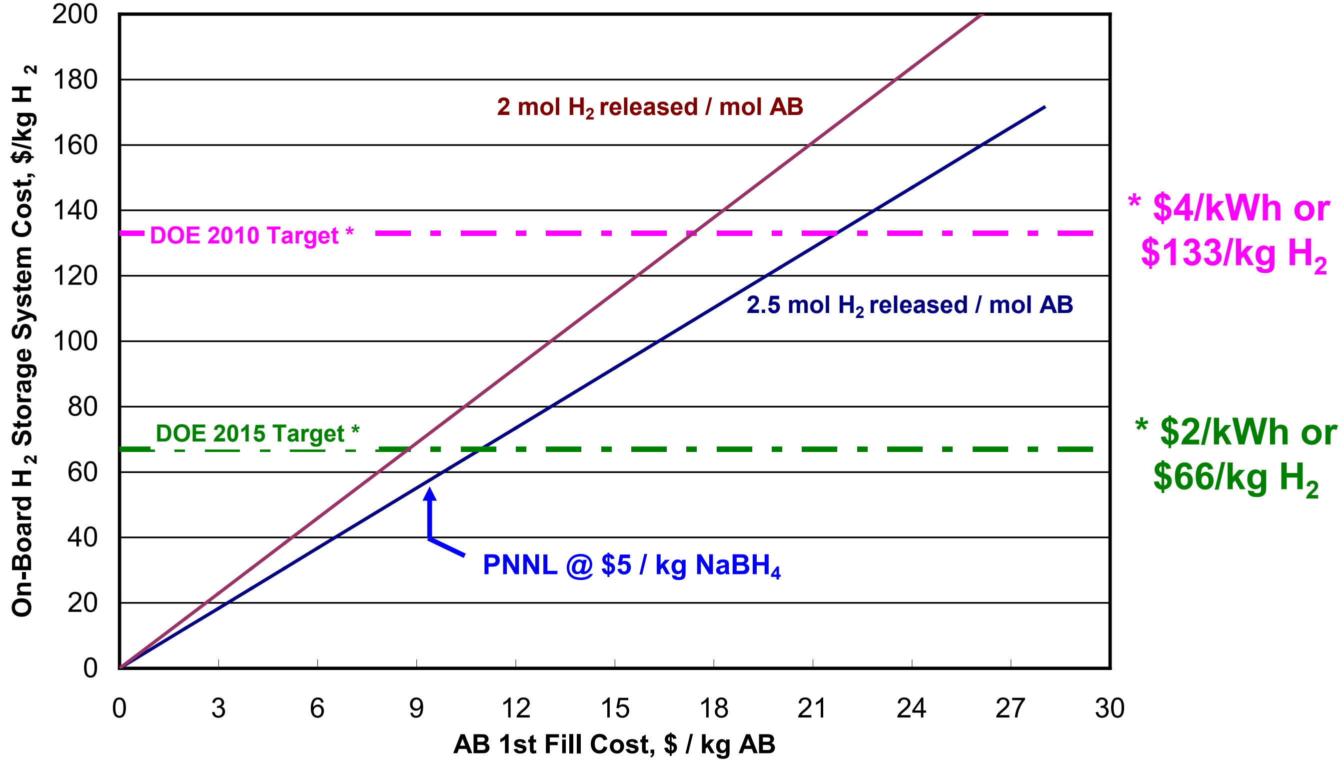
$$L\text{-}BH_3 + NH_3 \rightarrow NH_3BH_3 + L$$

- High AB yields (>95%) and purities (>99%) reported for dimethylaniline borane (Shore)
- Effective means to produce BH_3 adducts needed
  - $NaBH_4$ conversion to diborane and subsequent condensation in L
  - $NaBH_4$ reaction with amine hydrochloride avoids diborane

    $$L\text{-}HCl + NaBH_4 \rightarrow L\text{-}BH_3 + NaCl + H_2$$
  - Multi-step reactions involved - will not offer lower cost than PNNL route

Low-Cost $NaBH_4$ May Enable AB to Meet DOE Storage System Cost Targets

* Current storage system cost targets



$9/kg AB (produced from $5/kg $NaBH_4$) → $60/kg H_2 (for 2.5 mol H_2 released per mol AB)

Current fuel cost projection represents 45% of 2010 storage system cost target

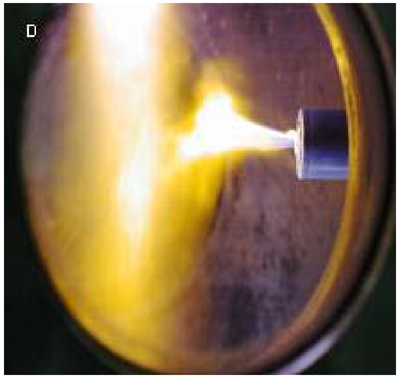
Current fuel cost projection represents 90% of 2015 storage system cost target (only 10% remaining for rest of system)

Accomplishments:
Low Cost $NaBH_4$ for 1^{st} Fill Ammonia Borane

Carbothermal Reduction of Borate

Approach

- Reproduce prior INL studies where $NaBH_4$ was produced
- Year 1 Go/No Go Milestone: INL experimental results should confirm a consistent plasma carbothermic conversion of borate to $NaBH_4$ of at least 40%
- Detail process window, separation / purification needs



$NaBO_2 + 2CH_4 \rightarrow NaBH_4 + 2CO + 2H_2$

Experimental - $NaBH_4$ formation remains elusive

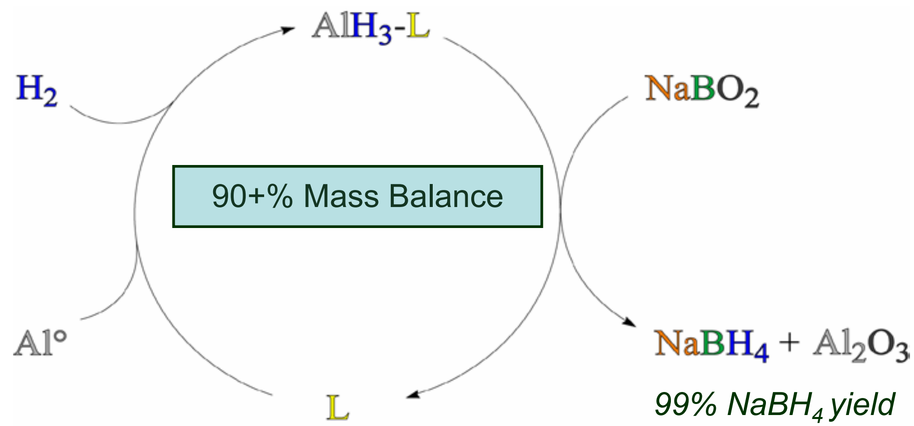
- $NaBH_4$ has not been produced, but unidentified water-reactive material has
- Studies plagued by equipment issues & analytical challenges - exact repetition of prior run conditions has proven difficult
- Extensive troubleshooting has failed to identify the same set of conditions under which $NaBH_4$ was produced

Year 1 Go/No Go Criterion Not Met → ***No Go Decision for Carbothermal***
Metal Reduction Selected for Development

Metal Reduction of Borate

Recyclable process identified based on solid-solid reactive milling (high-energy laboratory mill)

- Good material balance
- Full accountability for all products
- No intractable by-products
- Isolation and purification steps identified



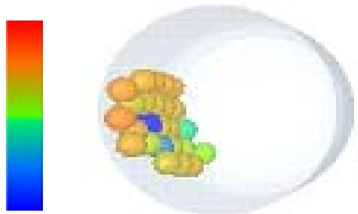
Quantitative recovery of L

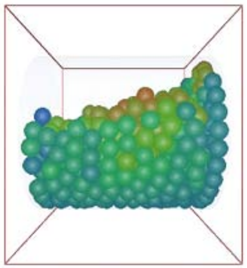
99% $NaBH_4$ yield
99% purity

Identification of a <u>scalable</u>, solid-solid reactive milling technology has been met with challenges: low $NaBH_4$ yields

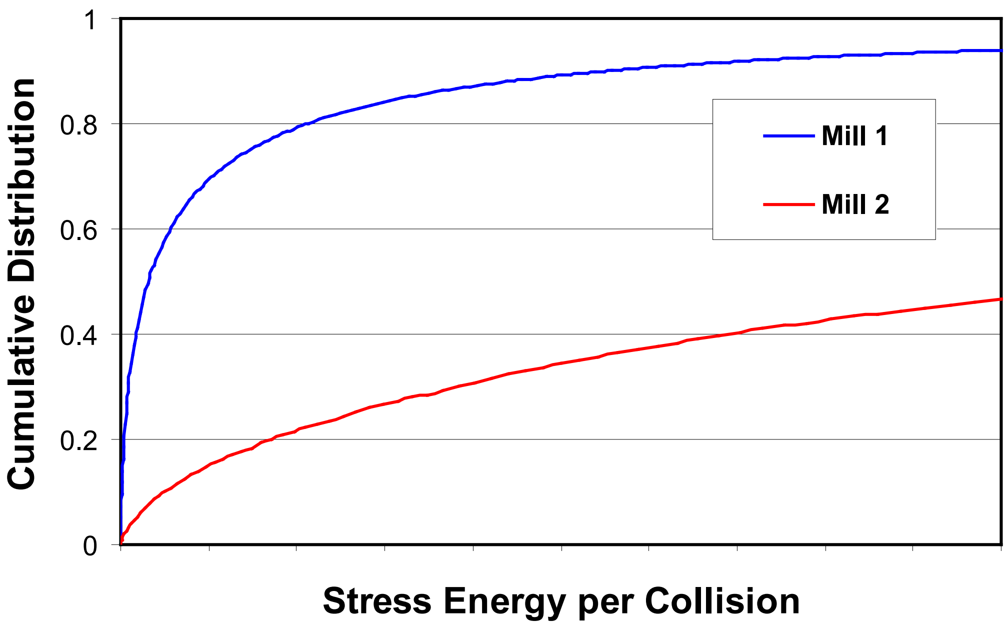
- Implications for the Metal Hydrides Center

Modeling Defines Reactive Milling Scaleup Challenges





Stress Energy Distribution during Milling



Discrete-element method modeling applied to obtain fundamental understanding of ball motions and particle collisions

Difficult to achieve sufficient milling energy in large scale mills ($NaBH_4$ volume to supply 10,000 MTA AB plant)

Alternatives to Solid-Solid Reactive Milling

Slurry milling

- Scalable, but insufficient $NaBH_4$ yields

Solution-based approach

- Scalable with potential use of conventional reactors and unit operations
- All steps of reaction scheme demonstrated
- Focus on defining chemistry and process window for each reaction step
  - » Identification of byproducts
  - » Separation and purification needs
  - » Establish material balance

Results to date very promising…

Solution-Based Metal Reduction: Results Point to Scalable Process

Alane formation step: 99+% yield

- Pressure, temperature, Al source, ligand, reaction medium

$NaBH_4$ formation step: 94% yield

- Pressure, temperature, B source, reaction medium

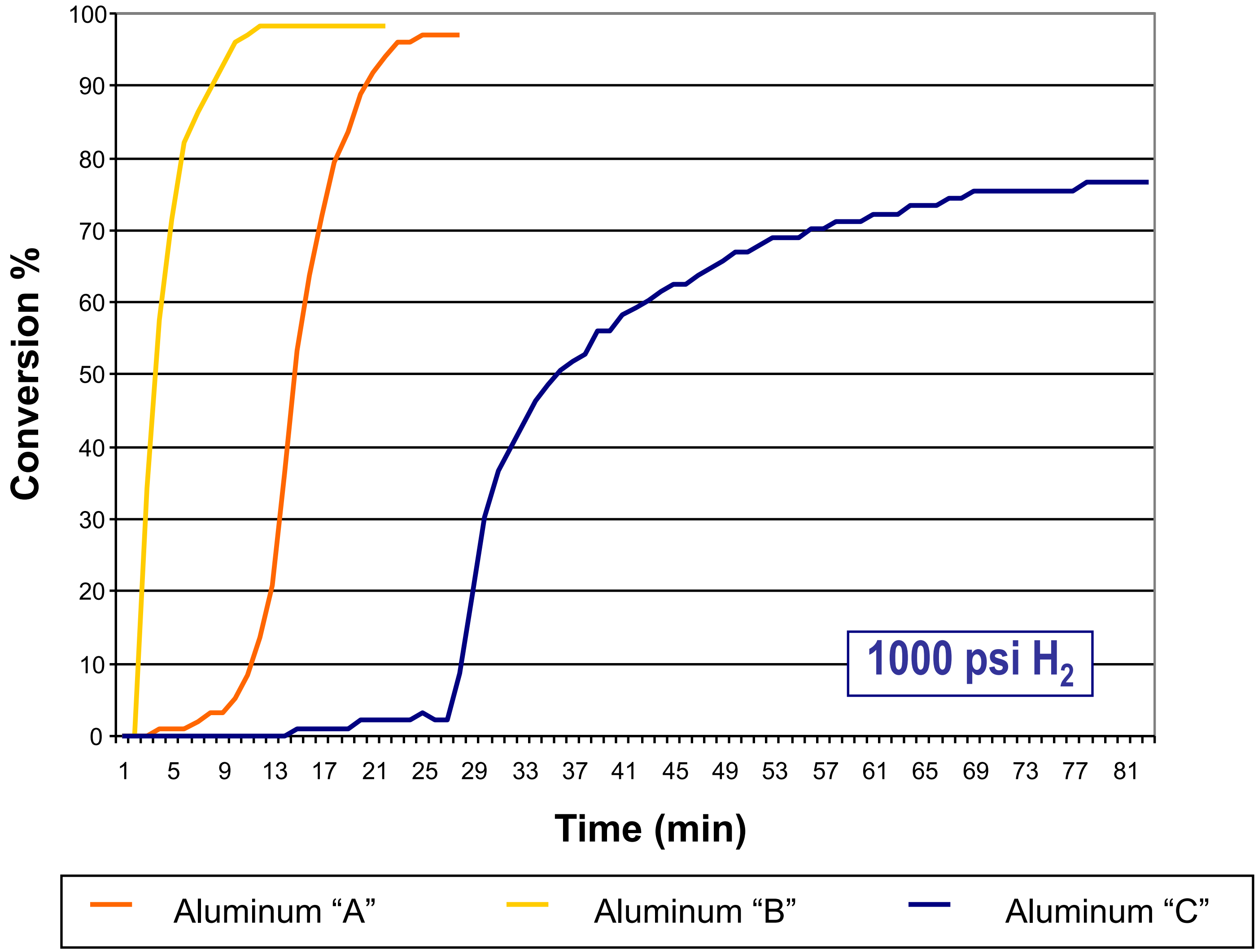
Product isolation and purification

- 99% $NaBH_4$ purity
- Separation scheme (crystallization, extraction, etc.)
- Full impurity profile characterization in progress (ICP, NMR, etc)

Recycle streams

- 97% ligand recovery, 99+% purity
- 99% recovery of aluminum by-product

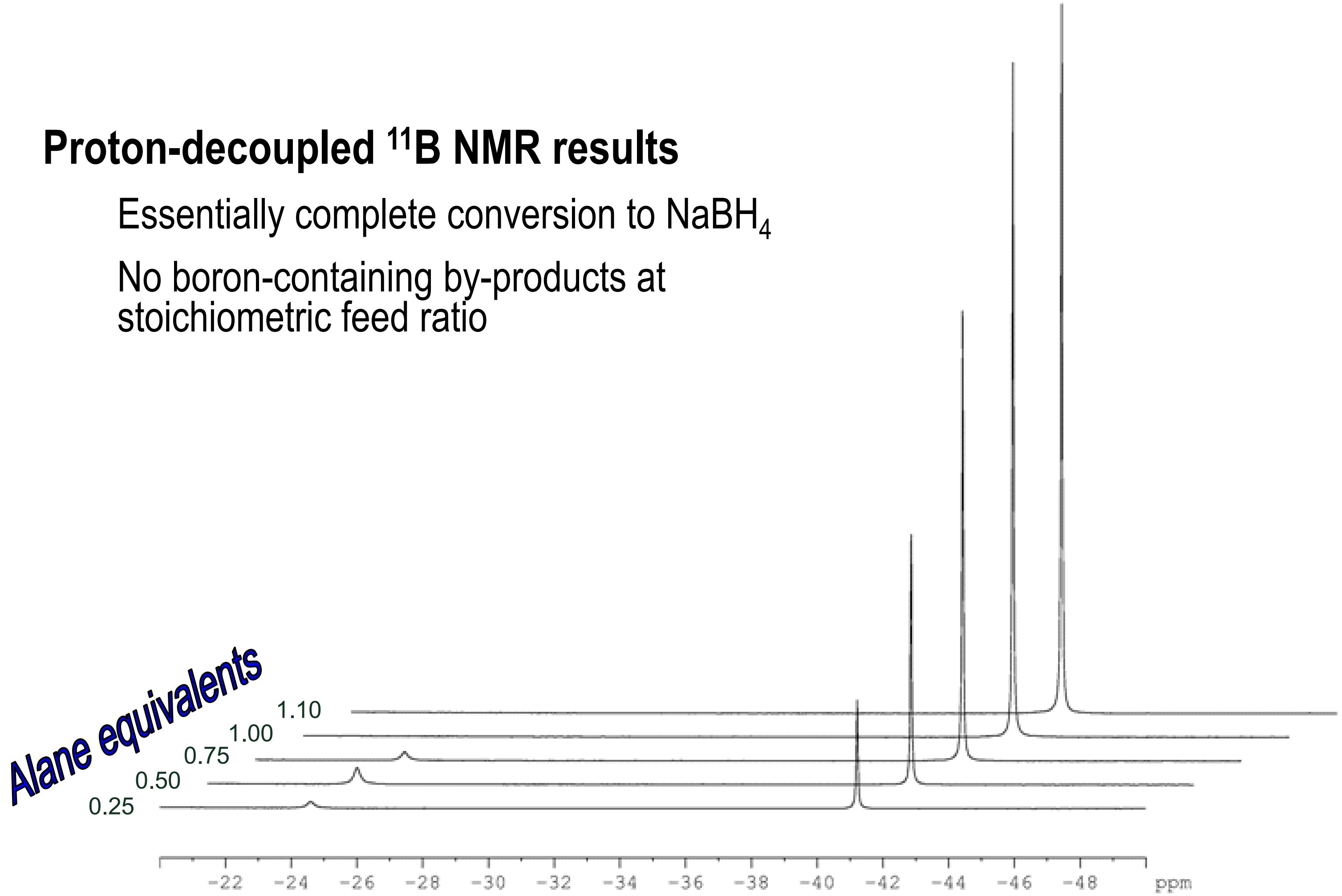
Excellent Alane Formation Kinetics Obtained



Excellent $NaBH_4$ Yield and Selectivity Achieved

Proton-decoupled ^{11}B NMR results

- Essentially complete conversion to $NaBH_4$
- No boron-containing by-products at stoichiometric feed ratio



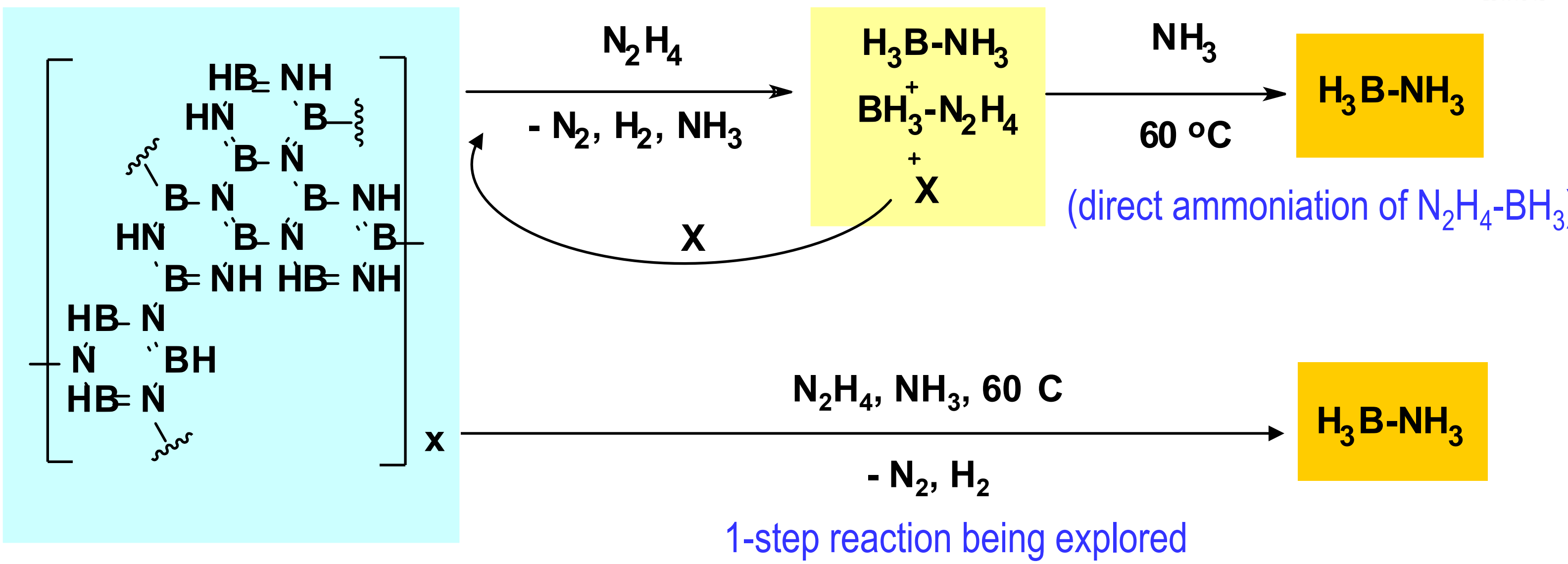
Accomplishments:
AB Regeneration

LANL 2nd Generation AB Regen Process

Hydrazine-based digestion and reduction

Significantly simpler process compared to thiol/tin-based pathway

Optimal regeneration path being identified by LANL :



Reaction basis being defined to proceed with cost analysis

LANL 2nd Generation AB Regen Process

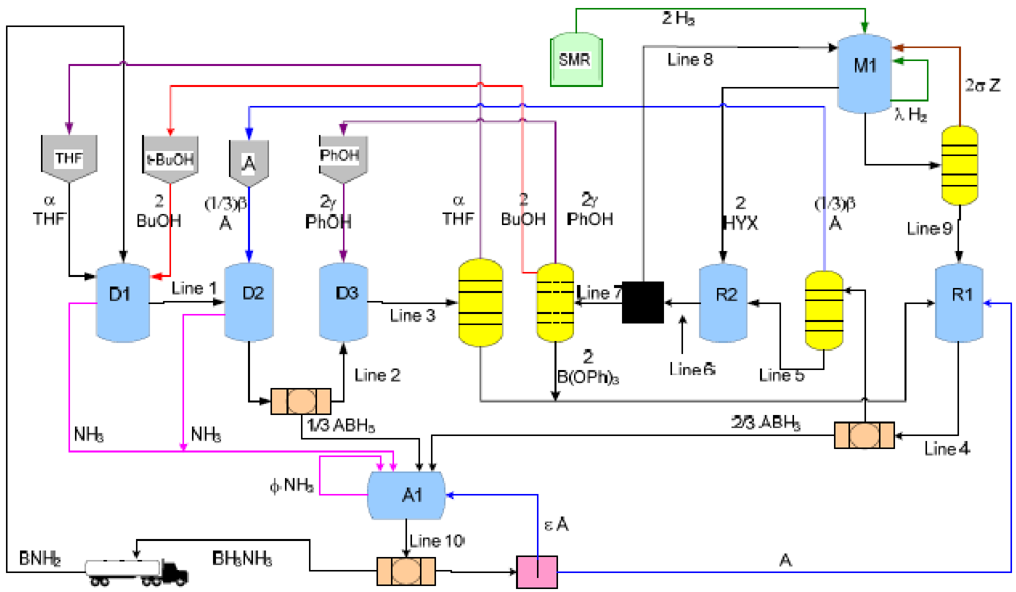
Hydrazine usage likely to dominate cost and energy demand instead of regen operations

- Minimum requirement of 8:1 hydrazine:H_2 released (wt/wt)
- Current anhydrous hydrazine manufacturing routes energy intensive and costly
- New approaches to N_2H_4 will be needed for regeneration scheme to be viable

PNNL Alcohol-based AB Regen Process

Chemistry steps and process options still being defined

Factored approach being pursued based on block flow diagram for cost estimate



Collaboration – Leveraging Expertise Across the Center

AB regeneration processes

- LANL, PNNL: Experimental results input
- U Alabama: Thermochemical calculations
- Dow engineering guides Center development work

First fill AB process analysis

- PNNL: Experimental results input

Low cost $NaBH_4$ for 1st fill AB

- INL (sub-contractor): Carbothermal studies

Future Work – Issues and Recommendations

Low Cost $NaBH_4$

- Refine process definition and development for solution-based alane reduction route
- Confirm recyclability
- Update flowsheets and economics
- Future work: conduct pilot studies to demonstrate fully integrated, scalable process

First Fill and Regen AB

- Early process analysis to ensure focus on cost-effective chemistries

Summary

AB First Fill

- Low cost $NaBH_4$ is key for producing 1st fill AB at cost required to meet 2010/2015 DOE hydrogen storage system cost targets.
- PNNL's moderate pressure AB route based on formation and decomposition of NH_4BH_4 provides best overall cost and purity/performance.
- At $5/kg $NaBH_4$ price using new technology, PNNL route can produce AB on a commercial scale at about $9/kg.

Low-Cost $NaBH_4$ for 1st Fill AB

- Attempts to reproduce 2007 carbothermal reduction of borate to $NaBH_4$ were not successful; No Go decision recommended
- Best scalable metal reduction process identified: solution-based alane reduction route
  - » Good yields and recoveries. Appears recyclable
  - » Currently defining process window, updating economics

AB Regeneration

- LANL's hydrazine-based pathway will need low cost hydrazine to be viable.