# 2008 Overview
## DOE Chemical Hydrogen Storage Center of Excellence


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***Project ST4***

# Overview

## Timeline

- Start: March 2005
- End: March 2010
- 60% 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 of the Chemical Hydrogen Storage Center

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

- Develop chemistries, materials, catalysts and new concepts to control thermochemistry and reaction pathways for hydrogen release
- Regeneration -- develop and demonstrate chemical steps leading to off board regeneration of fuel from spent fuel.
- Assess concepts and systems using engineering analysis and studies using DOE targets as guidance; *engineering-guided research*
- Down select most promising chemical systems for more detailed work and engineering development
- Develop life cycle analysis

- ~~Demonstrate a 1 kg storage system~~ ($\Rightarrow$ DOE Engineering CoE)
- Transfer chemical hydrogen storage systems information to Engineering CoE when operating, and receive feedback from its analyses

# Approach to technical barriers

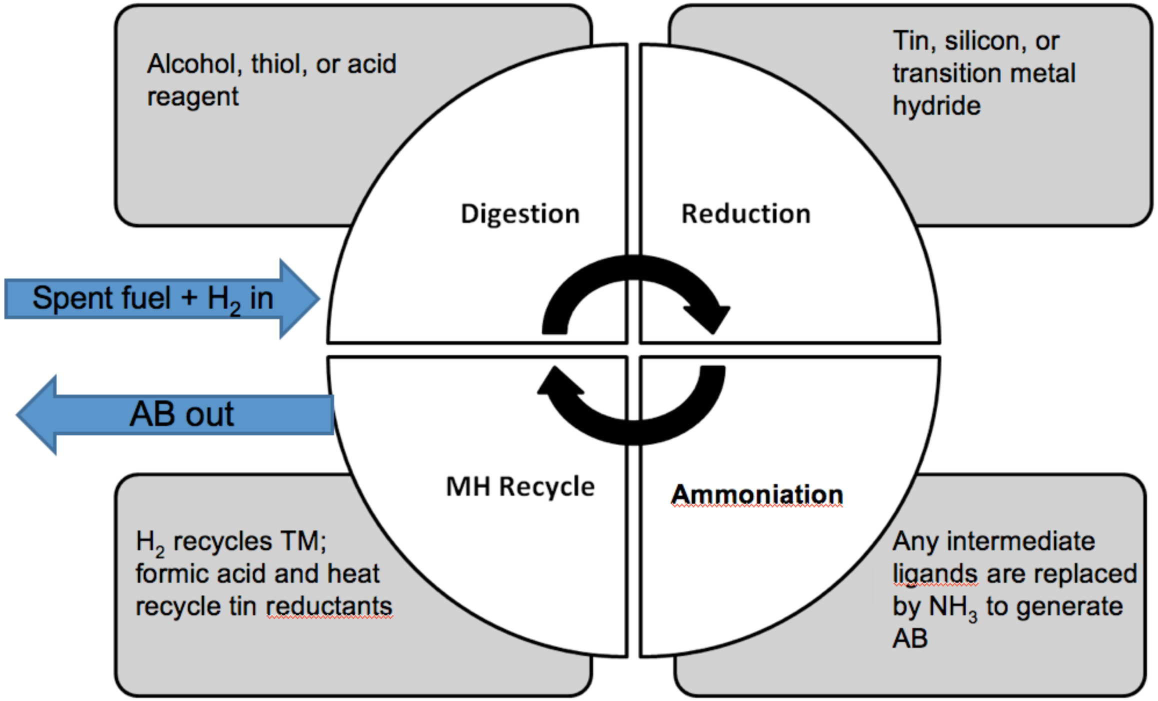
- ENGINEERING ASSESSMENT to GUIDE DOWN SELECTION
  - Provide early assessment of viability based upon potential to provide an engineered solution
  - Guidance to research to move chemistries to efficient processes
- HYDROGEN CAPACITY
  - Develop, synthesize, test compounds with hydrogen densities of > 7 wt. % and favorable energetics for release; materials with potential pathways for direct regeneration with $H_2$
  - Theory and modeling for insight to materials discovery and optimization
- 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 non-productive byproducts and minimize gas-phase impurities
  - Study mechanisms to enhance rates, extents of release, and to aid in the design of catalysts
- REGENERATION -- MAXIMIZE ENERGY EFFICIENCY
  - Develop off board regeneration pathways close to thermodynamic limits
    - Avoid high energy intermediates
    - Use recyclable intermediates
  - Demonstrate integrated regeneration chemistries
  - Assess well-to-tank energy efficiency of processes

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

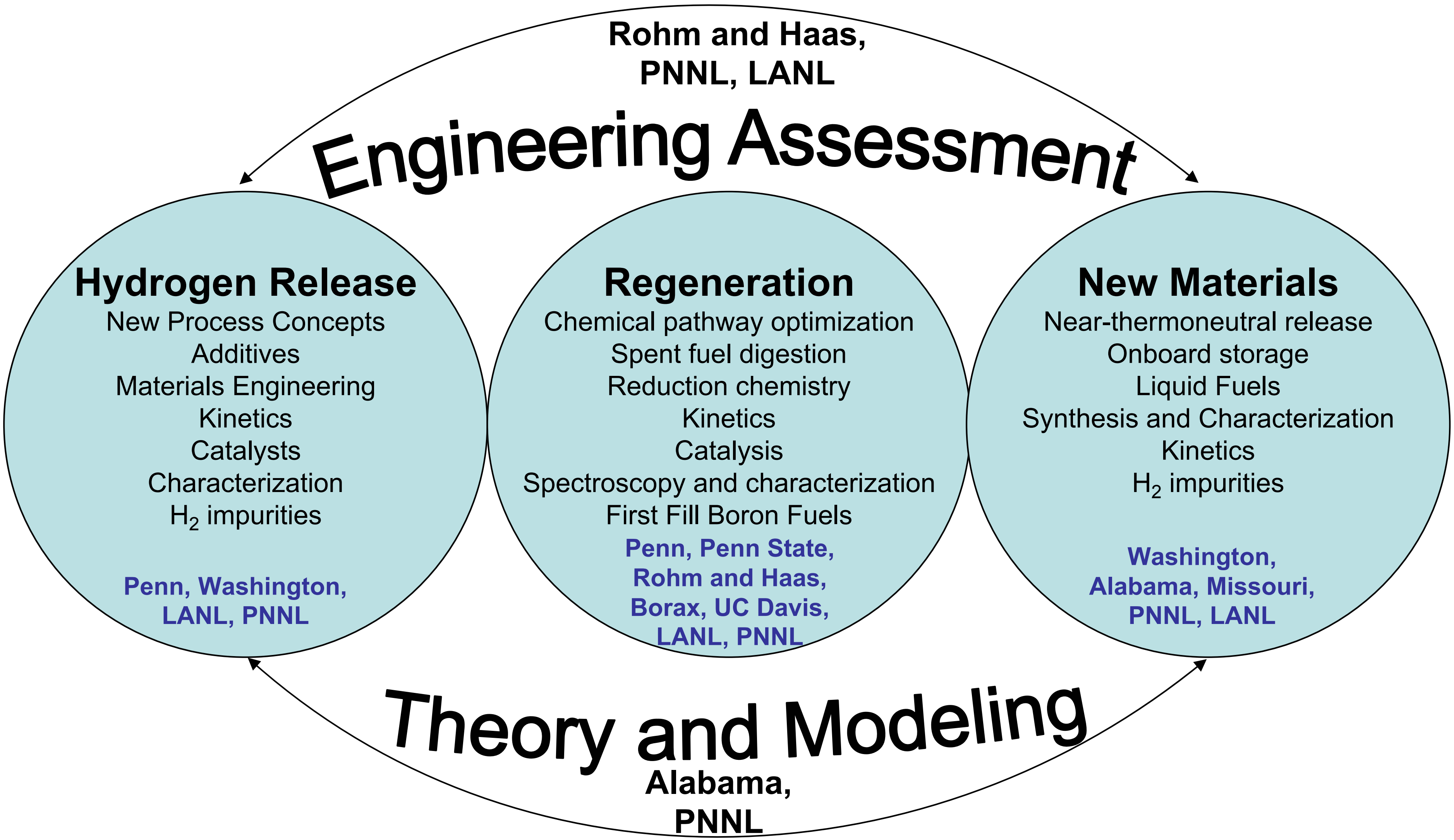
# Overview of current Center activities

- Hydrogen release approaches
  - Chemical additives
  - Thermolysis
  - Catalysis
  - Hydrogen gas purity
- New materials
  - Designed with high capac
    and near-thermoneutrality
    goal
  - Enable on-board regenera
  - Liquid fuel compositions
- Cross-cutting, underpinnin
  capabilities to guide resear
  - Engineering assessments
  - Theory and modeling

- Regeneration of spent fuel -- 60 to 70% of current Center efforts

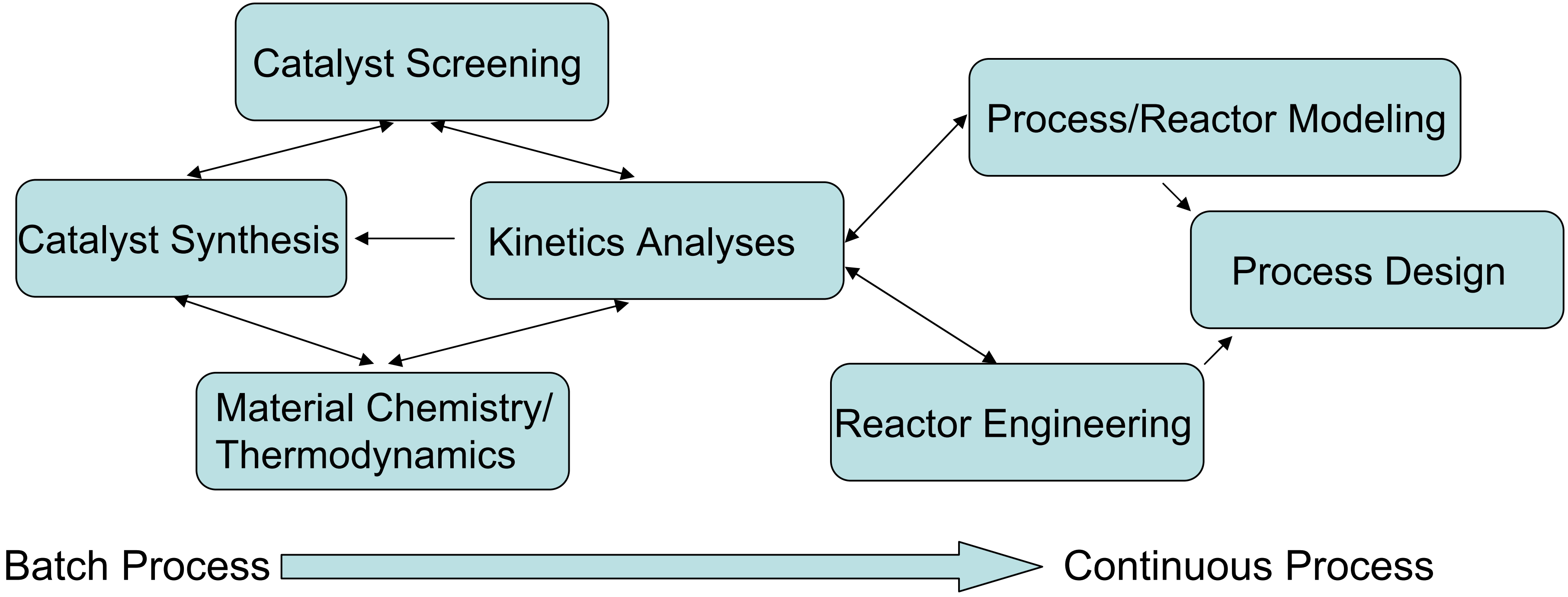


# Communication between Center partners key to moving forward



# Engineering Guided Approach to Materials and Processes

- Process engineering is playing increasingly important role
  - Provides early assessments of feasibility
  - Yields insights to achieve SYSTEM targets
  - Guides regeneration chemistries based on efficiency, scale up requirements
  - Guides materials, process down select decisions



# Engineering Assessment & Coordination Crosscuts Center Activities (PNNL Lead)

- First Fill: Rohm & Haas (lead), PNNL, LANL, US Borax
- Materials engineering and fuel formulation: PNNL (lead), Rohm & Haas, LANL, Penn
- New process concepts for $H_2$ release: PNNL, LANL, Penn
- AB Regeneration: LANL, Rohm & Haas, PNNL, Penn
- Catalysis requirements: LANL, Penn, PNNL

# Theory and modeling guide experiment toward energy efficiencies

- Regeneration (Alabama, Penn, PNNL, UC Davis, LANL)
  - Computation of thermodymic properties of reactants, intermediates, and products
  - Computation and evaluation of reaction pathway energetics
- 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 heteroatom organics (Alabama, Washington, PNNL)
  - Thermochemistry of metal amidoboranes (Alabama, LANL, PNNL)

# Milestones and Go/ No Go Decisions

## Sodium Borohydride (SBH) Go/ No-Go Decision

- Independent Review Panel (University and National Lab members)
- Recommendations
  - No-Go for hydrolysis of SBH for on-board vehicular $H_2$ storage
  - Continue research activities on low cost $NaBH_4$ pathways (Rohm& Haas)
    - $NaBH_4$ 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
- Go/No Go process provided valuable experience in understanding the life cycle of a chemical hydrogen storage system
  - Data requirements
  - Analysis assumptions
  - Contributed to developing Center down select processes

# Lessons Learned from SBH G/NG (Sept. 2007)

- Independent reviewers were extremely knowledgeable
- Regeneration and on board issues had equal weighting
- Identify show stoppers early!
  - Solvent-based approaches should target high concentration
  - Phase changes
    - Liquid to solid conversion during dehydrogenation must be avoided, e.g. crystallization of supersaturated spent fuel borates in the SBH case
    - Liquid to liquid or solid to solid conversions or solid to slurry, liquid to slurry conversions more workable
- Feasibility of scale up from bench scale a key consideration
- Chemical yields and energy efficiency are paramount in regeneration
- GNG exercise provided valuable experience for the Center in developing processes for Center down select decisions

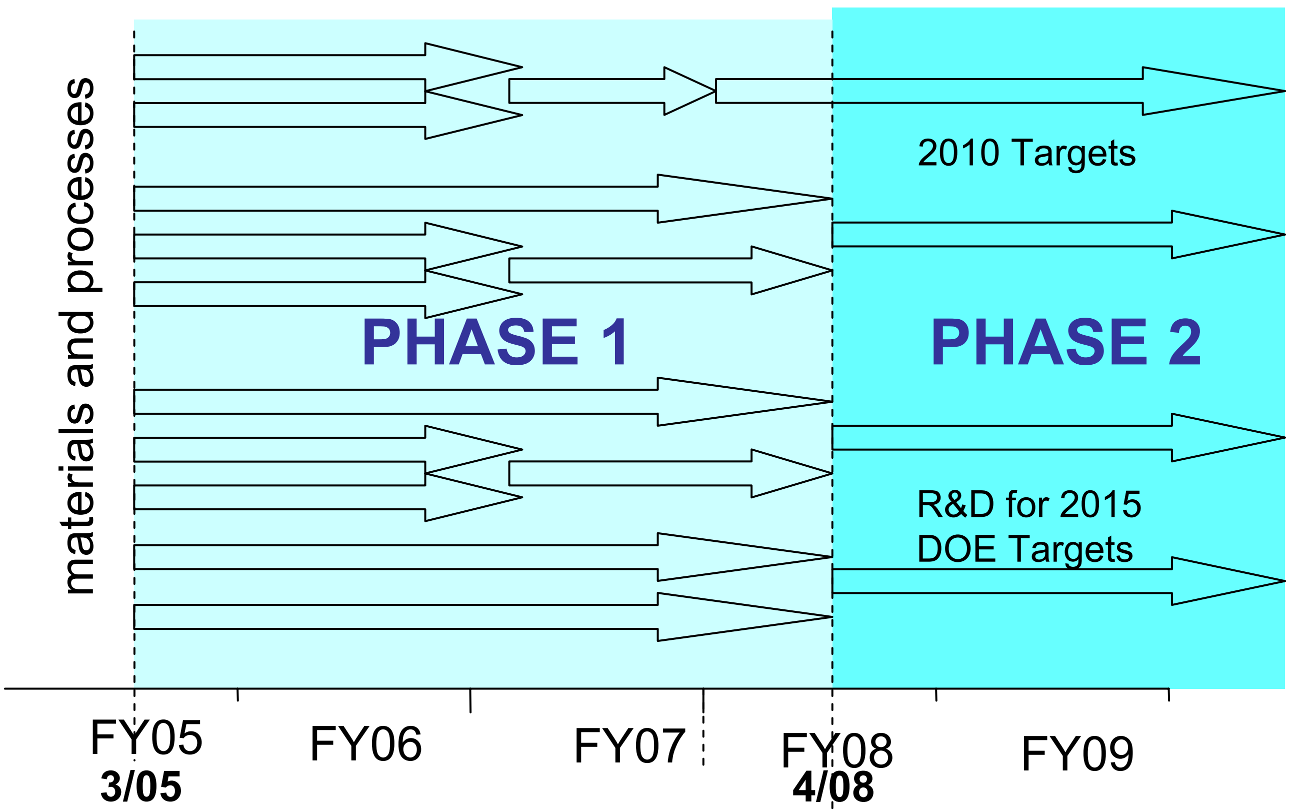
# Additional key milestones being addressed during this review period

- Chemical Hydrogen Storage Phase 1 Down Select
  - Down-select materials and processes within the Center for engineering and development studies to meet 2010 targets
- $H_2$ release from AB: achieve >2 equiv. $H_2$ at higher rates and lower temperatures; mitigate foaming and gas-phase impurities
  - Achieved with additives, scaffolds, and using catalytic release
  - Identified solutions to foaming
- Discover heterogeneous catalysts for AB
  - Found PGM and non-PGM catalysts with high rates and extent of release
- Develop liquid fuel formulations
  - Mixtures of AB with AB derivatives have shown preliminary promise
- Demonstrate individual steps, yields, and thermodynamic efficiencies of regeneration of spent fuel. Demonstrate integrated cycle and efficiency. (DOE Joule Milestones)
  - Demonstrated high yield, high thermodynamic efficiency steps
  - Demonstrated integrated spent fuel to $BH_3$ cycle

# Milestones and Go/ No Go Decisions

## Chemical Hydrogen Storage Phase 1 Down Select (Nov. 07)

- Focused Center efforts and transitioned work into Phase 2



# Down select process for chemical hydrogen storage materials and processes (Nov. 07)

- Collected up-to-date status of relevant materials-related storage parameters on all materials examined within the CoE
- Developed consensus on down select metrics at Center-wide meeting
- Constructed decision tree using down select metrics
- Coordinating Council assessed all of Center's portfolio of materials and processes against the decision tree
- Output was categorized
  - Down selected and proceed with priority
  - Down selected and proceed, but address short-term issues, concerns
  - No go -- halt work
- Recommendations were presented to DOE and guidance implemented for Phase 2

"*Down Select Report of Chemical Hydrogen Storage Materials, Catalysts, and Spent Fuel Regeneration Processes*"
June 2008

http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage

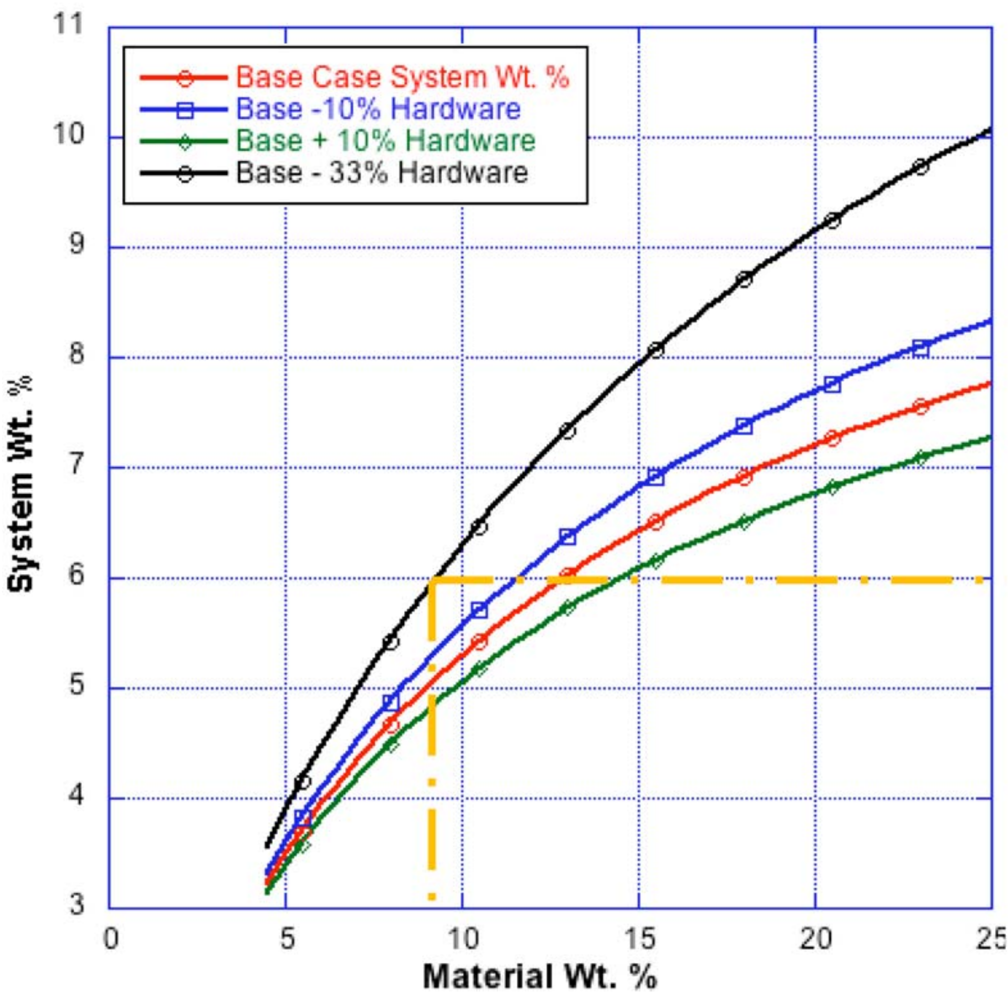
# Down Select Metrics

| Criterion | Description | Metric |
|---|---|---|
| Gravimetric Capacity | Maximum calculated hydrogen weight fraction | > 7 wt. % $H_2$ |
| Potential to Regenerate On-Board | Potential to rehydrogenate spent fuel directly | yes/no/? |
| Regenerable | Ability to chemically reprocess spent fuel off board | yes/no/? |
| Acceptable Phase Change | Problematic liquid to solid phase change, or volatile byproducts | yes/no/? |
| Acceptable Release Rate | Maximum rate of hydrogen release, T< 125 °C | > .02g $H_2$/s/kg material |
| Material Stability | Stable in fuel tank< 50 °C | yes/no/? |
| Endothermic Release | Hydrogen release occurs endothermically | yes/no/? |
| Low Temperature | For endothermic reactions, temperature of release <200 °C (with potential for lower T, i.e., 80 °C, release) | Temperature |

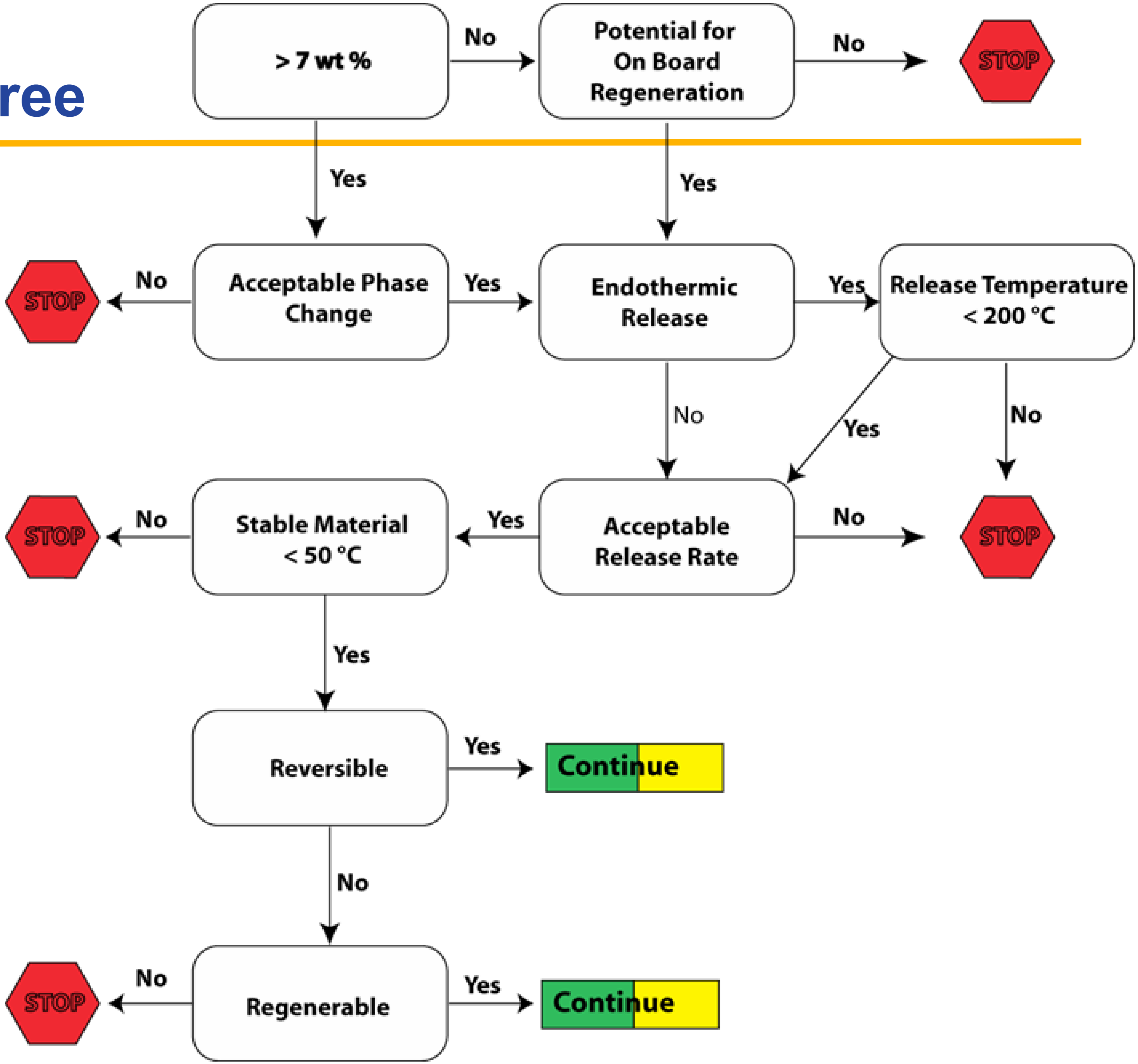
# System Gravimetric Guiding Rule Developed from SBH G/NG Experience

- SBH 7.5 wt % material ≈ 4.5 wt% system -- Millennium Cell
- To meet 2010 gravimetric target, need > 10 wt. % $H_2$ material
- Center's Criterion > 7 wt. %
- Consider lower values for potentially directly regenerable systems

$$\text{System Wt\%} = \frac{\text{Hydrogen Mass}}{\text{Hardware Mass} + \dfrac{\text{Hydrogen Mass}}{\text{Material Wt\%}}}$$



# Decision Tree




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

# Down Select Output from Decision Tree Process

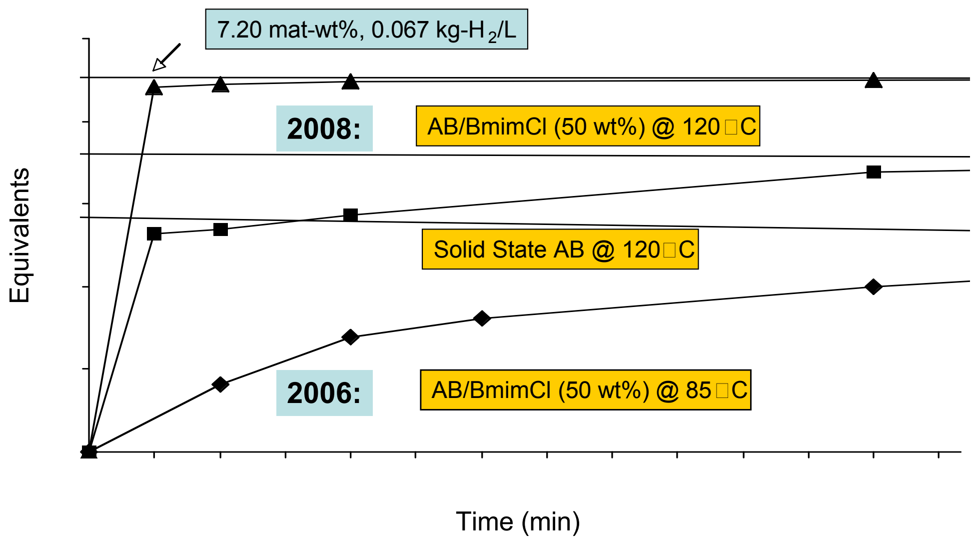
- CHSCoE has investigated more than 60 materials or classes of materials
- 50% Deselected
  - Endothermic organic compounds (low capacity)
  - Nanoparticles (low capacity)
  - Magnesium alkoxide/hydrolysis (release temp > 200 °C)
  - SBH (liquid to solid phase change during release)
  - Bronsted acid catalyzed release from ammonia borane (slow)
  - Substoichiometric LiH/AB mixtures (better compositions found)
  - Ammonia borane/solvent mixtures < 50 wt. % AB (capacity)
  - Polyhedral boranes (requires regen of borate B-O bonds to B-H)
- 30% Conditionally down selected, need resolution of certain performance concerns -- e.g. carbenes, methylamine borane, certain metal amidoboranes
- 20% Down selected for priority development -- e.g. ammonia borane, some metal amidoboranes, certain alkylamine boranes
- Redirected partners involved in SBH/hydrolysis to first fill, regeneration efforts, and new materials exploration

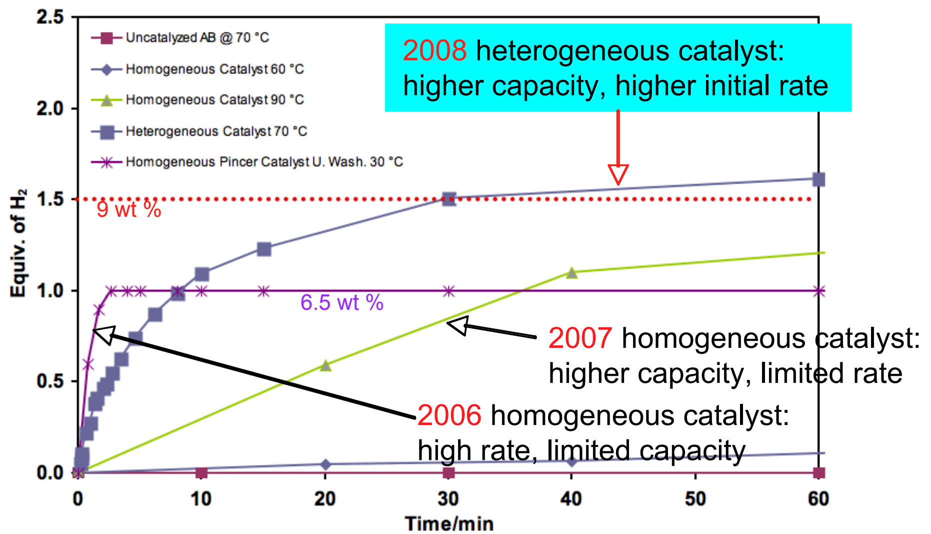
# Technical Accomplishments - Hydrogen Release from AB

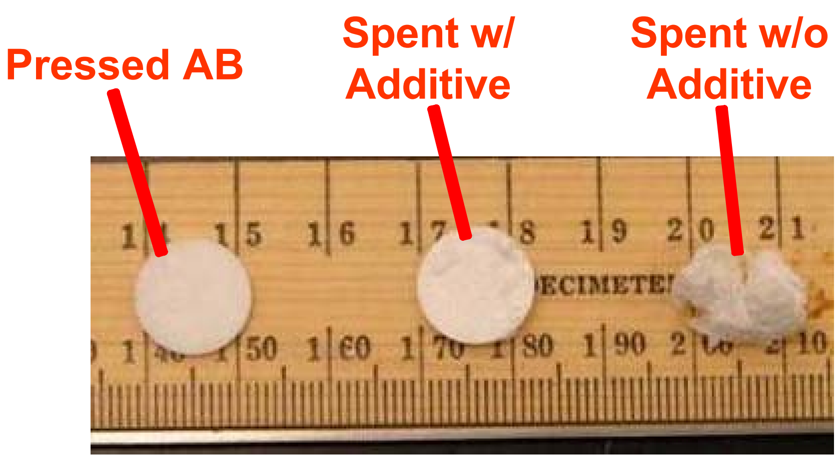
- Demonstrated non-PGM heterogeneous catalysts for AB -- increased rates (2x the DOE target rate), > 9 wt. % $H_2$, and reduced gas-phase impurities
- Demonstrated use of minor additives to reduce impurities and eliminate foaming of solid AB - enables monolithic fuels of higher volumetric density
- Demonstrated faster rates from AB/IL mixtures to yield 10 wt % $H_2$ in 15 minutes; >3x the DOE target rate, reduced impurities & foaming
- Quantified gas-phase impurities in $H_2$; and developed routes/materials to minimize or avoid certain impurities
- Designed, fabricated, and now operating a bench scale continuous flow reactor for catalyst screening and activity studies -- enables catalyst optimization lifetime studies, transient studies, kinetics
- Demonstrated hydrogen purity testing using single cell fuel cell

ST-5, -6, -7,-10,-11

# Improvements in hydrogen release: Kinetics, capacities, physical properties, impurities



# Accomplishments - Spent Fuel Regeneration

- Improved all three current AB regeneration pathways
  - Integrated some steps into single steps
  - Increased yield of integrated chemistries for portions of regeneration cycle
  - Demonstrated metal-hydride recycle chemistries
  - Demonstrated hydride transfer to spent fuel - potentially enabling to the alcohol-based route
- For one pathway, demonstrated all steps to complete regeneration of spent fuel to AB
- Modified regeneration approach based on on preliminary well-to-tank energy efficiency analysis
- Accomplishments support the goal of demonstrating energy and chemically efficient regeneration

- Effective use of theory and modeling to more rapidly assess regen chemistries and strategies prior to doing experiments.
  - Identified most promising digestion reagents to generate B-X bonds with most favorable energetics
  - Identified most promising energetically efficient reducing agents to reduce B-X with M-H
  - Assisted in matching digestion with reduction chemistries for efficiency
  - Aided selection of co-ligand for L-B-X reduction with M-H to enhance kinetics, yields
  - Identified most promising selection of optimal metals and ligands for hydride transfer
  - Computational analysis of direct rehydrogenation pathways

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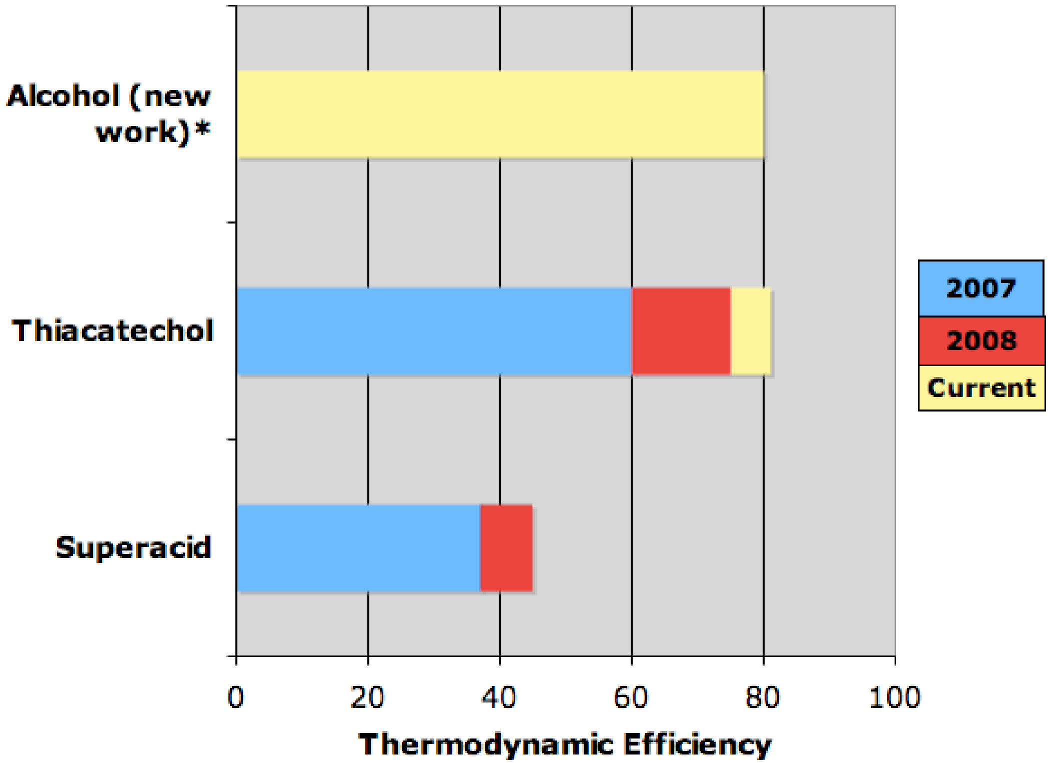
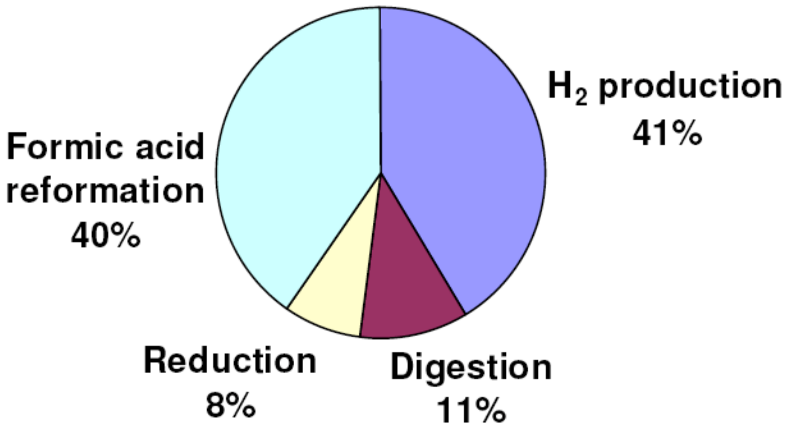
# Regeneration efficiencies and chemical yields improving with continued research




Thiacatechol route -- 35% improvement over 2007
Superacid route -- 22% improvement over 2007

Primary Energy Distribution




Argonne NATIONAL LABORATORY

* Not all steps demonstrated, new work

# Accomplishments - New Materials Development

- Liquid fuel compositions have been expanded in number, and liquid range to - 30 °C has been demonstrated
  - Goal is to enable design of continuous catalytic reactors for $H_2$ release
- Search for onboard regenerable materials *via* molecular design of near-thermoneutral hydrogen release materials
  - With guidance from theory, designed and are synthesizing novel C-B-N-$H_x$ molecular systems -- coupled endo/exothermic dehydrogenation systems
  - Prepared numerous metal amidoboranes that are less exothermic than AB; > 7 wt.% $H_2$, acceptable kinetics, reduced impurities, reduced or no foaming
  - Computationally explored alane - amine and alane - amine - borane systems. Results are guiding new materials development at Missouri, and has relevance to MHCoE efforts

ST-5,-6,-9,-10

# Accomplishments - Engineering Supporting Research

- Developed engineering-guided criteria to underpin Center down select process
  - Brought focus to Center efforts in materials discovery and development
- Developed preliminary spreadsheet analysis of regeneration schemes
  - Guides efficient regeneration chemistry process research
  - Responded quickly to ANL input on process efficiency concerns of AB regen by developing and providing proof-of-principle direct rehydrogenation scheme
- Operating bench scale continuous flow, heterogeneous catalyst reactor
  - Enables heterogeneous catalyst activity, lifetime, kinetics, transient studies, and long-term hydrogen purity studies
- Demonstrated simple hydrogen gas-cleanup chemistry using a fuel cell dosimeter to detect and determine any influence of impurities on FC performance
  - Preliminary data for release systems gas cleanup considerations

ST-5,-6,-8

# Materials Comparisons and Progress; Selected Results

| Metrics | AB Thermolysis/Chemical Promoters | | | | | | |
|---|---|---|---|---|---|---|---|
| | *2007 AB/Ionic Liquids ( 50 %)* | AB/Ionic Liquids (50 %) | AB/Ionic Liquids ( 20 %) | *2007 PNNL AB solid 155 °C* | PNNL AB solid 160 °C | PNNL AB solid 145 °C | PNNL AB solid 130 °C |
| Grav. density (Mat. wt%) | *4.2* | 7.2 | 10.2 | *6.5*<br>*13* | 6.5<br>9<br>13<br>>16 | 6.5<br>9<br>13 | 6.5<br>9 |
| $H_2$ Flow Rate (g/s) per kg* | *.0038* | 0.08 | 0.114 | *.84*<br>*.22* | 1.3<br>1.2<br>.54<br>.16 | .93<br>.50<br>.11 | .43<br>.1 |
| Vol. density (kg-$H_2$/L | *.023* | 0.067 | 0.086 | *.048* | .048 | .048 | .048 |

* DOE target = .02 g/s/kW;
rate/kg is roughly equal to rate/kW

**DOE System Targets for Hydrogen Storage Systems**

**Gravimetric Density (wt%)**
4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***

**Volumetric Density (Kg-$H_2$/L)**
0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

# Materials Comparisons and Progress; Selected Results

| Metrics | New Materials | | | AB Catalysis | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CaAB_2$ | $LiZnAB_3$ | $ScAB_3$ | Homog. Fe catalyst-2 *2007* | Heterog. Pt | Heterog. Cu | Heterog. Mn | Heterog. Ni |
| Grav. density (Mat. wt%) | 7.2 | 10.5 (tga) | 11.1 | 1.8 eq. $H_2$/AB | 1.91 (Eq. $H_2$ per AB) | 1.82 (Eq. $H_2$ per AB) | 0.16 (Eq. $H_2$ per AB) | 0.11 (Eq. $H_2$ per AB) |
| $H_2$ Flow Rate (g/s) per kg* | .02 | .02 | N/A New Work | .008 *0.00015* | 0.057 | 0.076 | 0.004 | 0.002 |
| Vol. density (kg-$H_2$/L | .05 (est.) | .07 (est.) | .05 (est.) | Not measured | .048 | .048 | .048 | .048 |

* DOE target = .02 g/s/kW;
rate/kg is roughly equal to rate/kW

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0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

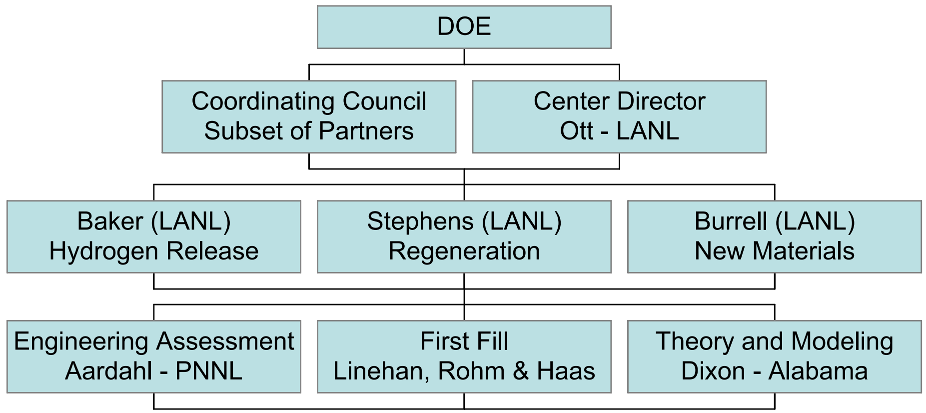
# Future work is aimed at providing diversity of options

- **Regeneration**: maintain diversity of processes to provide options, off-ramps
  - Explore M-H recycle via direct rehydrogenation; develop catalytic routes
  - Demonstrate complete recycle of 1 gram actual spent fuel at high yield
  - Initiate assessment of impact of additives on regeneration schemes
- **Engineering Support**: analyze progress with respect to key barriers, develop contingencies
  - Continue to provide early identification of gaps, opportunities in processes
  - Assess new well-to-tank results from ANL and address opportunities for improvement in efficiency
  - Hold Center-wide process chemistry brainstorming session to address regeneration process integration, separations chemistry issues
- **New Materials**: develop alternatives to existing materials, processes
  - Measure $H_2$ reversibility of existing and new near-thermoneutral materials
  - Continue search to add new promising storage materials and concepts to portfolio
- **Hydrogen Release**: maintain diversity of processes to provide for contingencies (solids, slurries, and liquids -based processes)
  - Solids handling innovations to enable solid-solid reactor design
  - Heterogeneous catalyst lifetime and release kinetics for AB dehydrogenation
  - Continue to expand capacity and improve kinetics of liquid fuels, and promoter- and ionic liquids-based fuels

# Summary of Center's Technical Accomplishments

- Center down select process has focused Center to continue to address key barriers
- Engineering- and theory-guided approach allows Center to make rapid progress
- Center has shown significant progress in demonstrating a regeneration process for AB
  - Improved yields, energetics
  - Some steps integrated to provide process simplification
  - Demonstrated regeneration cycle yield of 70% on a batch
- Center has demonstrated improvements in hydrogen release
  - Mitigated foaming of solid AB
  - Demonstrated heterogeneous catalyst for release from AB at 70 °C having rates and capacities in excess of DOE targets
  - Demonstrated AB-additive and scaffold systems that have rates and capacities in excess of DOE targets
  - Demonstrate processes and materials for release that reduce gas-phase impurities
- Center continues to add new promising storage materials to portfolio, while continuing to de-select less promising systems

# Center Management and Communication




- Maintain IP agreement that allows free exchange of ideas and materials among Center partners
- 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
- Quarterly tracking of Partner's progress toward DOE targets
- Develop materials down selection criteria and decision tree process to guide Center decisions
- Hydrogen Storage Centers conference calls with DOE to foster cross-Center information exchange with Carbon- and Metal Hydride Storage Centers
- Biannual Center meetings coincident with Tech Team and Annual Review; Fall meeting in Denver
- Participation in Storage Systems Analysis Working Group:  cross-Center engineering issues
- Organize Annual Review, Tech Team Review

# Key Impacts of Center Communications

- Mid-year Center down select meeting (Denver)
  - Developed engineering-guided decision tree approach to down select
  - Down select process has focused Center efforts
  - Identified crucial engineering issues facing Center in both release and regeneration
  - Brainstormed, identified, and have started work on new materials, new catalysts, regeneration chemistries
- Regular focus area conference calls
  - Conduit for free flow of information on progress, generate new ideas, share results
  - Regeneration, hydrogen release, B-O to B-H for first fill
  - Provide feedback mechanism to increase rate of progress, Center-wide
  - Develop and prioritize capital equipment needs for Center
- Coordinate technical personnel exchange and international collaboration
  - PNNL and LANL staff to Japan
  - PNNL, LANL, Washington, Hawaii PIs to Tokyo Nov. 07 for Joint NEDO/AIST - LANL hydrogen workshops (next in series is San Diego, September 2008)
  - LANL staff to Oxford/UK FY07
  - PNNL staff to Singapore FY07
  - Visitors from Oxford, Singapore, Japan, New Zealand: experimental work at National Labs
- Coordinate and promotes collaboration, exchange of materials
- Students from academic partner's labs working alongside National Lab staff and using National Lab instrumentation

# Collaborations: Leveraging our efforts to rapidly assess new developments

- Argonne National Lab -- WTT analysis of regeneration efficiency
- Storage Systems Analysis Working Group -- technical exchange among Centers to discuss technical progress to address key barriers
- IPHE partners (UK, NZ, Singapore) -- new materials, personnel exchanges
- Joint Japan NEDO/AIST - LANL Hydrogen Workshops (3rd in series -- San Diego, September 2008)
  - MHCoE and CHSCoE participation; anticipate expanded scope this year
  - Technical exchange with Japanese scientists in fuel cells and storage
  - LANL - AIST joint work on neutron scattering on storage materials
- Upcoming PNNL and LANL extended visits in Japanese laboratories
- Preliminary discussions with A*STAR/ICES on collaborations with Singapore government research lab in hydrogen projects
- *Looking ahead -- key collaboration with Engineering Center of Excellence*