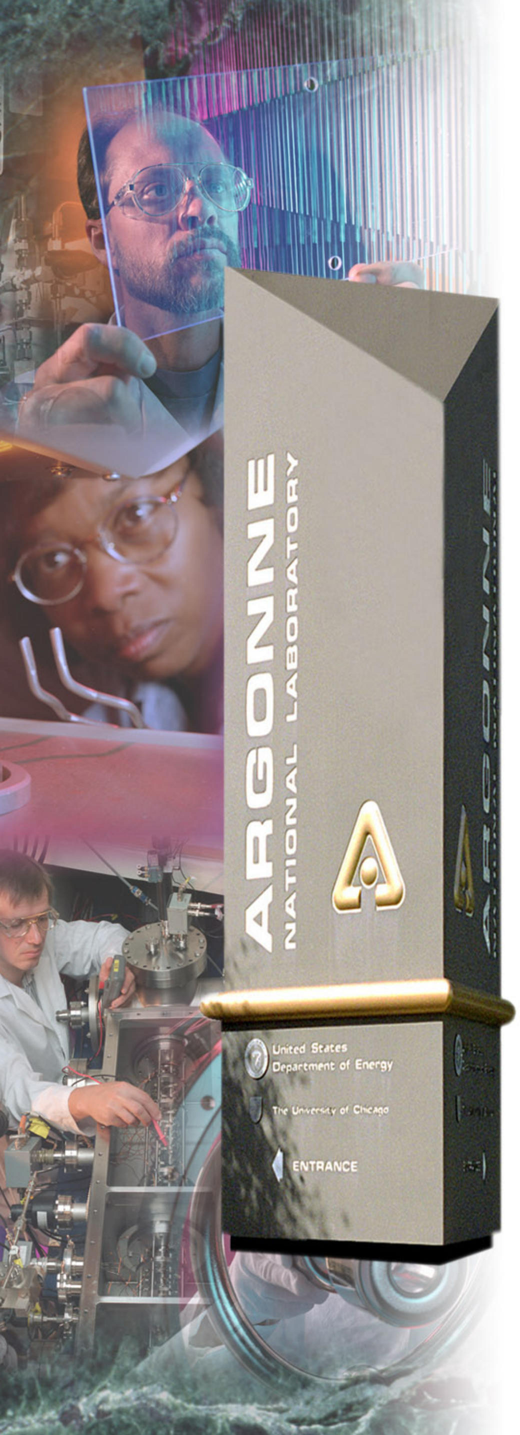


System Level Analysis of Hydrogen Storage Options

R. K. Ahluwalia, J-C Peng, and R. Kumar

This presentation does not contain any proprietary or confidential information

Project ID: ST20

Argonne National Laboratory

A U.S. Department of Energy Laboratory
Operated by The University of Chicago

Overview

Timeline

- Start date: Oct 2004
- Project end date: Sep 2009
- Percent complete: 20%

Budget

New Project in FY 2005

- FY '05: $250 K

Barriers

- Addresses H_2 Storage Technical Barriers:
  - A: Cost
  - B: Weight and Volume
  - C: Efficiency
  - E: Refueling Time
  - M: Hydrogen Capacity and Reversibility
  - Q: Thermal Management
  - R: Regeneration Processes
  - T: Heat Removal

Interactions

- FreedomCAR Technical Team
- Hydrogen Storage Analysis Working Group
- TIAX, UTRC, SNL, other Labs

Objectives and Approach

Objectives:

Working with DOE contractors and Center researchers:

- Model various developmental hydrogen storage systems
- Analyze hybrid systems that combine features of more than one concept
- Develop models “reverse-engineer” particular approaches
- Identify interface issues and opportunities, and data needs for technology development

Approach:

- Develop thermodynamic and kinetic models of processes in complex metal, carbon, and chemical hydrogen storage systems
- Assess improvements needed in materials properties and system configurations to achieve H_2 storage targets

Current activities

1. $NaAlH_4$ systems

- Adapted from TIAX and constrained to satisfy targets for:
  - amount of recoverable H_2 (5.6 kg)
  - discharge rate (1.6 g/s)
  - refueling rate (0.5 to 1.5 kg/min)
  - H_2 delivery pressure (FC: 8, 3 atm; ICE: 10, 35 atm)

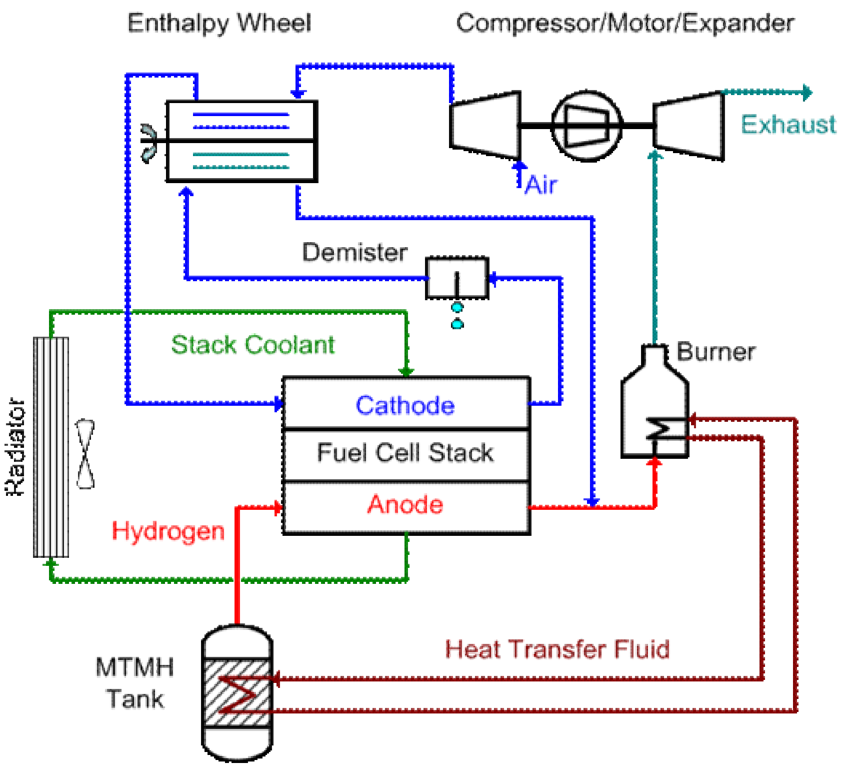
2. Activated carbon, low T/ medium P, systems

- Temperature, pressure, and operating conditions needed to meet near-term and long-term targets

Availability of fuel cell waste heat limits consideration to low-temperature hydride storage

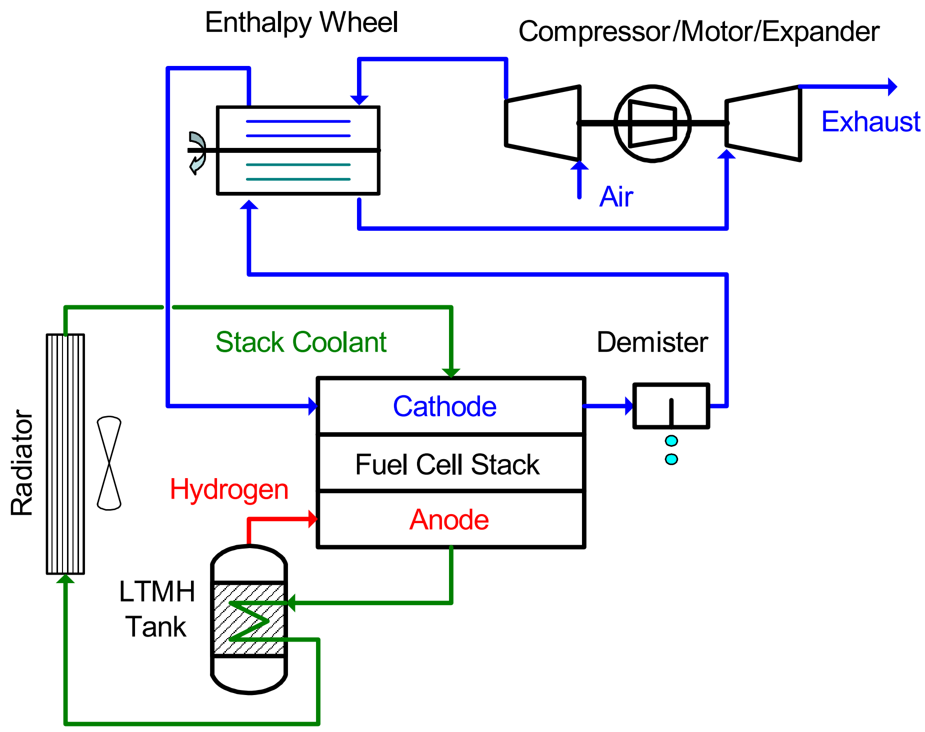
Medium-Temperature Hydride (MTMH)

- H_2 desorption T > stack coolant T
- Must burn H_2 to liberate H_2 from MTMH.
- **18-25% penalty in system efficiency**



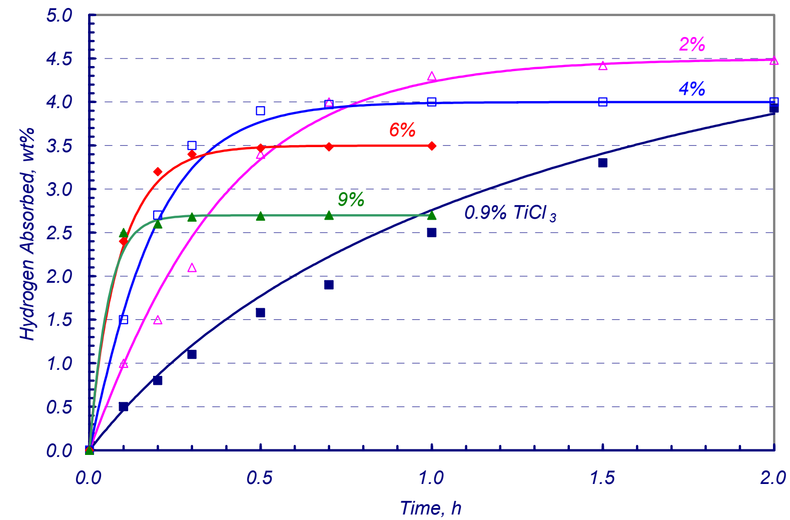
Low-Temperature Hydride (LTMH)

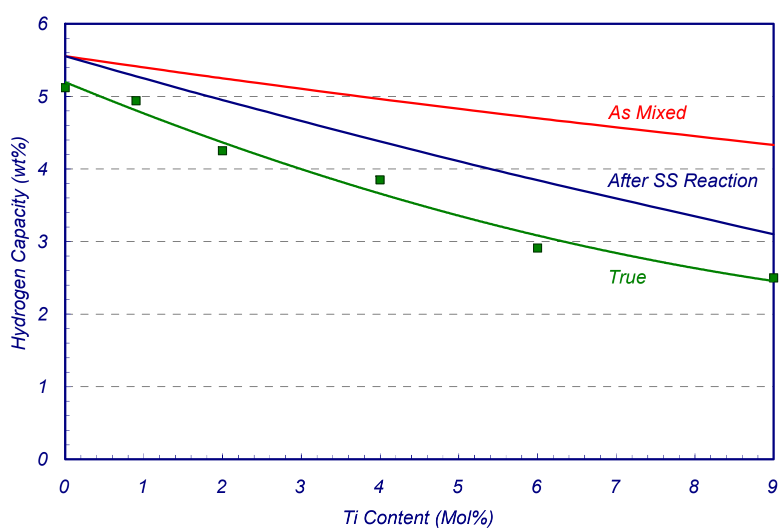
- H_2 desorption T < stack coolant T
- Waste heat to liberate H_2 from LTMH.
- Reduction in radiator heat duty

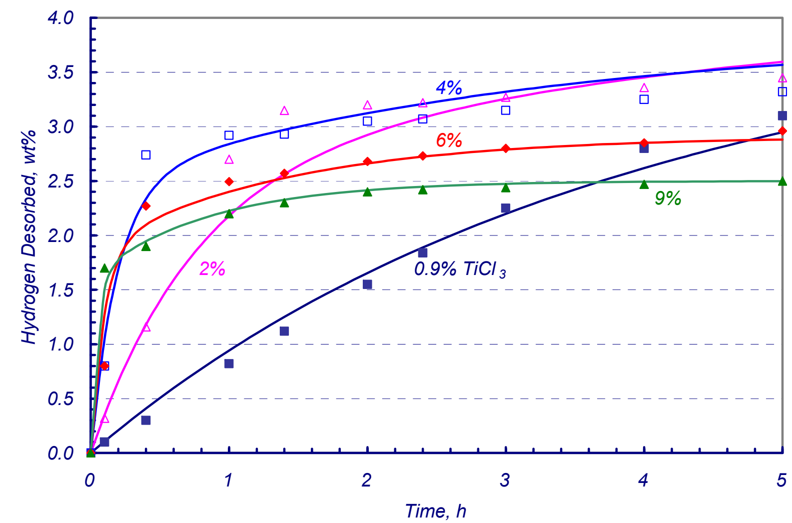


Developed GCtool model for sodium alanate system

- $NaAlH_4$-Na_3AlH_6 thermodynamics
- Successfully fitted SNL data to first-order kinetics for charging & discharging
- Transient thermal model for HT fluid, HXT, foam, hydride media, liner, carbon fiber (CF), glass fiber (GF), and insulation
- Hydrogen pressures and flow rates







Sodium alanate system characteristics

Discharge H_2 using stack coolant at 115°C

- Minimum tank pressure = 3 to 8 bar
- H_2 capacity limited to only the first dehydriding step, i.e., 3.7%, because equilibrium pressure of H_2 for Na_3AlH_6 dissociation is only 1.7 bar at 115°C
- Under transient conditions, tank can reach a maximum pressure of 24.4 bar

Charge H_2 at 100 bar

- Limit MH temperature to 165°C as equilibrium pressure of H_2 for re-forming $NaAlH_4$ is 100 bar at 169.4°C
- 104 MJ cooling load for charging 5.6 kg H_2, 173 kW avg (10-min refueling); ~1 MW max

Key design constraints

1. First-order sorption kinetics limit
   - minimum state-of-charge to be able to provide full flow of H_2 (0.02 g/s per kW)
   - maximum state-of-charge to permit acceptable refueling rates (0.5 to 1.5 kg/min)
   - recoverable amount of H_2 (the difference)
2. Heat removal during tank filling determines the heat transfer area (number of tubes)
   - 165^{o}C max temperature for 100-bar fill pressure
   - tube-to-foam contact resistance is significant
   - 100-105^{o}C coolant temperature, not too low (poor kinetics), not too hot (poor heat transfer)

Base Case: Reference Kinetics, 4% $TiCl_3$, L/D=2

- SOC: min = 40.4%, max = 95%, range = 54.6%
- Recoverable H_2 in MH media = 1.4 wt%
- 0.99 kg/min refueling rate
- Number of heat transfer tubes = 258, Peak Q = 993 kW
- Recoverable H_2 in tank = 0.7 wt%

	Weight (kg)	Volume (L)
Metal Hydride Media	400	500
Al Foam	56	521
Heat Transfer Tubes	186	68
Liner	63	8
Carbon Fiber	16	10
Glass Fiber	21	10
Total	812	656

Increased desorption kinetics would help, but not enough

- 10X enhancement in desorption kinetics can yield 90% recoverable H_2
- Refueling rate target is satisfied
- Energy density and specific energy still too low

		Desorption Kinetics			DOE 2007 Target
		1X	5X	10X	
Recoverable H_2 in $NaAlH_4$	%	54.6	82.7	88.4	90
SOC, Min/Max	%	40.4/95	12.3/95	6.6/95	
H_2 Refueling Rate	g/min	990	860	840	500
Weight of MH	kg	400	264	247	
Tank Weight	kg	813	613	588	125
Tank Volume	L	656	457	431	155
Recoverable H_2 in MH	kg H_2/kg %	1.4	2.1	2.3	
Recoverable H_2 in Tank	kg H_2/kg %	0.7	0.9	1.0	4.5
Specific Energy	kWh/kg	0.23	0.30	0.32	1.5
Energy Density	kWh/L	0.28	0.41	0.43	1.2

Heat transfer needs to be improved

- In addition to high kinetics, 10X decrease in contact resistance between Al foam and HX tubes, and Al-alloy vs. SS, help but still not enough

10X Desorption Kinetics No Inerts		1X h_c SS HX	10X h_c SS HX	10X h_c Al HX	DOE 2007 Target
Recoverable H_2 in $NaAlH_4$	%	87.9	88.4	88.4	90
SOC, Min/Max	%	7.1/95	6.6/95	6.6/95	
H_2 Refueling Rate	g/min	840	840	840	500
Number of HX Tubes		280	175	166	
Weight of MH	kg	192	191	191	
Tank Weight	kg	506	421	328	125
Tank Volume	L	350	323	321	155
Recoverable H_2 in MH	kg H_2/kg %	2.9	2.9	2.9	
Recoverable H_2 in Tank	kg H_2/kg %	1.1	1.3	1.7	4.5
Specific Energy	kWh/kg	0.37	0.44	0.57	1.5
Energy Density	kWh/L	0.53	0.58	0.58	1.2

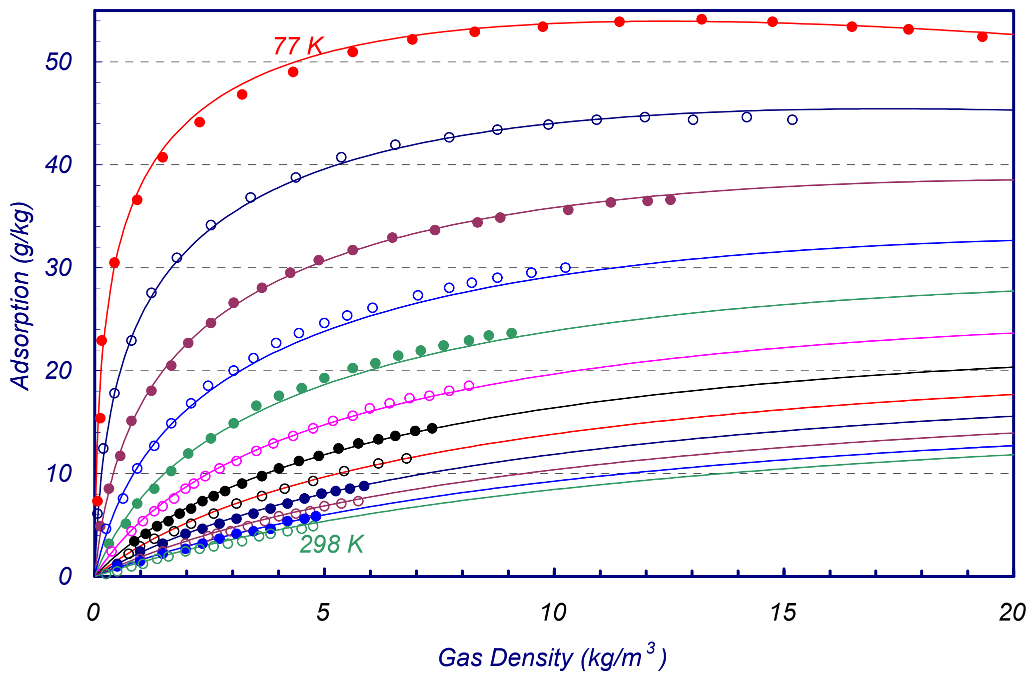
Summary: Sodium Alanate System

- To avoid excessive efficiency penalty, can only consider LTMH configuration with 120°C fuel cell operating temperature
- 2nd dehydogenation step does not occur at 115°C
- Need $\geq$10X enhancement in desorption kinetics to achieve $\geq$90% H_2 recovery
- Removing inerts from sorption media reduces MH weight by 25%
- Heat transfer subsystem size and mass dictated by
  - cooling during refueling
  - contact resistance (reduce by >10X ?)
- Faster refueling reduces recoverable hydrogen

Activated carbon system model

- Ono-Kondo theory for adsorption isotherms using model parameters derived by Benard et al.
- Peng-Robinson equation of state for H_2

$$\rho_s = N_{ads}\rho_b + \left(1 - \rho_b / \rho_c\right)\rho_g$$

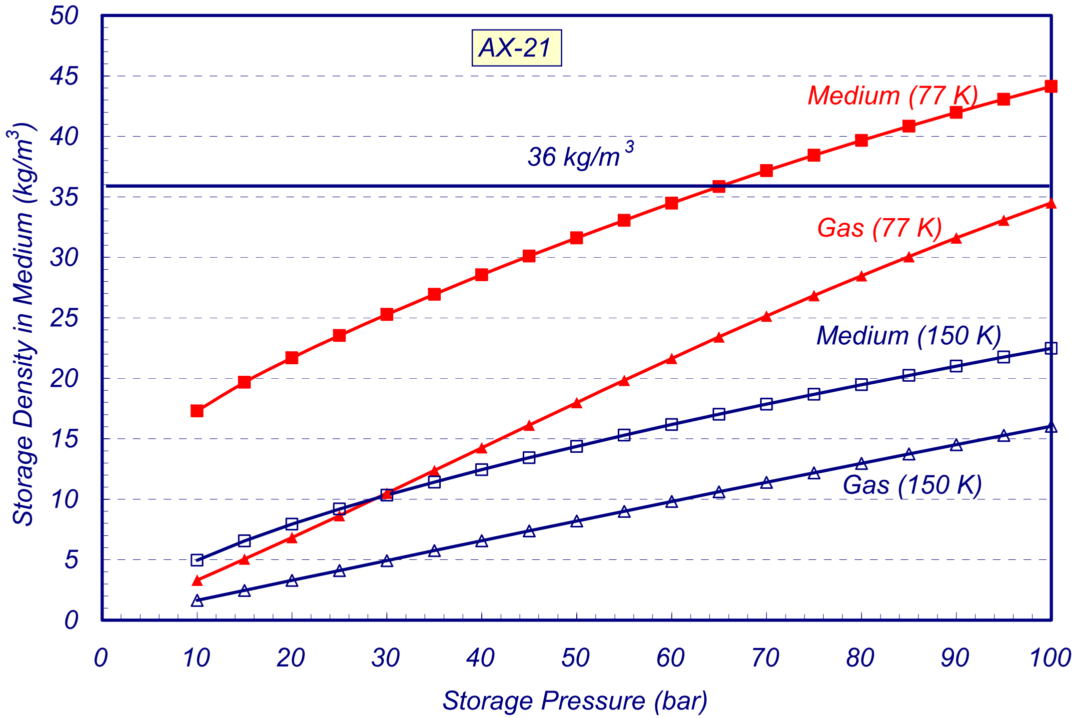


Preliminary Results
H_2 storage density of AX-21 carbon

Increase in storage density with AC, $\Delta\rho_s$, depends on P & T

- At 77 K, $\Delta\rho_s$ = 423% at 10 bar, 28% at 100 bar
- At 150 K, $\Delta\rho_s$ = 202% at 10 bar, 40% at 100 bar

Even w/o enclosure, ρ_s > 36 kg/m^3 only at 77 K, P > 65 bar

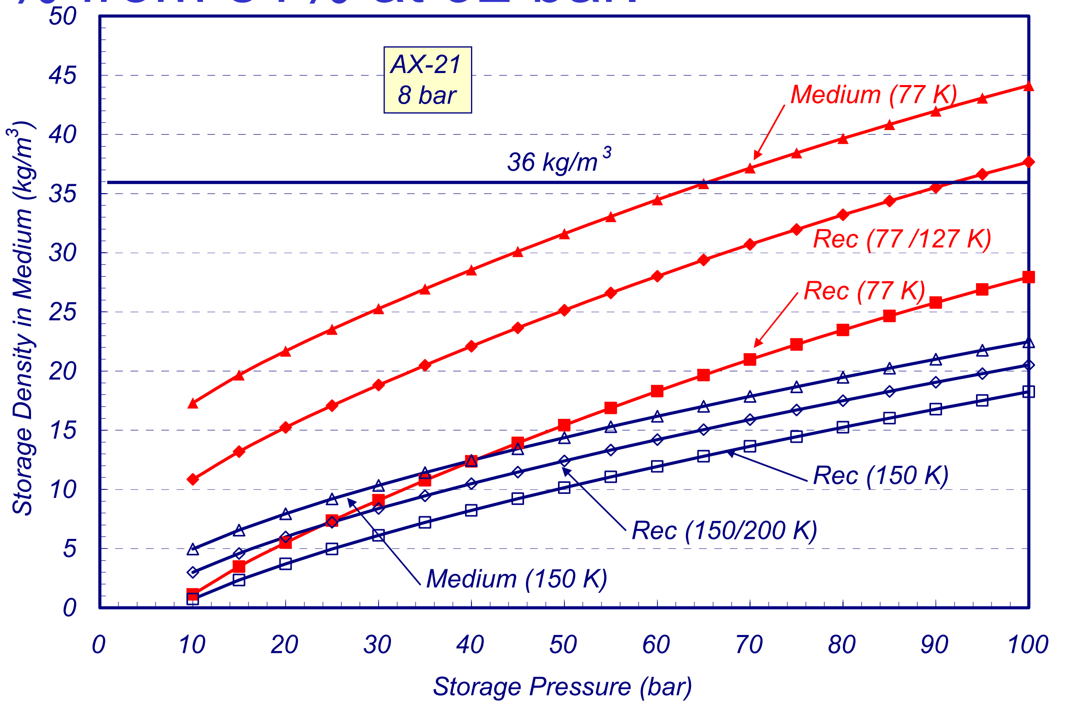


Preliminary Results

Temperature swing can facilitate H_2 recovery

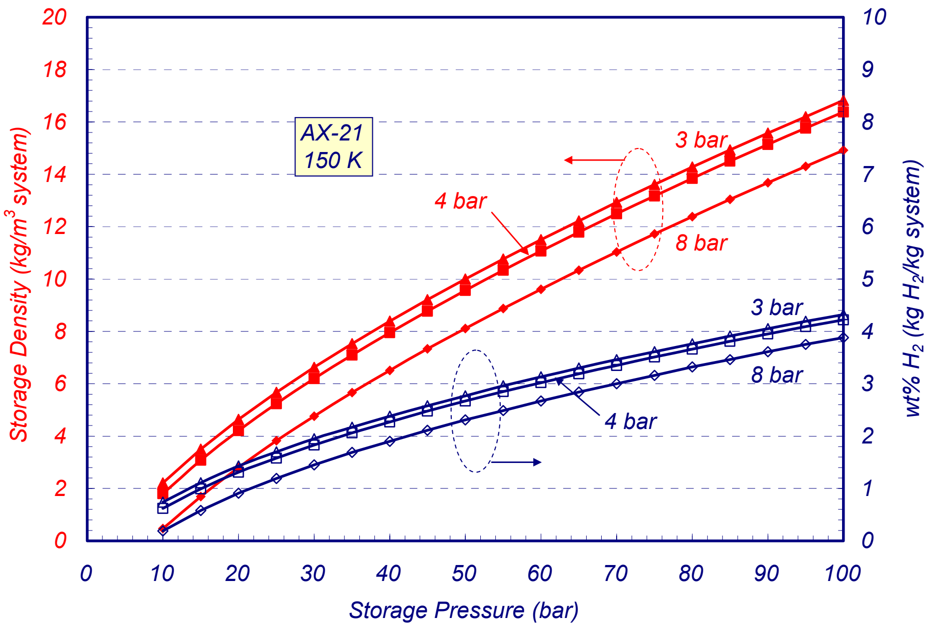
Improvement in recoverable H_2 fraction (Φ) with 50-K T swing.

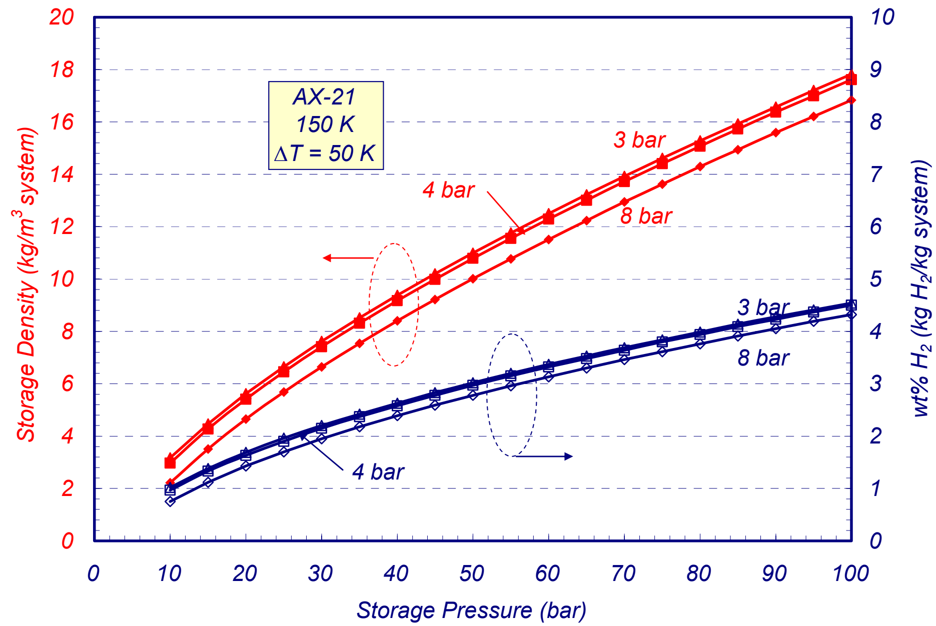
- At 77 K, Φ improves to 63% from 6.5% at ΔP = 2 bar, and to 85% from 63% at 92 bar.
- At 150 K, Φ improves to 60% from 15% at ΔP = 2 bar, and to 91% from 81% at 92 bar.



Preliminary Results
Weight and volume of 150 K system

- At 150 K, AX-21 may not meet either the 4.5 wt% target or the 36 kg/m^3 target.
- With 50-K T swing, the 4.5 wt% target may be met at P > 100 bar, P_{min} < 4 bar.





Preliminary Results

Engineered carbons may meet near-term targets

- AX-21: 300 kg/m^3 bulk density
- Densified AX-21: 700 kg/m^3 bulk density
- EAC-07: engineered activated carbon may meet targets

Development effort: 1 < 2 < 3 < 4 < 5 < 6.

T	P	ΔT	AX-21		Densified AX-21		EAC-07	
(K)	(bar)	(K)	wt% H_2	kg/m^3	wt% H_2	kg/m^3	wt% H_2	kg/m^3
77	50	0	3.2	11.6	1.6	10.6		
77	50	50	5.0	19.5	3.2	23.0	4.5[2]	36
77	100	0	5.4	21.7	2.5	17.4		
77	100	50	7.1	29.6	4.1	29.9	4.5[1]	36
150	50	0	2.3	8.1	1.4	9.4	4.5[6]	36
150	50	50	2.8	10.0	1.8	12.4	4.5[5]	36
150	100	0	3.9	14.9	2.2	15.8	4.5[4]	36
150	100	50	4.3	16.8	2.6	18.8	4.5[3]	36

Summary: Activated Carbon Systems

Commercial Activated Carbon at 77 K:

- Potential to meet the 4.5 wt% target isothermally at P = 60-75 bar
- Highest storage density is 30 kg/m^3 with ΔT = 50 K

Commercial Activated Carbon at 150 K:

- Need ΔT > 50 K & ΔP > 96 bar to meet the 4.5 wt% target
- Highest storage density is 20 kg/m^3

Engineered Activated Carbon:

- At 77 K, T swing may be needed to meet the weight and volume targets at 100 bar
- At 150 K, may meet the targets isothermally at 50-100 bar

On-going work to define cooling/heating needs, dormancy and boil-off

Future Work

Next Steps

- Verify capacity data (tank only vs. storage medium)
- Verify sorption kinetic data
- Conduct sensitivity analysis, including coupled parameters
- Develop a modeling tool that materials developers can use to determine properties needed to meet storage targets
- Analysis of chemical hydrogen storage systems – life cycle efficiency

FY 2005 milestones and progress

- **Working with TIAX, UTRC, Centers of Excellence, etc., develop specific tasks for the ANL analysis project (01/05)**
  - *Following discussions with individual researchers, conducted first working group meeting; presented preliminary analyses and obtained feedback for continued work*
- **Determine preliminary gravimetric and volumetric capacities of hybrid (low temperature/high pressure/adsorbent concepts) approaches (07/05)**
  - *Have initiated hybrid system analyses – preliminary results are presented here*
- **Develop storage system and interface models, (09/05)**
  - *Activity is getting underway*

Acknowledgments

- Funding from the U.S. Department of Energy, Energy Efficiency, Renewable Energy: Hydrogen, Fuel Cells, and Infrastructure Technologies Program is gratefully acknowledged

- DOE Technology Development Managers

Hydrogen safety

- This is an analytical and computer modeling project. There are no hydrogen safety issues involved.

Preliminary Results
Weight and volume distribution

	Units	AX-21	EAC-07[4]
P Swing	bar	100-8	100-8
T Swing	K	150-150	150-150
Recoverable H_2	%	81.2	68.8
H_2 Stored in AC	%	38.0	82.3
N_{ads}	g H_2/kg	28.4	73.1