IV.B.1a 2008 Overview - DOE Chemical Hydrogen Storage Center of Excellence (CHSCoE)

Kevin C. Ott
Los Alamos National Laboratory (LANL)
J514
Los Alamos, NM 87545
Phone: (505) 667-4600; Fax: (505) 667-9905
E-mail: kcott@lanl.gov

DOE Technology Development Manager:
Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

Start Date: March 1, 2005
Projected End Date: September 30, 2010

Objectives of the Center

- Implement a coordinated approach to identify, research, develop, and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet DOE Hydrogen Storage 2010 system goals.
- Design, synthesize, and test materials and compositions to control the thermochemistry and kinetics of hydrogen release.
- Develop energy and chemically efficient off-board spent fuel regeneration for the complete fuel cycle.
- Assess concepts and systems for hydrogen release and spent fuel regeneration using supporting engineering analysis and validation to rank viable candidates.
- Down-select most promising chemical systems for more detailed materials and engineering development.
- Develop most promising chemical hydrogen storage materials with potential to meet 2010 targets.
- Perform lab-scale engineering studies to evaluate performance of hydrogen storage systems.
- Develop life cycle analysis.
- Transfer chemical hydrogen storage systems information to the Engineering Center of Excellence (CoE) when operating, and receive feedback from its analyses.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

(A) System Weight & Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging & Discharging Rates
(J) Thermal Management
(K) System Life-Cycle Assessments
(R) Regeneration Processes
(S) By-Product/Spent Material Removal

Technical Targets

While all of the relevant targets detailed in the DOE MYRDDP will be addressed, our main emphasis focuses on the material requirements. The Center has developed interim technical guidelines to facilitate down-selection of promising materials for further development. The Center's key criteria for down selection of storage materials include gravimetric and volumetric hydrogen capacities, as well as hydrogen release rate and temperature. The Center's criteria for materials down-selection, which are mapped to the DOE technical targets for storage systems, are tabulated in Table 1. Gravimetric capacity of materials must exceed 7 wt%, with the potential to exceed 9 wt%. The latter value was determined via an analysis of Millennium Cell's very aggressive process design for hydrogen release form aqueous sodium borohydride (SBH). The goal for temperature is for hydrogen release to occur with high rate below 100°C, with an interim goal of release occurring at high rates below 200°C. The Center's criterion for the rate of hydrogen release, 0.02g H_2/s/kW, is the DOE 2010 target.

Accomplishments

Using the criteria in Table 1, the Center down-selected materials and processes with the potential to meet DOE 2010 technical performance targets. The Center evaluated all of the more than 60 materials systems studied to date within the Center, and down-selected 20% of these for priority development. Research and development (R&D) on 50% of the systems was discontinued, and another 30% were conditionally down-selected, awaiting further data. The process for down-selection is described below in the Results section. A summary of the Center's progress toward meeting the technical targets is tabulated in

TABLE 1.

Criterion	Description	Metric
Material Wt%	Maximum calculated hydrogen weight fraction, potential to exceed 9 wt%	>7 wt% H_2
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/potential
Regenerable	Ability to chemically reprocess fuel offboard	yes/no/potential
Acceptable H_2 Release Rate	Problematic liquid to solid phase change	yes/no/potential
Acceptable H_2 Release Rate	Maximum rate of hydrogen release	>0.02 g H_2/s/kW material
Stable Material <50°C	Stable in fuel tank<50°C to H_2 release, or decomposition	yes/no/potential
Temperature of Release	Demonstrated, or potential for release at T<100°C	<200°C

TABLE 2.

(a)

Metrics	AB Thermolysis/Chemical Promoters							
	DOE Systems Targets	*2007 AB/Ionic Liquids (50 %)*	AB/Ionic Liquids (50 %)	AB/Ionic Liquids (20 %)	*2007 AB solid 155 ?C*	AB solid 160 ?C	AB solid 145 ?C	AB solid 130 ?C
Grav. density (Mat. wt%)	*6 wt. % (system)*	*4.2*	7.2	10.2	*6.5 13*	6.5 9 13 >16	6.5 9 13	6.5 9
H_2 Flow Rate (g/s) per kW	*0.02*	*0.006*	0.07	0.07	*0.81 0.11*	1.25 0.83 0.26 0.06	0.90 0.35 0.05	0.41 0.07
Vol. density (kg-H_2/L	*0.045*	*0.023*	0.067	0.086	*0.048*	0.048	0.048	.048

(b)

Metrics	New Materials			AB Catalysis				
	$Ca(AB)_2$	$LiZn(AB)_3$	$Sc(AB)_3$	Homog. Fe catalyst-2 *2007*	Heterog. Pt 70 ?C	Heterog. Cu 70 ?C	Heterog. Mn 70 ?C	Heterog. Ni 70 ?C
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 kW	.02	.01	New Work	.008 *0.00015*	0.03	0.04	0.02	0.017
Vol. density (kg-H_2/L	.05 (est.)	.07 (est.)	.05 (est.)	Not measured	.048	.048	.048	.048

Tables 2a and 2b. The values for some of the ammonia borane (AB) release processes (additives, thermolytic, catalytic) are compared to previously obtained data from Fiscal Year 2007, and indicate that substantial improvements in materials properties has occurred during FY 2008, particularly in the area of rates of release. In some systems an improvement in release rate of 10-fold over 2007 values has been realized.

The Center's progress in spent fuel regeneration as measured against the DOE goal of achieving >60% energy efficient regeneration has shown substantial progress. Three routes are being developed. Hybrids of these three approaches are evolving as we gain experience in the reactivity of spent fuels, and as we gain knowledge that we have received from extensive computation and modeling of the thermodynamics of the individual steps that make up the spent fuel regeneration schemes. The three approaches rely on digestion of spent fuel that arises from dehydrogenation of AB to a highly crosslinked polyborazylene polymer. Three digestion approaches using a superacid, a thiol, or an alcohol to digest the fuel to a more chemically processable intermediate have all shown improvements in overall computed thermodynamic efficiencies. The calculated thermodynamic efficiencies of these three processes are shown in Figure 1.

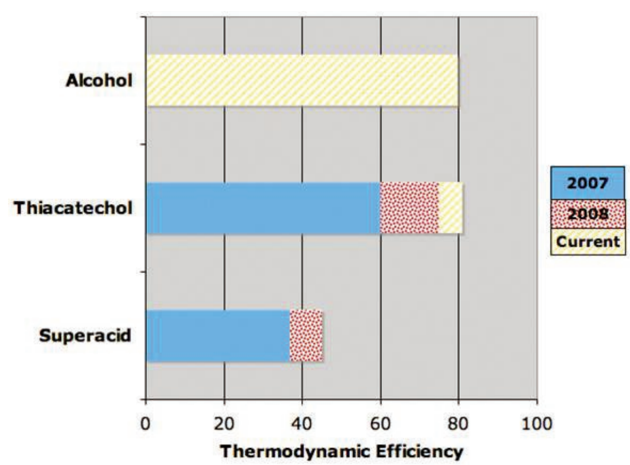

FIGURE 1. Calculated Thermodynamic Efficiencies of the Three Current Spent Fuel Regeneration Approaches the CHSCoE is Developing

During FY 2008, the thiacatechol route has shown a 35% improvement in efficiency over FY 2007, and the superacid route has improved by 22% over FY 2007. The alcohol route is relatively new work during FY 2008, and thus is not compared to earlier work. Following is a list of the Center's FY 2008 key accomplishments:

- Hydrogen Release from Ammonia Borane:
  - Demonstrated non-platinum group metal heterogeneous catalysts for release from AB -- increased rates (2x the DOE target rate), and the quantity of hydrogen, >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/ionic liquid mixtures to yield 10 wt% H_2 in 15 minutes; >3x the DOE target rate, and reduced impurities and foaming.

   - Quantified gas-phase impurities in H_2 arising from different processes for release from AB; and developed routes/materials to minimize or avoid certain impurities.
   - Designed, fabricated, and now operating a bench-scale continuous flow reactor for heterogeneous catalyst screening and activity studies that enables catalyst optimization lifetime studies, transient studies, kinetics.
   - Demonstrated hydrogen purity testing using single-cell fuel cell.
- Spent Fuel Regeneration:
   - Demonstrated individual steps for three individual pathways for regeneration.
   - Integrated theory and modeling with experiment to accelerate regeneration R&D.
   - For two regeneration pathways, demonstrated all steps to complete regeneration of spent fuel to AB.
   - Modified and improved this regeneration approach based on preliminary well-to-tank energy efficiency analysis.
   - Accomplishments support the goal of demonstrating energy and chemically efficient regeneration.
   - Developed 'first-fill' cost and efficiency analysis capability from experience gained from SBH regeneration analyses.
- New Materials Development:
   - New liquid fuel compositions have been discovered with liquid range to -30°C has been demonstrated.
   - Liquid fuels enable design of continuous catalytic reactors for H_2 release.
   - Designed (using input from theory and modeling) and are synthesizing novel potentially coupled endo/exothermic C-B-N-Hx molecular systems.
   - Prepared numerous metal amidoboranes that exhibit lower exothermicity of hydrogen release than AB; materials with >7 wt% H_2 with rates of release that meet the DOE target, and exhibit reduced impurities and reduced or no foaming upon release of hydrogen.
   - Computationally explored alane-amine and alane-amine-borane systems. Results are guiding new materials development at the University of Missouri, and has relevance to Metal Hydride Center of Excellence efforts.
- Engineering-supporting R&D:
   - Developed engineering-guided criteria to underpin the Center down-select process and to lend guidance to materials discovery efforts.
   - Developed preliminary spreadsheet analysis of regeneration schemes.
   - Provided proof-of-principle direct rehydrogenation scheme to improve regeneration energy efficiency for one regeneration approach.
   - Designed, fabricated, and demonstrated bench-scale continuous flow, heterogeneous catalyst reactor for hydrogen release R&D.
   - Demonstrated fuel cell dosimetry approach for determining hydrogen purity, and demonstrated a simple hydrogen gas-cleanup separation of borazine and other potential impurities.

✧ ✧ ✧ ✧ ✧

Introduction

Chemical hydrogen storage involves storing hydrogen in molecular chemical bonds where an on-board chemical reaction is used to release hydrogen. The resulting spent fuel is regenerated off-board using chemical processing. In addition to the importance of on-board storage capacity and hydrogen release rates, the energy efficiency of the off-board regeneration of spent fuel is a key contributor to the overall energy efficiency of the fuel cycle. Chemical hydrogen storage provides a diversity of options to enable hydrogen for transportation and could also be used for hydrogen delivery where it offers the opportunity for a liquid or solid fuel infrastructure with the potential for no direct hydrogen handling by the consumer.

Researchers in the Center are advancing a number of integrated projects involving the development of storage compounds, thermochemical and catalytic processes for on-board release from those compounds, catalysts to accelerate hydrogen release from compounds at lower temperatures, and development of regeneration processes of resulting spent fuels. These activities are guided by a well-integrated theory and modeling effort, as well as by an engineering supporting R&D function that informs Center R&D of engineering issues and concerns. The objectives of the Center are to develop and assess new methods for on-demand release of hydrogen from chemical systems that can achieve DOE targets and to develop high-yield, energy-efficient off-board methods for regeneration of spent storage material. The key elements in the Center's collaborative activities are computation and modeling; the design, synthesis, and testing of structures and compositions to control the thermochemistry and kinetics of hydrogen release and spent fuel regeneration; development of chemical processes and catalysts for hydrogen release and regeneration; and iterative engineering assessment including evaluation, modeling and testing ranging from process identification through optimization of hydrogen release and regeneration reaction conditions.

Approach

The overall Center approach capitalizes on its broad spectrum of expertise to carry out R&D in chemical hydrogen storage. The Center's activities fall into four general areas. The researchers that work across these four areas communicate efficiently across the Center to maintain a focus on achieving the DOE technical targets, and collectively move the Center's R&D forward, making adjustments in strategy and direction as new results from R&D become available. In addition to the four major areas of focus, the crosscutting area of theory and modeling is integrated into each area as required. Much of the theory and modeling effort is directed at computational chemistry of the regeneration approaches. An additional area that underpins the Center's activities is in the area of 'first-fill', the synthesis of the first load of fuel from mined borate minerals, a task that is one of Rohm and Haas' primary focus areas.

The four major areas of Center R&D are outlined below.

1. **Hydrogen Release from Ammonia Borane.** This activity is populated by a number of Center partners, and is directed at developing processes for the release of hydrogen from AB. The goal is to simultaneously improve the quantity of hydrogen released while improving the rate of hydrogen release at the lowest temperatures achievable, and with mitigation of foaming or the release of volatile byproducts that could be deleterious to the eventual utilization of the hydrogen in for example, a fuel cell.
2. **Regeneration of Spent Fuel.** This activity is directed at the energy and chemically efficient regeneration of spent fuel that arises from dehydrogenation of ammonia borane. This represents a majority of the current work being performed within the Center. The Center's regeneration efforts are directed at digesting of the spent fuel to a readily chemically processable material, then adding hydrogen to this material, and recycling any auxiliary components required along the to provide for a chemically integrated spent fuel to fuel regeneration loop.
3. **Materials Discovery.** Much of the Center's focus is on developing AB as a hydrogen storage material. The Center maintains a smaller research effort to discover other potentially useful storage materials. These areas are currently focused on developing storage materials that release hydrogen less exothermically than AB, with the goal of discovering a material that releases hydrogen with little or no heat lost or gained. This could lead to a potentially reversible, on-board regenerable fuel.
4. **Engineering Supporting R&D.** This activity, along with theory and modeling, crosscuts all of the other activities within the Center, as engineering analyses are used to inform the R&D efforts as to what the practical implications of the systems targets entail for development of an efficient hydrogen storage system. This activity provides chemical engineering and process engineering expertise for analysis of potential hydrogen storage systems and spent fuel regeneration, and provides guidance for materials down selection processes.

Pursuing these four major areas of Center R&D in parallel will maximize our ability to achieve the DOE targets for hydrogen storage. The goal is to provide DOE with several working options for chemical hydrogen storage, as well as an evolving knowledge and critical evaluation to assist future R&D, technology demonstration, and policy decision-making. The overall approach of the Center is to screen and assess concepts and ideas against a set of hierarchical criteria that are derived from the DOE technical targets for hydrogen storage.

Table 3 tabulates the four areas of Center R&D focus along with the Center partners who are involved in the research. Our collaborative project structure enables the close coupling of experimental and computational R&D with engineering assessment to facilitate the transition from discovery of new concepts through development to implementation. The Center is addressing storage capacity by developing, synthesizing, and testing molecular compounds with high hydrogen density, appropriate energetics, and potential pathways for hydrogen release. The Center is organized as shown in Figure 2, with the key people that help to coordinate the four areas of R&D activities, and the underpinning first-fill and theory and modeling efforts. Center communication challenges across such a diverse, and technically broad spectrum of partners are met by task and sub-task conference calls, face-to-face meetings,

TABLE 3.

Task	Partners
Hydrogen Release from Ammonia Borane	U. Alabama, LANL, PNNL, U. Pennsylvania, U. Washington
Regeneration of Spent Fuel	U. Alabama, U. California, Davis, LANL, PNNL, Pennsylvania State U., U. Pennsylvania, Rohm and Haas
New Materials Discovery	U. Alabama, LANL, U. Missuri, PNNL, U. Washington
Engineering Supporting R&D	PNNL, Rohm and Haas, LANL

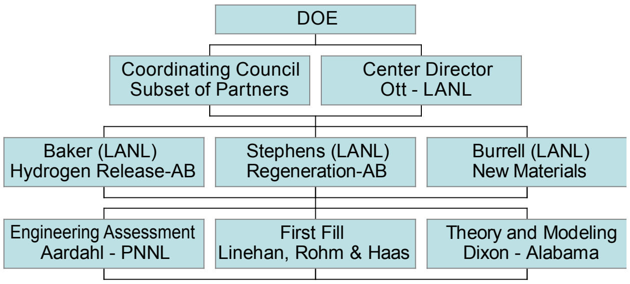

FIGURE 2. The Organizational Structure of the CHSCoE

one-on-one phone conversations, and three annual Center-wide meetings at the annual Hydrogen Program Merit Review, a mid-year meeting in Denver, and the annual Tech Team Review held in early spring. In addition, co-workers from Pacific Northwest National Laboratory and Los Alamos National Laboratory collaborate with a group of international scientists that are participating in an International Partnership for the Hydrogen Economy project that also allows for additional opportunities to meet and discuss the science and technology of chemical hydrogen storage.

In addition, this Center communicates with the Metal Hydride and Sorption Storage Centers through our participation in the Storage Systems Analysis Working Group, a sub-group that examines engineering and integrations aspects that are common to all of the hydrogen storage concepts being developed within the individual Centers.

Results

The selected Chemical Hydrogen Storage Center technical accomplishments listed above are further detailed and extended in the associated partner reports. In addition to the technical progress that will be described in those individual annual progress reports from the partners, the Center participated in DOE's sodium borohydride hydrolysis go/no-go decision making processes and completed a down-select process to focus Phase 2 research on the most promising candidates with the potential to meet or exceed DOE's 2010 technical targets.

A Center-wide accomplishment in meeting a Q2 FY 2008 Center milestone was in down-selecting materials and processes with potential to meet and exceed DOE's 2010 targets. The Center's down selection process and results are documented in the report "Down Select Report of Chemical Hydrogen Storage Materials, Catalysts, and Spent Fuel Regeneration Processes", June 2008, and is available online: http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html - h2_storage

Using a decision tree process (Figure 3) based upon the criteria developed by the Center (Table 1), the Center evaluated all of the more than 60 materials systems studied to date within the Center, and down selected 20% of these for priority development. Approximately 50% of the systems were discontinued, and another 30% were conditionally down selected, awaiting further data.

A few of these materials or processes that were selected and serve as examples of the Center's progress towards meeting these targets is tabulated in Tables 2a and 2b for different processes for hydrogen release from AB, and also from some metal amidoborane derivatives.

Prior to the Center's down-select process, the Center was also involved in the determination of a go/no-go decision on the use of aqueous sodium borohydride as an on-board storage medium. An independent review panel evaluated progress in using aqueous sodium borohydride to meet DOE's near-term hydrogen storage targets as well as the potential to meet longer-term targets. Based on the recommendations of the review panel, the DOE Hydrogen Program made the following decisions: 1) discontinue hydrolysis of sodium borohydride R&D for vehicular hydrogen storage applications, and 2) continue related R&D applicable

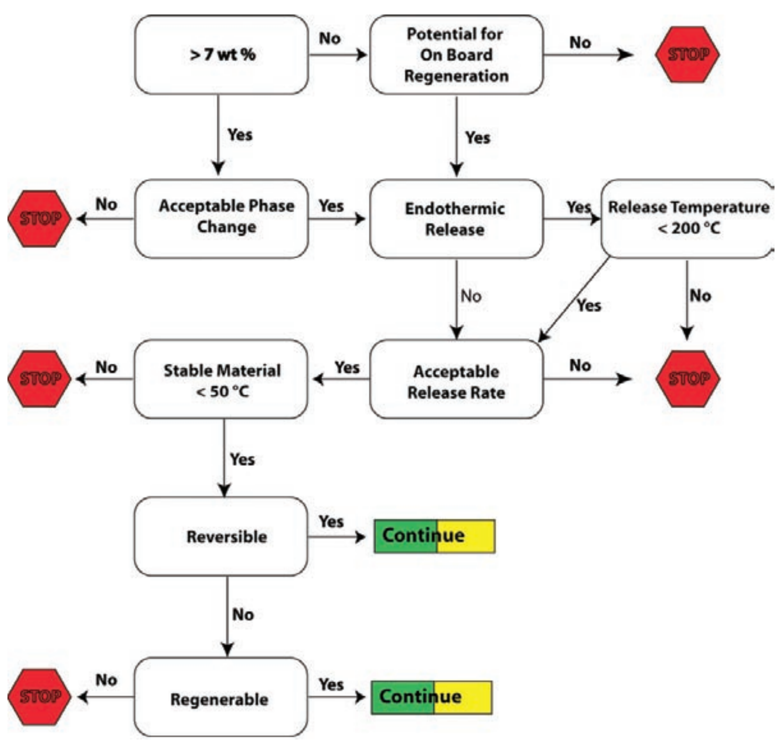

FIGURE 3. The Chemical Hydrogen Storage Center's Decision Tree Tool for Materials Down-Selection

to cost effective initial production of other borane-based species for amine borane vehicular hydrogen storage approaches. This decision is documented in the following report: "No-Go Decision on Sodium Borohydride Hydrolysis for Vehicular Hydrogen Storage", also available on line at the same Web address given previously.

Conclusions and Future Directions

Even with the significant progress the Center has made this year and in years past, on-board chemical hydrogen storage remains a significant scientific and technical challenge. Adding to this challenge is the requirement to achieve a highly chemically and energetically efficient regeneration of spent fuel off-board. The Center will continue to focus on improvements on materials performance, how such materials can meet engineering systems requirements, and continuing to refine and improve the chemical processing of spent fuel back to fuel. The Center will also bring more focus to an engineering study of the synthesis of the 'first-fill' load of fuel from mineral boron sources. Specifically, the Center's future directions for each area are:

- Regeneration – maintain diversity of processes to provide options, off-ramps:
  - Explore metal hydride 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.
- First-Fill – develop cost and efficiency analysis of mined borate to first load of fuel.
- 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 system analysis results from Argonne National Laboratory 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.

Special Recognitions & Awards/Patents Issued

All Awards, Patents, Publications and Presentations resulting from work within the Chemical Hydrogen Storage Center are given in the accompanying partner reports.