DOE Chemical Hydrogen Storage Center of Excellence

Low-Cost Precursors to Novel Hydrogen Storage Materials

Project ID# ST8

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Overview

Timeline

- Start: March 1, 2005
- End: February 28, 2010
- 60 % complete

Barriers

- Cost
- Energy efficiency
- Regeneration processes
- System life cycle assessment

Budget

	Phase 1	Phase 2	Total Funding
DOE	$1,136K	$632K	$1,768K
ROH	$537K	$285K	$822K
Overall 68:32 DOE:ROH Split			

Partners

Los Alamos National Laboratory

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

PennState

Penn
University of Pennsylvania

The University of California Davis

A Continuation Application with new scope and budget has been submitted to DOE.

Objectives

- Overall: Develop and advance novel hydrogen storage materials to meet DOE 2010 targets and with potential to meet 2015 targets
  - Leverage expertise and experience across Center: engineering requirements, economics, life cycle analysis
  - Support DOE Chemical H_2 Storage Systems Analysis Sub-Group
- Define and evaluate novel chemistries and processes for producing chemical hydrides (Phase 1)
  - Emphasis on low-cost routes to regenerate sodium borohydride from spent fuel leading to Go/No-Go Review
- 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

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Go/No-Go Process: Basis of Center Evaluations Moving Forward

- $NaBH_4$ process provided valuable experience in requirements for the life cycle of a chemical hydride system
  - Data requirements
  - Analysis assumptions
  - Applicable to AB and other systems of promise
- Independent Review Panel
  - University and National Laboratory experts
- Recommendations
  - No-Go for hydrolysis of $NaBH_4$ for on-board vehicular H_2 storage
  - Continue research activities on low cost $NaBH_4$ pathways
    - $NaBH_4$ is a key starting material for AB and other borane-based on-board H_2 storage systems under consideration
    - Improvements in $NaBH_4$ production will lead to cost-effective production (first fill) of these systems

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Low Cost $NaBH_4$ is Essential to Center Success

- Low Cost Ammonia Borane (and other borane-based materials) requires low cost $NaBH_4$ for initial system fill
  - $NaBH_4$ is dominant component to AB costs

    $$nNaBH_4 + (NH_4)_nX = nNH_3BH_3 + Na_nX + nH_2$$

  - Lower cost $NaBH_4$ technologies needed

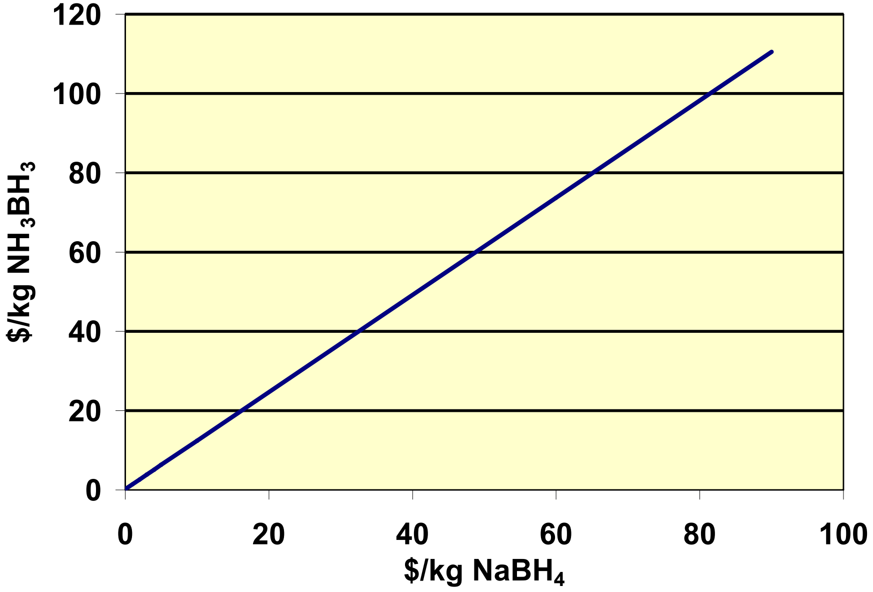
DOE Storage System Cost Targets

	$/kg H_2	$/kg AB *
2007	200	8.7
2010	133	5.8
2015	67	2.9

* assume media is 33% of system cost (from TIAX SAH study)

Need < $5/kg $NaBH_4$ for 2010, <$3/kg for 2015

Impact of $NaBH_4$ on AB RM Costs



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Milestones

Month/Year	Milestone or Go/No Go Decision
June 2007	Key chemistries demonstrated to validate leading $NaBH_4$ chemical pathways.
September 2007	Feasibility of leading $NaBH_4$ pathways established based on laboratory-scale experimental demonstration and cost analysis.
November 2007	No Go decision for $NaBH_4$ for on-board hydrogen release; ***Go decision to progress R&D on $NaBH_4$ synthesis for low cost first fill AB***
July 2009	Top $NaBH_4$ synthesis route selected for development

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Technical Approach

Identify Leading Pathways	Determine Feasibility of Leading Pathways	Detail Performance to Select Single Pathway	Single Pathway Selected
▪ 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	▪ Demonstrate key chemical and process steps in laboratory studies ▪ Develop flow sheets and preliminary energy requirements and cost estimates for leading systems	▪ Establish complete material balance to determine intermediates and purification requirements ▪ Demonstrate all chemical and process steps ▪ Investigate scalability	▪ Develop single $NaBH_4$ process ▪ Update economics

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Technical Accomplishments Overview

- Feasibility of 2 new low-cost $NaBH_4$ routes identified
  - Metal reduction of borate
  - Carbothermal reduction of borate
- Key chemistry step of $NaBH_4$ formation demonstrated
- Conceptual processes developed show significantly improved energy efficiency and lower cost compared to current Schlesinger technology
- Research on electrochemical reduction pathways to $NaBH_4$ discontinued (Penn State)
- Spent AB regeneration analysis support initiated

Leading $NaBH_4$ Pathways Identified

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

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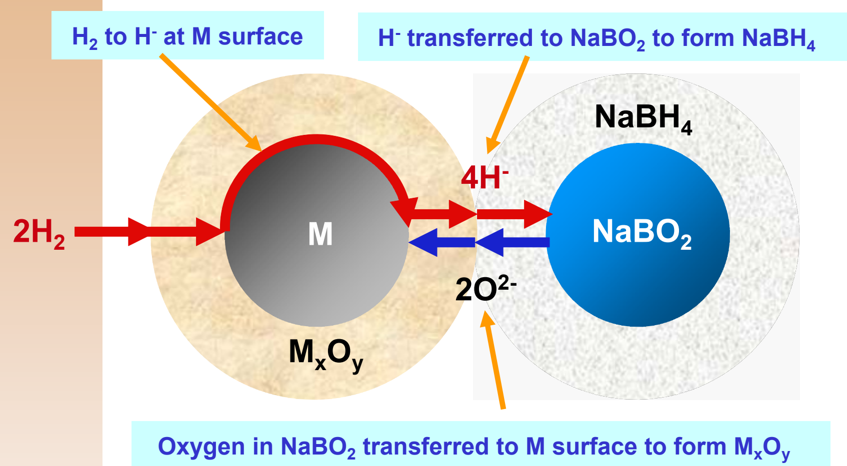
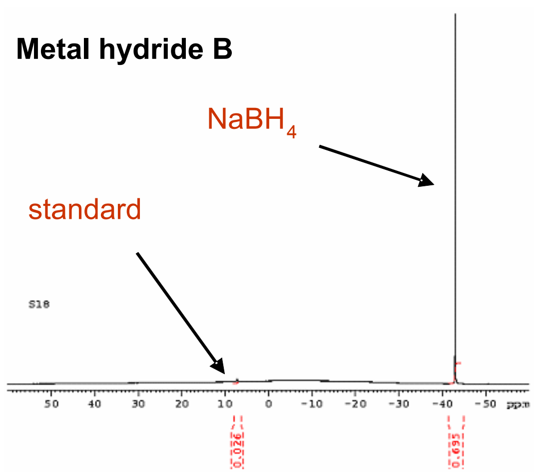
Metal-Based Reduction Feasibility Established

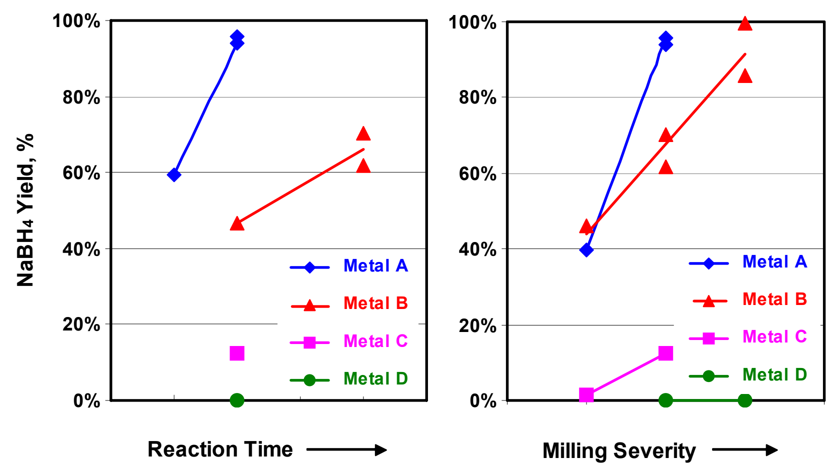


Lab reactive milling capabilities established

[11]B NMR confirms and quantifies $NaBH_4$ formation

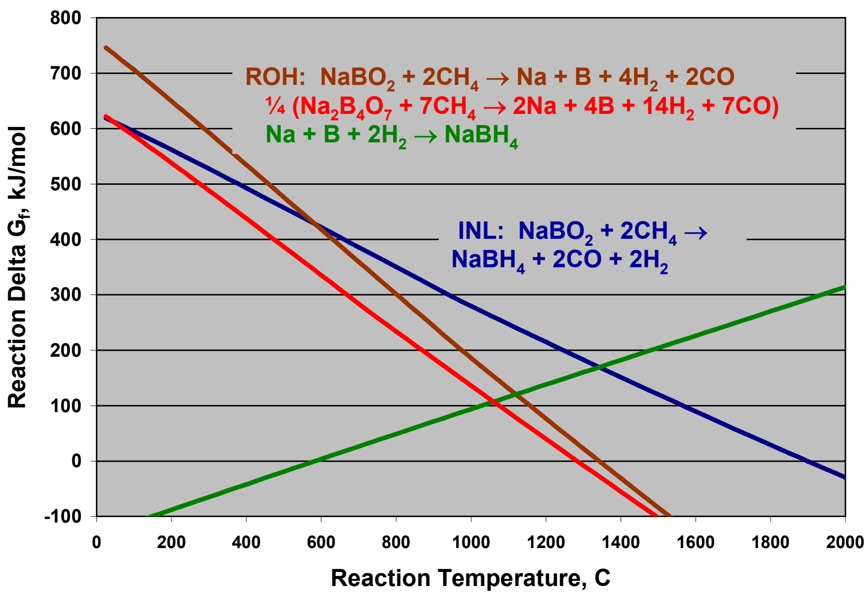


High $NaBH_4$ yields demonstrated with metal hydrides

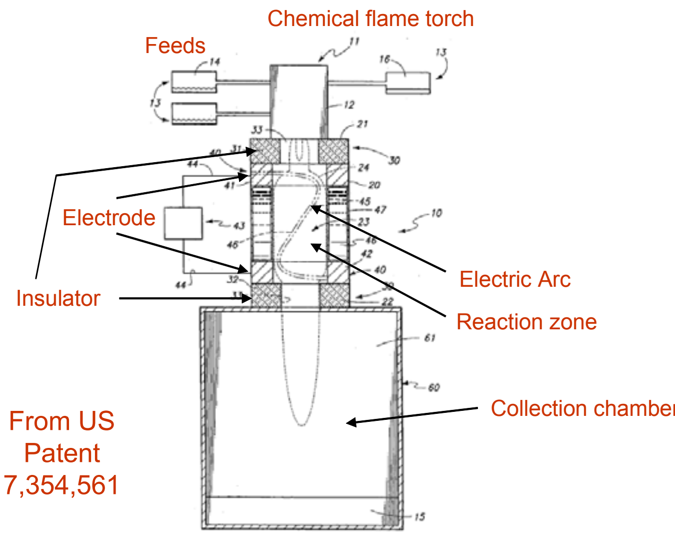


Carbothermal Reduction Feasibility Established

Reactions favored at high temperatures



INL claims $NaBH_4$ formation under plasma conditions



From US Patent 7,354,561

<u>Pre-combustion</u>:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2$

Net: $4CH_4 + 2O_2 \rightarrow 4CO + 8H_2$

<u>Borate Reduction</u>:

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

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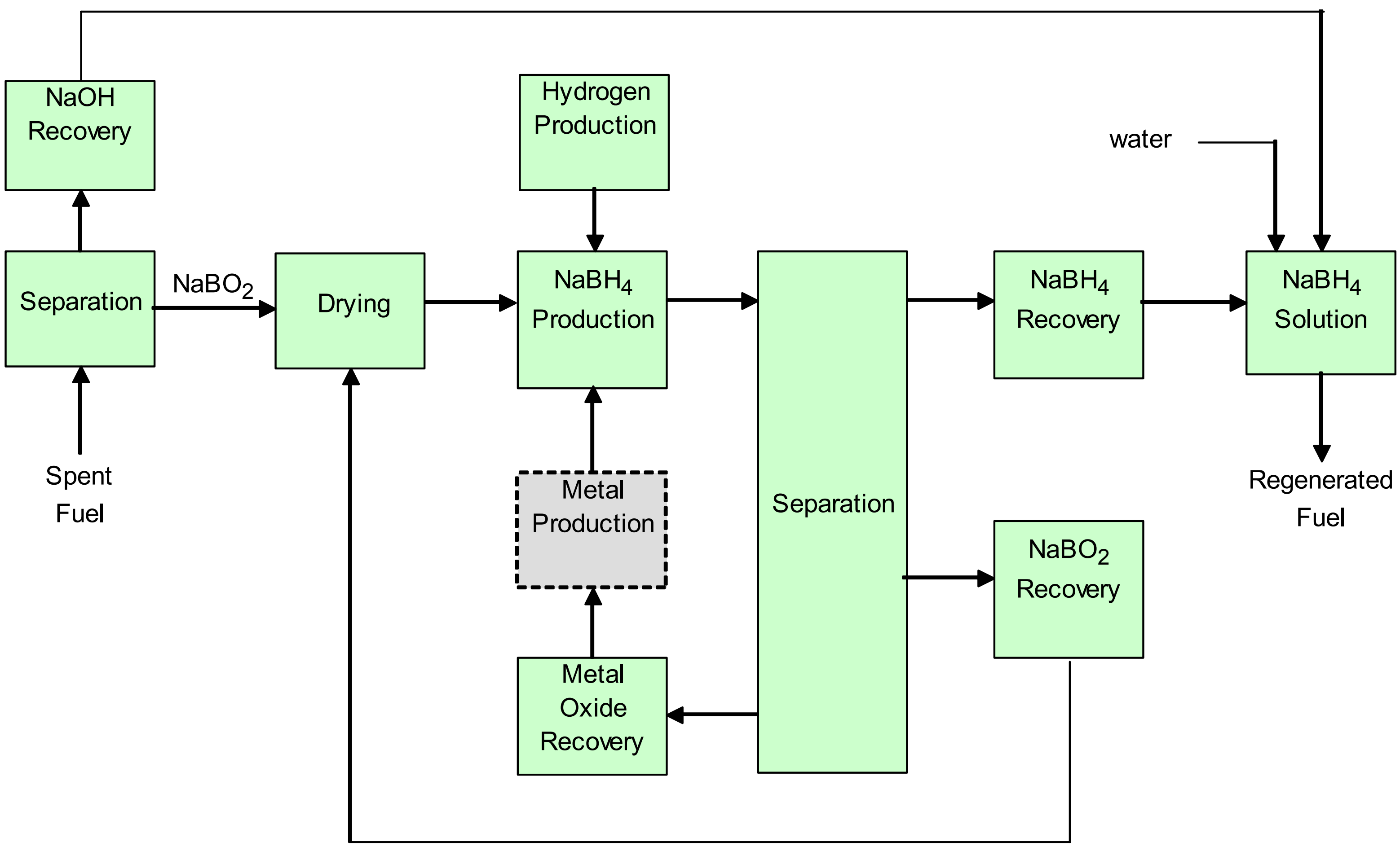
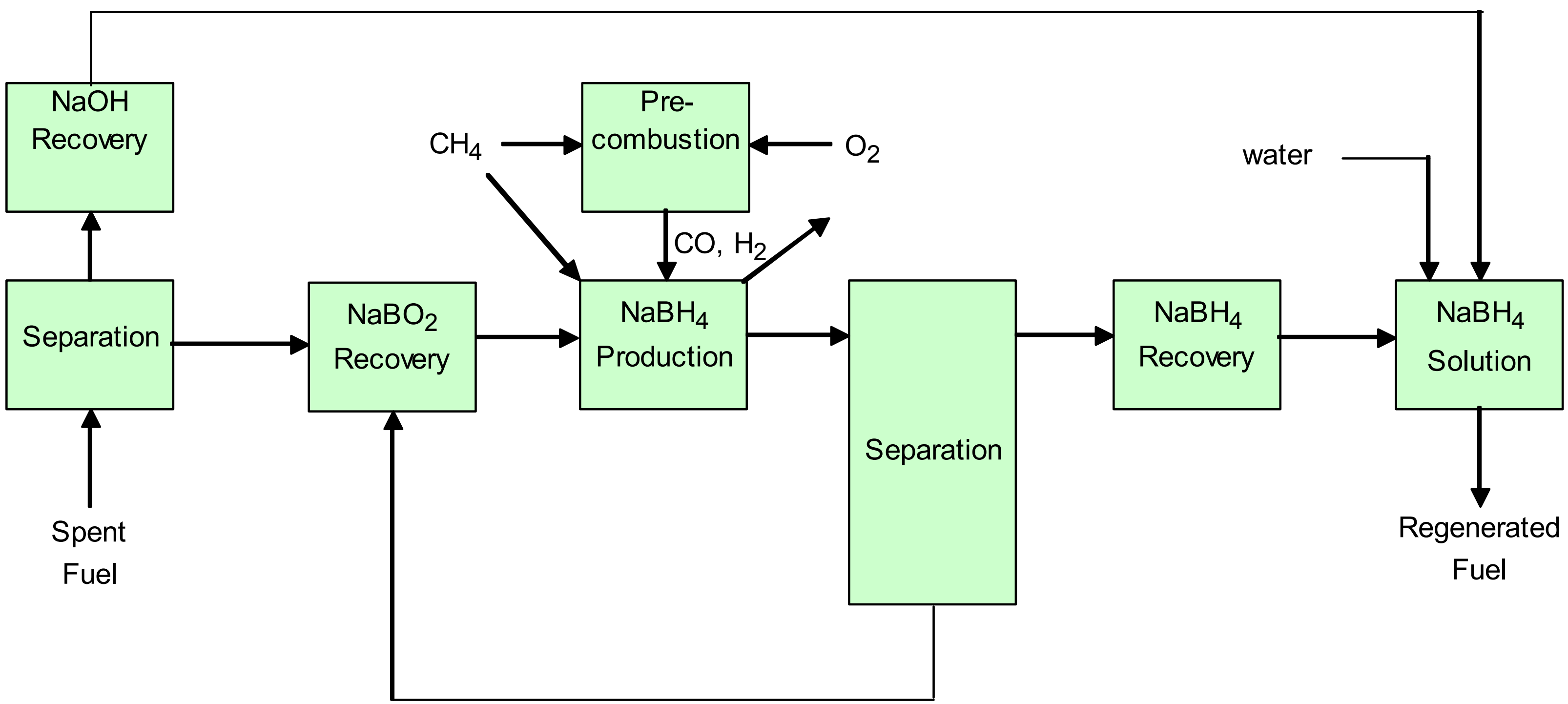
$NaBH_4$ Regeneration Conceptual Process Using Metal Reduction

$$NaBO_2 + 2x/y\ M + 2H_2 \rightarrow NaBH_4 + 2/y\ M_xO_y$$



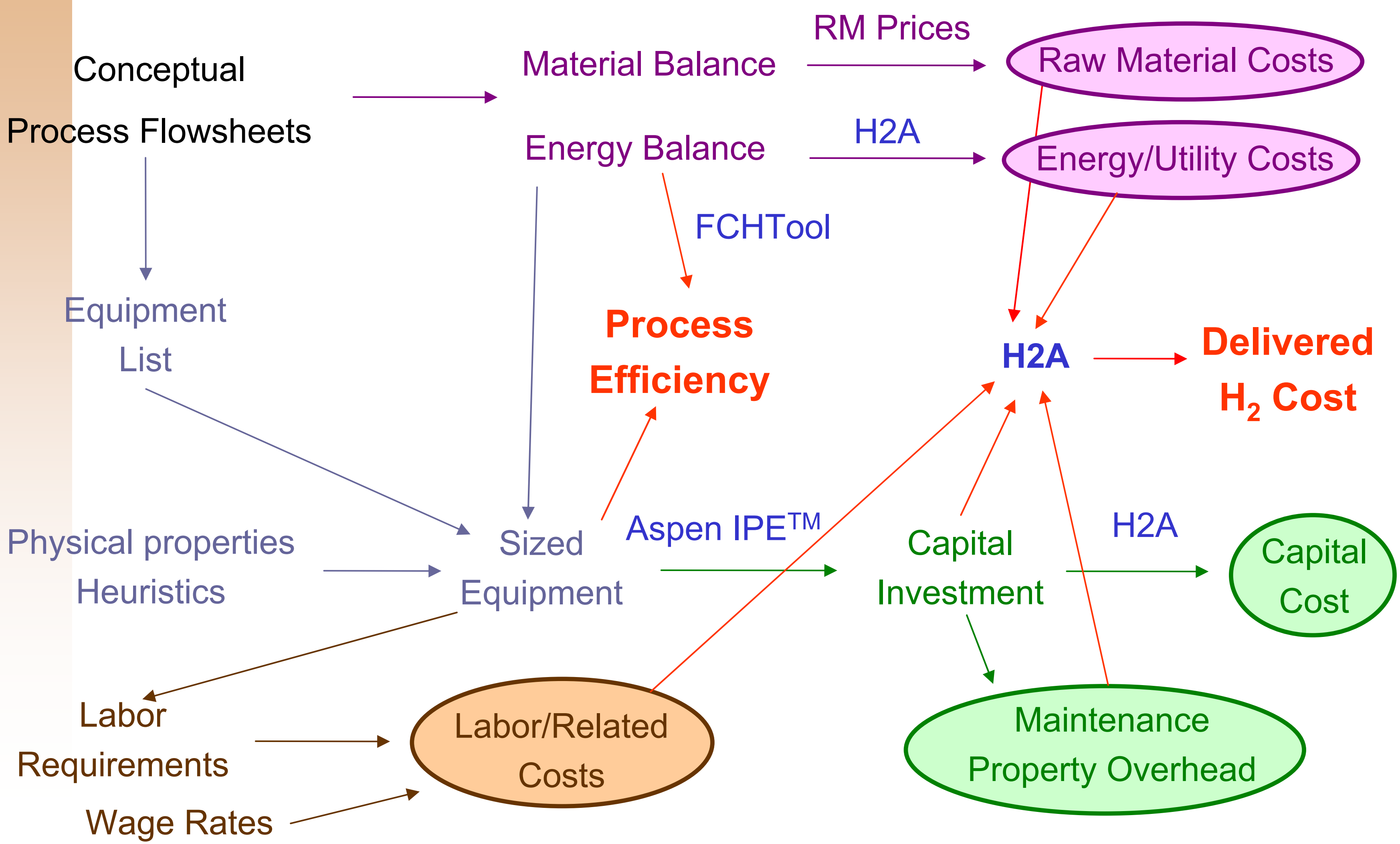
$NaBH_4$ Regeneration Conceptual Process Using Carbothermal Reduction

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



Lower cost and higher efficiency process expected with elimination of metal recovery.

Cost Estimating Methodology Established



Regenerated $NaBH_4$ Costs Approach DOE Fuel Targets

Pathway	Cost, \$/kg H_2 [1]	Fuel Energy Efficiency [2]
DOE 2010 Target	2-3	60%
Metal Reduction	6-12	43(19)%
Carbothermal Reduction	2-7	50(19)%

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

1 - Delivered H_2 cost to auto

2 - Energy content of H_2 delivered to auto relative to total energy to process including fuel input energy of H_2 and any other fuel streams used for generating process heat and electrical energy. Electricity from hydroelectric. () indicates efficiency based on US Electrical Grid.

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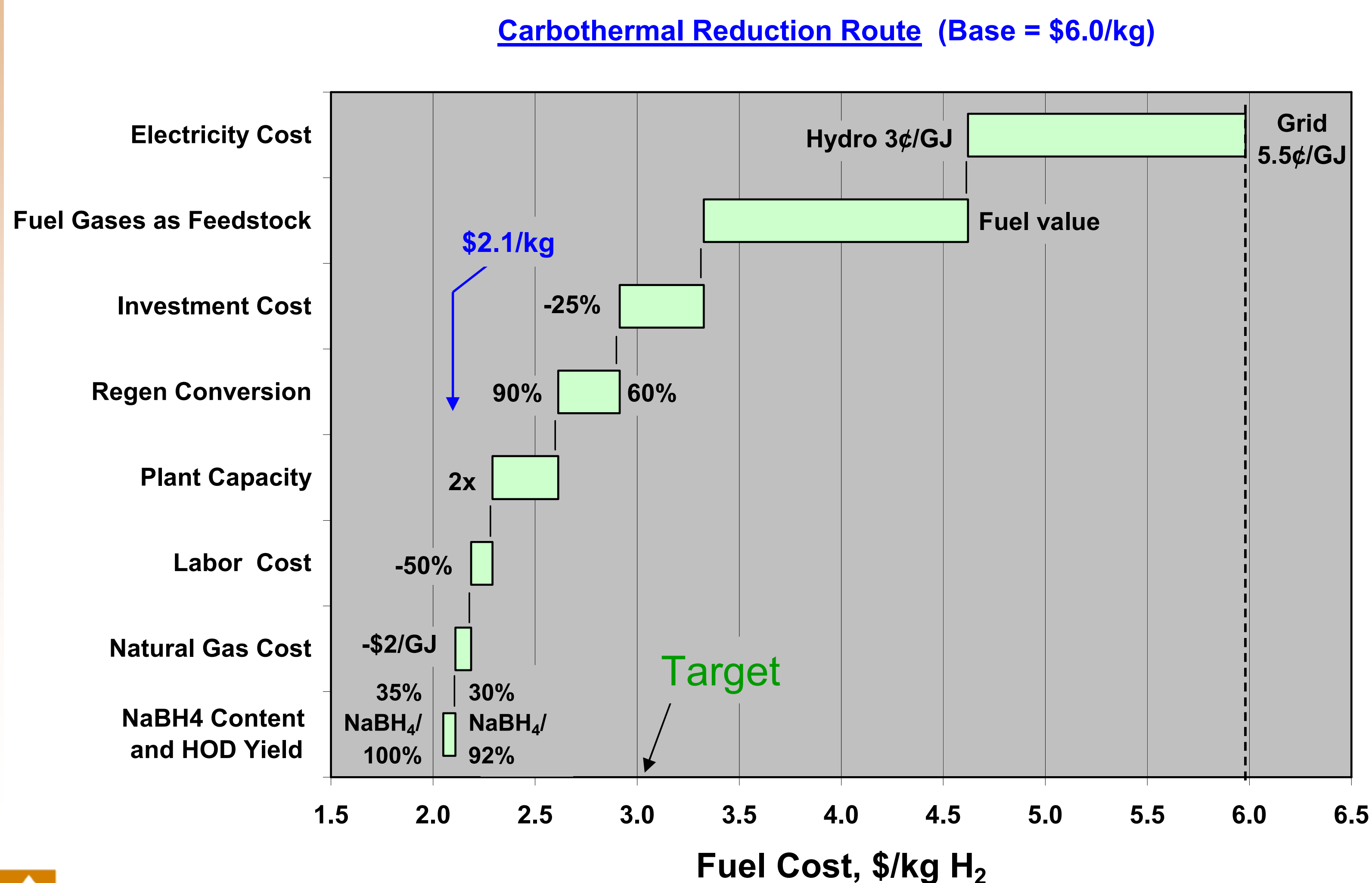
Sensitivity Analysis Shows Scenarios to Achieve DOE Fuel Cost Targets



Low Cost $NaBH_4$ Routes Will Help AB Meet DOE Storage System Cost Targets

- With No-Go decision for on-board $NaBH_4$ hydrolysis, focus turns to low cost means for first charge of fuel (AB)
- Project scope unchanged - $NaBH_4$ paths applicable to borate as raw material or as spent fuel
- With lower $NaBH_4$ demand, efficient energy sources (i.e., hydroelectric) may be practical

Pathway	H_2 Cost, $/kg	AB Cost, $/kg * ($NaBH_4$ RM)
Metal Reduction	6-12	1.6-3.1
Carbothermal Reduction	2-7	0.5-1.8

* Excludes borate feed cost; 100% yield to AB

Assuming AB media is 33% of storage system costs, AB media cost targets are $5.8/kg AB in 2010 and $2.9/kg AB in 2015.

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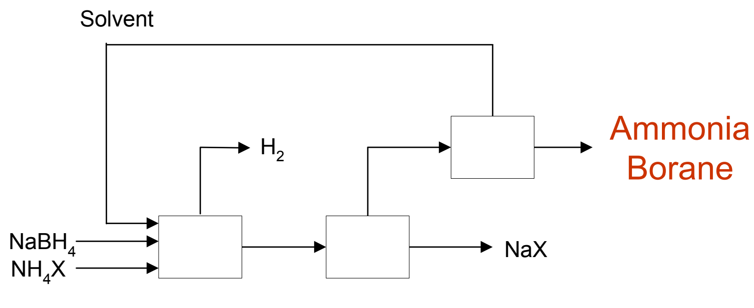
Future Work

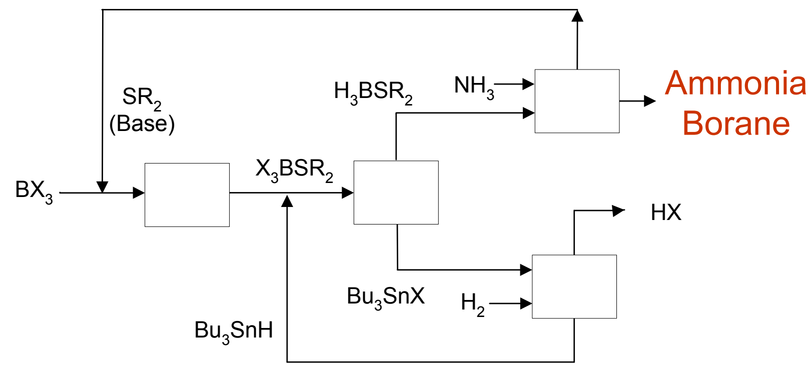
- Progress process R&D to create high-yield, low-cost scalable $NaBH_4$ process for first fill AB
  - Continue studies on both metal-based and carbothermal reduction
    - Identify byproduct formation
    - Define chemistry and process window
    - Identify scale-up options and evaluate viability
    - Develop separation and purification needs
    - Detail conceptual process and costs
  - Select single top pathway
    - Continue R&D to define and develop process
    - Update flowsheets and economics
    - Develop life cycle impacts

Future Work (cont.)

- Support AB synthesis and regeneration research
  - Apply $NaBH_4$ metrics-based process to select top AB pathways
  - Provide conceptual process development and cost estimates
  - Conduct “first fill” AB synthesis process analysis



1st Fill AB Synthesis



UPenn Halo-Superacid AB Regen

Define high yield, low cost, scalable processes

- Leverage Rohm and Haas competencies across Center
  - Process development
  - Engineering assessment

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Summary

- Experimental studies confirmed feasibility of two leading pathways for regenerating $NaBH_4$ from spent borate fuel
  - Metal reduction
  - Carbothermal reduction
  - ***Both show potential for significant cost improvement over current Schlesinger process***
- Independent Panel Review found
  - Sound chemistry, but early stage
  - $NaBH_4$ analysis methodology valuable: tool applicable to AB and other promising storage materials
- Research on low-cost pathways to $NaBH_4$ will continue
  - $NaBH_4$ is a key starting material for AB and other borane-based materials under consideration
  - Improvements in $NaBH_4$ production will lead to cost-effective "first fill" for these systems
- Phase 2 focus
  - Detailing conceptual process and cost for top $NaBH_4$ pathway
  - Applying metrics-based $NaBH_4$ pathway analysis to AB assessments

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Collaboration and Technology Transfer Phase 2

- AB regeneration processes
  - Rohm and Haas, PNNL, LANL, U. Penn
- "First fill" AB process analysis
  - Rohm and Haas, PNNL, LANL

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Los Alamos NATIONAL LABORATORY

Penn UNIVERSITY of PENNSYLVANIA

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