DOE Chemical Hydrogen Storage Center of Excellence

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

Project ID# ST6

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This presentation does not contain any proprietary or confidential information

Project Overview

Timeline

- Start: March 1, 2005
- End: February 28, 2010
- 20% 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	FY07	FY08	FY09	Total
DOE	$229K	$250K	$353K	$370K	$389K	$1,591K
ROH	$103K	$112K	$176K	$168K	$168K	$727K

Overall 69:31 DOE:ROH Split

Partners

Rohm and Haas
Los Alamos National Laboratory
Pacific Northwest National Laboratory (Operated by Battelle for the U.S. Department of Energy)
Millennium Cell
Penn State
The University of Alabama
Borax
Northern Arizona University

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 Tier 1 Research: energy efficient and cost-effective options for B-OH to B-H conversion • Leverage expertise and experience across Center Tiers 1, 2, 3: engineering requirements, economics, life cycle analysis • Support DOE Chemical H_2 Storage Systems Analysis Sub-Group
FY05	Define goals/strategies, boundaries/assumptions; establish performance criteria/metrics
FY06	• Identify chemical pathways and process options • Complete computational analysis of SBH regeneration routes (chemical and electrochemical) • Develop experimental program • Provide engineering support to H_2 Storage Systems Analysis program

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Approach: Engineering-Guided R&D

Potential Regeneration Chemistries

Identify chemical routes

Compile & organize concepts

Define basic reaction envelopes & regeneration efficiency

Perform preliminary technical & economic viability analysis

Establish experimental & computational needs

Define leading options

Viable Regeneration Chemistries and Process Options

Engineering Assessment Reduces Technical Risk

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Accomplishments

- Established performance-based metrics
- Identified potential regeneration routes
  - Metal reduction of borate
  - Electroreduction of borate
  - Borane-based routes
- Established framework for Analysis
  - Life Cycle Inventory
- Ammonia borane
  - Conducted preliminary cost and thermal stability assessments

Accomplishments : Performance-Based Metrics

			Baseline Cases		Performance of Option			
	CRITERIA	Criticality	Compressed H2 (700 bar)	Liquid H2	Brown-Schlesinger Process	Metal Reduction	Electrochemical	Borane-Based
0	Safety Score (Risk Analysis)	Paramount						
1	H2 weight density meets 2010 DOE requirements (2 kWh/kg or 6 wt%)	Must						
	H2 weight density meets 2015 DOE requirements (3 kWh/kg or 9 wt%)	Desirable						
2	H2 volume density meets DOE 2010 requirements (1.5 kWh/L or 0.045 kg/L)	Must						
	H2 volume density meets 2015 DOE requirements (2.7 kWh/L or 0.081 kg/L)	Desirable						
3	Storage system cost meets DOE targets: 2010 = $4/kWh ($133/kg H2) 2015 = $2/kWh ($67/kg)	Must						
4	Operating Ambient Temp. (DOE targets): 2010 = -30/50 (sun) °C 2015 = -40/60 (sun) °C	Must						
5	Loss of Useable Hydrogen (DOE targets): 2010 = 0.1 [(g/h)/kg H2 stored] 2015 = 0.05 [(g/h)/kg H2 stored]	Must						
6	Fuel cost meets DOE requirements: $2-$3/ gal gasoline equivalent	Must						
7a	High energy efficiency: Ideal thermo. efficiency based on 'burn ratio' of > 60%	Desirable						
7b	High energy efficiency: Measured energy efficiency of 60%	Desirable						
8	Low capital cost (complexity, # UOps, technical risk)	Optional						
9	Low operating cost	Optional						
10	Low raw material (RM) cost	Optional						
11	No Path, Clear Path, or Demonstrated	Optional						
12	Logistics (availability of RM's)	Optional						
13	Low EHS risk	Optional						
	RESULT							

Options Generated

Key Metrics for Selection of Regeneration Process:

- Fuel cost $2 - $3 gal gasoline equivalent
- Ideal thermodynamic efficiency based on "burn ratio" of >60%
- Measured energy efficiency of 60%

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Accomplishments: Identification of $NaBH_4$ Regeneration Chemistries

- Metal reduction of borate
- Electrochemistry
- Borane-based routes
- Elemental synthesis
- Metathesis reactions
- Transfer hydrogenation

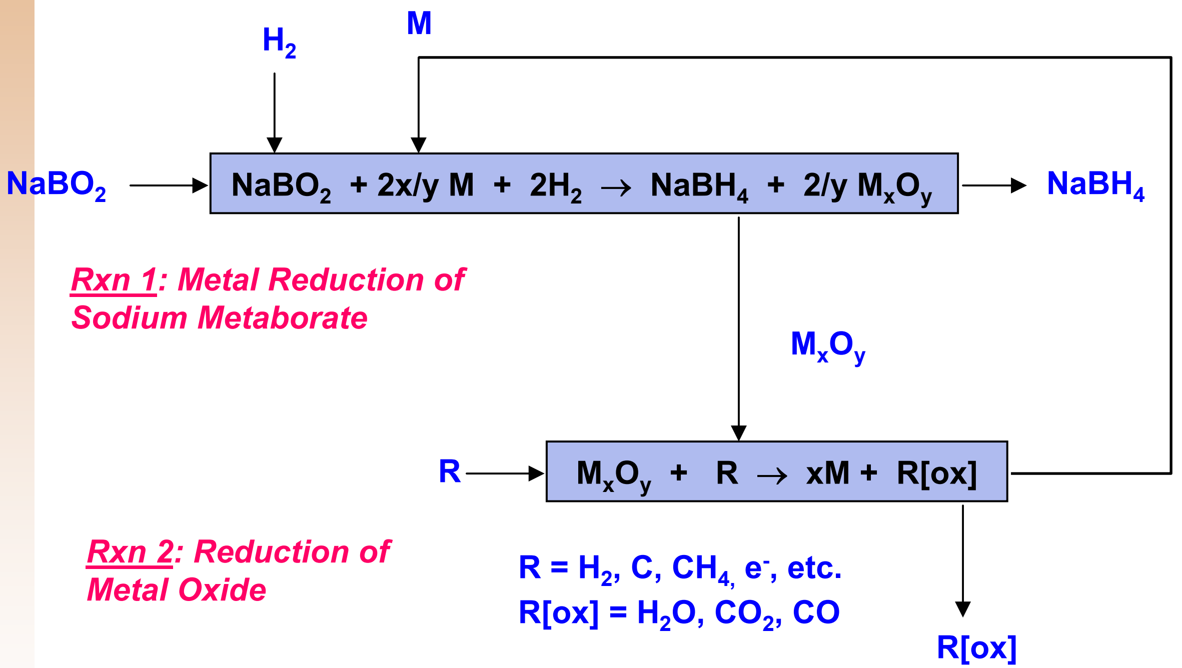
→

Construct overall reaction pathway

Fast-fail Metrics

- Theoretical energy efficiency
- Reductant regeneration requirements
- Energy costs
- Raw material cost and availability

Accomplishments: General Pathway for Metal Reduction of Borate



Fast-fail Metrics

- Energetics of both reaction steps
- Metal reductant regeneration requirements
- Energy costs
- Raw material cost and availability

Net: $NaBO_2 + 2H_2 + R \rightarrow NaBH_4 + R[ox]$

% Regen Eff = Usable Energy Released / Total Energy Used*

= 100 * ΔG_{cmb} H_2 prod / (ΔG_{cmb} reductant + ΔG_{rxn} $NaBO_2 \rightarrow NaBH_4$)

= 75% ideal

* Described at DOE H_2 Storage Engineering Analysis meetings, Argonne National Lab (10/12/05) and Palm Springs (11/18/05)

Accomplishments: Leading Metal Systems Identified

Group		Reaction 1: NaBO2 + H2 ΔG 25C kcal/mol SBH	Reaction 1: NaBO2 + H2O ΔG 25C kcal/mol SBH	ΔG neg?	Overall Regen Efficiency, No Heat Recovery, Reaction 2 Metal Oxide Reductant: H2	C	e-	Other	Minimum Theoretical Energy MJ/kg SBH	Eff>60%?	Global Supply	Leading Options
Current B-S via NaCl									40.6			
Ideal Regen (4H2)		76			75%				8.4			
IIA	Mg	-82.8	-241.6	→	59%	57%	48%	59%	17.6			
	Ca	-99.0		→	56%				19.4			
IIIB	Sc	-100.5		→	56%				19.5			
	Y	-100.0		→	56%				19.5			
	La	-82.7		→	59%				17.6			
	Ce	-56.1	-188.2	→	63%				14.6	→		
IVB	Ti	-23.2	-122.4	→	70%			48%	11.0	→	→	Work needed to define reductant regeneration
	Zr	-59.8	-195.6	→	63%				15.0	→	→	
VB	V	8.6	-58.9	→	63%				14.9	→	→	
VIB	Cr	21.6	-32.9	→	68%				12.0	→	→	
VIIB	Mn	15.9	-44.2	→	65%				13.3	→	→	
VIII	Fe	71.3	66.6									
	Co	87.0										
	Ni	88.2										
IB	Cu	128.1										
IIB	Zn	36.2	-3.6	→	74%	82%	57%		8.8	→	→	Zn
IIIA	Al	-62.7	-201.5	→	62%	60%	62%		15.3	→	→	Al
IVA	Si	-15.3	-106.7	→	71%	69%			10.1	→	→	Si
	Ge	64.8										
	Sn	66.1										

Mixed metals

Commerical Route

Accomplishments: Electrolytic Reduction of B-OH to B-H

- Collaboration with Penn State, LANL, MCEL
  - Validated analytical methods and electrolytic cell
  - Established reporting criteria and metrics
  - Previous Rohm and Haas successes shared with Team
  - Concepts suggested for improvement
  - Guide experimental activities
  - Testing at Penn State University
- Two electrolytic process routes identified
  - Laboratory evaluations
    - Boron substrate: borate, alkyl borates, alkoxyborohydrides
    - Solvent systems: aqueous, non-aqueous
    - Cathode materials: hydrophobic composites, high hydrogen overpotential systems, gas diffusion cathodes
  - 1-step direct conversion to $NaBH_4$
  - 2-step conversion through $NaBH(OCH_3)_3$

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Accomplishments: Positive Results for One-Step Electroreduction

Cathode Material	Catholyte	Current Density, $mAmps/cm^2$	Current Efficiency
Teflon / Ni flag	0.5M boric acid 1M TMAH	50	**2.9%**
$LaNi_5$ flag	10M NaOH 0.5M boric acid 1% TMAH	20 – 65	**0.1%**
Nickel / carbon gas diffusion electrode	10M NaOH 0.5M boric acid 1% TMAH	150	**0.15%**

- Advanced cathode materials (hydrophobic cathodes, high surface area cathodes)
- High current densities
- Alkylammonium salts and other means to minimize water electrolysis and favor borate reduction
- Analytical method : RDE voltammetry, detection limit ~50μM $NaBH_4$
- Typical operating parameters
  - Membrane divided Astris acrylic resin test cell
  - Nafion® 324 membrane
  - Anode : Pt or Pt-clad niobium
  - 1M NaOH anolyte

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US patent application US 2005/0224365 A1, October 13, 2005 (Example 1)

Accomplishments: Positive Results for Two-Step Electroreduction

- Overall Process
  - Trialkylborate → trialkoxyborohydride → borohydride
  - $B(OCH_3)_3 \rightarrow NaBH(OCH_3)_3 \rightarrow NaBH_4$
  - Competing disproportionation reaction : $NaB(OCH_3)_4$
- Embodiments
  - H_2 gas feed
  - Nonaqueous solvents
  - Regenerable redox species at cathode
- Positive confirmation by ^{11}B NMR
  - Conversion of $B(OCH_3)_3$ to $NaBH(OCH_3)_3$
  - Conversion of $NaBH(OCH_3)_3$ to $NaBH_4$ **(current efficiencies 15 – 47%)**

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US patent application US 2005/0224364 A1, October 13, 2005

Accomplishments: Borane-Based Pathways

- Demonstrated chemistry to form $NaBH_4$
  - $NaH + \frac{1}{2} B_2H_6 \rightarrow NaBH_4$
  - $2/3\ Na_2CO_3 + 2/3\ B_2H_6 \rightarrow NaBH_4 + 1/3\ NaBO_2 + 2/3\ CO_2$
- Low cost, energy efficient method needed for B_2H_6 (or BH_3) generation
- Current industrial routes are inadequate
  - $3/2\ NaBH_4 + 2BF_3 \rightarrow B_2H_6 + 3/2\ NaBF_4$
  - $2NaBH_4 + H_2SO_4 \rightarrow B_2H_6 + 2H_2 + Na_2SO_4$

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Accomplishments: Alternate Diborane Pathways

Path	Reaction
1. Disproportionation	$6BX_3 + 6H_2 \rightarrow 6HBX_2 + 6HX$ (X=F, Cl, Br) $6HBX_2 \rightarrow$ **B_2H_6** $+ 4BX_3$ Net: $2BX_3 + 6H_2 \rightarrow$ **B_2H_6** $+ 6HX$
2. Hydrogenolysis (Hyd)	$2B(OR)_3 + 6H_2 \rightarrow$ **B_2H_6** $+ 6ROH$ (R=H, C_1-C_4)
3. Hyd via Red Metal	$2B(OR)_3 + 2Al + 3H_2 \rightarrow$ **B_2H_6** $+ 2Al(OR)_3$ (other electro-positive metals)
4. Boron alkyl reduction	$2B(OR)_3 + 2AlEt_3 \rightarrow 2BEt_3 + 2Al(OR)_3$ $2BEt_3 + 6H_2 \rightarrow$ **B_2H_6** $+ 6EtH$
5. Amine borane I	$2B(OH)_3 + 6RNCO \rightarrow 2B(NHR)_3 + 6CO_2$ (R=H, C_1-C_4) $2B(NHR)_3 + 6CO \rightarrow$ **B_2H_6** $+ 6RNCO$ Net: $2B(OH)_3 + 6CO \rightarrow$ **B_2H_6** $+ 6CO_2$
6. Amine borane II	$2B(OH)_3 + RNH_2 \rightarrow 2B(NHR)_3 + 6H_2O$ (R=H, C_1-C_4) $2B(NHR)_3 + 6H_2 \rightarrow$ **B_2H_6** $+ 6RNH_2$ Net: $2B(OH)_3 + 6H_2 \rightarrow$ **B_2H_6** $+ 6H_2O$
7. Carbon	$B_2O_3 + 3C + 3H_2 \rightarrow$ **B_2H_6** $+ 3CO$
8. Elemental	$2B + 3H_2 \rightarrow$ **B_2H_6**

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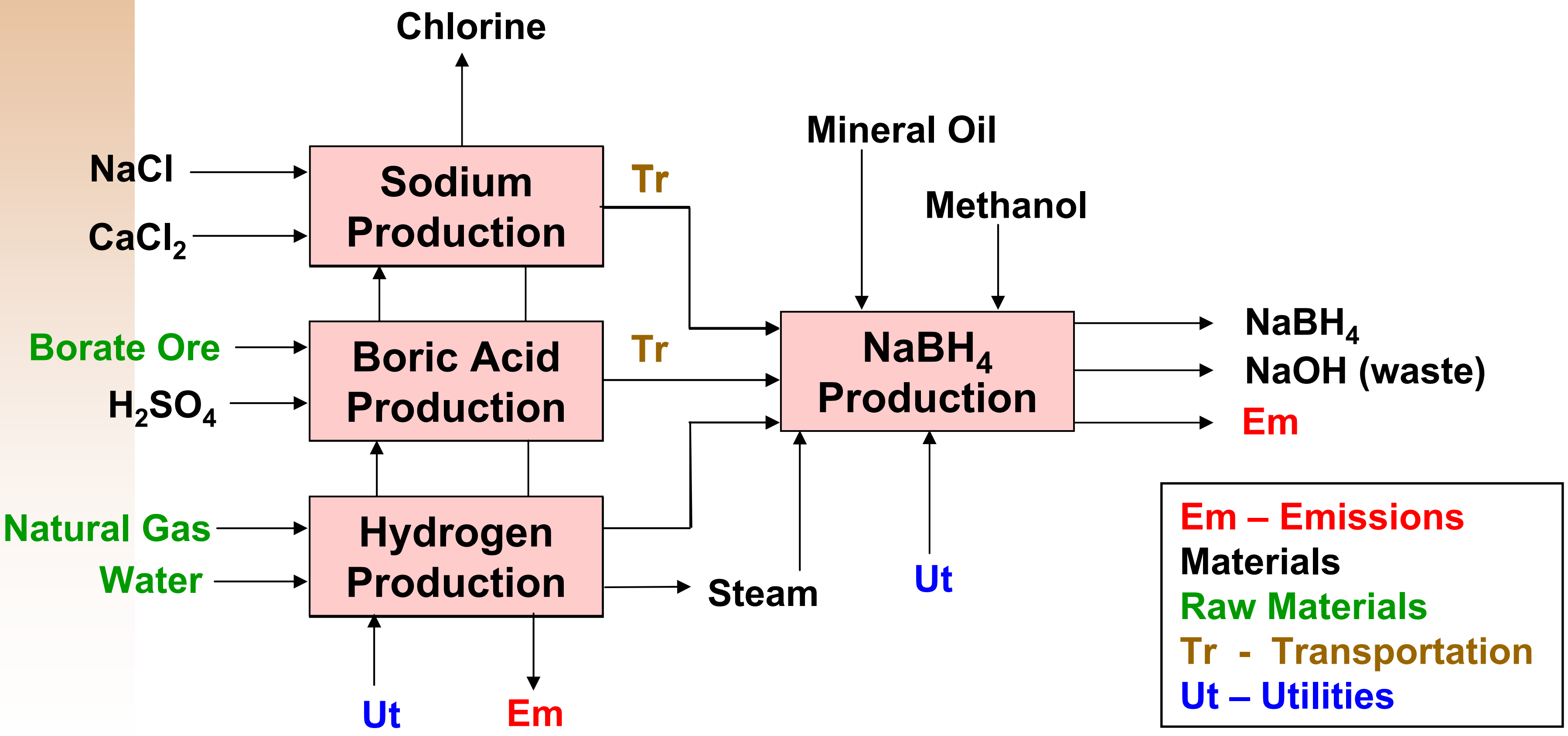
Accomplishments: Analysis

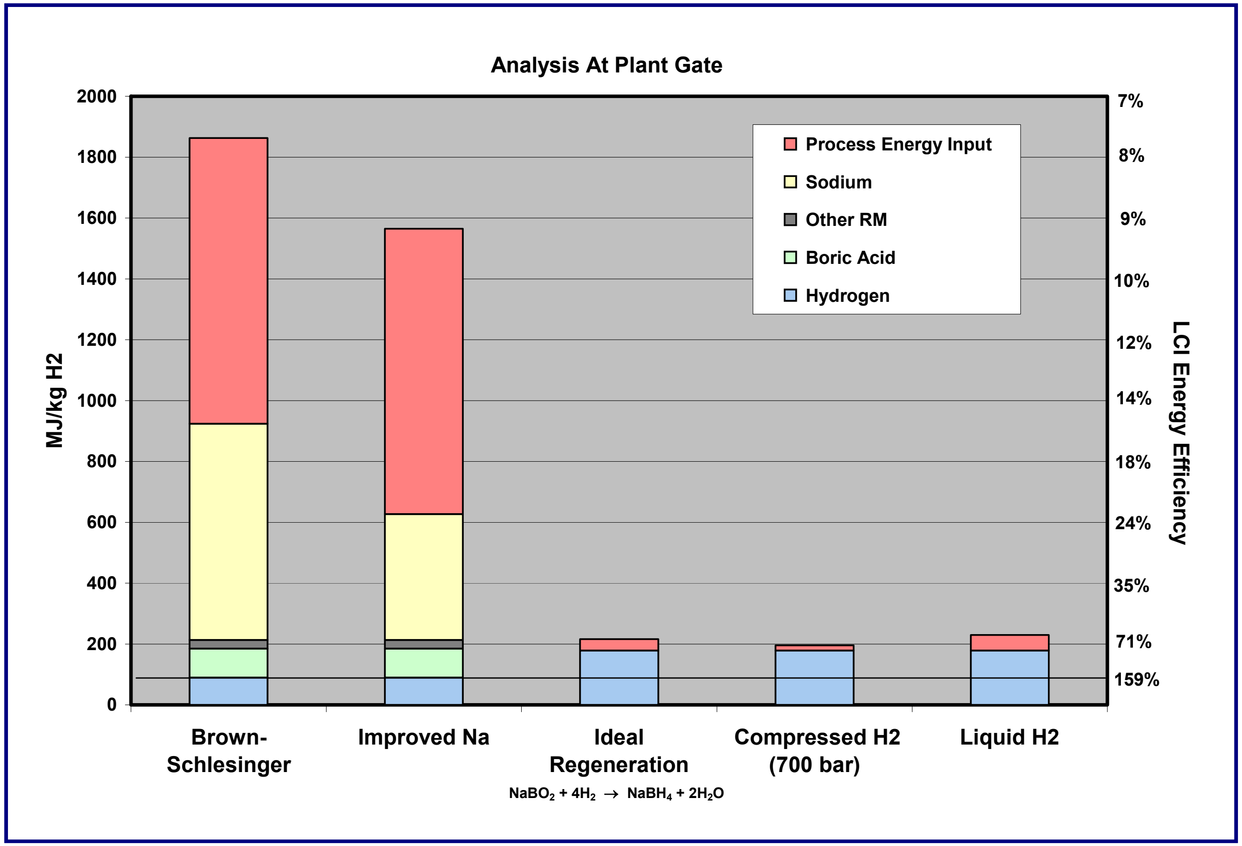
Life Cycle Inventory (LCI) Established for $NaBH_4$ via Current Brown-Schlesinger Process



Life cycle analysis addresses technical barrier: Lack of understanding of environmental impacts (energy usage and emissions) of the generation process

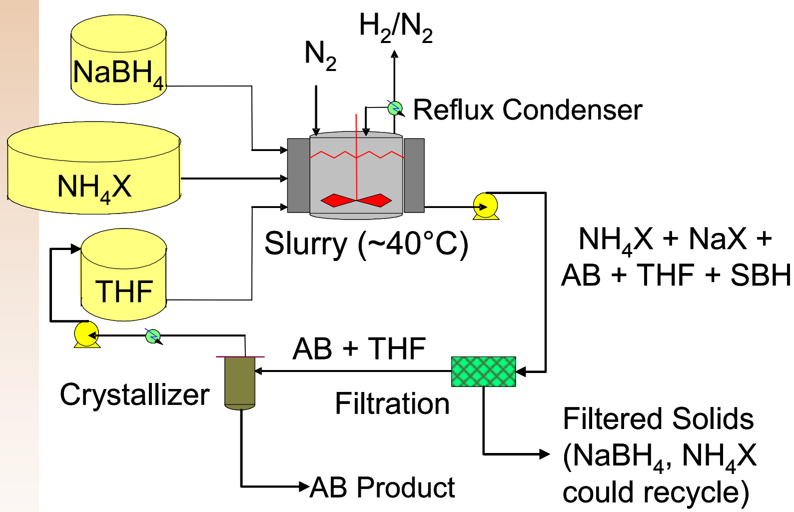
Accomplishments: Analysis

Comparison of LCI Gross Energy for H_2 at Regeneration Plant Fenceline



Ideal Regeneration, Compressed H_2 and Liquid H_2 data based on use of hydroelectric power with 70% efficiency of conversion. Boustead model uses High Heating Values.

Accomplishments: Ammonia Borane Preliminary Cost Assessment



Hu *et al*. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2147-2150.

- Current cost of ammonia borane is very high because it is priced as a specialty chemical. Low cost AB is needed to meet 2010 system cost targets.

- Initial fill chemistry will require $NaBH_4$

  NH_4^+ salt route:

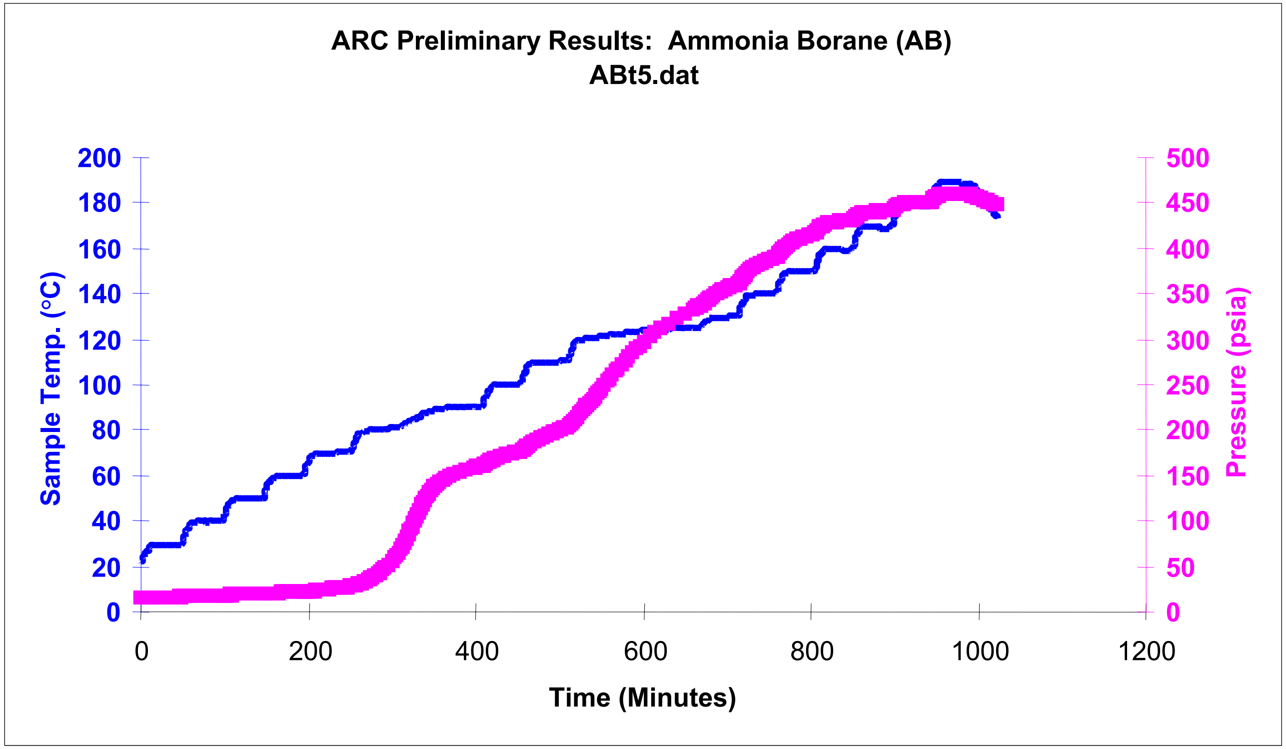
  $NaBH_4 + 1/n\ (NH_4)_nX \rightarrow$
  $NH_3BH_3 + 1/n\ Na_nX + H_2$

  Diborane route:

  $\frac{1}{2}\ B_2H_6 + NH_3 \rightarrow NH_3BH_3$
  B_2H_6 from $NaBH_4$)

- AB regeneration should not involve $NaBH_4$ to meet regeneration fuel cost targets

Accomplishments: Ammonia Borane Thermal Stability



- DOE Stability Targets
  - 2010: <0.01% H_2 loss/hr at 50°C
  - 2015: <0.005% H_2 loss/hr at 60°C
- PNNL - DSC and TGA data; no adiabatic stability data
- Rohm and Haas - advanced calorimetry capabilities
  - ARC (accelerated rate calorimeter)
  - Uses small samples to test system stability under a wide range of conditions

Future Work

- $NaBH_4$ Regeneration Routes
  - Complete compilation of other chemical routes and conduct computational analysis to identify at least one option for laboratory demonstration (12/31/06)
  - Laboratory demonstration of at least one process with overall efficiency $\geq$ 80% of theoretical (6/30/07)
  - Develop conceptual design for laboratory demonstrated regeneration process and associated on-board system (9/30/07)
  - **Go/no go decision for $NaBH_4$ (9/30/07)**
- Ammonia Borane
  - Develop conceptual AB manufacturing process and cost estimate
  - Complete reaction calorimetry studies
    - Determine stability as function of time and temperature (50°C and 60°C)
    - Determine impact of aging and impurities on stability
- Leverage ROH competencies
  - Across Center
  - Support DOE Chemical H_2 Storage Systems Analysis Sub-Group

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Summary

- $NaBH_4$ Regeneration Routes
  - Leading metal reduction systems with lower energy usage have been identified
  - Potential electroreduction routes identified
  - Completing data-mining of other regeneration options
  - Building efficient conceptual processes around them
  - Estimate manufacturing cost
- LCI
  - Methodology developed for current Brown-Schlesinger process
  - Build LCI models for regeneration alternatives
  - Interface with H2A analysis tool
- Ammonia Borane
  - Lower cost $NaBH_4$ required
  - ROH ARC stability data complements PNNL research

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Publications and Presentations

F. Lipiecki, “Sodium Borohydride Regeneration and Analysis,” Presentation to FreedomCAR Hydrogen Storage Tech Team, Houston, TX, Feb. 16, 2006

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Critical Assumptions and Issues

- Intellectual Property
  - Agreements to cover jointly invented IP are critical, but difficult to establish with large number of Center partners
  - Lack of agreements can inhibit collaboration and co-invention
  - Separate IP agreements, involving fewer parties, therefore established for each sub-project (i.e., electrochemistry, engineering, etc.)

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