DOE Chemical Hydrogen Storage Center of Excellence

Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides

Project ID# ST25

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Overview

Timeline

- Start: March 1, 2005
- End: February 28, 2010
- 40 % complete

Barriers

- High cost and energy requirements for regenerating spent fuel from irreversible chemical H_2 storage systems
- Lack of understanding of cost and environmental impact of regeneration process

Budget

	FY05 Actual	FY06 Actual	FY07 Budget	Total Funding
DOE	$275K	$300K	$433.8K	$1,768K
ROH	$129K	$141K	$214K	$822K
Overall 68:32 DOE:ROH Split				

Partners

ROHM AND HAAS

Los Alamos NATIONAL LABORATORY

PENNSTATE 1855

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

Millennium Cell

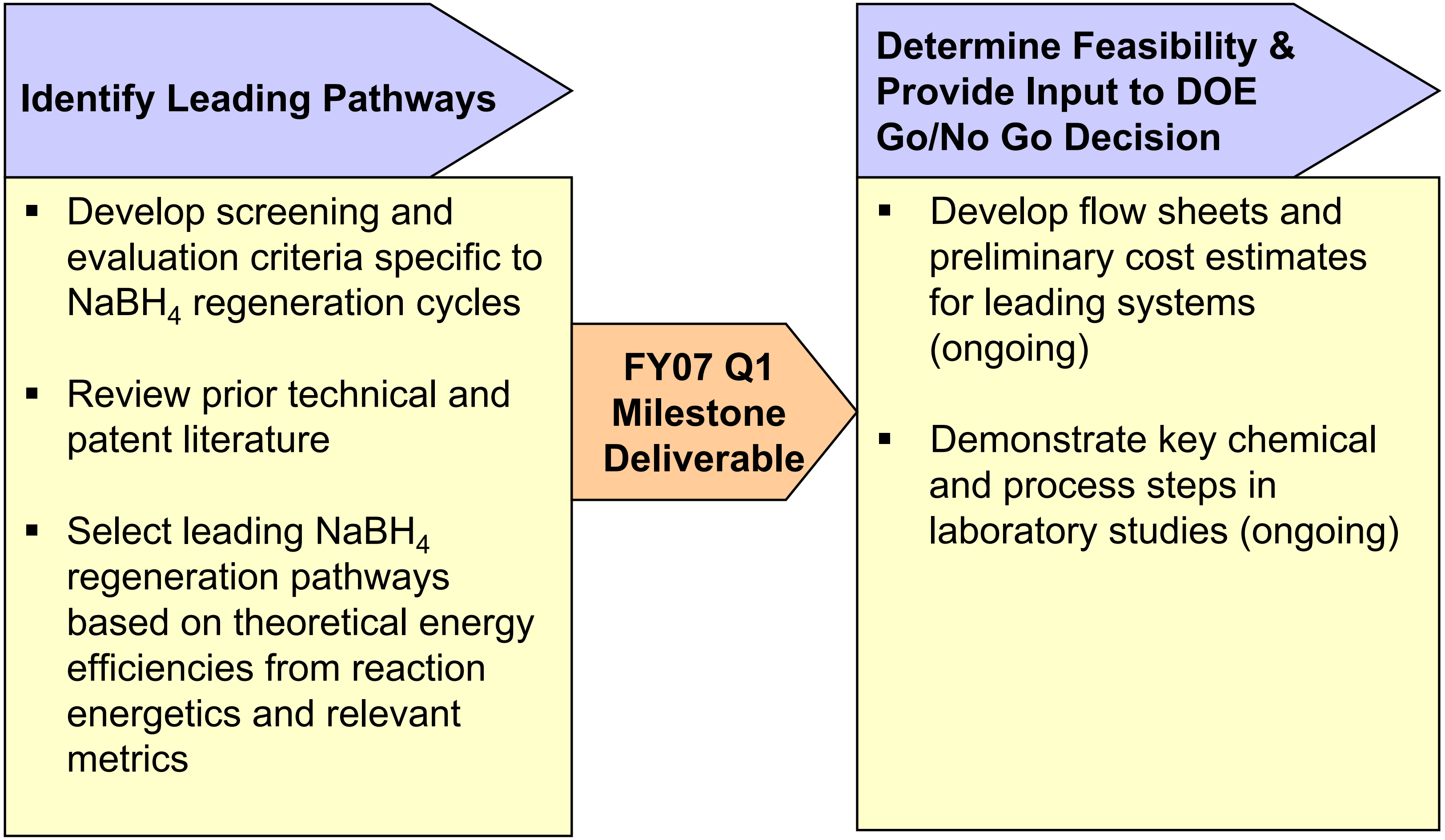
THE UNIVERSITY OF CALIFORNIA DAVIS

THE UNIVERSITY OF ALABAMA

Objectives

Overall	**Define and evaluate novel chemistries and processes to produce chemical hydrogen storage materials to meet DOE 2010 targets and with potential to meet 2015 targets** • Focus on energy efficient and cost-effective options for B-OH (borate) to B-H conversion • Leverage expertise and experience across Center: engineering requirements, economics, life cycle analysis • Support DOE Chemical H_2 Storage Systems Analysis Sub-Group
FY06	**Identify chemical pathways and process options** • Complete computational analysis of sodium borohydride (SBH) regeneration routes: chemical and electrochemical • Develop experimental program **Center-wide** • Engineering analysis • Ammonia Borane stability studies
FY07	**Provide input to DOE Go/No Go decision for SBH** • Demonstrate laboratory feasibility • Estimate efficiency of process • Prepare preliminary SBH production/regeneration cost estimate

Technical Approach



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

FY07 Q1 Milestone Deliverable

Determine Feasibility & Provide Input to DOE Go/No Go Decision

- Develop flow sheets and preliminary cost estimates for leading systems (ongoing)
- Demonstrate key chemical and process steps in laboratory studies (ongoing)

Results Overview

- **Chemical reduction of borates**
  - Compiled regeneration pathways
  - Issued report literature review (FY07 Q1 deliverables completed)
  - Developed system of metrics
  - Selected systems for experimental work
  - Began experimental program; SBH production confirmed

- **Electrochemical reduction of borates**
  - Investigating aqueous and non-aqueous systems with PSU
  - Recent studies suggest successful production of $NaBH_4$

- **Ammonia borane stability**
  - Collaborated with PNNL on adiabatic calorimetry studies

- **Analysis**
  - Received and applied H2A model
  - Developed conceptual regeneration processes

Result: Literature Review of $NaBH_4$ Routes Completed

- Metal reduction
- Electrochemistry
- Borane-based routes
- Carbothermal reduction
- Elemental synthesis
- Metathesis routes

All result in higher energy efficiency and improved metal utilization over current Schlesinger process

Review of literature and patents from 1950’s to current. Over 30 chemical pathways considered, with numerous variations/combinations within each class (total >100)

Result: Regeneration Chemistries Identified

Pathway	Illustrative Chemistry
Schlesinger (current)	**$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$**
Metal reduction	**$NaBO_2 + 2x/y\ M + 2H_2 \rightarrow NaBH_4 + 2/y\ M_xO_y$**
Electrochemical	**$B(OH)_4^- + 4H_2O + 8e^- \rightarrow BH_4^- + 8OH^-$**
Carbothermal	**$NaBO_2 + 2H_2 + CH_4 + O_2 \rightarrow NaBH_4 + CO_2 + 2H_2O$**
Elemental synthesis	**$Na + B + 2H_2 \rightarrow NaBH_4$**
Borane-based	**$1/2\ B_2H_6 + NaH \rightarrow NaBH_4$** **$2/3\ B_2H_6 + NaOCH_3 \rightarrow NaBH_4 + 1/3\ B(OCH_3)_3$**
Metathesis	**$Na + Al + 2H_2 \rightarrow NaAlH_4$** **$NaAlH_4 + B(OR)_3 \rightarrow NaBH_4 + Al(OR)_3$**

Result: Energy Efficiency Analysis

Procedure

- Define complete reaction cycle
- Calculate ΔG° for each step to determine reaction spontaneity under range of conditions and eliminate disfavored routes
- Calculate $\Delta H^\circ_{25^\circ C}$ for theoretical minimum energy. Reaction enthalpy change is sum of endothermic steps minus 0-75% heat recovery of exothermic steps
- Usable energy of product and reactants based on $\Delta H^\circ_{25^\circ C}$ (LHV)
- Determine theoretical regeneration efficiency

$$\textbf{Theoretical Efficiency} = \frac{\textbf{Usable Energy Released in Product}}{\textbf{Reactant Energy Value} + \textbf{Reaction Enthalpy Change}}$$

Result: Energy Efficiency Analysis

Example – Silicon Reduction of Borate

- **Hydrolysis reaction:** $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$
- **Regeneration path:**

		$\Delta H°_{25°C}$ (kcal/mol)
	$NaBO_2 + Si + 2H_2 \rightarrow NaBH_4 + SiO_2$	-30.4
	$SiO_2 + 2C \rightarrow Si + 2CO$	164.9
	$2CO + 2H_2O \rightarrow 2H_2 + 2CO_2$	1.4
Overall	$NaBO_2 + 2C + 2H_2O \rightarrow NaBH_4 + 2CO_2$	143.5 – 166.2**

- **Heating values (LHV):**

H_2 product	-57.8
C feed	-94.1

Theoretical Efficiency $= \dfrac{\textbf{Usable Energy Released in Product } (4H_2)}{\textbf{Reactant Energy Value + Reaction Enthalpy Change}}$

= 4(57.8) / [2(94.1) + (143.5 to 166.2)] = 65-70%

** For 0-75% heat recovery of exothermic reactions

Result: Energy Efficiency Analysis

Primary Energy Basis

$$\text{Efficiency (Primary Energy)} = \frac{\text{Usable Energy Released in Product}}{\dfrac{\text{Reactant Energy Value}}{\eta_1} + \dfrac{\text{Reaction Enthalpy Change}}{\eta_2}}$$

$$\text{Efficiency (Si reduction)} = \frac{4(57.8)}{\dfrac{2(94.1)}{0.88} + \dfrac{164.9}{0.62} + \underset{**}{(1.4 \text{ to } -21.4)}} = 48\text{-}50\%$$

** (1.4 - 0.75 * 30.4)

- η_1 = efficiency to produce reactant fuel (primary energy) [0.88 for coke]
- η_2 = energy efficiency of controlling endothermic reaction [0.62 for Si]

Result: Energy Efficiency Drivers Identified

- Ideal $NaBH_4$ regeneration <76% theoretical efficiency
  - loss due to unrecoverable exotherm for $NaBH_4$ hydrolysis
- Heat recovery from regen exothermic reactions important
- Process selected to recover metal has substantial impact
- Pathway must be coupled with efficient fuel source to achieve efficiency targets based on primary energy

	$\Delta H_{rxn,\ 25C}$ kcal/mol	Efficiency to Fuel, η	Max Efficiency (Primary)
$NaBO_2 + \mathbf{4H_2} \rightarrow NaBH_4 + 2H_2O_{(g)}$	72	68% (H_2 : SMR)	56%
$NaBO_2 + 2H_2O_{(l)} \xrightarrow{e^-} NaBH_4 + 2O_2$	324	32 (e^- : 2015 US grid)	24
$NaBO_2 + 2H_2O_{(l)} \xrightarrow{e^-} NaBH_4 + 2O_2$	324	80-100 (e^- : CHP - hydro)	58-71

Result: Energy Efficiency Summary

Pathway (metal recovery route)	Theoretical Efficiency @ Heat Recovery 0%	Theoretical Efficiency @ Heat Recovery 75%	Primary Energy * 2015 US Grid (32%) @ Heat Recovery 0%	Primary Energy * 2015 US Grid (32%) @ Heat Recovery 75%	Primary Energy * Electricity (50%) @ Heat Recovery 0%	Primary Energy * Electricity (50%) @ Heat Recovery 75%	Primary Energy * Hydro (100%) @ Heat Recovery 0%	Primary Energy * Hydro (100%) @ Heat Recovery 75%
Metal Reduction								
Na (Downs w/Schlesinger)	45%	52%	9%	9%	13%	13%	23%	25%
Na (MCEL w/Schlesinger)	62%	76%	28%	31%	36%	40%	47%	54%
Mg (e-)	57%	70%	16%	17%	23%	25%	39%	45%
Al (carbon)	57%	67%	47%	53%	47%	53%	47%	53%
Ti (e-)	68%	74%	20%	21%	29%	30%	47%	50%
Si (carbon)	65%	70%	48%	50%	48%	50%	48%	50%
Zn (carbon)	76%	77%	58%	58%	58%	58%	58%	58%
Electrochemical Reduction								
1-step (B(OH)4- + 8e-)	71%	71%	17%	17%	26%	26%	50%	50%
2-step through NaBH(OCH3)3	69%	72%	24%	25%	33%	34%	51%	53%
Carbothermal Reduction	75%	75%	62%	62%	62%	62%	62%	62%
Carbothermal/Elemental	77%	82%	55%	57%	55%	57%	55%	57%
B2O3 Reduction via Mg/Elemental	55%	70%	19%	20%	25%	28%	38%	44%
Borane Routes								
BHCl2 disproportionation	44%	65%	33%	43%	33%	43%	33%	43%
BH(OR)2 disproportionation	68%	78%	44%	48%	44%	48%	44%	48%
B2O3 + M + H2	64%	69%	47%	50%	47%	50%	47%	50%
Metathesis								
B(OR)3 + NaAlH4	53%	65%	14%	15%	20%	21%	34%	38%
Formaldehyde	54%	69%	39%	47%	39%	47%	39%	47%

Several pathways satisfy efficiency target

Electrochemical routes require high efficiency electricity source

Additional metrics needed to select top routes

*** Includes efficiency of metal oxide reduction to metal; use 70% electrical efficiency for electrochemical reduction**

Applied Evaluation Criteria - Metrics

Criterion	Weighting
Chemistry demonstrated	**Strong preference**
Manufacturing cost	
– high theoretical energy efficiency	**25**
– high conversion and yield	**25**
– low operating severity	**5**
– few chemical reactions	**5**
– few separation / processing steps	**5**
Capital cost	
– low complexity	**10**
– low technical risk	**5**
EHS	
– low emissions, wastes, greenhouse	**10**
– high safety profile: low toxicity, corrosivity, flammability, H_2O-reactivity	**5**
Logistics	
– abundant raw materials	**5 (G/NG)**

Score = 1-10

Overall Score = $\sum_i$ (Weighting x Score)$_i$

Result: Leading Regeneration Pathways Identified

Goal: Define energy efficient and cost effective process to regenerate spent borate to NaBH4 to meet DOE targets

Option Criterion	Weighting	Schlesinger	Metal Reduction					Carbothermal	Elemental *	Echem			Borane			Metathesis
			Mg	Al	Ti	Si	Zn			1-stop	2-step	HT melts	BCl3	TMB	M + B2O3	
Chemistry demonstrated	Pref	Yes	Yes	Yes	No	Yes	No	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
Cost/per unit H2 (NaBH4)																
Energy consump (theor efficiency)	**25**	1	5	7	7	7	9	9	8	7	7	7	4	6	7	3
Raw material consump - high conv / yields	**25**	3	8	7	7	7	7	5	7	1	3	5	7	3	3	7
Low operating severity	**5**	7	8	8	8	8	8	5	3	10	10	5	5	3	5	7
Few chemical reactions	**5**	5	8	8	8	8	8	9	8	10	8	8	4	7	4	5
Few separation / processing steps	**5**	5	8	8	8	8	8	9	6	10	8	6	3	7	5	5
Capital cost, $ per unit H2 (NaBH4)																
Low complexity	**10**	6	8	8	8	8	8	8	6	9	8	6	5	7	5	5
Low technical risk	**5**	10	7	7	7	7	7	5	5	7	7	5	6	7	5	7
EHS (environmental / health / safety)																
emissions, wastes, CO2	**10**	10	8	8	8	8	8	7	8	10	9	8	7	7	7	6
toxicity, safety, flammability, H2O-reactive	**5**	8	7	6	7	7	7	7	7	10	9	7	5	6	6	6
other ecological components?																
Logistics (supply / distribution)																
abundant raw materials	**5**	10	7	10	7	8	6	10	8	10	10	10	10	10	8	10
Total Score		**485**	**710**	**745**	**735**	**740**	**780**	**725**	**700**	**675**	**680**	**645**	**560**	**565**	**535**	**560**

* Elemental - B by carbo, 600 if B by Mg

Rankings:

Metal reduction # 1

Carbo and elemental (B via carbo) # 2 and 3

Electrolytic # 4

Borane, metathesis # 5 and 6

Key Findings: $NaBH_4$ Pathways Analysis Summary

- **Metal reduction pathway most advanced**
  - Highest yields demonstrated
  - Fewest processing steps for direct conversion of $NaBO_2$
  - Potential for low severity operations
  - Numerous metal candidates with satisfactory energy efficiency
  - Existing large scale industry for metal recycle, but process advances will significantly improve efficiency
- **Electrochemical route attractive but remains elusive**
  - Improved yields needed from Penn State program
- **Carbothermal/elemental route has high potential efficiency**
  - Does not require introduction of metal reductant
- **Borane pathway commercial but requires more efficient path**
  - Multi-step processes involving multiple complex chemistries
  - Higher hazard class
- **Metathesis route "proven" but has lower efficiency**

Result: Experimental Program Established

Goal: Demonstrate/validate key reaction steps to define top route

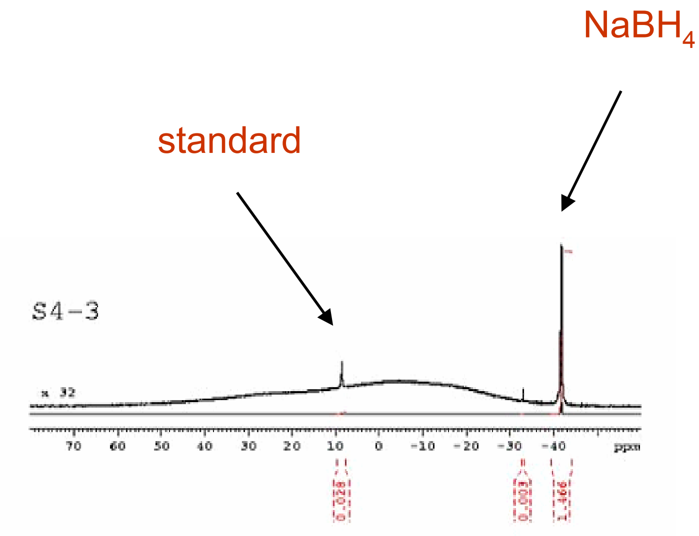
- **Metal reduction studies initiated at ROH**
  - Defined equipment and testing needs
  - Screen feasibility of Mg, Al, Si, Ti, Zn and/or their hydrides to reduce $NaBO_2$
  - Explore with UCDavis potential of H-terminated Si nanoparticles
  - Identify operations providing optimum yields and energy efficiency
  - Validate process flowsheets for more rigorous cost and energy calculations

- **Electrochemical reduction studies ongoing at PSU**
  - Provided details of prior 1-step and 2-step ROH studies to reproduce
  - Shared concepts on modified electrodes, non–aqueous systems

- **Carbothermal reduction**
  - Exploring options to address lack of carbothermal reduction experimental capability

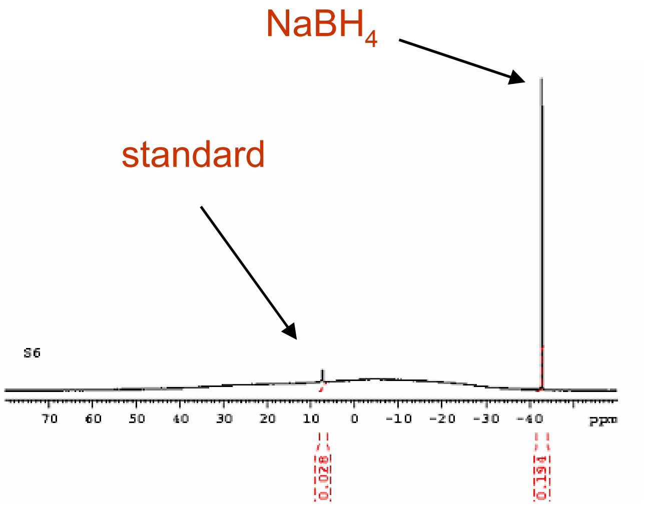
Result: Reduction of Borate Using Metal Hydride Demonstrated

Metal Hydride A


NaBH$_4$

standard

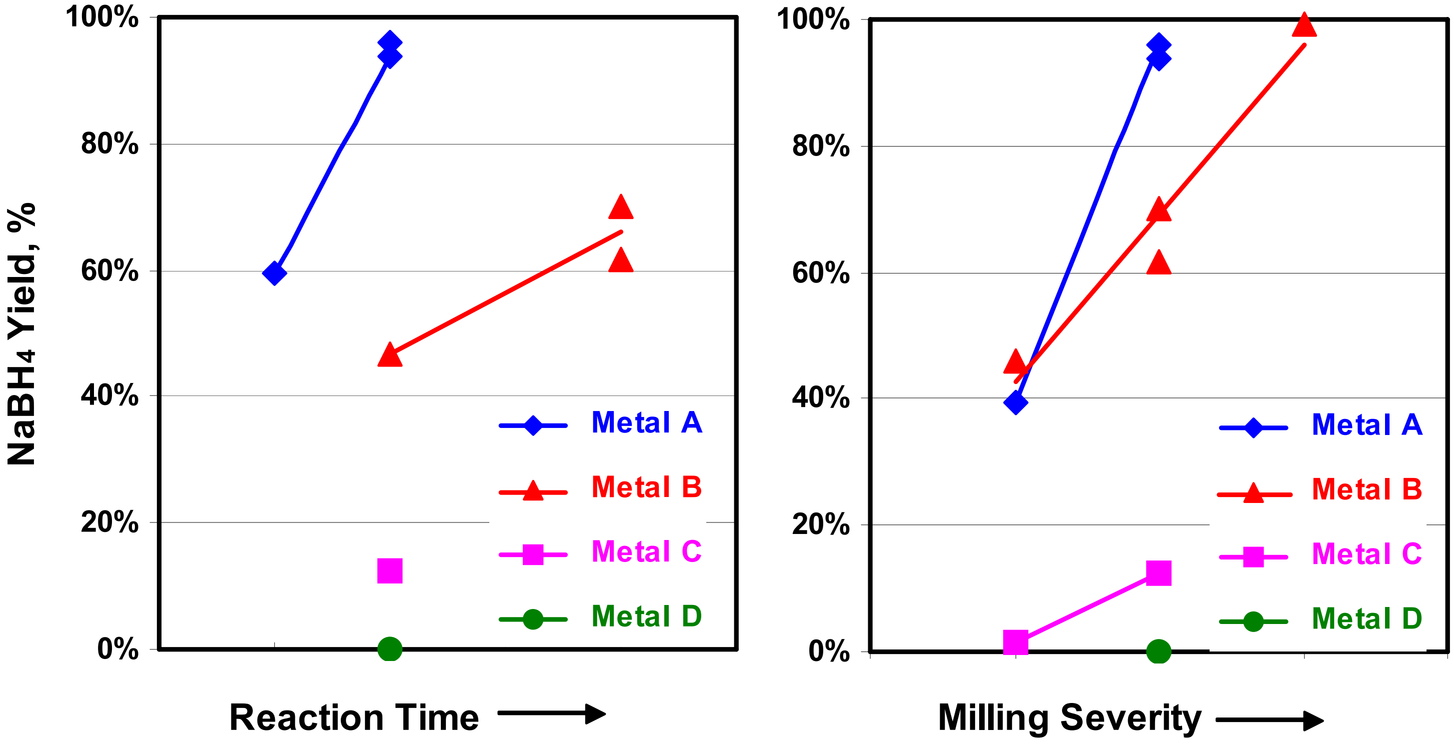
Metal Hydride C


NaBH$_4$

standard

Proton-decoupled ^{11}B NMR analysis confirms and quantifies NaBH$_4$ formation

Result: Feasibility of Metal Reduction Process Established

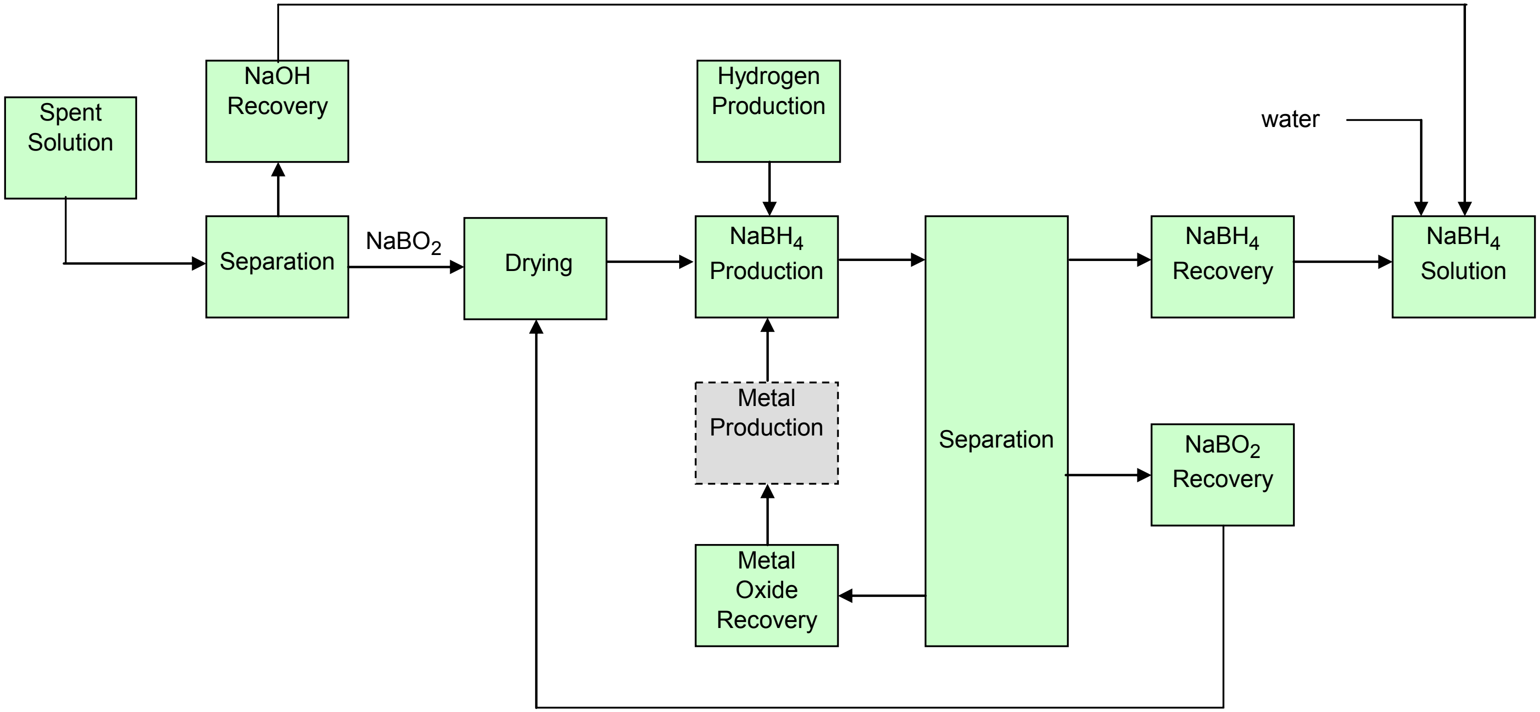


Key Results: Reaction milling studies of $NaBO_2$ and metal hydride (T_{init} = 25°C)

- Order of reactivity defined for candidate metals
- Processing parameters identified to improve yields and lower costs

Result: Conceptual Regeneration Processes Developed

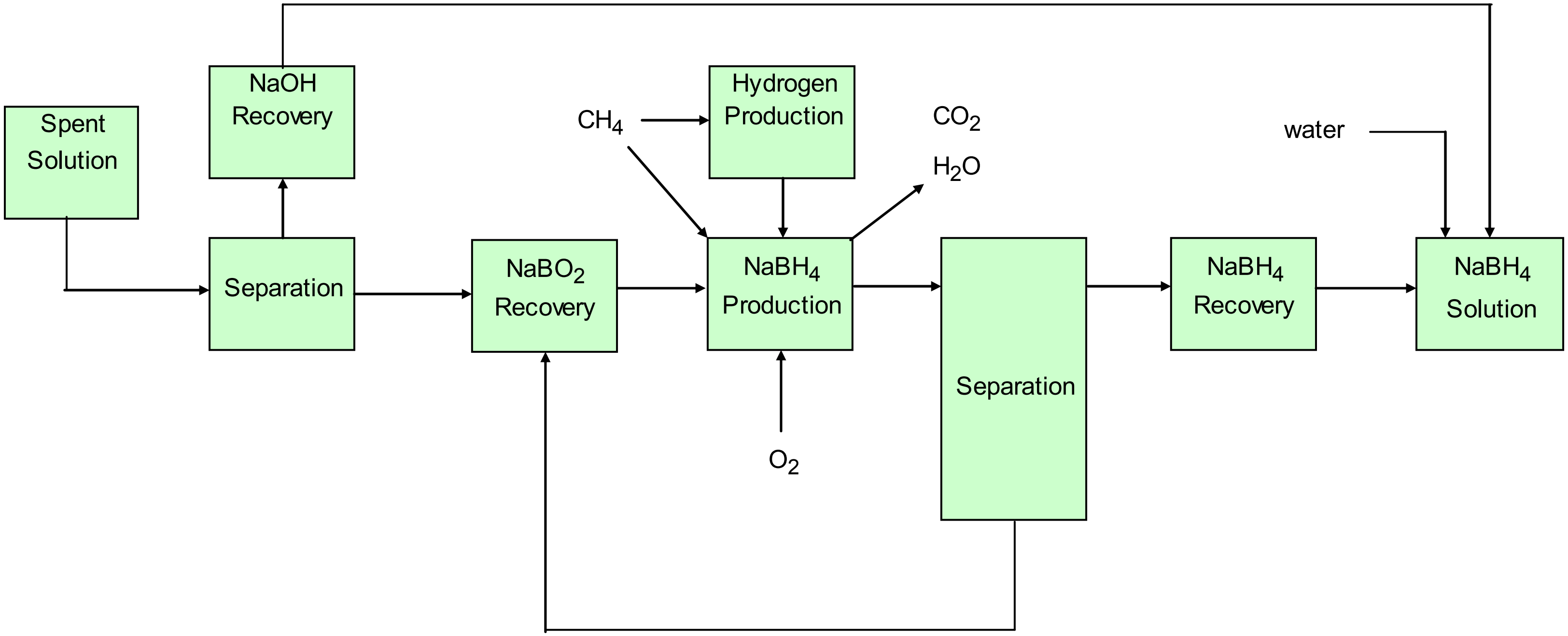
Metal Reduction: $NaBO_2 + 2x/y\ M + 2H_2 \rightarrow NaBH_4 + 2/y\ M_xO_y$



Basis: 100 mt H2/day, 470 mt $NaBH_4$/day

Result: Conceptual Regeneration Processes Developed

Carbothermal: $NaBO_2 + 2H_2 + CH_4 + O_2 \rightarrow NaBH_4 + CO_2 + 2H_2O$



Basis: 100 mt H2/day, 470 mt $NaBH_4$/day

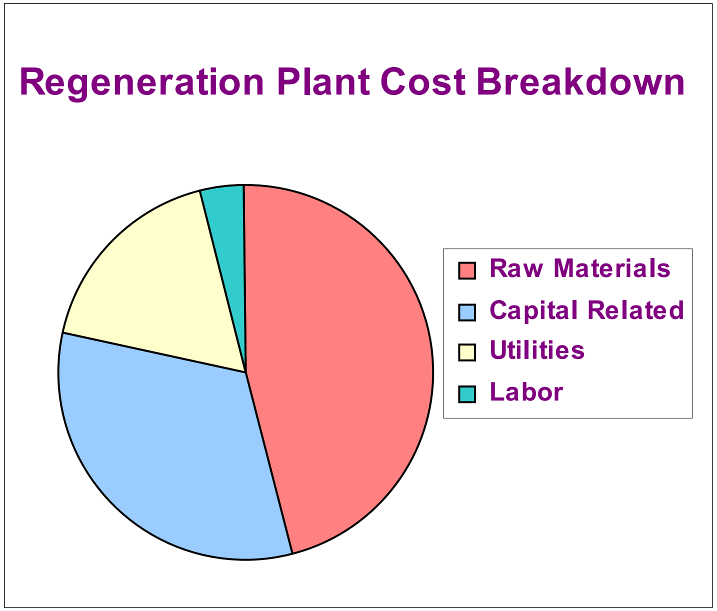
Result: Manufacturing Cost Estimate and Analysis Underway

Material and Energy Balance

Equipment Sizing/ Capital Investment

Operational Requirements

Energy Efficiency



Interface with H2A and FCHTool to estimate cost and energy efficiency

Future Work

- Program milestones accelerated

June 2007	Determine if laboratory demonstration of all non-commercial or unproven SBH formation steps are possible and estimate the efficiency** of the overall process. Demonstrate key chemistries to validate process flowsheets and build conceptual process to estimate cost and energy efficiency.
July 2007	Prepare preliminary SBH production/regeneration cost estimate that contains a sensitivity analysis and qualifies the estimate in terms of degree of confidence.
Sept 2007	Determine feasibility based on laboratory-scale experimental demonstration of energy-efficient** regeneration off-board. Provide results to Go/No Go Review Panel.
Phase 2 FY08-FY09	Pending outcome of DOE Go/No Go decision: Define top options. Develop and optimize process. Detail selected pathways.

- Leverage Rohm and Haas competencies across Center

****Based on the primary energy consumed in regenerating the spent material and the lower heating value of hydrogen that is released on-board the vehicle. Electricity consumed during regeneration must be converted back to the primary energy on the basis of 2015 US grid.**

Summary

- Preliminary estimates identify a series of chemistry paths with potential to achieve high energy efficiency in $NaBH_4$ regeneration
  - Metal reduction
  - Electrochemical
  - Carbothermal/elemental
- Work scope defined to generate specific information to determine cost and energy requirements for Go/No-go decision

Collaboration and Technology Transfer

Partner	Technology Focus
PNNL / Millennium Cell	Engineering analysis of on-board hydrogen generation systems
LANL/ Penn State / MCEL	Electroreduction of borates to borohydride
PNNL	Ammonia borane (AB) stability Synthesis of metal hydrides
U Penn	Engineering assessment of AB regen processes Exchange of starting materials for synthesis
UC Davis	Hydrogen-terminated Si nanoparticles
U Alabama	Computational analysis of reaction pathways
TIAX / ANL	Analysis / H2A

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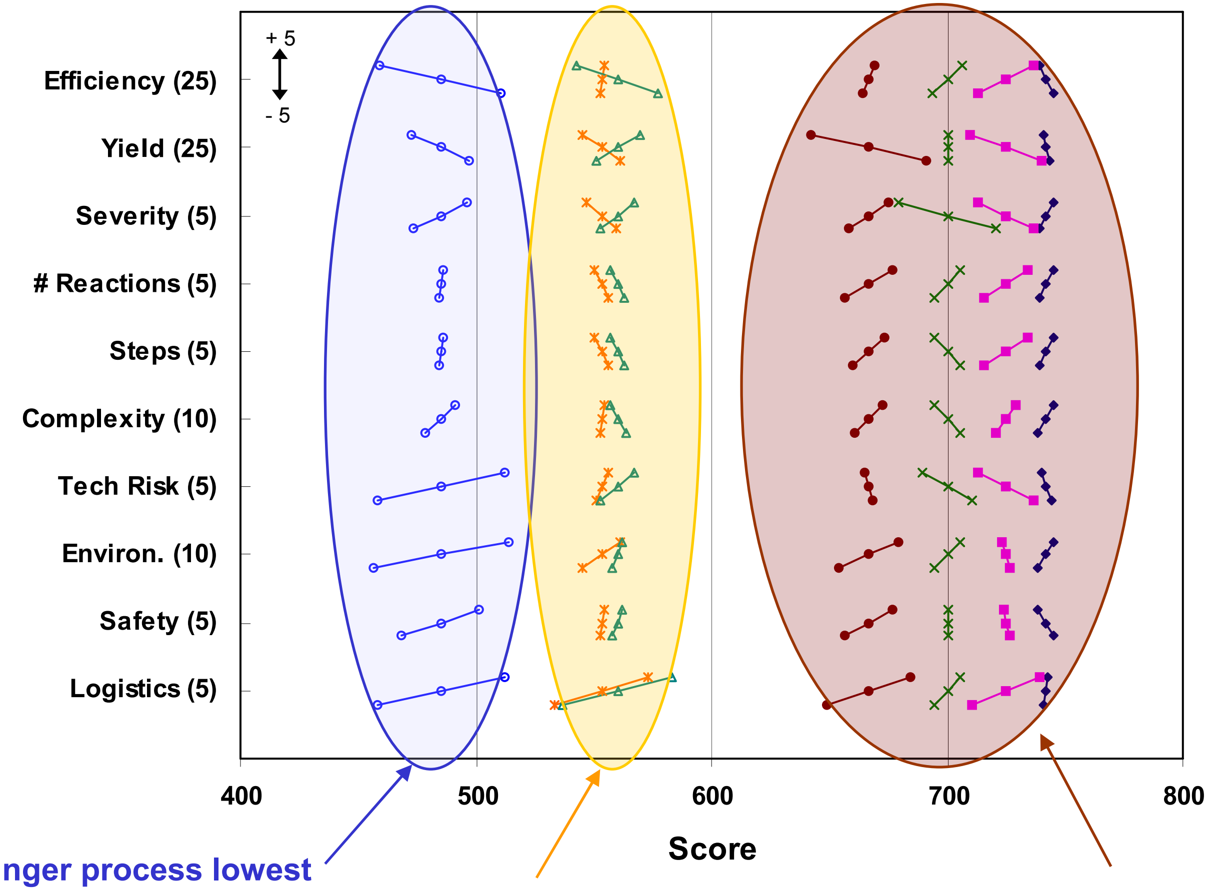
Supplemental Information

Top Regen Pathways Superior to Others

Variation of ± 5 in criteria weighting factor has minimal effect on rankings



Schlesinger process lowest

Borane* and metathesis paths provide only moderate improvement

Metal reduction *, carbothermal, elemental, and electrochem * paths provide highest scores

* average

Metal Reduction

Chemistry

- Use lower cost, lower usage reducing metal in place of sodium
- **$NaBO_2 + 2x/y\ M + 2H_2 \rightarrow NaBH_4 + 2/y\ M_xO_y$**

  (or $NaBO_2 + 4x/y\ M + 2H_2O$)
- Convert M_xO_y back to M using existing or advanced metal technology

Features

- Theoretical energy efficiencies of 60-76% (Al, Si, Ti, and Zn) with no heat recovery of exothermic reactions
- Can achieve >50% efficiency based on primary energy
- Potential for single-step process
- Na and B feed does not need to be separated for reaction

Demonstrated

- Past lab studies conducted predominantly with Mg
- Achieve yields >95% using high intensity milling at low T as well as higher T reaction studies
- Lower yields achieved with Al (~70%)

Recommendation / Plan

- Demonstrate high yields for metals other than Mg
- Identify optimal metal recovery process

Carbothermal Routes

Chemistry

- Direct carbothermal reduction using CH_4 and O_2

$$\mathbf{NaBO_2 + 2H_2 + CH_4 + O_2 \rightarrow NaBH_4 + CO_2 + 2H_2O}$$

- Coupled with combustion to provide favorable ΔG compared to direct $NaBO_2 + CH_4$

Features

- Potential for high efficiency: 75% theoretical energy efficiency and 62% based on primary energy
- Reductant does not require regeneration
- High degree of uncertainty

Demonstrated

- Suda (Kogakuin Univ) - proposed in JP 2004/224593
  - Reaction has not been demonstrated; 500-700°C, <300 atm proposed to achieve 70% yield
- Idaho National Labs - US2006/0103318

Recommendation / Plan

- Experimentation needed to confirm yields and detail individual reaction steps

Elemental Synthesis

Chemistry

- **$Na + B + 2H_2 \rightarrow NaBH_4$**
- B produced by carbothermal reduction of $NaBO_2$ or Mg reduction of B_2O_3

Features

- Direct production of $NaBH_4$, with potential for no or low byproducts
- High theoretical efficiency if carbothermal path feasible (77%); 55% if via Mg reduction
- Carbo can achieve 55-57% efficiency based on primary energy

Demonstrated

- Goerrig DE 1077644 (1960) - 81% yield for $Na + B + H_2$ (higher for K)
- Mg reduction of B_2O_3 is commercial route to produce elemental B
- B_4C produced in reaction $B_2O_3 + C$

Recommendation / Plan

- Verify production of B in carbothermal path, possibly in combination with carbo-only pathway studies.

Electrochemistry

Chemistry

- Reduction of spent borate in aqueous or organic media
- **$B(OH)_4^- + 4H_2O + 8e^- \rightarrow BH_4^- + 8OH^-$ (cathode)**
- $NaH + B(OCH_3)_3 \rightarrow NaBH(OCH_3)_3$
  $NaBH(OCH_3)_3 + 6H^+ + 6e- \rightarrow$ NaBH4...

Features

- Theoretical energy efficiency = 71%, but requires efficient electricity production to achieve 50% primary energy
- Potential for single-step process
- Na and B feed does not need to be separated for reaction
- No need to dehydrate borate spent fuel

Demonstrated

- Positive confirmation in prior Rohm and Haas studies with specific electrodes
- Recent Chinese, Japanese and Portuguese papers/patents but appropriate analytical tests needed
- Recent PSU studies confirm successful production of $NaBH_4$

Recommendation / Plan

- Support PSU studies including extension of prior ROH experimental studies
- Continue studies with modified electrodes
- Explore options identified to achieve higher yields
- Consider alternative high temperature, single phase borate melts

Borane-Based Routes

Chemistry

- Borane complex reacted with NaH or other Na compound

  $1/2\ B_2H_6 + NaH \rightarrow NaBH_4$

  $2/3\ B_2H_6 + NaOCH_3 \rightarrow NaBH_4 + 1/3\ B(OCH_3)_3$

- Must integrate with most efficient and cost effective pathway to produce borane (non-$NaBH_4$-based)

Features

- Potential for Na metal/$NaBH_4$ < 1
- Theoretical energy efficiency highest for H_2 reduction of borate ester (68%) and metal reduction of boron oxide (64%) with no heat recovery
- BCl_3-based route has <50% theoretical efficiency

Demonstrated

- ½ B_2H_6 + NaH reaction yield ~98%
- Aviabor (Russia) commercial $NaBH_4$ process from B_2H_6 via BCl_3 hydrogenation
- High efficiency borane routes ($B(OR)_3$ reduction or hydrogenolysis using metal) demonstrated at only low yields

Recommendation / Plan

- Will be difficult to reach 50% efficiency based on primary energy.
- Pursue if other routes do not show promise:
  - Validate efficient means to borane
  - Identify options using safer, more stable borane complexes rather than diborane gas

Metathesis Routes

Chemistry

- $Na + Al + 2H_2 \rightarrow NaAlH_4$
  $NaAlH_4 + B(OR)_3 \rightarrow NaBH_4 + Al(OR)_3$
- Need to separate $NaBO_2$ to process Na and B components separately

Features

- Theoretical energy efficiency = 53% using current Na and Al technologies, with no heat recovery, but <40% based on primary energy
- 50% reduction in metal usage compared to Schlesinger
- Chemistry steps all proven; low temperature reactions

Demonstrated

- Albermarle $NaAlH_4$ commercial process
  - US4081524 (1978)
- Metathesis chemistry:
  - US3063791 (1962): 65-70% yield
  - JP02-208218 (1990): 90% yield

Recommendation / Plan

- No-go due to difficulty in achieving 50% efficiency target based on primary energy.