2009 Overview
DOE Chemical Hydrogen Storage Center of Excellence

Kevin Ott

Los Alamos National Laboratory

May 21, 2009

Project ST_15_Ott

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: March 2005
- End: March 2010
- 80% Complete

Barriers

- Weight and Volume
- H_2 Flow Rate
- Regeneration Process
- Energy Efficiency
- Cost
- System Life-Cycle Assessments

Budget for Center Coordination: LANL - 300K; PNNL - 300K

Objectives and Approach – final year of Center

Conceive, research, develop and validate advanced on-board chemical hydrogen storage materials with the potential to overcome technical barriers and meet 2010 with potential to meet 2015 DOE system goals:

- *Regenerate* spent fuel by demonstrating energy and cost efficient chemical processes leading to off board regeneration of fuel
- *Assess* and down select concepts and systems using engineering analysis and studies using DOE targets as guidance in order to:
- *Develop* chemistries, materials, catalysts and new concepts to control thermochemistry and reaction pathways for optimal hydrogen release
- *Analyze* life cycle issues: boron resources, first fill and spent fuel regeneration costs
- *Make recommendations* to DOE of most promising chemical systems for more detailed work and engineering development
- *Transfer* information and prioritization of chemical hydrogen storage materials and processes to the Hydrogen Storage Engineering Center for analysis and development of systems

Approach to Technical Barriers (bold indicates current focus)

- ENGINEERING ASSESSMENT to GUIDE DOWN SELECTION
  - Provide early assessment of viability with potential to provide an engineered solution
  - Guidance to research to move chemistries to efficient processes
- HYDROGEN CAPACITY
  - Develop, synthesize, test compounds with hydrogen gravimetric densities of > 7 wt. % and favorable energetics for release; materials with potential pathways for direct regeneration
- HYDROGEN RELEASE RATES
  - Develop materials and pathways that release hydrogen at rates in excess of DOE performance targets at the lowest temperatures possible
  - Develop pathways that avoid byproducts and minimize gas-phase impurities
- REGENERATION -- MAXIMIZE ENERGY EFFICIENCY
  - Develop off board regeneration pathways close to thermodynamic limits
  - Demonstrate integrated regeneration chemistries
  - Assess well-to-tank energy efficiency of processes
  - Develop baseline cost for spent fuel regeneration options
- THEORY AND MODELING underpins all of our Center's activities

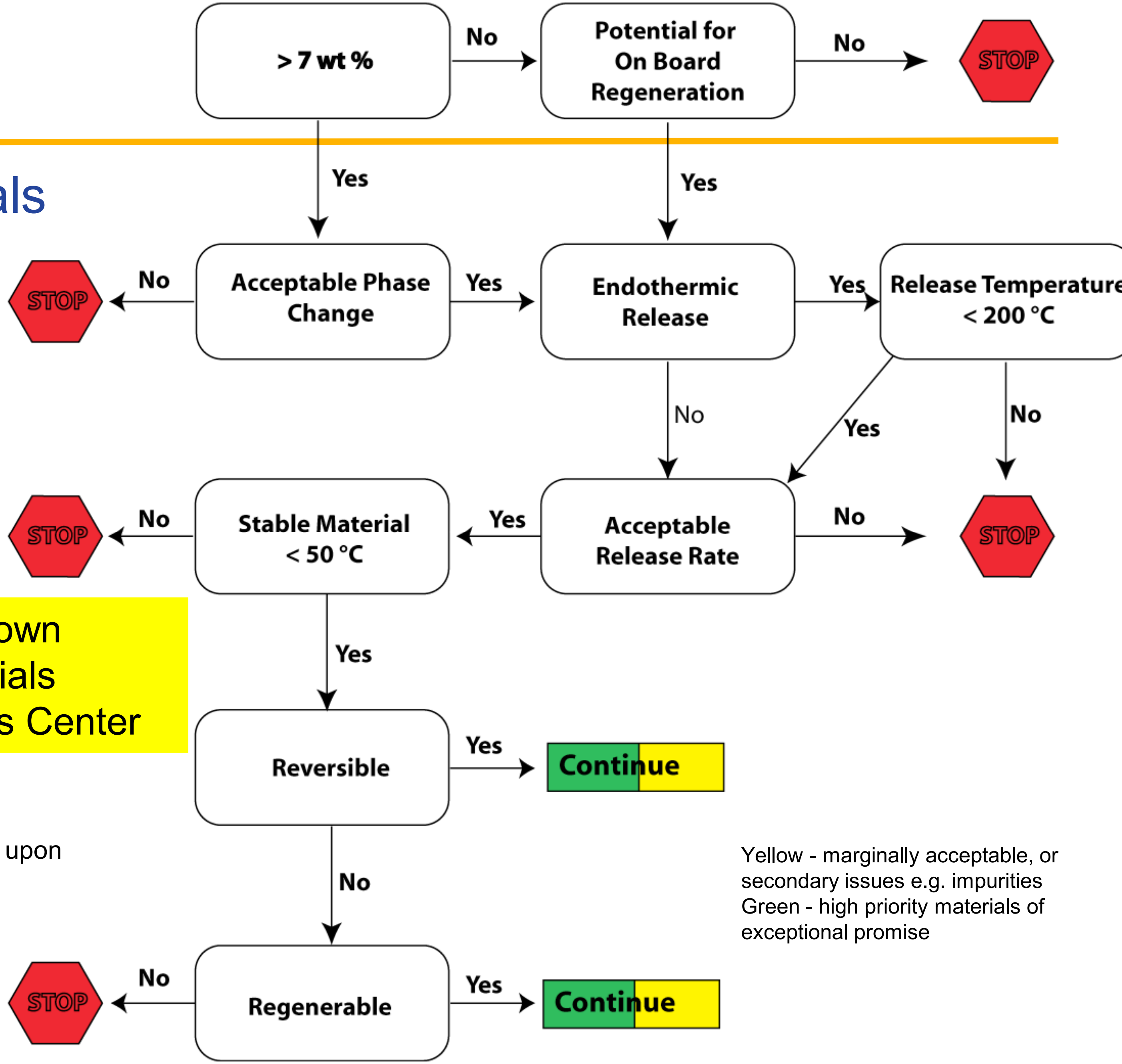
Coordination and communication between engineering, theory, and experiment critical to Center success

Approach: Theory, Modeling, and Well-Developed Down Select Criteria Guide Experimental Effort

- Regeneration (Alabama, Penn, PNNL, UC Davis, LANL)
  - Computation of thermodynamic properties of reactants, intermediates, and products
  - Computation and evaluation of reaction pathway energetics enable selection of optimal thermodynamic routes
  - Computation/calibration of physical properties of intermediates for input into R&H cost analyses
- Hydrogen Release
  - Calculation of energetics of dehydrogenation reactions and reaction intermediates (Alabama, LANL, PNNL)
  - Catalytic reaction pathway energetics to examine extent of release (Alabama, LANL, PNNL)
- New Materials
  - Heats of formation and reaction enthalpies for cyclo-CBN compounds (Oregon, Alabama, Washington) guides synthesis
  - Thermochemistry of metal amidoboranes (Alabama, LANL, PNNL) tests hypotheses for release and direct rehydrogenation

Approach

CHSCoE Materials Decision Tree

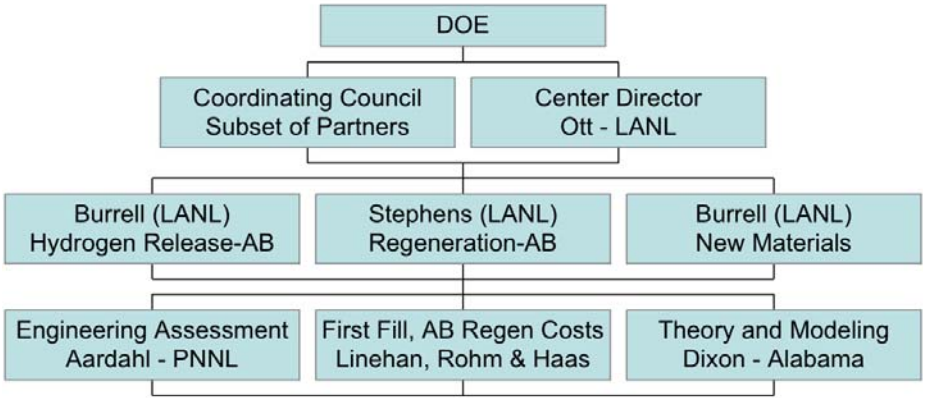


Criteria for materials down selection guides materials synthesis efforts across Center

Refer to supplementary slides for 'gravimetric guiding rule' upon which this is based

Yellow - marginally acceptable, or secondary issues e.g. impurities
Green - high priority materials of exceptional promise

Coordination, Collaboration, and Communication
Center Management and Communication



- Focus areas are coordinated through single LANL point of contact; Coordinating Council
- Regular conference calls and meetings, frequent one-on-one phone calls, site visits to exchange information in real time, develop plans
- Organize face-to-face brainstorming meetings (2-3/yr)
- Quarterly tracking of Partner’s progress toward DOE targets
- Apply materials down selection criteria and decision tree process to guide Center decisions
- 3 Center meetings coincident with Tech Team and Annual Review; Fall meeting in Denver
- Hydrogen Storage Centers conference calls with DOE to foster cross-Center information exchange with Sorption- and Metal Hydride Storage Centers
- Participation in Storage Systems Analysis Working Group: cross-Center engineering issues
- Maintain IP agreement that allows free exchange of ideas and materials among Center partners
- Organize Annual Review, Tech Team Review, Engineering meetings, Denver fall meeting

Coordination, Collaboration, and Communication
Teaming Key to Center Moving Forward

Spent Fuel Regen

- Regen process team
  - Rohm & Haas
  - Penn
  - PNNL
  - LANL
  - Alabama
- Cost analysis team
  - Rohm & Haas
  - PNNL
  - LANL
- M-H recycle team
  - PSU (STP19)
  - LANL
  - PNNL
  - UC Davis(STP18)
  - Alabama
- Digestion agents team
  - US Borax
  - PNNL
  - LANL
  - Alabama

H_2 Release Teams

- AB Solid
  - PNNL
- Scaffolds
  - PNNL
  - UC Davis (STP19)
- Liquid fuels
  - LANL
  - Penn
- Ionic liquid fuels
  - Penn
  - LANL
- Catalysis
  - LANL
  - Penn
  - U. Washington (STP17)

New Materials Teams

- Cyclo CBN team
  - U. Oregon (STP16)
  - U. Washington (STP17)
  - Alabama
- Metal Amidoboranes
  - PNNL
  - LANL
  - Missouri (STP20)
  - Alabama

First Fill AB team

- Process chemistry
  - Rohm and Haas/INEL
  - PNNL
- Cost analysis
  - Rohm and Haas
- Boron resources
  - US Borax

Theory, modeling, and engineering analysis crosscut and guide experimental efforts

Coordination, Collaboration, and Communication
Key Impacts of Center Communications

- Organized key Center meetings to maintain coordination of activities
  - Developed timeline and data needs for cost analysis
  - Communicated technical updates from all Center partners
  - Conducted brainstorming sessions on new materials, release approaches
  - Prioritized technical plan for ensuing 4-6 months and follow-up actions
  - Redirected research focus to meet current and expected future challenges
- Communicated via focus area conference calls updates on decision points, criteria
  - Maintain IP and free flow of information: progress, generate new ideas, lessons learned
  - Focus areas: regeneration, hydrogen release, regeneration process cost estimation
  - Provided feedback mechanism to increase rate of progress, Center-wide
  - Developed and prioritized capital equipment needs for Center
- Coordinated technical personnel exchange and international collaboration
  - PNNL and LANL staff to Japan, summer 2008
  - Center scientists participated in Joint NEDO/AIST - LANL hydrogen workshop San Diego 2008
  - Students from academic partner's labs working alongside National Lab staff
- Coordinated and promoted collaboration, exchange of materials

Frequent communication shared lessons learned, and helped to ensure complementary approaches were coordinated, and duplication or repetition of effort avoided

Key milestones being addressed during this review period (✓complete, • in progress, — not started)

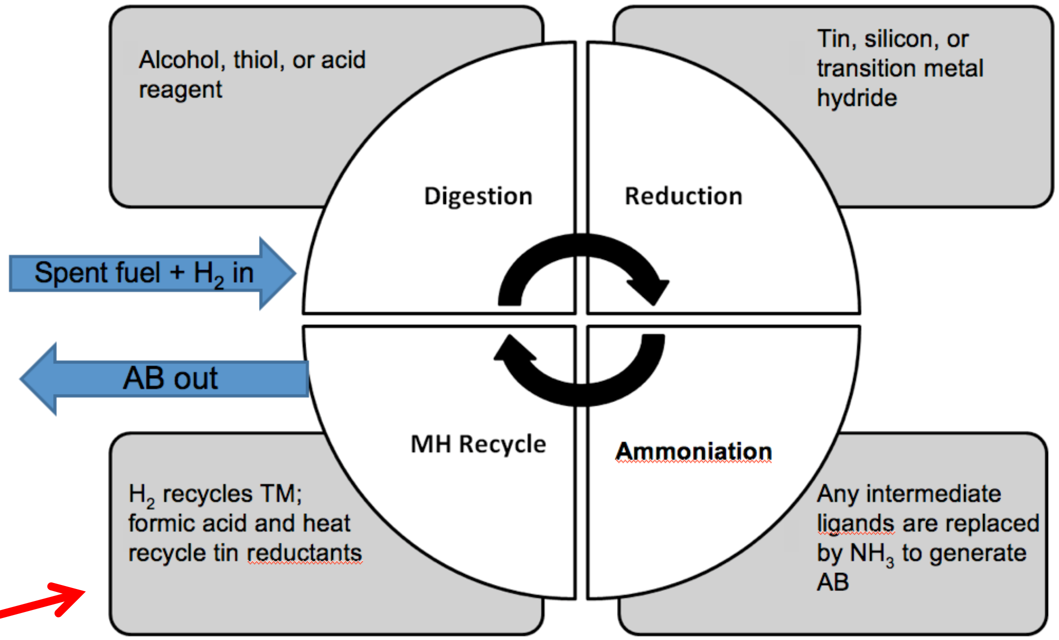
- ✓ Baseline cost analysis of spent fuel regeneration
- • Regeneration
  - Prioritize and address largest improvements in cost and efficiency
  - Address potential ‘hybrid’ approaches with additional analysis
- • H_2 release from AB
  - ✓ Continued improvement in rate and extent of release
  - Focus on identification and quantification of gas phase impurities and mitigation
  - Onboard approaches to solid handling
  - Move to continuous flow reactor for catalytic release from liquid materials
- • New materials
  - Complete assessment of metal amidoboranes, MABs
  - Cyclo-CBNs –synthesize, and identify catalysts for H_2 release
- • Down select and prioritize materials and release processes, prioritize regeneration processes from relative pros and cons, costs and efficiencies
- • Planned future communication and discussion with HSECoE of down select and prioritization of chemical hydrogen storage approaches

Overview of Current Center Activities

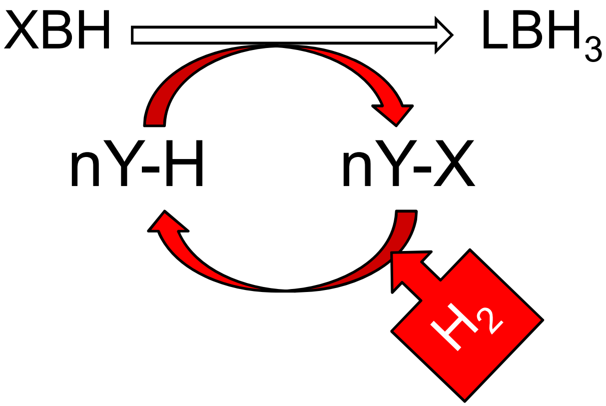
- Hydrogen release approaches
  - Chemical additives
  - Thermolysis
  - Catalysis
  - Hydrogen gas purity
- New materials
  - Designed with high capacities and near-thermoneutral release as goal
  - Enable on-board regeneration
  - Liquid fuel compositions
- First fill process development and costs
- Baseline cost analysis for off board regeneration of spent fuel

Center-wide focus

- Regeneration of spent fuel -- 60 to 70% of current Center efforts
  - Process refinements
  - ‘Hybrid’ processes
  - Supporting R&H baseline cost analyses with experiments



Coordination of Reducing Agent Recycle Effort: Now a Center-Wide Focus



electrochemical H· delivery

STP19

catalytic Sn-SR hydrogenolysis

Los Alamos NATIONAL LABORATORY

ST17

reducing agent recycle

transition metal hydride transfer

Pacific Northwest NATIONAL LABORATORY

ST18

CO_2 analogs, nano reductants

THE UNIVERSITY OF ALABAMA

ST19

Los Alamos NATIONAL LABORATORY EST. 1943

THE UNIVERSITY OF CALIFORNIA DAVIS

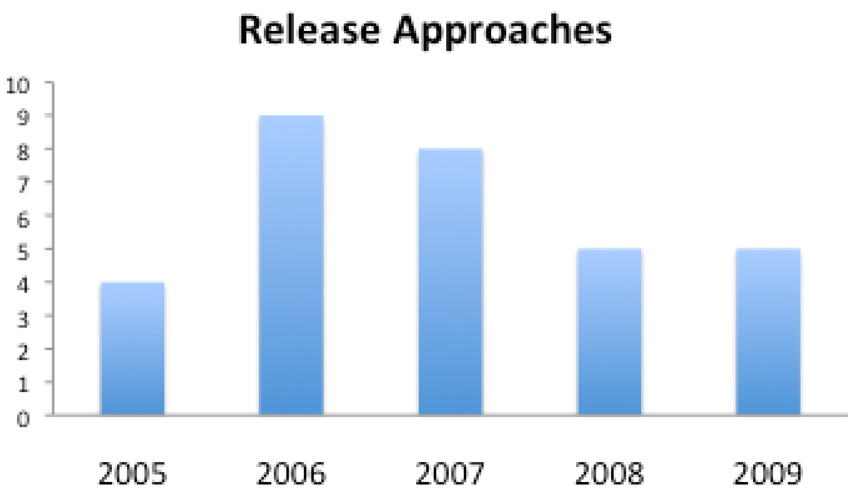
STP18

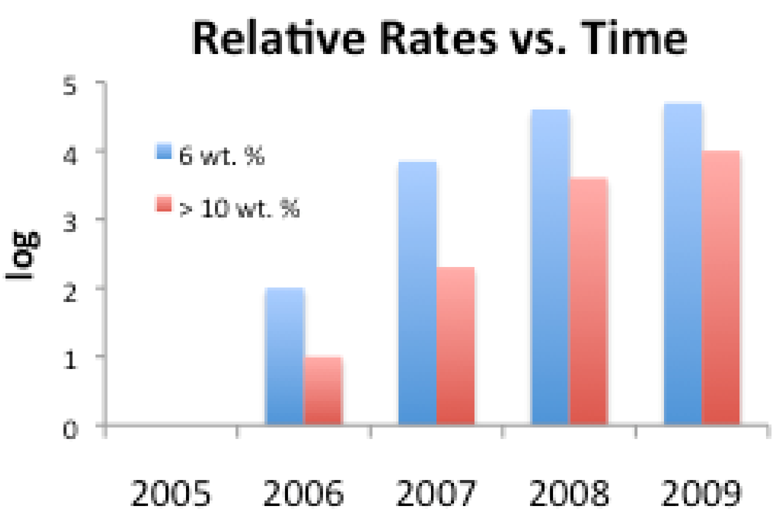
Accomplishments
Status of Center's Approach to Meet Technical Barriers

- Gravimetric (Center criterion > 7 wt. %)
  - Ammonia borane (AB):
    - solid >13 wt. % 130 °C
    - in ionic liquids 7 – 11 wt. % < 110°C
    - as liquid fuel 7 – 10 wt. % <120 °C
  - Metal amidoboranes
    - Solids 7 – 13 wt. % < 130 °C
  - Cyclo CBN compounds – potentially reversible; liquids, solids 5 – 7 wt. % (theoretical yield)
- Volume - all of the above compounds or mixtures exceed .045kg H_2/liter = DOE target
- H_2 release kinetics - demonstrated release rates from 70 °C – 110 °C that have potential to exceed the target
- Regeneration: Off board processes
  - Three promising processes, each with distinct advantages; high yield
  - Demonstrated complete cycle
- Energy efficiency analyses
  - Argonne has provided analyses for 4 CHSCoE regen processes
  - Steady improvements in energy efficiency
  - Started mid 'teens, now mid 30's (ANL)
- Cost – R&H has completed:
  - First fill of AB from SBH analysis
  - Cost of 1st regen process: $7-8/kg
- System life-cycle assessments
  - US Borax provided updated borax resource analysis

Summary
CHSCoE Technical Accomplishments

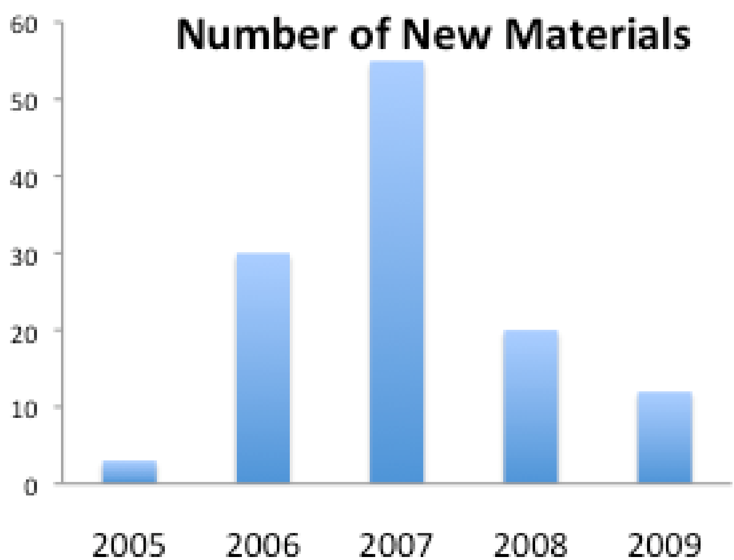
AB Release





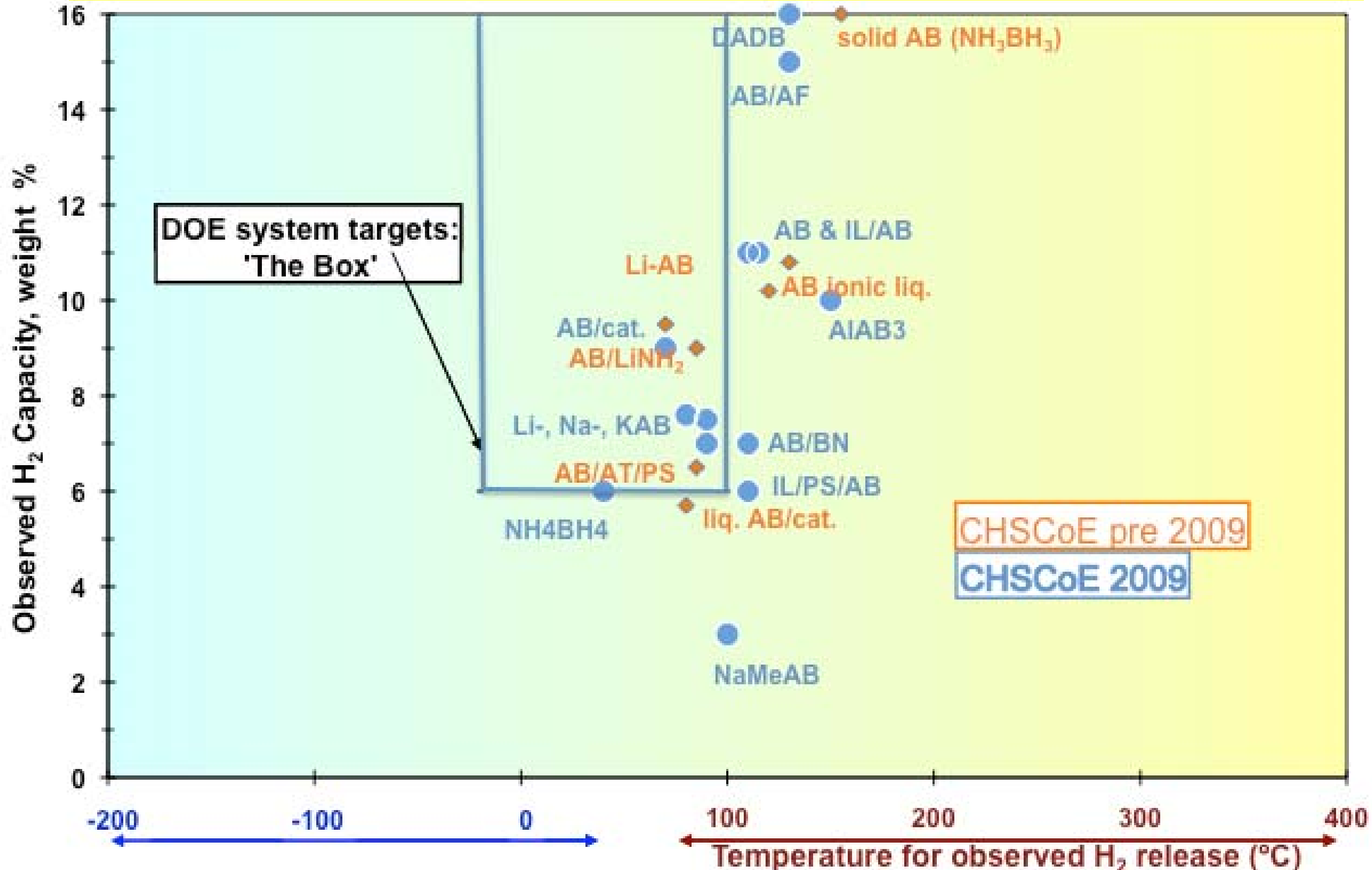
New Materials

- Non-AB materials being examined within CHSCoE
- Idea generation and down select continues



Summary
Progress in AB release routes and New Materials

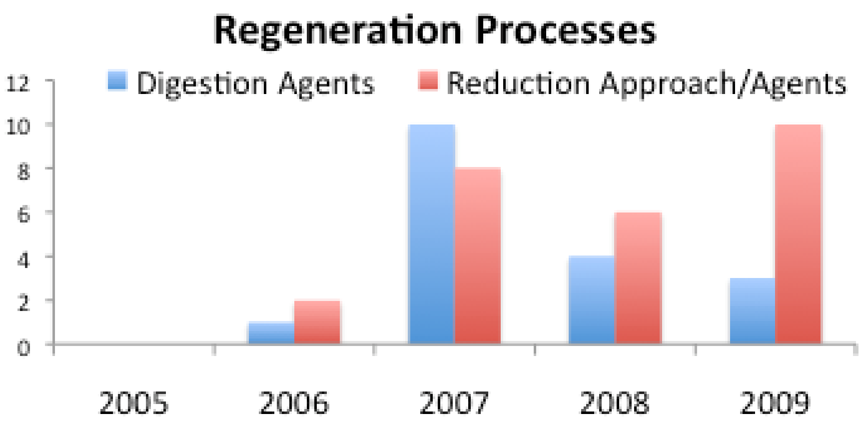
Exothermic release allows thinking 'outside the box'

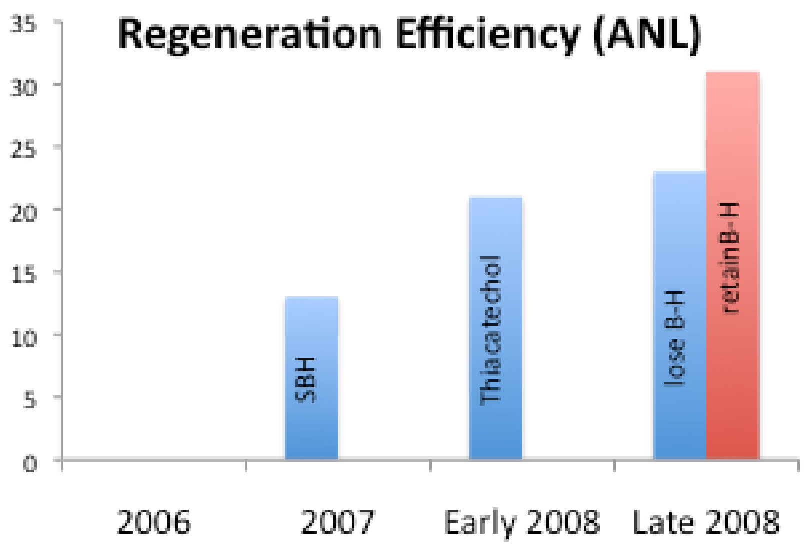


template courtesy of DOE

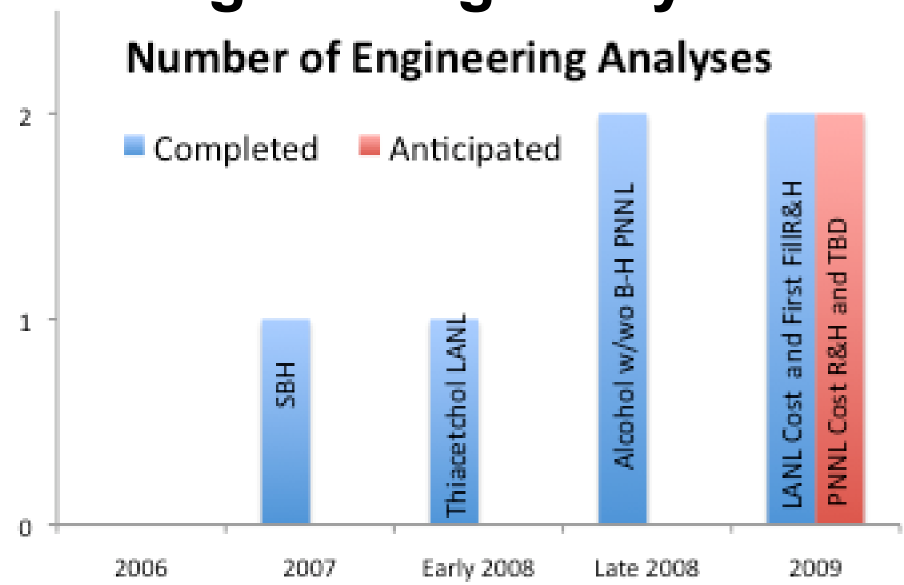
Summary
CHSCoE Technical Accomplishments

Regeneration





Engineering Analyses



- R&H baseline cost for LANL regen completed: \$7-8/kg H_2
- ANL analyses have driven efficiency improvements in regeneration
- R&H cost analysis identifies significant opportunity for additional improvements related to mass flow and separations requirements

Technical Accomplishments
Hydrogen Release from AB

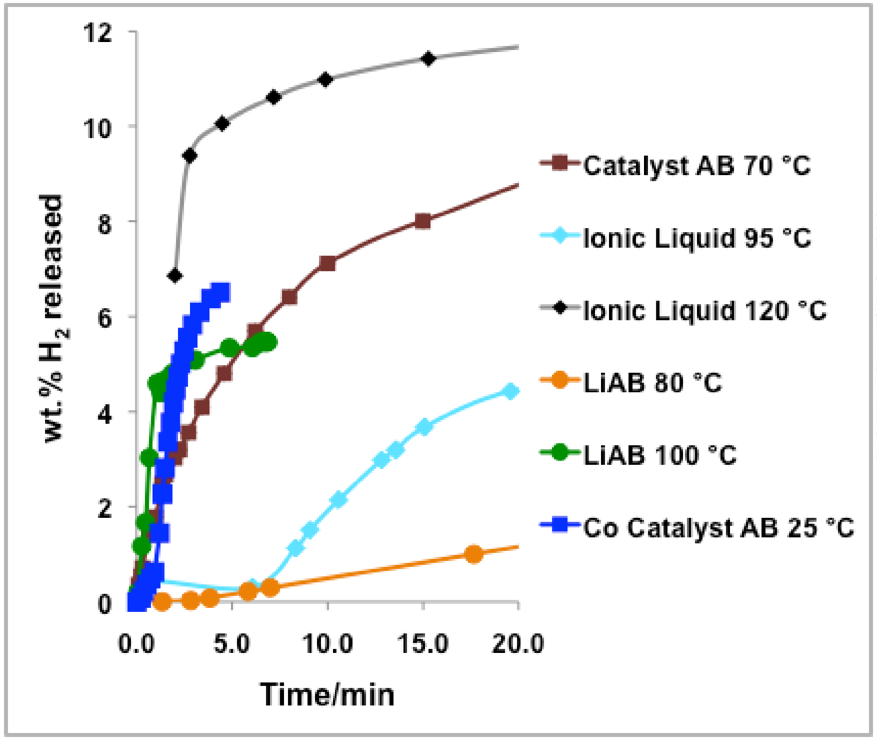
- Foaming mitigation well demonstrated for solid AB with scaffold, nano BN, methylcellulose
- AB with nano-BN decrease release temperature, decrease foaming, but increase levels of byproduct borazine
- Ionic liquid/AB mixtures demonstrated to release > 10 % H_2 by wt. < 110 °C
- Very high rates from IL/AB mixtures at ≤ 110 °C
  - Addition of bases increases rate of release of 2nd equivalent of H_2
  - Catalysts speed the release of the 1st equivalent of H_2
  - Synergy found in catalytic release in ILs
- High rates at T as low as 70 °C with heterogeneous catalysts demonstrated
  - Survey of several non-PGM catalysts completed, active catalysts identified
- Liquid fuels of alkylamine borane/AB eutectics expanded in number
- Impurity identification, mechanism of origin, and quantification
  - Thermolysis, additives, and catalytic release each give rise to differing byproducts and quantities of byproducts
  - Identifying time evolution of products
  - Potential mitigation approaches

ST16, -17, -18, STP18

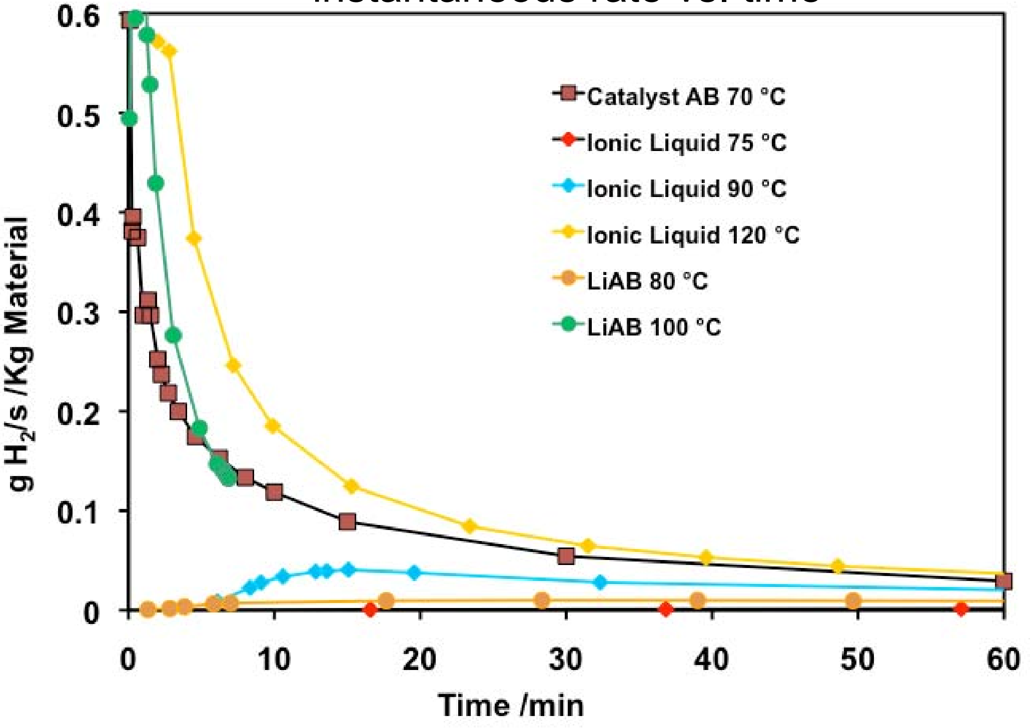
Improvements in hydrogen release:
Kinetics & capacities have potential to meet targets

- High rates of H_2 release from AB to a large extent of capacity at T< 110°C
- Activated processes, highly temperature dependent, allows control
- Release at high rates can be achieved as low as 70 °C with a catalyst

release vs. time



instantaneous rate vs. time



Technical Accomplishments
Timeline of Spent Fuel Regeneration Progress

ST16-21, STP18-19

2006 — 2007 — 2008 — 2009 — 201

⦿ANL SBH Regen Efficiency Analysis

⦿ANL thiocat regen efficiency analysis – indicates potential efficiency problem

⦿ANL alcohol regen efficiency analyses of residual B-H fate

⦿R&H thiocat Regen Baseline Cost Analysis

✓concept of 5 step regen cycle conceived

✓digestion, reduction, metal recycle demonstrated in model reactions

✓super acid digest'n, near-quantitative red'n, exchange to AB demo'd

✓thiocatechol digestion, high yield reduction to LBH_3 demonstrated

✓residual B-H bond retention demonstrated for t-BuOH

✓calculated thermodynamic effic. of thiocat regen cycle exceeds 60%

✗ intractable byproduct in superacid cycle, alternatives sought

✓single pass thiocat process demonstrated to LBH_3

✓metal-based deprotonation/hydride donor route to M recycle described, model system demo

✓Thermodynamic eff. to 90% estimated

✓'Tuning' of thiocat process in preparation for cost analysis

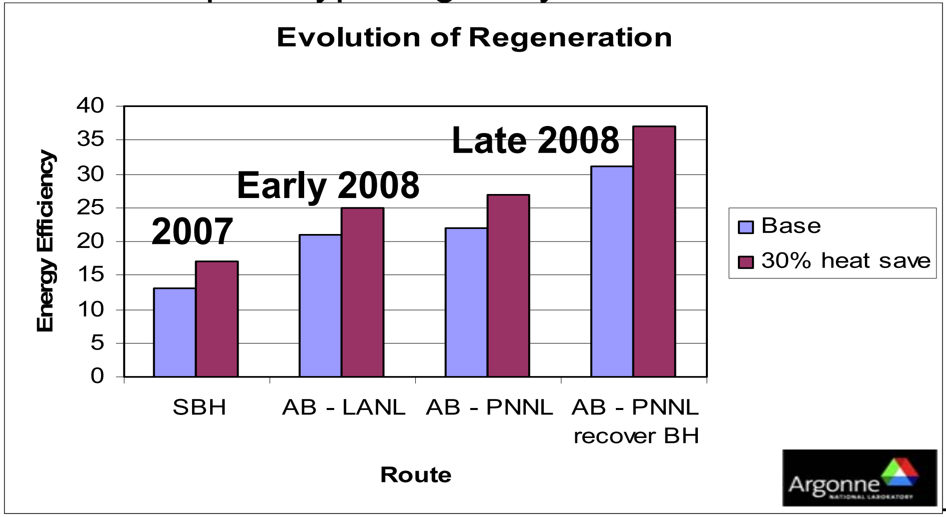
Technical Accomplishments
Spent Fuel Regeneration: Baseline Cost Estimate

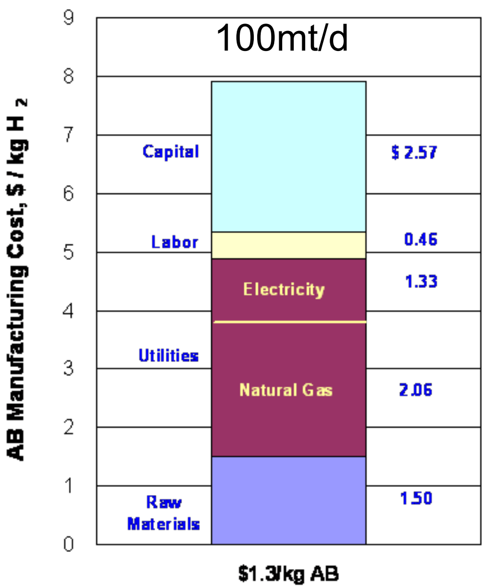
2008

- Thiocatechol route to ANL for 1st baseline efficiency analysis
- ANL identifies significant efficiency problem
- LANL modifies regen pathway
- ANL conducts additional analyses on alcohol routes
- Continuous improvement in efficiency of prototype regen cycles

2009

- Selected thiocat route for baseline cost assessment by Rohm and Haas
- Substantial iterative 'tuning' of process in lab and process flow sheet by R&H
- Cost analysis indicated significant opportunities for improvements in efficiency and cost





ROHM AND HAAS

ST-20

Technical Accomplishments
First Fill Processes and Borax Resource Analysis

- Leading chemistries for synthesis of first fill of AB identified
  - PNNL demonstrates another potential route with improved purity, yield
- Process flow sheeting accomplished
- Results and sensitivity of cost analysis will be discussed by R&H
- Analysis identified inexpensive $NaBH_4$ as key
- Metal reduction/reactive milling route promising

ST20

- Added US Borax as a funded partner
  - Developing updated boron resource and reserves estimates
  - Current US resource can meet anticipated US light duty vehicle demand

ST21

Technical Accomplishments
New Materials Development

2008

- LiAB – structurally characterized
  - different rates, temperatures, and reduced impurities relative to AB
  - 2nd equivalent of H_2 appears to release more readily than from AB
- A number of new metal amidoboranes had been synthesized, but not characterized

2009

- LiAB -- High activation energy of release, sharp onset of release with temperature
- NH_4BH_4 synthesized – valuable intermediate first fill, new materials
  - higher thermal stability than previous reports
  - NH_3 solutions stable
- K-, Mg-, Ca- ABs structurally characterized
  - cation changes solid state structure and reactivity
  - $Al(AB)_3$ synthesized by Missouri
- Metal amidoboranes – diversity of release properties demonstrated
  - All still 'too' exothermic for direct rehydrogenation
  - Not onboard regenerable
- Added new partner to Center, University of Oregon
  - Synthesis of cyclo-CBN compounds
  - Impact in the literature with U. Alabama
  - Early demonstration of rehydrogenation of some cyclo-CBNs
  - Working with U. Washington on catalysis for cyclo CBN H_2 release

ST17,-18,-19, STP16,-17, -20

Technical Accomplishments
Engineering Supporting Research

- Started working more closely with Argonne in FY08 and will continue
  - Efficiency analysis is primary driver
  - Yields feedback on energy/cost intensive steps crucial to moving forward
  - Worked with ANL on analysis of impact of retaining residual B-H in spent fuel
- First Fill and Regeneration of Spent Fuel
  - Cost and efficiency analysis is a core capability of Rohm and Haas
  - Generated first fill analysis from one process, examining additional routes
  - Identified that decreasing cost of SBH is crucial to minimizing first fill cost
- 2 Regeneration process workshops held in Summer 08
  - @ PNNL-- outlined major needs to move to analysis rapidly
  - @ R&H – detailed status of chemistries, identified process details necessary for baseline analyses, initiated data call for physical/chemical properties of intermediates
- Fall Center meeting charted a course to deliver baseline cost in early CY09
  - Rohm & Haas drove the process
  - Considered pros/cons of multiple regen processes for cost analysis
  - Selected LANL process for first baseline cost estimate
  - Subsequently developed timeline to produce baseline analysis
  - Completed baseline cost analysis on time, vetted with LANL and TIAX Feb 2009
  - R&H AB regeneration cost: $7-8/kg

Future work is aimed at providing prioritization and down selection as Center ends 2010

- **Engineering Support**: analyze progress with respect to key barriers, provide quantitative input to prioritization, down select processes
  - Additional cost, efficiency analyses to guide remaining experimental efforts are planned
  - Identification of remaining opportunities in processes
  - Identify and demonstrate most efficient route of borax to first fill AB
  - Continue borax resource analysis for impacts of H-vehicle introduction on market parameters: supply, prices
- **Regeneration**: use baseline cost analysis to prioritize improvements in efficiency, cost
  - ***Final task: reduce mass flow in M-H reduction, separations, recycle***
  - Combine steps, reduce separations and capital costs
  - Reduce separations energy requirements – crystallizations vs. distillations
  - Assess impact of additives, ionic liquids, anti-foam agents on regeneration schemes
  - Down select most energy and cost efficient ‘hybrid’ regeneration process

Future plans, continued

- **New Materials**: Continue search for reversibility in covalent materials: on board regenerable materials
  – Develop pros/cons of the variety of M-ABs now available
  – Prioritize potential of M-ABs for Center sunset
  – Synthesize key members of cyclo CBN family
  – Develop catalysts for de/rehydrogenation of cyclo CBNs
- **Hydrogen Release**
  – Finalize optimization of catalyst, ionic liquid, additive-mediated release processes
  – Develop and describe mitigation of impurities
  – Complete release studies for catalytic, IL-activated, and thermolytic approaches
  – **Analyze pros/cons; give final recommendations to DOE**

External Collaborations: Leveraging our efforts to rapidly assess new developments

- Argonne National Lab and TIAX -- WTT analysis of regen efficiency
- Storage Systems Analysis Working Group -- technical exchange among Centers to discuss technical progress to address key barriers
- IPHE partners (UK, NZ, Singapore/China) -- new materials, personnel exchanges (Autrey, Burrell in Japan, summer 2008).
- Joint Japan NEDO/AIST - LANL Hydrogen Workshops (4th in series – California, Fall 2009)
  - MHCoE and CHSCoE participation
  - Technical exchange with Japanese scientists in fuel cells and storage
  - LANL - AIST joint work on neutron scattering on storage materials
- University of Ottawa, Canada – maintain R. T. Baker's expertise in catalysis and synthesis of liquid fuels within Center
- *Initiated key collaboration with Engineering Center of Excellence*
  - *PNNL and LANL both have key roles as partners in Engineering Center led by SRNL; both have liaison roles with HSECoE*

HSECoE