2009 DOE Chemical Hydrogen Storage Center of Excellence

Low-Cost Precursors to Novel Hydrogen Storage Materials

Project ID# ST_20_Linehan

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Project Overview

Timeline

- **Start:** March 1, 2005
- **End:** March 31, 2010
- **Percent complete:** 80 %

Barriers

- **System cost**
- **Regeneration processes**
  - Cost
  - Energy efficiency
  - Environmental impacts

Budget

	Total Funding	FY08 Actual	FY09 Budget*
DOE	$3,438K	$642K	$1,300K
ROH	$1,524K	$275K	$557K

Phase 2 DOE:ROH 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
Penn University of Pennsylvania
The University of Alabama

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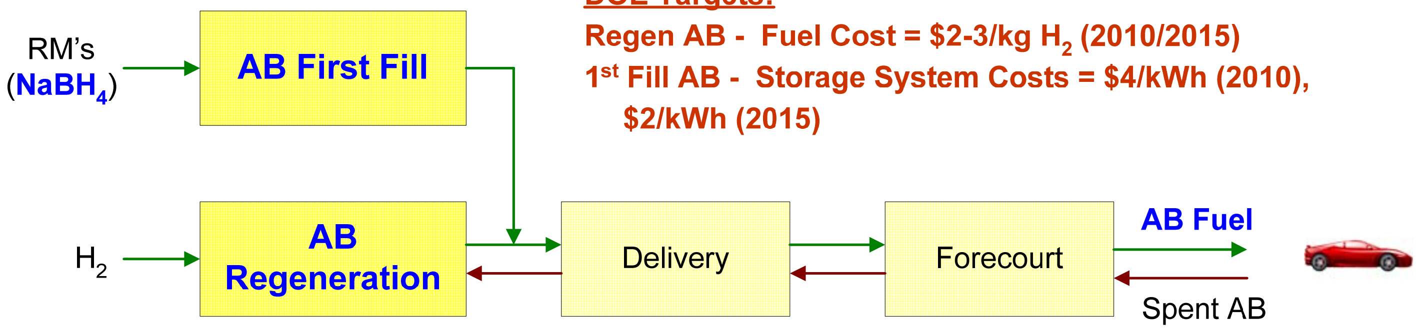
Objectives/Relevance

- Identify cost and energy efficient pathways to "first fill" and regeneration for ammonia borane (AB) and other borane materials (Phase 2)
  - Continue experimentation leading to selection of single pathway for low-cost $NaBH_4$ and further AB process technology development
  - Guide selection of a top AB regeneration scheme for experimental studies on most promising alternatives
- Low cost AB (and other borane-based materials) requires low cost $NaBH_4$ for initial system fill
  - $NaBH_4$ is dominant component to AB costs
  - Lower cost $NaBH_4$ technologies needed
- Low cost $NaBH_4$ also essential to Metal Hydride Center success

DOE Targets:

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

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



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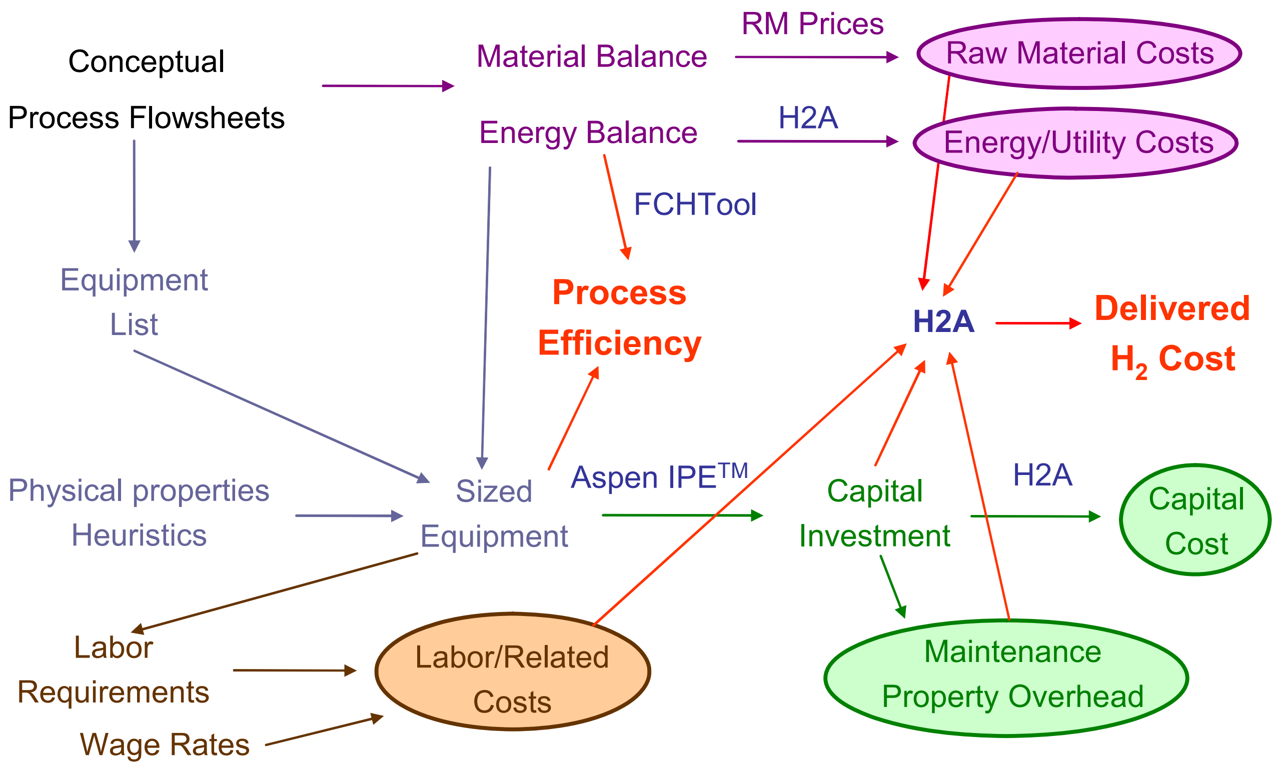
Approach/Milestones – AB Cost and Energy Efficiency Estimation



- **Methodology developed for determining energy efficiency and delivered costs**
- **Results reviewed with TIAX; feedback incorporated**
- **Baseline cost estimates developed February 2009 (1st fill AB and AB regen milestone reports)**

Approach/Milestones – Low Cost NaBH4 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 Go/No Go Decision for $NaBH_4$ as a storage material**

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 milestone**

Develop Single Pathway

- Develop single $NaBH_4$ process
- Update economics

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

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1st Fill AB: Leading Chemistries Identified

Metathesis of ammonium salt and MBH_4 in organic solvents

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

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

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

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

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

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

Ohio State: Shore et al, WO2007/120511 A2

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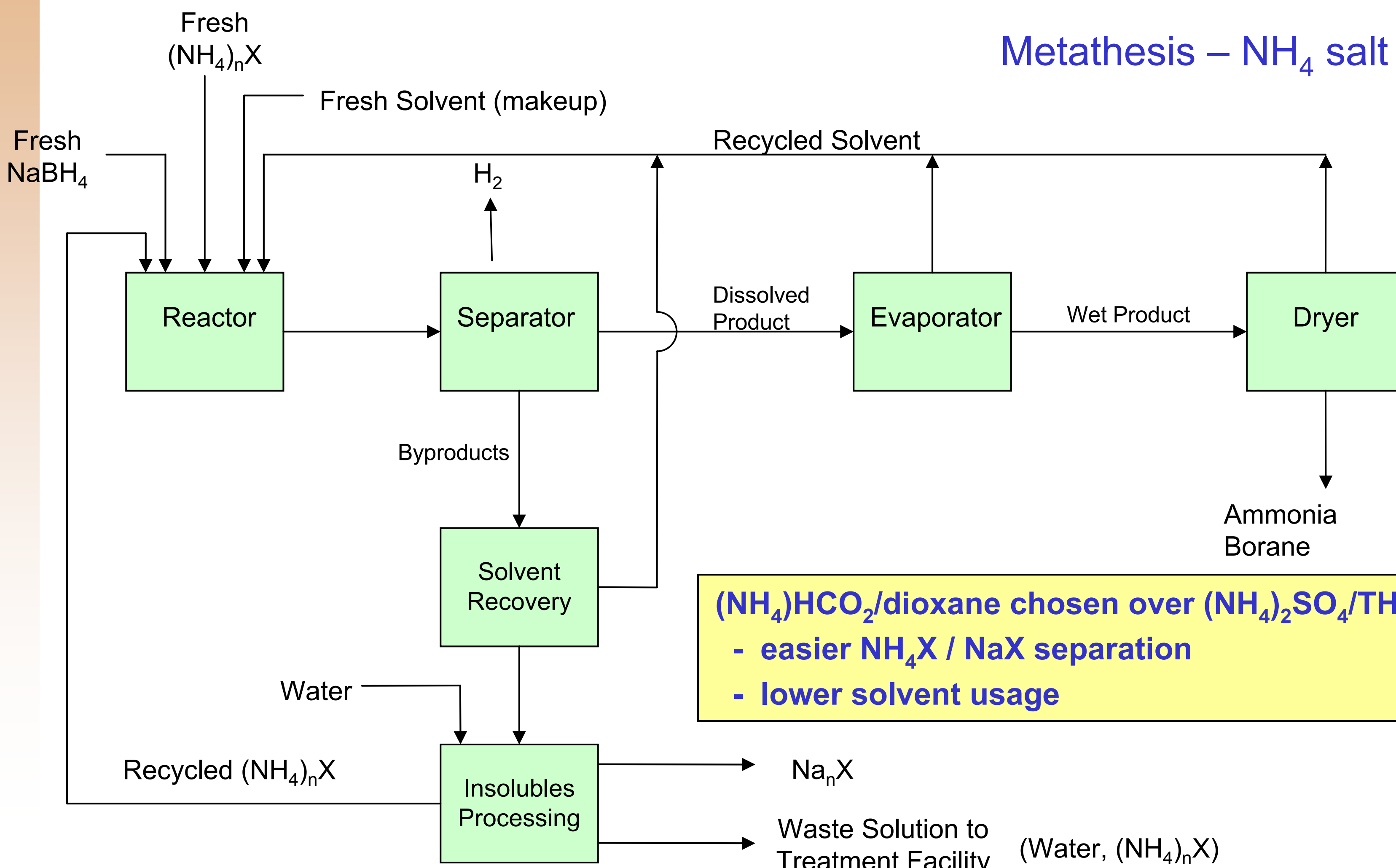
1^{st} Fill AB: Separation Requirements Determine Feasibility

Metathesis – NH_4 salt

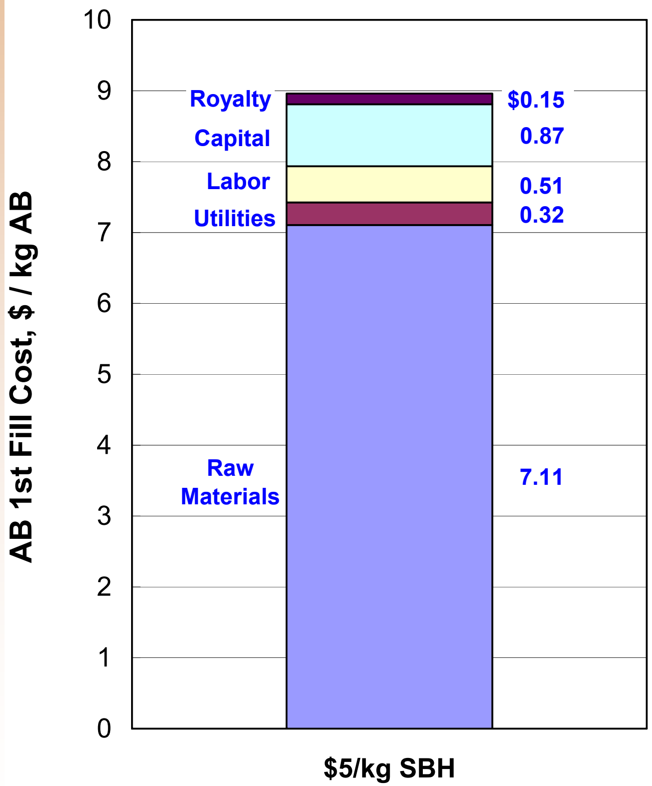


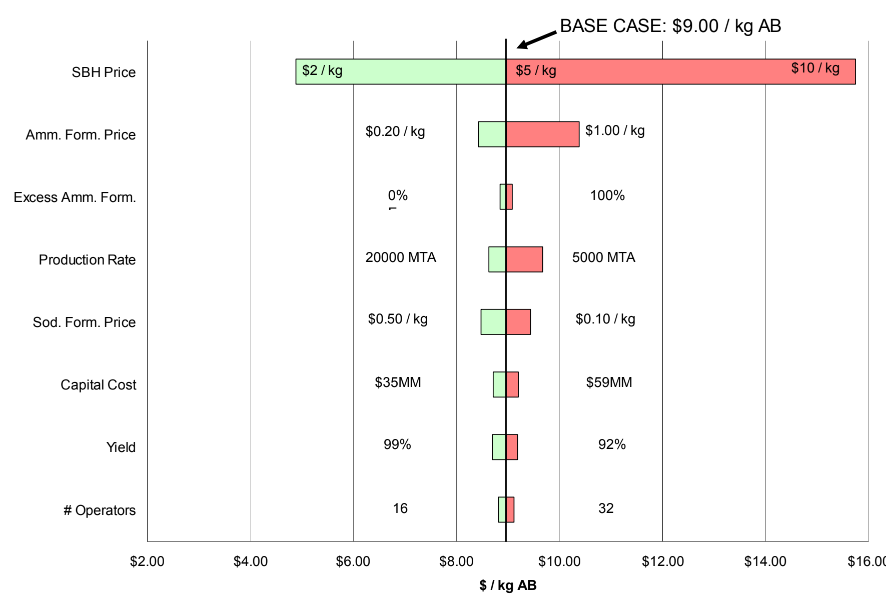
$(NH_4)HCO_2$/dioxane chosen over $(NH_4)_2SO_4$/THF
- **easier NH_4X / NaX separation**
- **lower solvent usage**

1st Fill AB Cost: $NaBH_4$ is Dominant Component

- Cost = \$9/kg AB
  - ~80% from raw materials
  - $NaBH_4$ at \$5/kg accounts for 95% of RMs; 75% overall
- AB cost would be \$55-85/kg at current \$40-\$60/kg $NaBH_4$
- Low cost $NaBH_4$ technologies under development
  - 2007 study indicates \$1-2/kg $NaBH_4$ at high volume production in regen plants
  - Use \$5/kg $NaBH_4$ as initial estimate for 1st fill AB scales

AB plant capacity = 10,000 MTA
Metathesis – NH_4 formate / dioxane





Sensitivity Analysis

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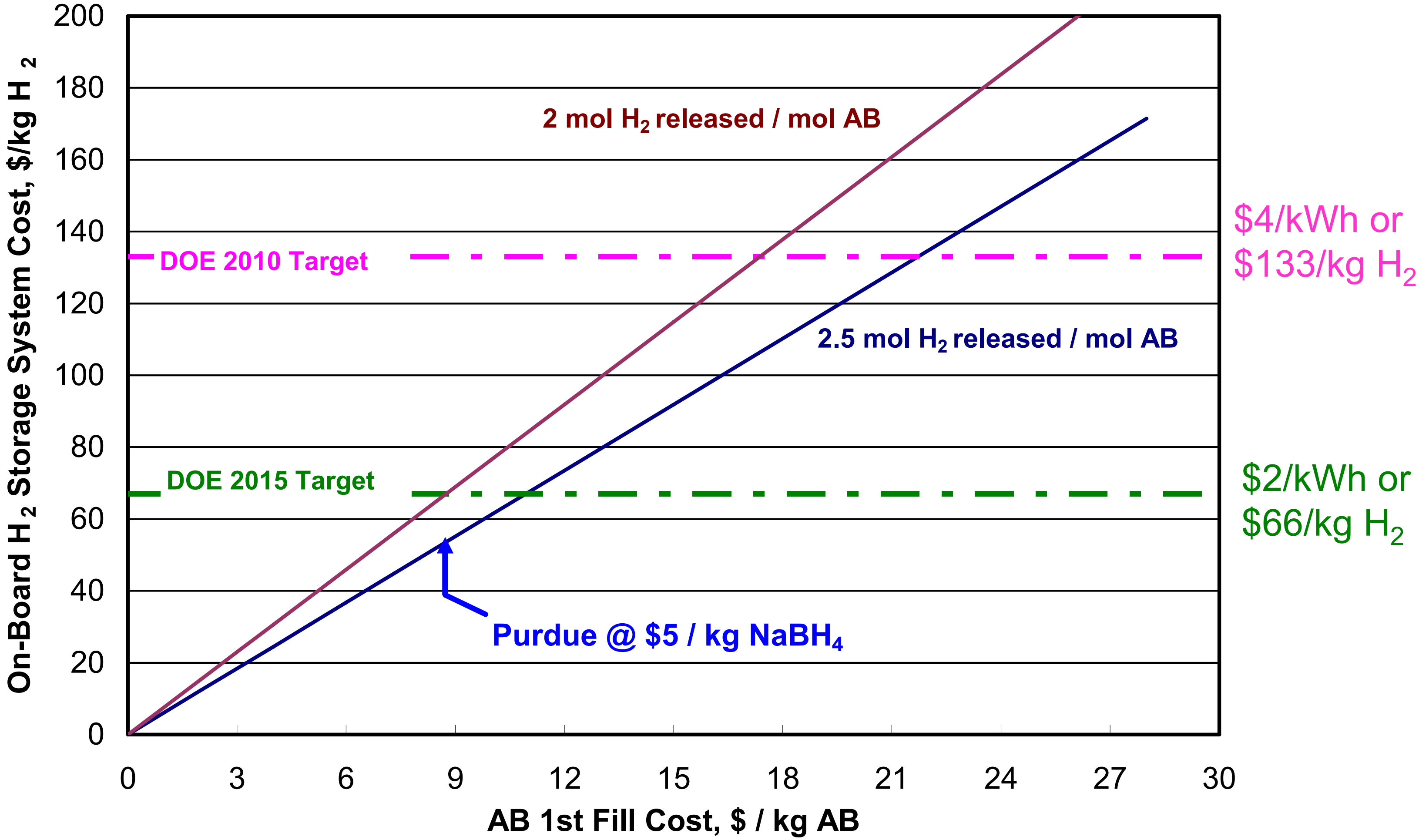
DOE Storage System Targets Require Low-Cost H_2 Storage Media



Two R&D Approaches to Low Cost $NaBH_4$ Under Development

Pathway	Chemistry
Schlesinger (current)	$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$ - 25% utilization of Na metal
Metal Reduction	1-step: $NaBO_2 + 2x/y\ M + 2H_2 \rightarrow NaBH_4 + 2/y\ M_xO_y$ 2-step: $2x/y\ M + 2H_2 \rightarrow 2x/y\ MH_{2y/x}$ $NaBO_2 + 2x/y\ MH_{2y/x} \rightarrow NaBH_4 + 2/y\ M_xO_y$ - lower-cost metal and lower usage vs. Na - reactive milling
Carbothermal Reduction	$NaBO_2 + 2CH_4 \rightarrow NaBH_4 + 2CO + 2H_2$ - methane instead of metal reductant - syn gas (CO/H_2) byproduct - high temperature to convert B-O to B-H

Objective: Select single pathway for low-cost $NaBH_4$ in 3Q2009

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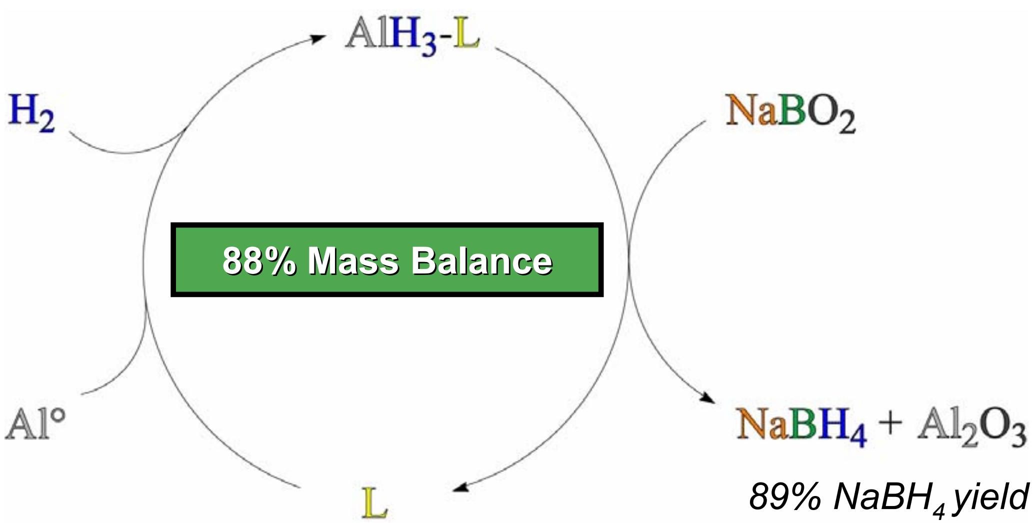
Chemical Pathway Established for Metal Reduction

Focus on 2-step process via metal hydride intermediate

- Offers advantage of higher yields and lower reaction severities



89% $NaBH_4$ yield
99% purity

Quantitative recovery of L

Lab material balance analysis points to recyclable process.

Full accountability for all products.

No intractable byproducts identified.

Isolation and purification steps identified.

Alane work may be relevant to Metal Hydride Center.

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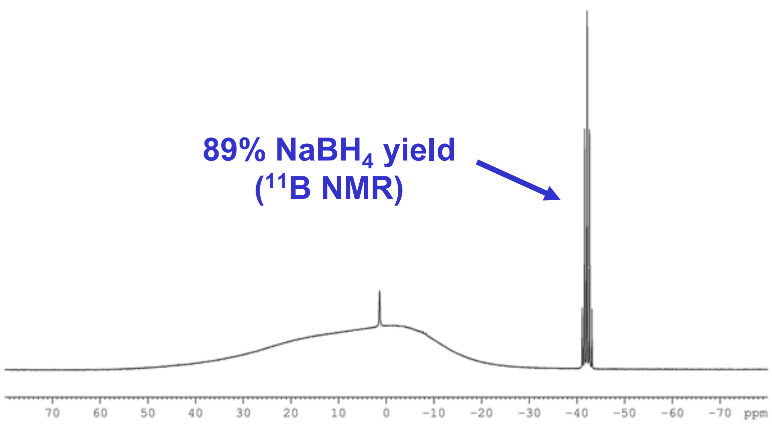
Metal Reduction – Key Chemistry for Reactive Milling Confirmed

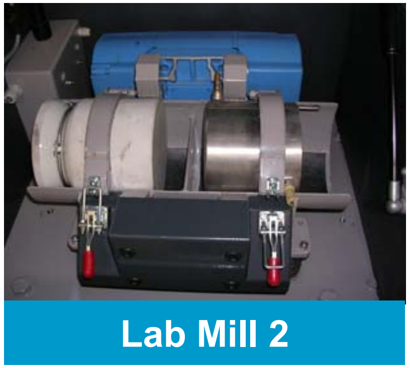
$3\ NaBO_2 + 4\ AlH_3{\cdot}L \rightarrow 3\ NaBH_4 + 2\ Al_2O_3 + 4\ L$

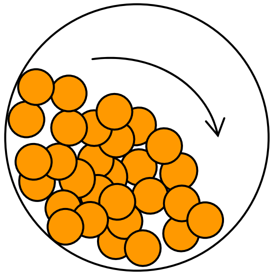
Chemistry (Ball Milling)	Borate source	• $NaBO_2$: **89% $NaBH_4$**, 5% BH • $Na_2B_4O_7$ + NaX: **62% $NaBH_4$**
	Alane adduct	• L^1 : **89% $NaBH_4$**, 5% BH • L^2 : **1% $NaBH_4$**, 29% BH • L^3: **2% $NaBH_4$**
	Stoichiometry	• 1.1 eq. AlH_3-L: **60% $NaBH_4$**, 1% BH • 2.0 eq. AlH_3-L: **77% $NaBH_4$**, 1% BH
Alternative Approaches	Slurry-based systems	• Borate + AlH_3-L → **29% $NaBH_4$** + 60% BH **89% boron conversion**

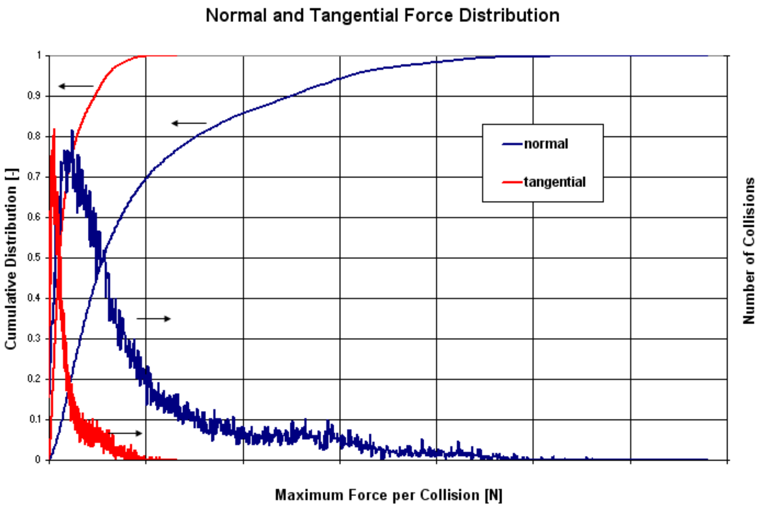
Results based on ^{11}B NMR analysis
BH = borane intermediate



Reactive Milling Modeling Guides Lab Studies, Defines Scalable Process







- Discrete-element modeling provides fundamental understanding of mill motions and particle collisions
- Obtain insight into mill operation, scaleup, and design
- Model also used to help guide lab studies

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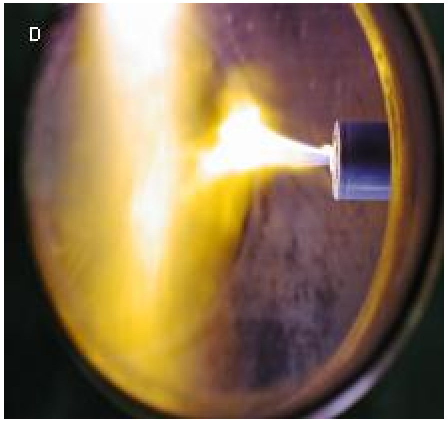
Carbothermal Reduction of Borate – Prior Results Still to be Validated

Established	To Be Defined
• Collaboration with INL • Prior INL studies: nearly 50% $NaBH_4$ yields for $NaBO_2$ reduction by reducing gases in plasma arc • High reaction temperatures (>1200°C) dictated by thermodynamics • Plasma arc process technology commercially viable	• Formation of intermediates and byproducts and required separation • Reaction quench and heat integration needs • Best mode for carbothermal reaction (temp sensitivity) • Scaleup options for commercial high temperature operations



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

- **Experimental - $NaBH_4$ formation remains elusive**
  - $NaBH_4$ has not been produced but some water-reactive material has (possibly boranes or Na/NaH)
  - Equipment issues - exact repetition of prior positive $NaBH_4$ studies difficult
  - Analytical challenges
  - Working closely to assist analysis and understand various aspects of previous results

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LANL AB Regen: Heats of Reaction Favorable for High Efficiency Process

Step	Reaction	ΔH,rxn, 25C kcal/mol AB
Reactor 1:		
✓ Digestion	(1a) $BNH + 1.5\ C_6H_4(SH)_2 \rightarrow 0.5\ HB(C_6H_4S_2){\cdot}NH_3 + 0.5\ (NH_4)B(C_6H_4S_2)_2$	5.7
Side Reactions:	(1b) $C_6H_4(SH)_2 + HB(C_6H_4S_2){\cdot}NH_3 \rightarrow (NH_4)B(C_6H_4S_2)_2 + H_2$	20.9
Reactor 2:		
✓ Reduction:	(2a) $0.5\ (NH_4)B(C_6H_4S_2)_2 + 0.5\ Bu_3SnH \rightarrow 0.5\ HB(C_6H_4S_2){\cdot}NH_3 + 0.5\ (C_6H_4)(SH)(SSnBu_3)$	-15.7
✓ Amine Exchange:	(2b) $HB(C_6H_4S_2){\cdot}NH_3 + Et_2NH \rightarrow HB(C_6H_4S_2){\cdot}NHEt_2 + NH_3\ (g)$	1.4
✓ Reduction:	(2c) $HB(C_6H_4S_2){\cdot}NHEt_2 + 2\ Bu_3SnH \rightarrow Et_2NHBH_3 + C_6H_4(SSnBu_3)_2$	6.5
Net:	(2d) $0.5\ HB(C_6H_4S_2){\cdot}NH_3 + 0.5\ (NH_4)B(C_6H_4S_2)_2 + 2.5\ Bu_3SnH + Et_2NH \rightarrow Et_2NHBH_3 + NH_3 + 0.5\ (C_6H_4)(SH)(SSnBu_3) + C_6H_4(SSnBu_3)_2$	-7.8
Side Reactions:	(2e) $C_6H_4(SH)_2 + Bu_3SnH \rightarrow C_6H_4(SH)(SSnBu_3) + H_2$	-10.5
	(2f) $C_6H_4(SH)(SSnBu_3) + Bu_3SnH \rightarrow C_6H_4(SSnBu_3)_2 + H_2$	- 4.0
Reactor 3		
✓ Ammoniation:	(3) $Et_2NHBH_3 + NH_3\ (l) \leftrightarrows H_3NBH_3 + Et_2NH$	-4.1
Reactor 4:		
Metal Recycle:	(4a) $0.5\ C_6H_4(SH)(SSnBu_3) + 0.5\ H_2 \rightarrow 0.5\ C_6H_4(SH)_2 + 0.5\ Bu_3SnH$	5.3
	(4b) $C_6H_4(SSnBu_3)_2 + 2H_2 \rightarrow C_6H_4(SH)_2 + 2\ Bu_3SnH$	14.5

Overall ΔH_{rxn} for target reactions (no side reactions) and no heat recovery of Rxr 2 and 4 product
= 25 kcal/mol AB
= 21 MJ/kg H_2 (potential for very high energy efficiency)

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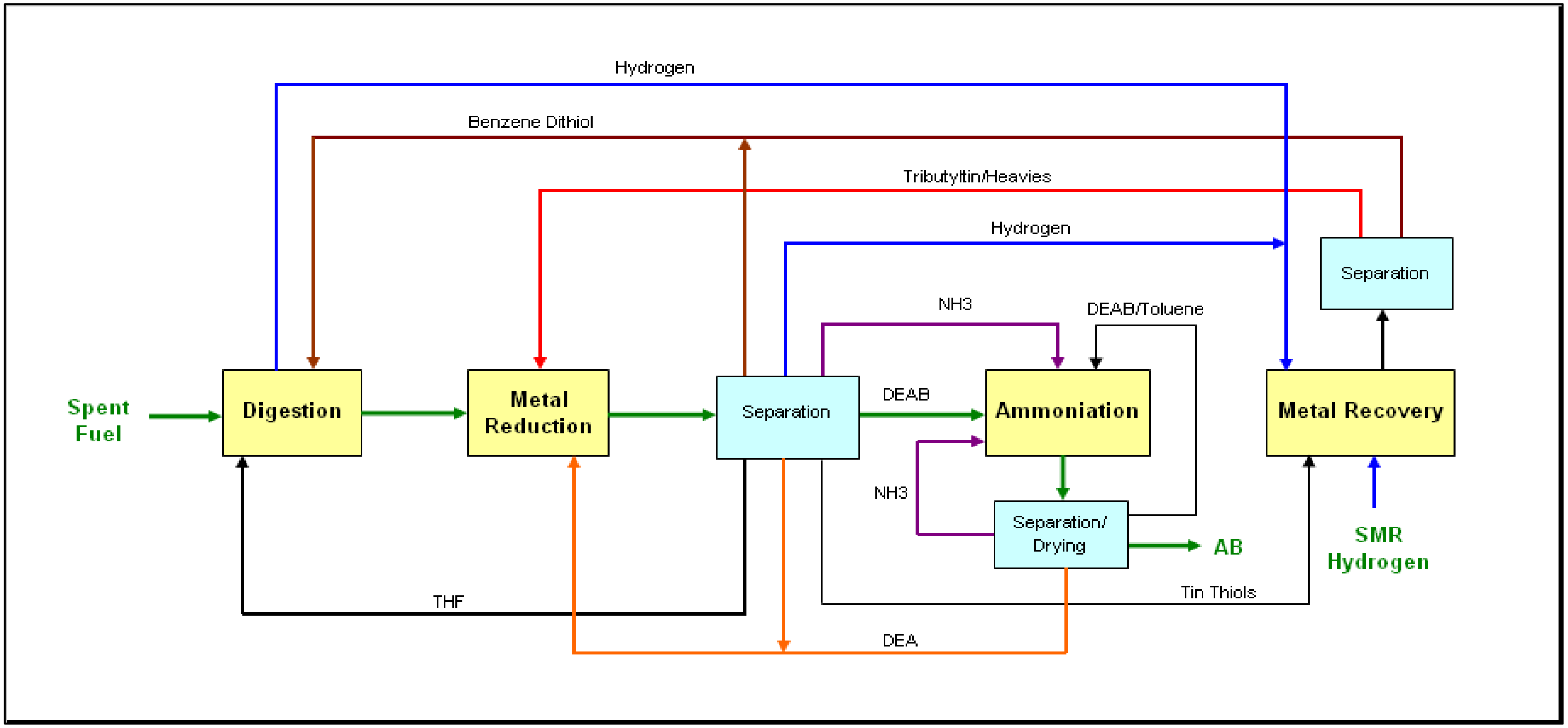
✓ demonstrated

LANL Spent AB Regeneration Route: Conceptual Process Flowsheet Developed

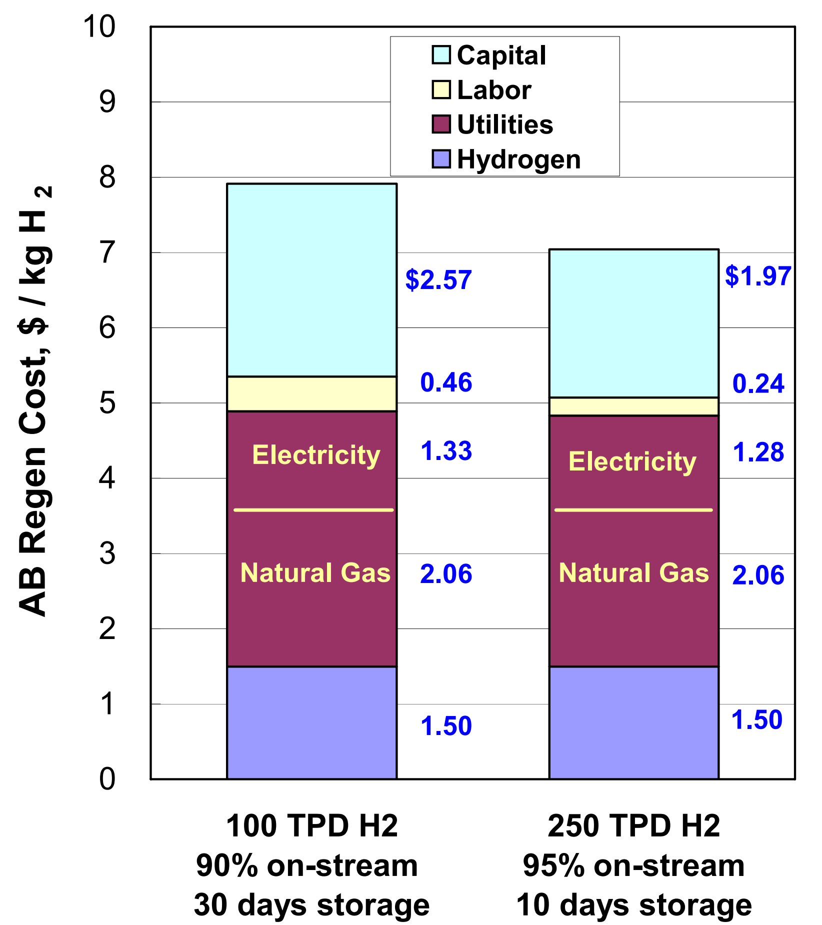


Plant Design Basis

- **225,000 MTA ammonia borane production**
  - Equivalent to 100 mt/day H_2 @ 90% on-stream and 2.5 mol H_2 release per mol AB
  - Negligible losses during fuel shipping and storage
  - AB not used to generate heat for on-board H_2 release
  - 250 mt/day H_2 production as sensitivity
- **Spent AB fuel delivered to plant and regenerated AB bulk powder leaves plant**
  - Delivery costs to auto not included since design of AB fuel is not yet defined

Capital Recovery and Utilities Dominate LANL AB Regen Cost

AB Production, TPD H_2 equivalent	100	250
Baseline AB Regen Plant Cost, $/kg H_2	**7.9**	**7.0**
Total Investment, $M	**520**	**1000**
Capital	**460**	**850**
First Fill Chemicals (dominated by tin)	**60**	**150**

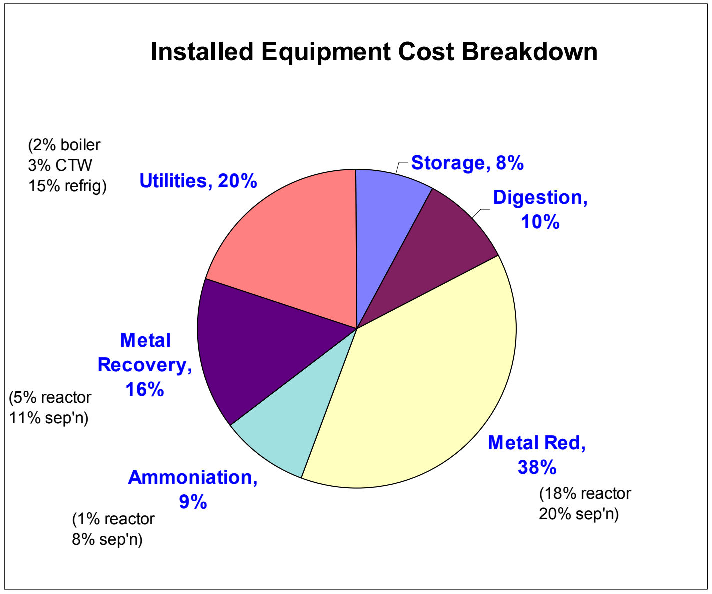


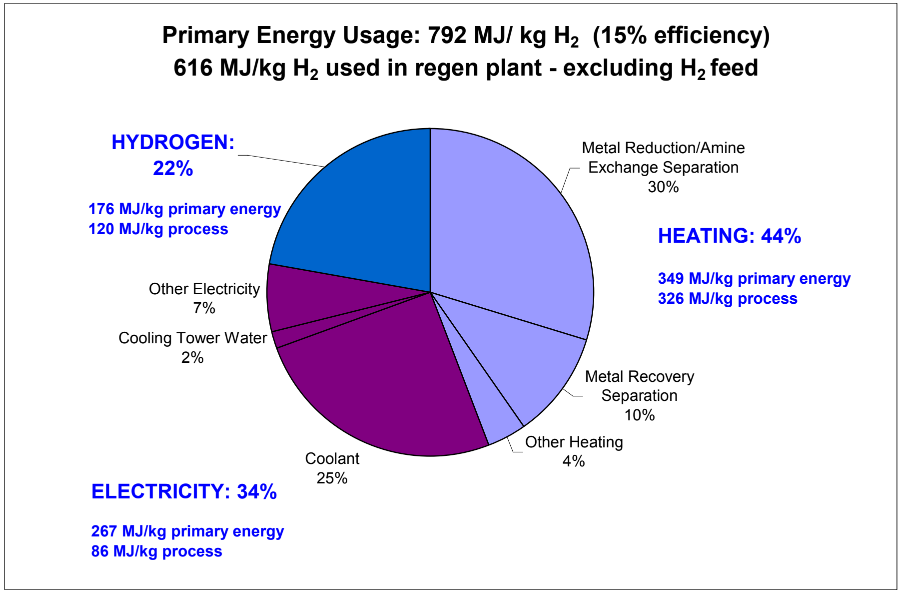
Capital recovery plus utilities account for 75% of regen cost

- necessitated by high mass flows and separation requirements

Nearly 60% of Capital Cost and 90% of Utility Cost Related to Separations

100 mt/day H_2 plant





Opportunities to Lower Cost/Energy Usage

- Reduce mass flow
- Minimize refrigeration - use alternative reagents to improve thermal stability
- Simplify separation scheme - eliminate unessential separations
- Reduce separation severity
- Consider alternatives to high energy distillation (e.g., crystallization)
- Improve heat integration

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Collaboration – Essential for Sound Process Development and Analysis Work

- AB regeneration processes
  - LANL, PNNL, UPenn: Experimental results input
  - U Alabama: Thermochemical calculations
  - Rohm and Haas guides Center development work
- First fill AB process analysis
  - PNNL: Experimental results input
- Low cost $NaBH_4$ for 1^{st} fill AB
  - INL (sub-contractor): Carbothermal studies

Future Work

- AB regeneration
  - Investigate options to reduce cost of LANL AB regen scheme
    - Reduce mass flow
    - Utilize less energy intensive separation schemes
  - Conduct baseline cost estimate for PNNL, hybrid AB regen routes
- First fill AB
  - Conduct baseline cost estimate for PNNL and Shore schemes:
    - $NaBH_4 + NH_4Cl \rightarrow NH_4BH_4 + NaCl \rightarrow NH_3BH_3 + NaCl + H_2$
    - $L\text{-}BH_3 + NH_3 \rightarrow NH_3BH_3 + L$
  - Refine cost estimates with updated $NaBH_4$ cost

Future Work (continued)

- Low cost $NaBH_4$ for 1st fill AB: continue R&D to identify high-yield, low-cost scalable process
  - Metal reduction: select best scalable process
    - Demonstrate alane formation
    - Define chemistry and process window
    - Identify byproduct formation, establish material balance
    - Develop separation and purification needs
    - Detail conceptual process and costs
  - Carbothermal: progress experimental program to validate prior positive results
    - Define process window, quench requirements, separation/purification needs
    - Detail conceptual process and costs
  - Select single top pathway: metal reduction or carbothermal
    - Continue R&D to define and develop process
    - Confirm scalability
    - Update flowsheets and economics
    - Develop life cycle impacts

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Summary

- AB First Fill
  - Low cost $NaBH_4$ is dominant factor for producing 1st fill AB at cost required to meet 2010/2015 DOE hydrogen storage system cost targets.
  - At \$5/kg $NaBH_4$ price using new technology, the metathesis reaction of $NaBH_4$ with NH_4 formate developed by Purdue University can produce AB on a commercial scale at about \$9/kg, which may meet DOE targets.
  - AB synthesis paths differ in separation requirements and could impact AB purity and performance.
  - PNNL and Shore routes are undergoing investigation.
- Low-Cost $NaBH_4$ for 1st Fill AB
  - Alane reduction of borate affords high-purity $NaBH_4$ with high yields.
  - Chemical pathway has been elucidated: good material balance with no intractable byproducts observed; points to recyclable process.
  - Carbothermal reduction of borate to borohydride remains elusive.
- AB Regeneration
  - Baseline cost estimate to regenerate AB using the thiol-based LANL route: \$7 - 8/kg H_2 (exit regen plant) for 100 – 250 MTD H_2 equivalent.
  - Capital recovery and utilities are dominant components of cost, due to high volume process flows and their separation requirements.
  - Opportunities are identified to lower processing and separation costs.

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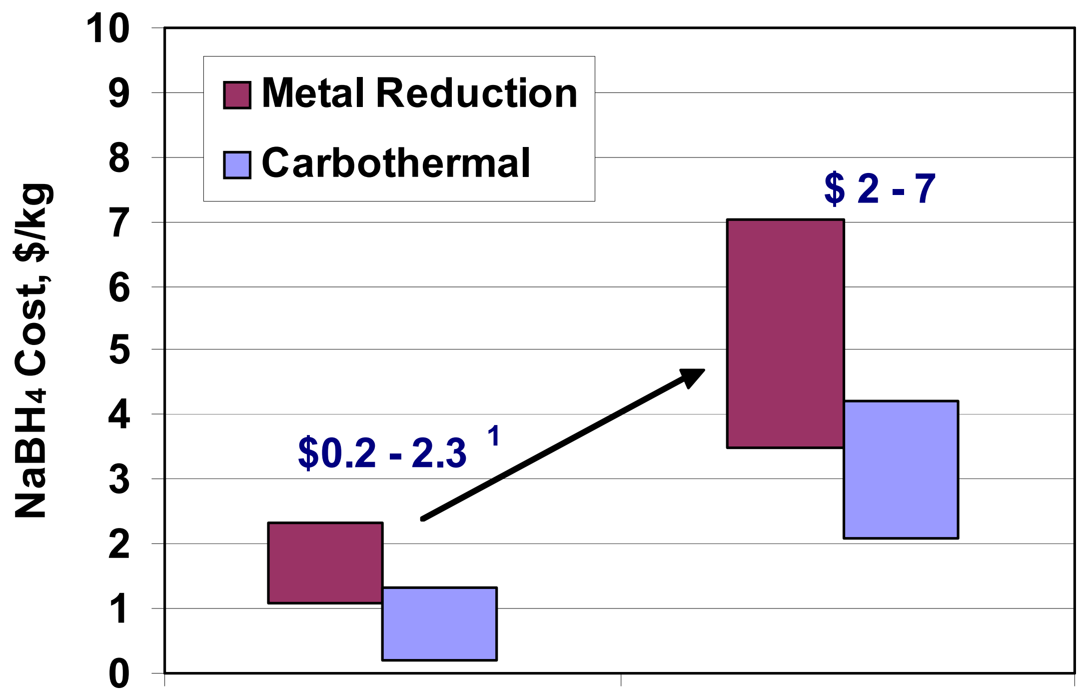
Supplemental Slides

Development of Low-Cost $NaBH_4$ Important at All Production Scales



$NaBH_4$ Plant :	**$NaBH_4$ Regen Plant**	**For 1st Fill AB**
Capacity, MTA :	**173,000**	**13,000**
	(100 mt/d H_2)	**(10,000 MTA AB)**

Cost ranges reflect sensitivities in yield, production volume, capital investment, utility costs, byproduct values, and labor costs

[1] Linehan et al, 2008 AMR : Carbothermal reduction = \$2-7/kg H_2, metal reduction = \$6-12/kg H_2

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