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The Hydrogen Battery Technology Company

Development of an Advanced Chemical Hydrogen Storage and Generation System

- Participants in the Chemical Hydrogen Storage Center of Excellence -

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DOE Annual Program Review
Washington, D.C., May 16-19, 2006

Project ID #: ST 7
Contract #: DE-FC36-05GO15056

Overview

Timeline

- Project start date: February 2005
- Project end date: February 2010
- Percent complete: 20%

Barriers

- Weight and Volume
- Efficiency
- Heat removal

Budget

Total project funding (5 Year)

- DOE share: $2.4 million (80%)
- MCEL share: $0.6 million (20%)

Funding received for FY05:

- $200 K

Funding for FY06:

- $400 K requested
- $250 K obligated

Project Targets

	2005	2006	2007
System volumetric capacity (kWh/L)	**1.0**	**1.1**	**1.2**
System wt%	**3.9**	**4.2**	**4.5**

Partners

Center of Excellence – Chem. H_2 Storage
PNNL – System modeling and eng.
RandH, PSU, LANL – Regeneration

Objectives

Overall:

- To Improve capability to store and release H_2 from chemical hydride
- To Meet DOE 2007 target and beyond:
  - 1.2 kWh/L (36 g H_2/L) and 1.5 kWh/kg (45 g H_2/kg).
- To leverage MCEL engineering expertise and guide Center research

◆

Last Year:

- Data mining on the synthesis and regeneration of B-O → B-H.
- Rapid screening of options
- Initiate system analysis and reactor module development.

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This Year:

- Develop modeling tool for hydrogen generation reactor
- Validate modeling results with experimental data
- Conceptual design based on modeling
- Maintain progress to meet DOE go/no-go decision on SBH

Status at Start of Project

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Hydrogen Generation System Metrics

Criteria	2007	2010	MCEL current	MCEL target for Phase I
Specific energy	4.5 wt% 1.5 kWh/kg	6 wt% 2.0 kWh/kg	3.9 wt%	4.5 wt%
Flow rate	0.02	0.02	0.02	✔
Density	36 g/L (1.2 kWh/L)	45 g/L (1.5 kWh/L)	33 g/L (1.0 kWh/L)	36 g/L (1.2 kWh/L)
Storage system cost	$6 /kg H_2 stored	$4 /kg H_2 stored	$ 6.7 /kg H_2 stored	$ 6 /kg H_2 stored

Accomplishments to Date

- Reactor modeling activity started and progressing well
  - Developed reactor packing sub-module
  - Completed Lattice Boltzmann microscopic modeling of reactant flow in the reactor
  - Established macroscopic reactor model that matches the experimentally observed parameters
- Generated experimental data to validate modeling results.
- Started to use the model to predict performance parameters
- Begin to build the experience and modeling tool that can be applied to other chemical hydrogen storage systems

Improve System Level Storage Capacity

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Reduce Fuel Volume

- Increase fuel concentration
- Improve catalyst's ability to process concentrated fuel
- Volume exchange tank design

Reduce Volume of Balance of Plant (BOP)

- Relationship between reactor liquid hold-up and size of ballast
- Manage heat exchange – size of exchanger
- Improve gas-liquid separation – size of separator

System Development Approach

Using $NaBH_4$ as Example

CFD	Reactor Modeling	Conceptual Design	System Design
Oct. – Dec. 05	Jan.- Aug. 06	Sept. 06 - Sept 07	Oct. 07 –Sept. 08

PNNL Collaboration

- Develop modeling tools
- Lattice Boltzmann calculations
- Macroscopic modeling
- Star-CD data processing
- Validate model

- Optimize Conversion
- Optimize reactor dimensions
- Increase throughput
- Fluid dynamics

- Reactor features
- BOP designs
- Safety evaluation

09/30/07

Go/no-go Decision

- Sub-system testing
- BOP testing
- System testing
- Prototype Demo:

> $45 g H_2/kg$

> $36 g H_2/L$

System Development Approach

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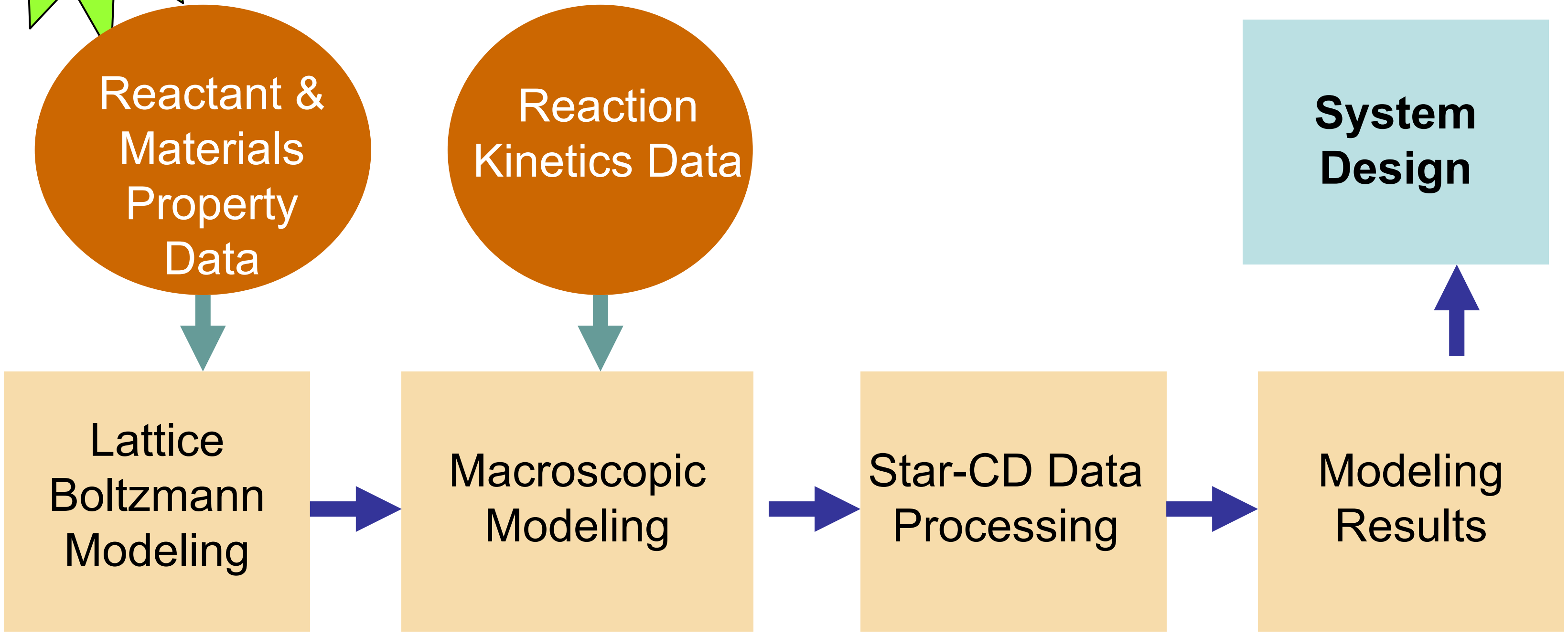
PNNL-MCEL Collaboration

Modeling Approach Overview



Reactant & Materials Property Data

Reaction Kinetics Data

System Design

Lattice Boltzmann Modeling

Macroscopic Modeling

Star-CD Data Processing

Modeling Results

Develop “Tool Box” applicable to other chemical hydrogen storage systems

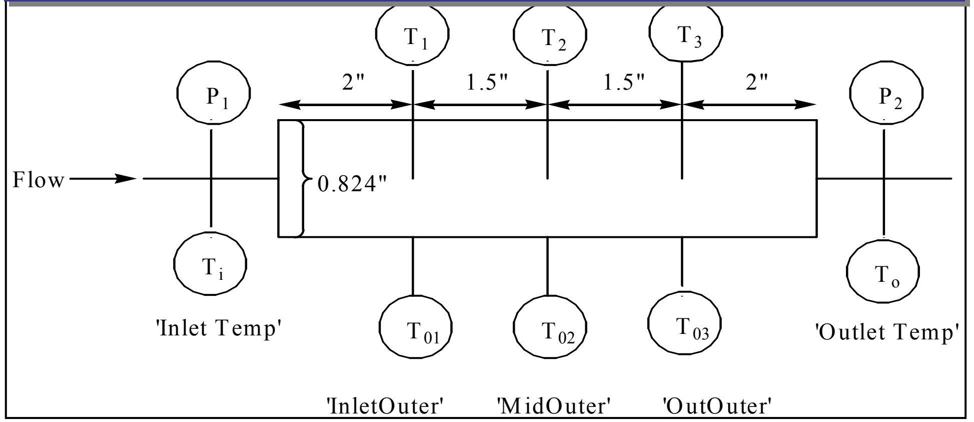
- Means to handle microscopic reaction basics
- Means to handle multi-phase reactions
- Means to incorporate thermodynamic and kinetic data
- Means to apply to other chemical hydride systems

Reactor for H_2 Generation

Preliminary Modeling

- 10 x 100 segmentation of reactor – simplifies overall heterogeneous microscopic properties into 1,000 individual homogeneous sections
- Solves the flow, energy and species transport equations for multiphase flow through a catalyst bed reactor
- Two-dimensional (axial and radial) finite-volume formulation
- Transient solution to reach a steady state

Reactor Schematic

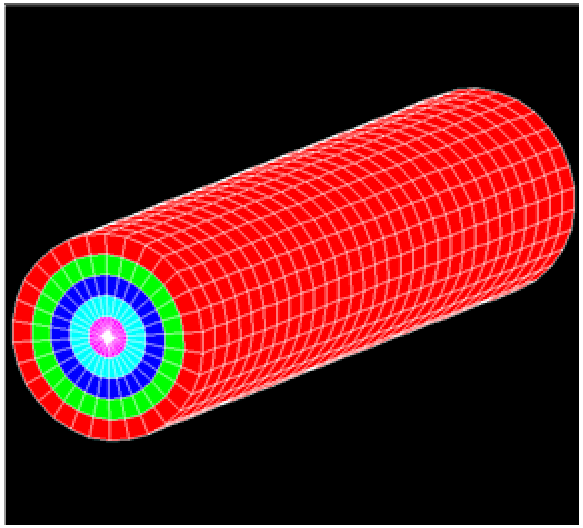


Technical Accomplishments

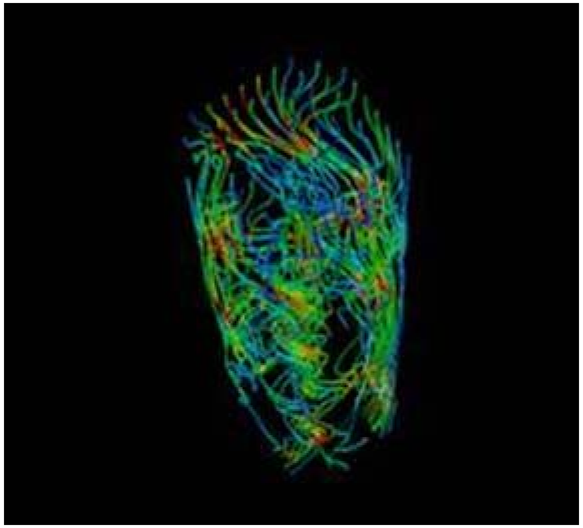
STAR-CD Data Process

- CFD reactor modeling program
- Commercially available from CD-adapco
- Customized subroutines for specific reactions (PNNL/MCEL)
  - Utilizes code from Fortran method
- Powerfully post-processing functions
- Complex to use for modeling heterogeneous catalytic surface reactions

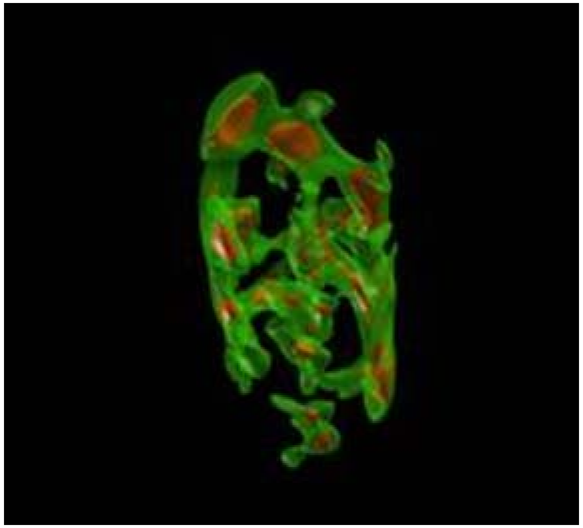
Reactor Geometry



Streamlines



High Velocity Regions

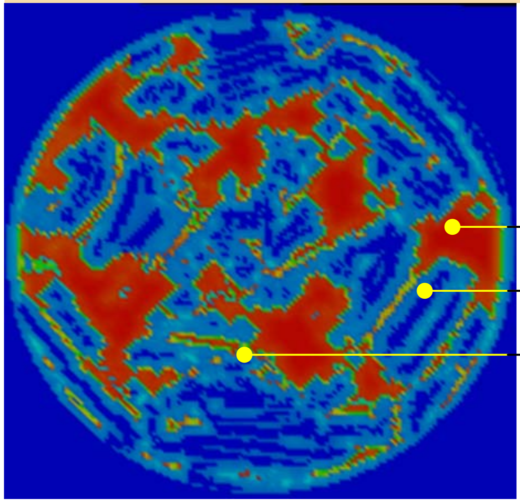


Technical Accomplishments

Lattice-Boltzmann Modeling (PNNL)

- **Microscopic discreet modeling**
  - Detailed nodes model separate solid, liquid, and gas regions/interfaces
  - Determine transport and reaction parameters for use in macroscopic model
- **Advantage** - includes effect of catalyst geometry, less empiricism
- **Process Design Implication**
  - Need efficient gas separation mechanism
  - Design of catalyst

Example Data



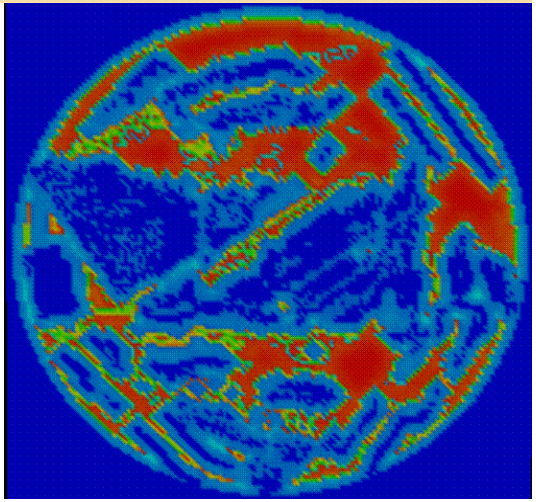
Radial slices at different lengths along the reactor

(Red) Liquid phase

(Dark Blue) Solid phase

(Light Blue) Gas phase

"Gas Shielding"



Technical Accomplishments

Macroscopic Reactor Modeling

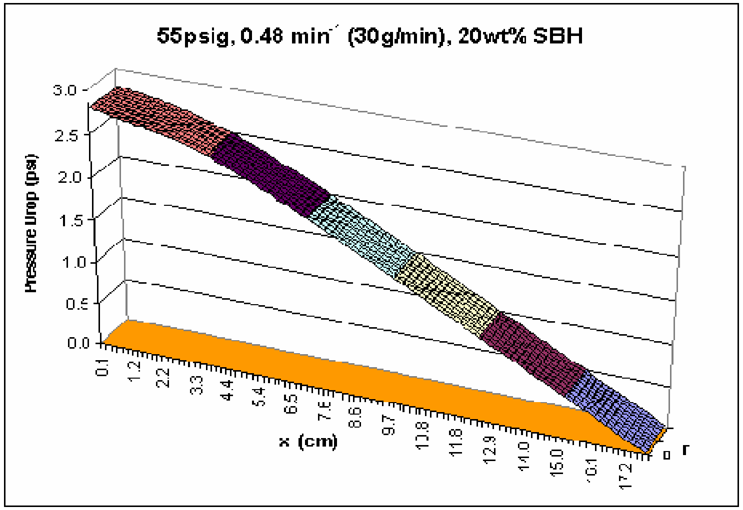
- **Validation parameters**
  - SBH conversion
  - Axial reactor temperature
  - Overall reactor pressure drop
  - Hydrogen flow rate

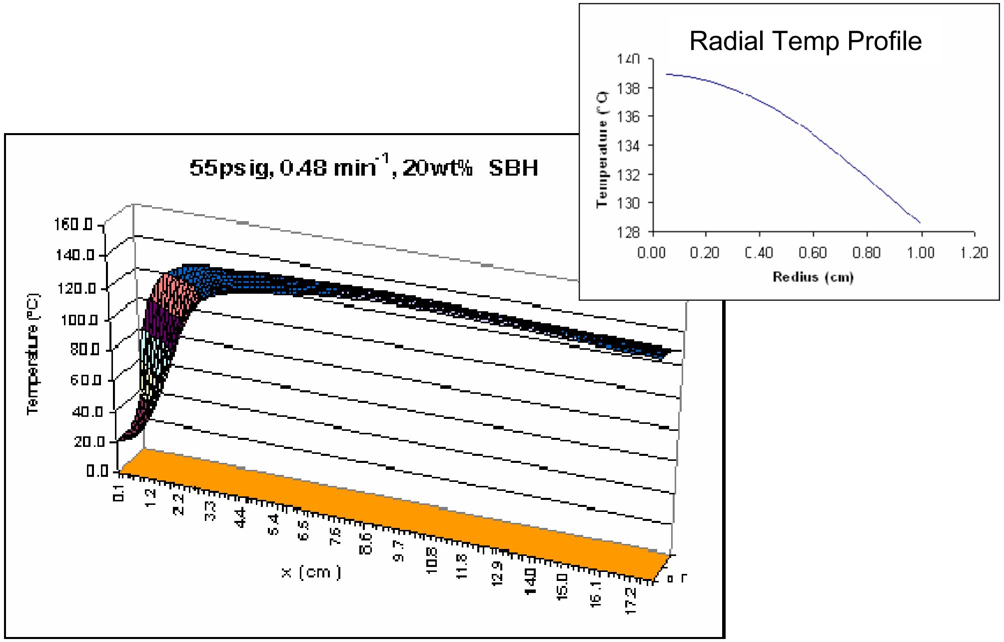
- **Simulation**
  - $NaBO_2$ liquid flow
    - ($NaBO_2$ concentration)
  - Water vapor flow
  - Hydrogen distribution
  - Void fraction

- **Optimization**
  - Fuel space velocity
    - (flow rate)
  - Reactor parameters
    - Total volume
    - D/L ratio
    - Geometry
    - Pressure
  - Heat removal
  - Fuel concentration
  - Catalyst packing density

Validating the Model:

- Pressure Drop and Reactor Temperature



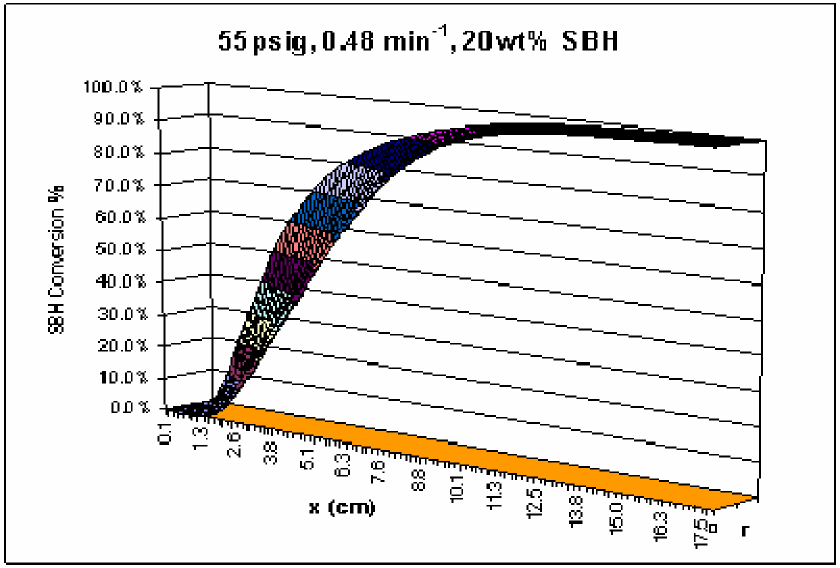


- **Pressure drop is affected by catalyst porosity & packing density**
- **Temperature profile varies with:**
  - **system pressure; space velocity,**
  - **fuel concentration; water vaporization**
- **Simulated parameters match experimental measurements**

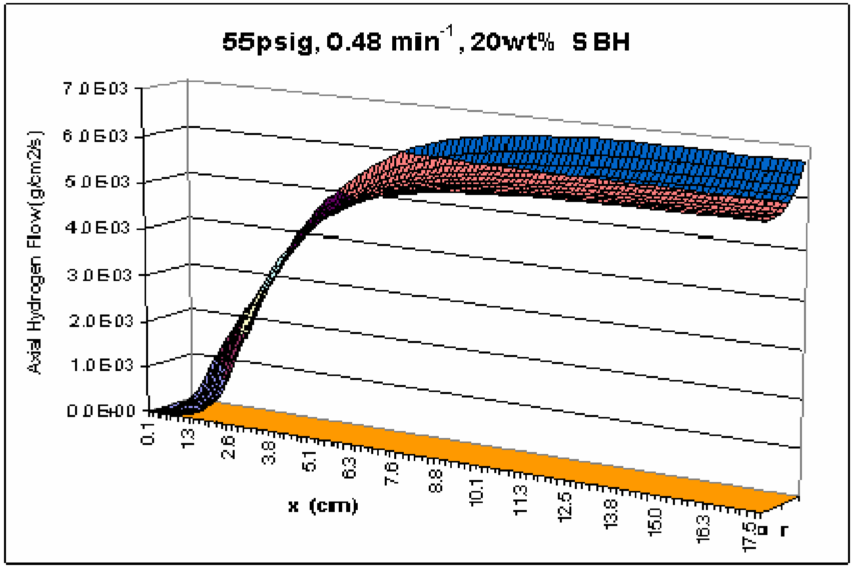
Validating the Model:

- SBH Conversion and H_2 Flow

SBH % Conversion



H_2 Flow Rate

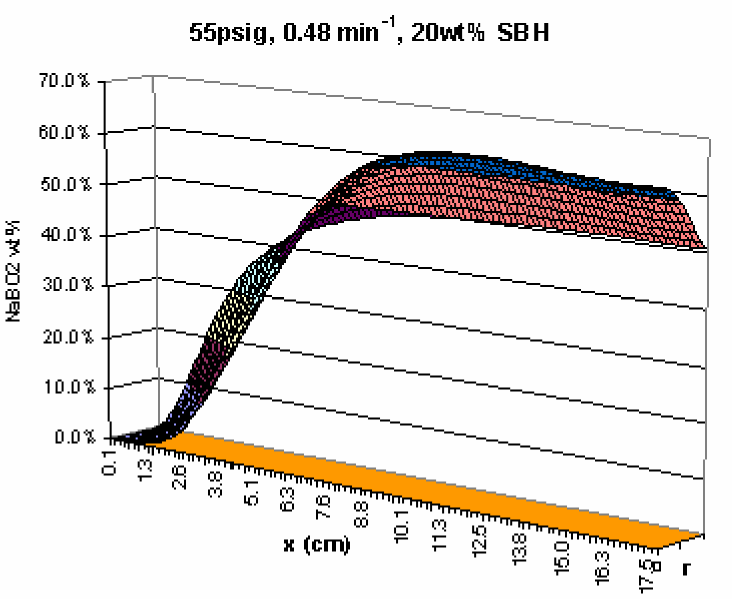


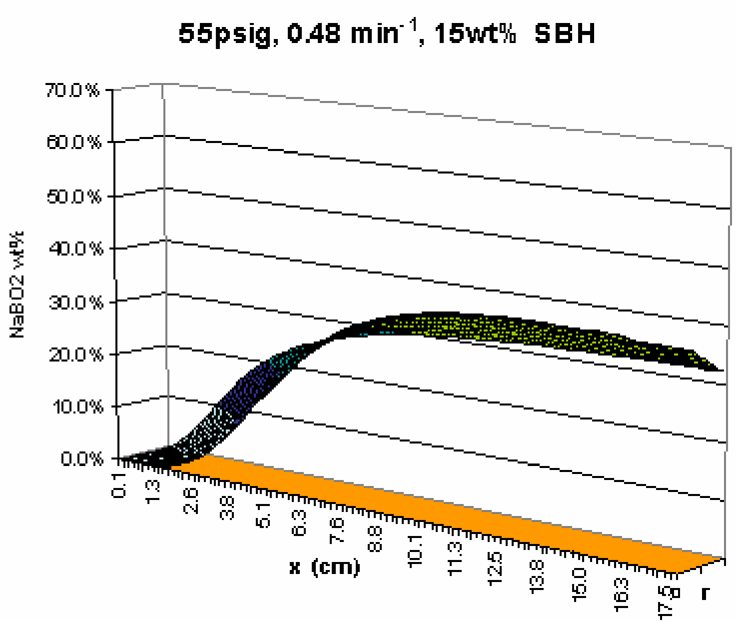
$$-rA = k_0 e^{-Ea/RT}\left[BH_4\right]$$

Accuracy of model generated conversion profile relies on the accuracy of kinetics equations describing the reactions

Simulated Results:

- "$NaBO_2$" Concentrations





- High $NaBH_4$ concentration can result in $NaBO_2$ concentrations that exceed the solubility limits
- Super-saturation has been observed experimentally
- Active management of reactor temperature (via reactor pressure) can mitigate the problem of borate precipitation

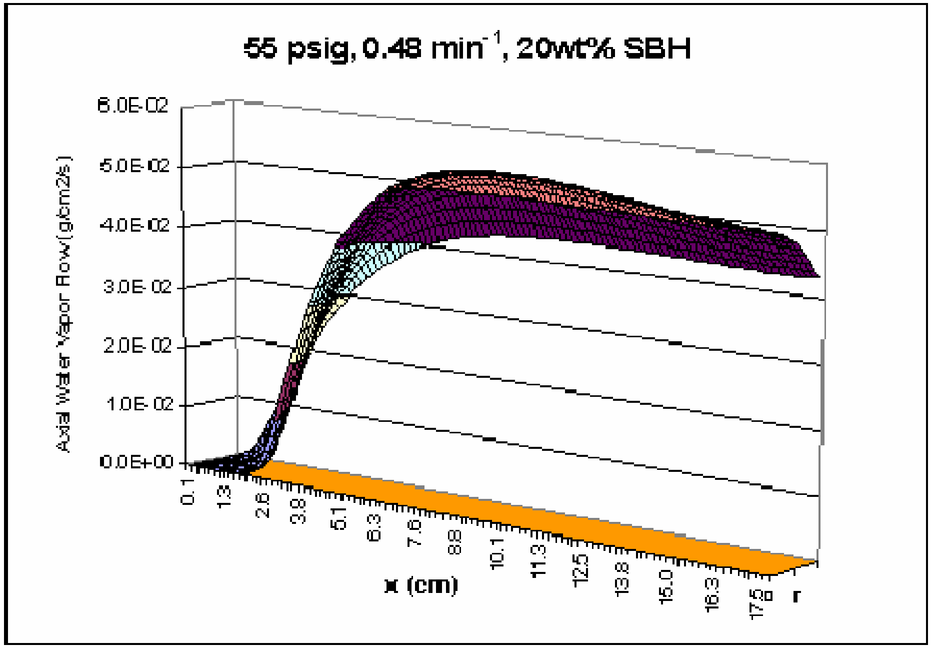
Solubility Table

Temp.	$NaBO_2$ wt%
0°C	14.50
10°C	17.0
20°C	20.0
30°C	23.6
40°C	27.9
50°C	34.1
60°C	38.3
70°C	40.7
80°C	43.7
90°C	47.4
100°C	52.4

Simulated Parameters:

- Flow of Water Vapor

Profile of Vapor Phase Water Flow



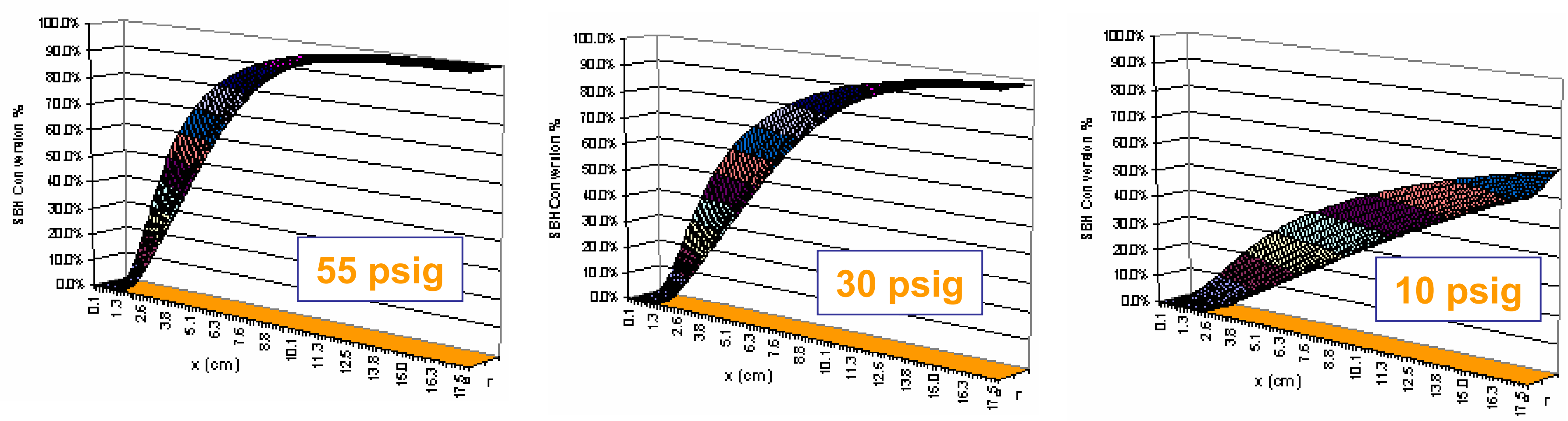
- High press. and low temp. → low H_2O vapor pressure
- Low gas volume → low void space → better contact between reactants and catalyst
- **Liquid water is favored to solubilize borate by-product.**

Optimization Using the Model

- Effect of System Pressure

NaBH$_4$ Conversion Profile At Various Reactor Pressures

0.48 min^{-1} for 20 wt.% SBH



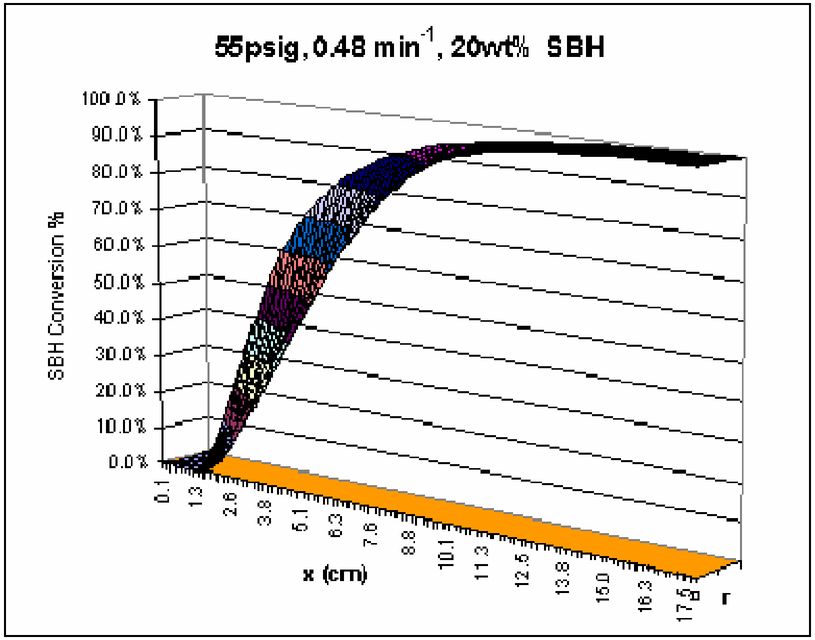
- Simulation provides additional insight within the reactor
- System pressure governs peak temperature in the reactor
- High system pressure is favored to increase SBH conversion

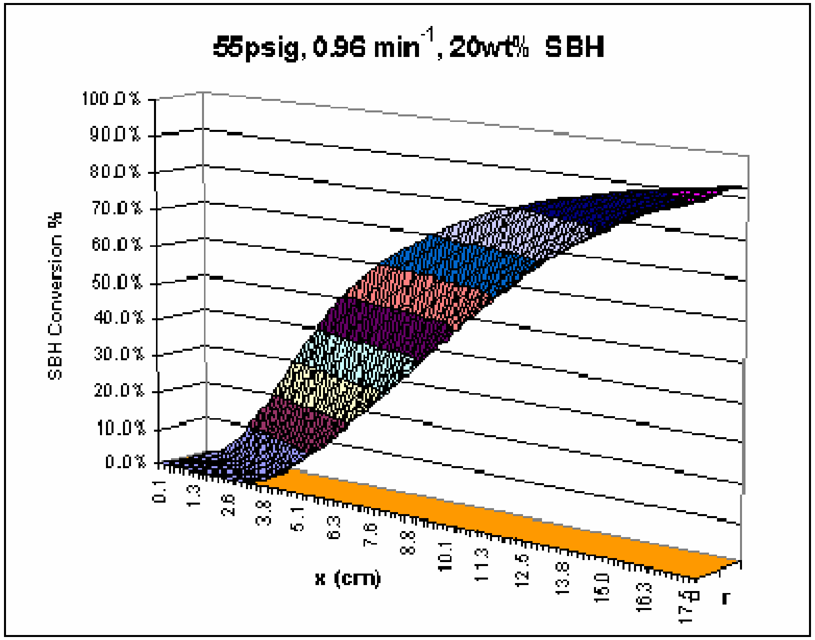
Will Affect BOP

Optimization Using the Model:

- Effect of Fuel Space Velocity

NaBH$_4$ Conversion as a Function of Space Velocity

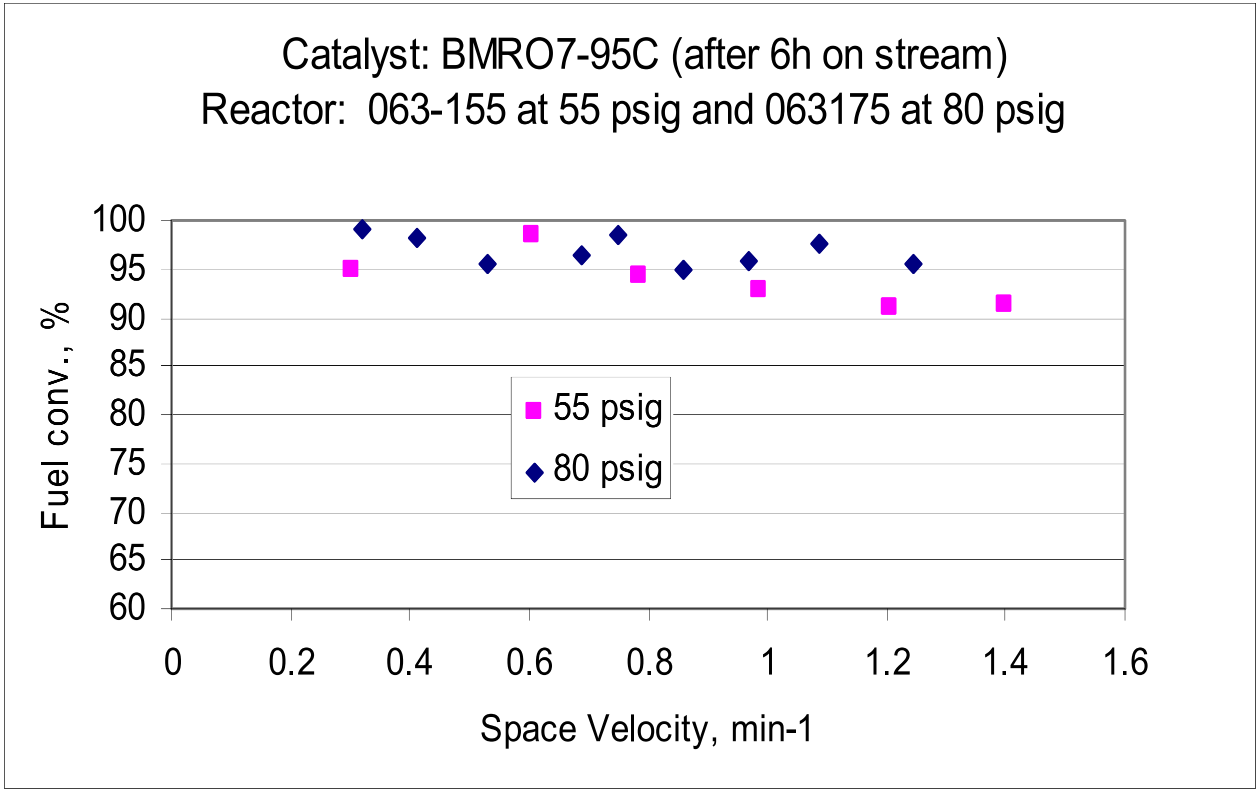

55psig, 0.48 min^{-1}, 20wt% SBH


55psig, 0.96 min^{-1}, 20wt% SBH

- Increase in fuel space velocity reduces NaBH$_4$ conversion
- Space velocity also affects reactor temperature

Comparison to Experimental Data

Experimental data confirms that high reactor pressure will allow more rapid processing of fuel



Main Observations

1. **Modeling Method** has been validated as a tool to simulate and predict the experimental results.
2. **Reaction Kinetics** is critically important to establishing the validity of the model.
3. **Validation**: Steady state profiles of temperature, $NaBH_4$ concentration, pressure drop, and H_2 flow rate correspond to experimental data.
4. **Simulation:** Effects of fuel flow rate, fuel concentration, and system pressure were determined.
5. **Design Optimization**: reactor geometry, catalyst porosity, active control of pressure and temperature will have strong influence on the simulation results.
6. **Benefits:** Initial simulation results already generated additional insights to be used to optimize system design and operation.

Future Work

FY06

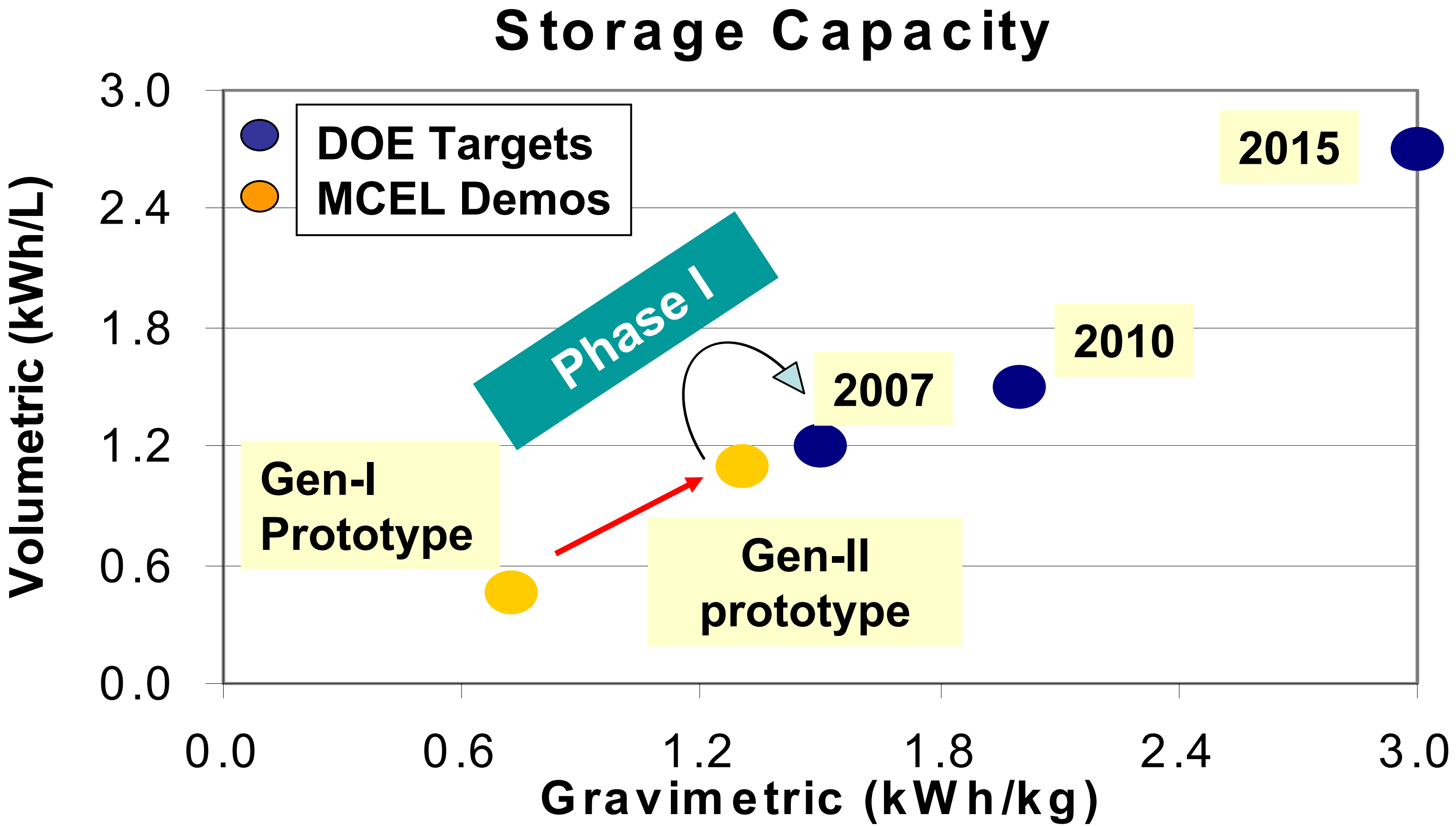
- **Complete reactor simulations**
  - Improve accuracy of reaction rate equation
  - Use Star-CD program to improve visualization of simulation results
  - Optimize operational parameters
- **Initiate reactor design**

FY07

- **Complete reactor design**
  - Optimize performance and parameters
- **Develop other sub-modules in BOP of system**
  - Use optimization results to guide H_2 generation system development
  - Evaluate possible system performance against FY07 DOE targets
- **Safety evaluation**
  - Individual sub-module components
  - Overall System

Storage Capacity Progress

Towards DOE Targets



Summary

Center Collaboration:

- Collaboration with PNNL has been very productive
- Insightful information has been generated from the modeling activities in a short period of time
- Microscopic and Macroscopic level modeling tools being developed for use with additional chemical hydrogen storage systems

System Development:

- Developed accurate tool/method that will be utilized to generate an optimized and improved on-board hydrogen generator
- Heat and water management can be accomplished by better understanding of operating conditions
- Borate precipitation can be managed by balancing fuel concentration and reactor pressure and temperature

Acknowledgements

- Center of Excellence for Chemical Hydrogen Storage
- Project Collaborators:
  - PNNL: modeling activities
    - Dave Rector, Scot Rassat
  - ROH, PSU, LANL, PNNL : SBH regeneration
- DOE program managers:
    - Grace Ordaz, Jim Alkire, Sunita Satyapal
- Center Coordinators
    - Chris Aardahl, Bill Tumas

Response to Previous Year Reviewers' Comments

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- Comments received mostly pertain to Center as a whole, very few directly for this project.
  - MCEL's role:
    - develop modeling and engineering for on-board system;
    - Improve system level storage density
- Check the system gravimetric and volumetric capacity data from the previous DCX system demo (Natrium) and compare values by DCX and Millennium Cell.
  - Available information only limited to publicly disclosed data. DCX proprietary information not available.
- DOE request that the PI coordinate more closely on the overall efficiency analyses with TIAX and ANL.
  - Provided feedback to Argonne's paper on WTT calculations; learned the Excel tool for calculation WTT efficiency.
  - Became familiar with the H2A model for cost and efficiency.
- Communicate with Hydrogen Delivery Team, delivery has a capacity target of 13.2 wt% (though less stringent volumetric target of 27 g/l)
  - Presented to the Delivery Tech Team in October 2005 conference call.

Publications & Presentations

“Reactor Development for Hydrogen Generation from Sodium Borohydride”
Presentation by Ying Wu, MRS Spring Meeting, San Francisco, CA, April 18, 2006

Critical Assumptions & Issues

Accuracy of reaction kinetics

- Affects fluid dynamics and operational parameters
- Inaccuracy in kinetic expressions will alter design parameters of other system sub-modules

Application to other Chemical Hydride systems

- Adaptability to other chemical hydride (e.g. NH_3BH_3)
- Liquid vs. solid fuel

System design of a Chemical Hydride Prototype

- Detailed system design will occur after go/no-go evaluation
- Optimizing overall unit
- Assuring complete safety