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System Level Analysis of Hydrogen Storage Options

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Project ID: ST_13_Ahluwalia

Overview

Timeline

- Project start date: Oct 2004
- Project end date: Sep 2014
- Percent complete: 50%

Barriers

- H_2 Storage Barriers Addressed:
  - A: System Weight and Volume
  - B: System Cost
  - C: Efficiency
  - E: Charging/Discharging Rates
  - J: Thermal Management
  - K: System Life-Cycle Assessments

Budget

- FY08: $525 K
- FY09: $725 K

Interactions

- FreedomCAR and Fuel Partnership
- Storage Systems Analysis Working Group, MH COE, CH COE
- BNL, LANL and PNNL, LLNL, SRNL, TIAX, H2A, UH/UNB, UTRC, and other industry

Objectives

- Perform independent systems analysis for DOE
  - Provide input for go/no-go decisions
- Provide results to CoEs for assessment of performance targets and goals
- Model and analyze various developmental hydrogen storage systems
  - On-board system analysis
  - Off-board regeneration
  - Reverse engineering
- Identify interface issues and opportunities, and data needs for technology development

Approach

- Develop thermodynamic and kinetic models of processes in physical, complex metal hydride, sorbent, and chemical hydrogen storage systems
- Calibrate, validate and evaluate models
- Work closely with the DOE Contractors, CoEs, Storage Tech Team, other developers, and Storage Systems Analysis Working Group
- Assess improvements needed in materials properties and system configurations to achieve H_2 storage targets

Technical Accomplishments

Compressed Hydrogen (March 2009): Backup slides

- Gravimetric/volumetric capacity of compressed H_2 tanks, well-to-tank efficiency, validation with “Learning Demo” data
- Issuing a final joint report with TIAX on 350 and 700-bar systems

Metal Hydrides (August 2008): Backup Slides

- Performance of on-board system with alane slurries
- WTT efficiency for off-board regeneration of alane

Hydrogen Storage in Metal Organic Frameworks (June 2009)

- Performance of on-board system with off-board liquid N_2 cooling (storage capacity, charge and discharge dynamics, dormancy)
- Electricity consumed for cryogenic cooling
- Adiabatic refueling option

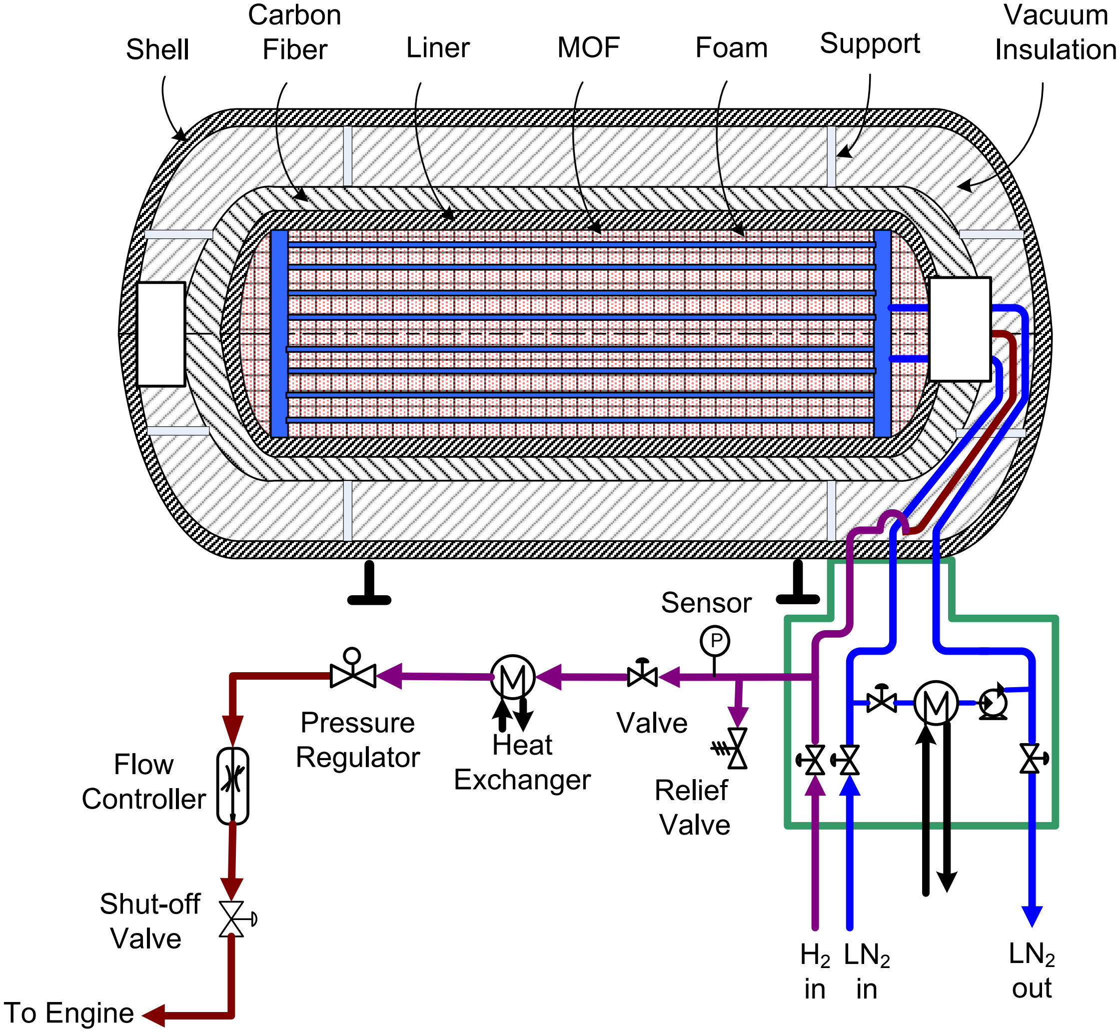
Hydrogen Storage in Ammonia Borane (December 2008)

- WTT efficiency of AB regeneration (CHCoE/LANL/PNNL schemes)

Hydrogen Storage in Lithium Alanate (September 2009)

- WTT efficiency of $LiAlH_4$ regeneration by UH/UNB Method

On-Board Storage of Hydrogen in Metal Organic Frameworks at Cryogenic Temperatures



Key System Requirements

Storage Medium

- 5.6 kg recoverable H_2
- 4-bar minimum delivery P

Containment Vessel

- 2.35 safety factor

Heat Transfer System

- 1.5 kg/min H_2 refueling rate
- 1.6 g/s H_2 min flow rate
- 0.1 (g/h)/kg H_2 loss rate
- 2 W in-leakage rate

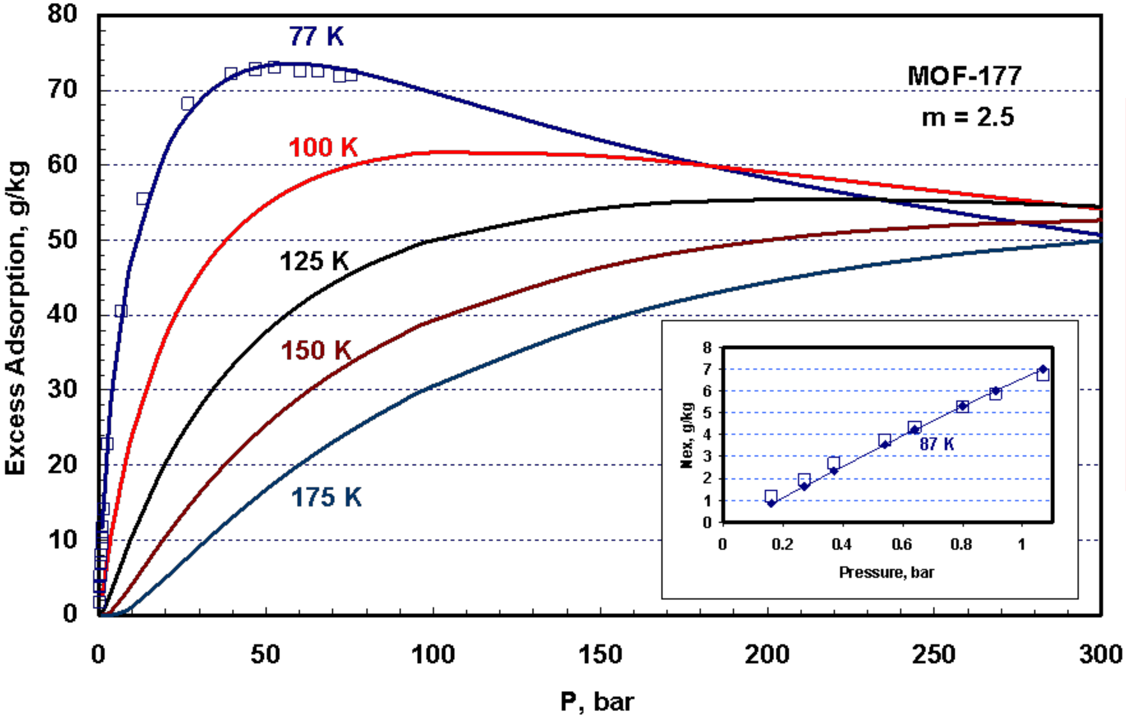
*Reference system configuration, other layouts and options also being analyzed

Key Assumptions

	Parameter	Reference Values
Sorbent	**MOF-177**	J. Mater. Chem., 2007, 17, 3197-3204
	Skeletal density	1534 kg/m^3
	Crystallographic density	427 kg/m^3 (1.56 cm^3/g pore volume)
	Bulk density	342 kg/m^3 (0.8 packing fraction)
	Thermal conductivity	0.3 W/m.K
Conductive Support	**40-PPI Al 2024 Foam**	2-wt%
	Thermal conductivity	2.4 W/m.K
	Contact resistance	1000 W/m^2.K
Thermal	**U-Tube Heat Exchanger**	
	Material of construction	Al 2024 alloy
	Tube ID/OD	9.5/11.9 mm
	Tube sheet thickness	0.9 mm
Insulation	**Multi-Layer Vac. Super Insulation**	Aluminized Mylar® sheets, Dacron® spacer
	Layer density	28 cm^{-1}
	Density	59.3 kg/m^3
	Pressure	10-5 torr
	Effective conductivity	5.2×10^{-4} W/m.K
Tank	**T700S Carbon Fiber**	Toray Carbon Fiber
	Tensile strength	2550 MPa
	Density	1600 kg/m^3
	L/D	3
	Liner	2.4-mm thick Al 2024 alloy
	Shell	3-mm thick Al 2024 alloy
System	Miscellaneous weight	30 kg
	Miscellaneous volume	25 L

Modeled Hydrogen Adsorption Isotherms

- H Furukawa, M Miller, M Yaghi (J. Mater. Chem. 2007, 3197 – 3204)
  - MOF-177, Zn_4O(1,3,5-benzenetribenzoate) crystals
  - Volumetric high-P gas adsorption measurements at SWRI®
  - Gravimetric high-P gas adsorption measurements at UCLA
  - Peak 75 g-H_2/kg surface excess at 77 K, 70 bar;110 g/kg absolute
- Low-T data fitted to Dubinin-Astakhov (D-A) isotherm with m=2.5

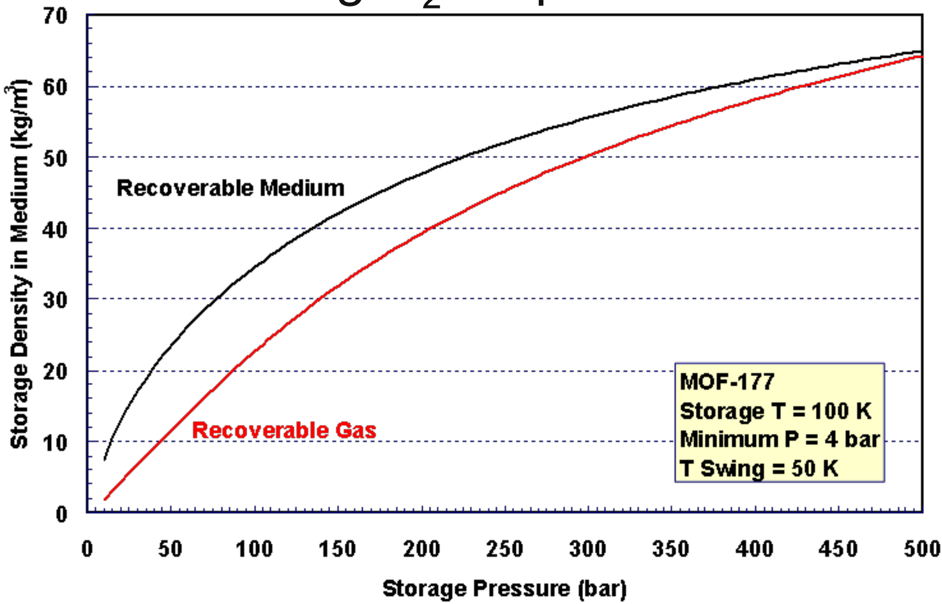


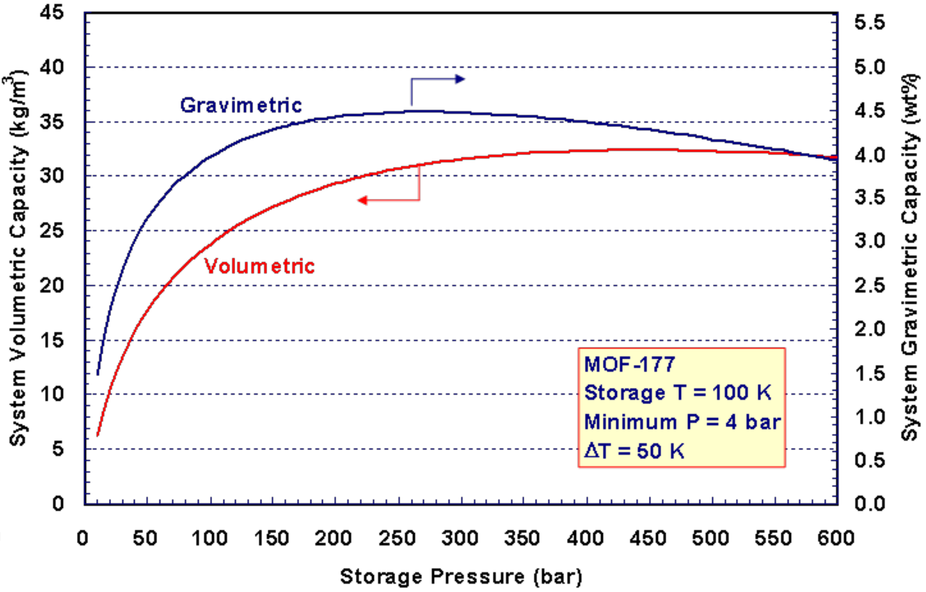
Modeled Uptake at 100 K

- 62 g-H_2/kg peak excess adsorption at 100 bar
- 101 g-H_2/kg peak absolute adsorption at 100 bar

System Storage Capacity

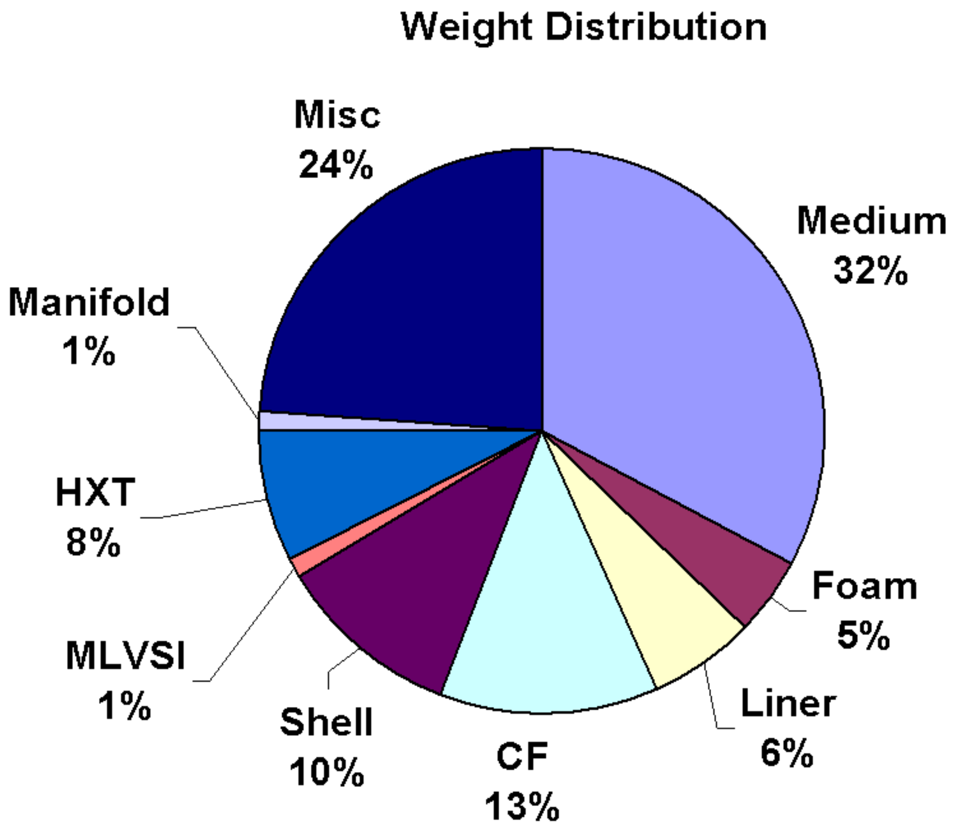
- MOF-177 enhances the gas density by ~50% at 100 bar, but by <12% at 250 bar
  - At 250 bar, 93% of stored H_2 recoverable with 24% on MOF and 76% within pores and void space
  - At 60% volumetric efficiency, need 75 kg/m^3 medium storage density to achieve 45 kg/m^3 system capacity
- System cannot reach 6-wt% and 45 kg/m^3 (meets revised 2010 targets)
  - 4.5 wt% peak gravimetric capacity at ~250 bar
  - 32.4 kg-H_2/m^3 peak volumetric capacity at ~425 bar

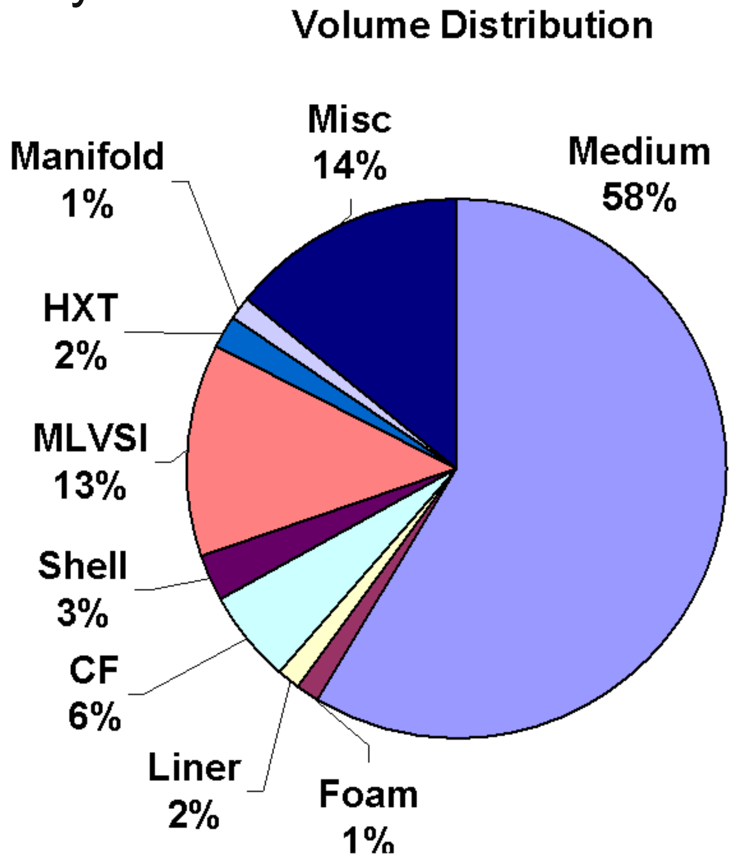




Weight and Volume Distribution

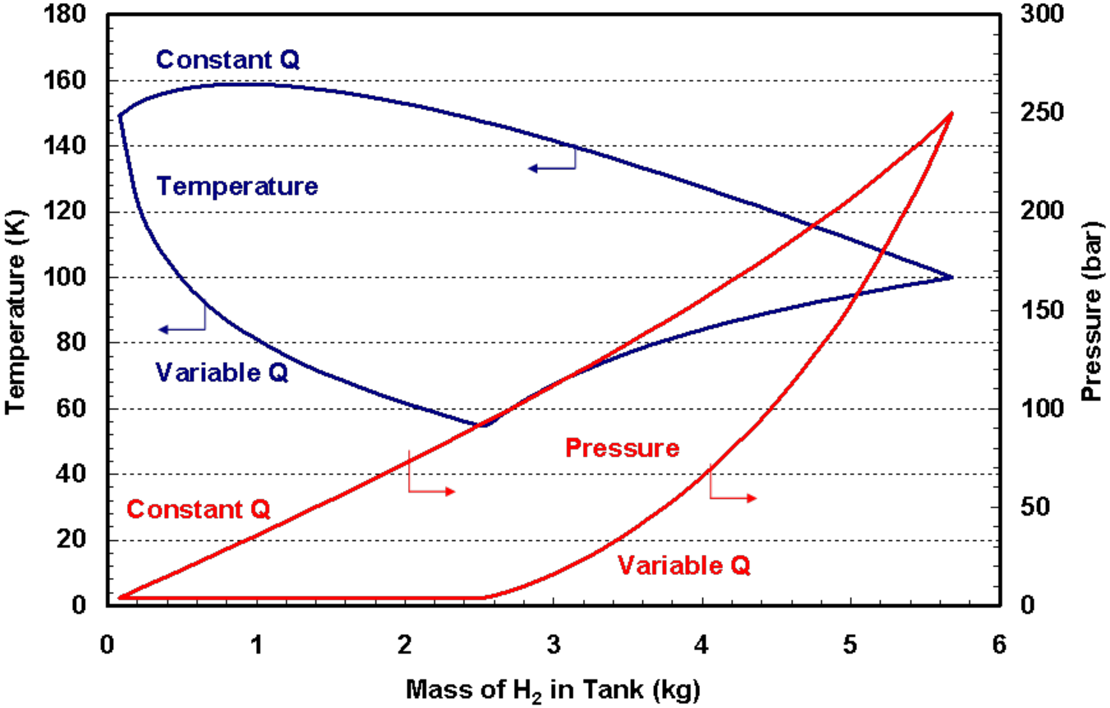
- 4.5-wt% gravimetric and 31.2 kg/m^3 volumetric capacity at 250 bar
  - Medium and containment contribute almost equally to the overall weight
  - 58% volumetric efficiency which can be improved by reducing insulation at the expense of dormancy





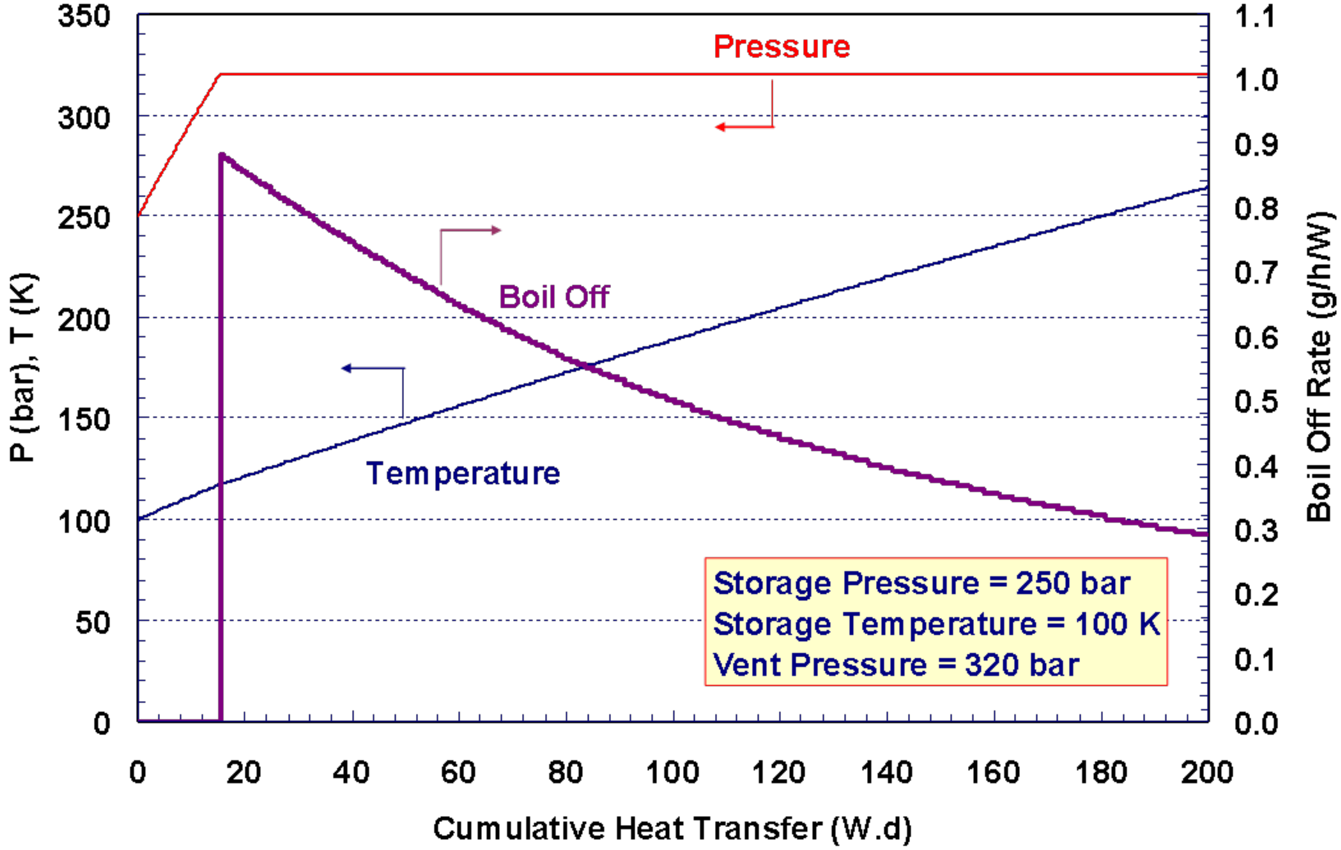
Refueling and Discharge Dynamics

- 7.2 MJ on-board cooling duty, 32.2 kW average heat transfer rate
  - 82% of the cooling duty is due to heat of adsorption
- Options for thermal management during discharge
  - Constant Q (1.8 kJ/g of H_2 discharged), 2.9 kW, 10.1 MJ heat duty
  - Variable Q, heat supplied only if tank pressure drops below 4 bar, peak heat transfer rate can exceed 20 kW (difficult to implement)



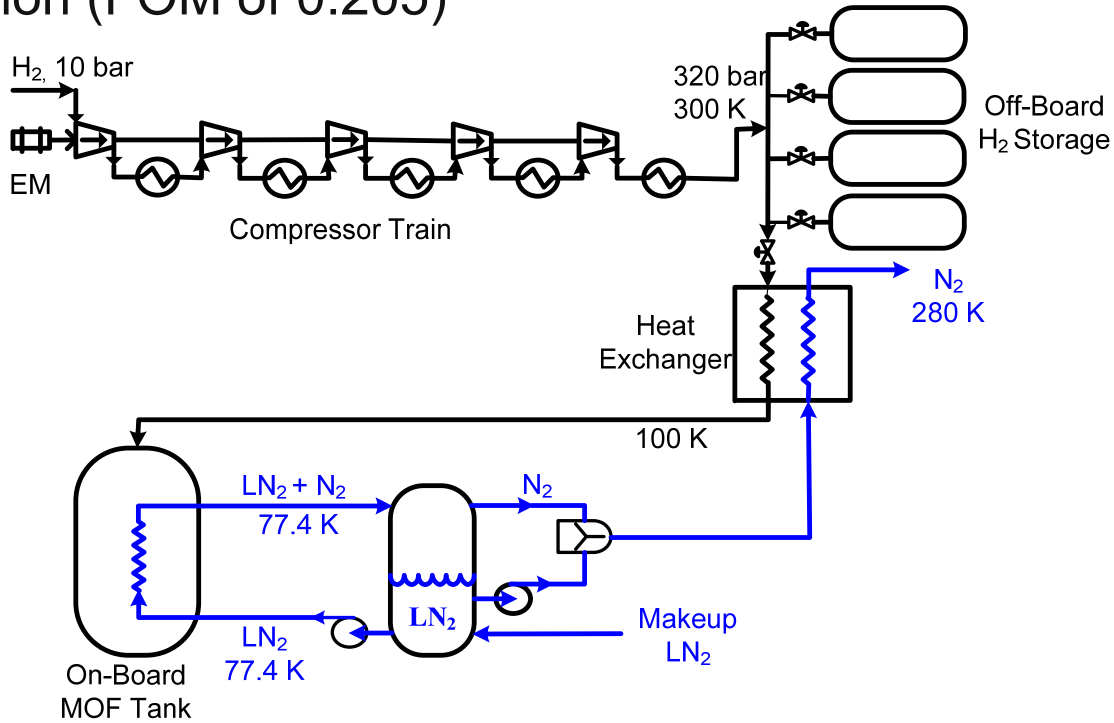
Dormancy

- Dormancy: Function of amount of H_2 stored and P/T at start of the event
  - Minimum dormancy is 15.4 W.d (7.8 days at 2 W in-leakage rate)
  - Peak H_2 vent rate is 0.9 g/h/W (1.8 g/h at 2 W in-leakage rate)
  - 116.7 W.d for venting of all stored H_2



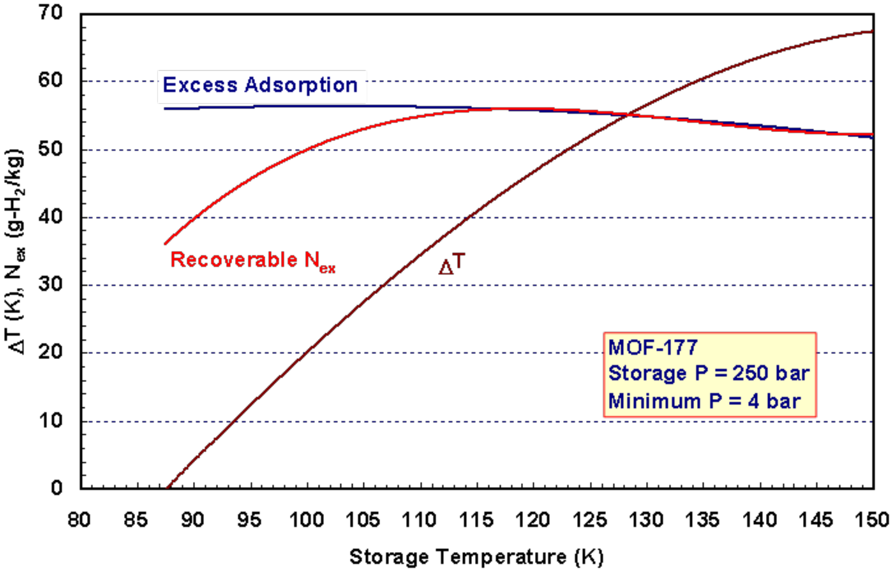
Off-Board Refueling with LN_2 Cooling

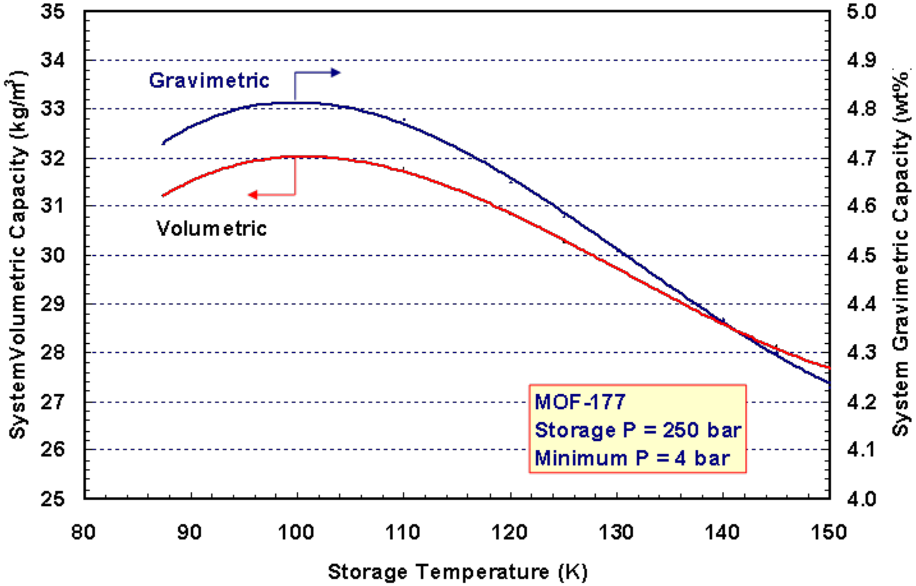
- Estimated electric energy for cryogenic cooling is 10 kWh/kg-H_2
  - Off-board cooling duty to precool H_2 to 100 K: 2.8 MJ/kg-H_2
  - On-board cooling duty to remove heat of adsorption and cool tank internals: 1.3 kW/kg-H_2
  - LN_2 requirement: ~10 kg-LN_2/kg-H_2
  - ~1 kWh/kg-LN_2 electric energy for distributed LN_2 production by air liquefaction (FOM of 0.205)



Adiabatic Refueling Option

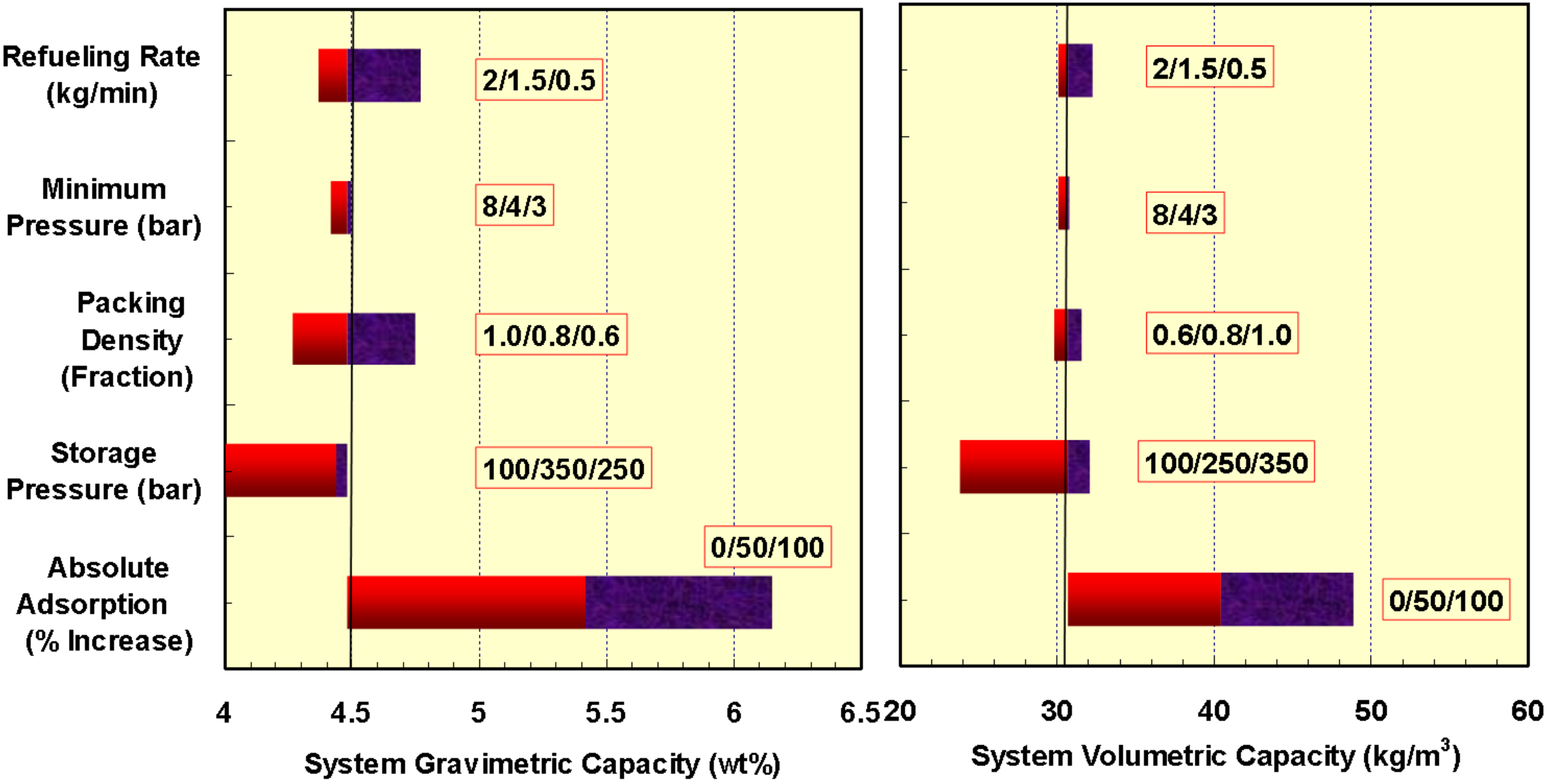
- Adiabatic refueling with LH_2
  - On-board heat exchanger still needed but sized for discharge
- Optimum storage temperature (115 K) for maximum recoverable N_{ex}
  - Allowable ΔT increases with increase in storage T, ΔT = 0 at 87K
  - Excess N_{ex} decreases with increase in storage T
- Optimum storage T (100 K) for maximum system capacity is < T at which recoverable N_{ex} is maximum
  - 4.8 wt% maximum system gravimetric capacity
  - 32 kg-H_2/m^3 maximum system volumetric capacity





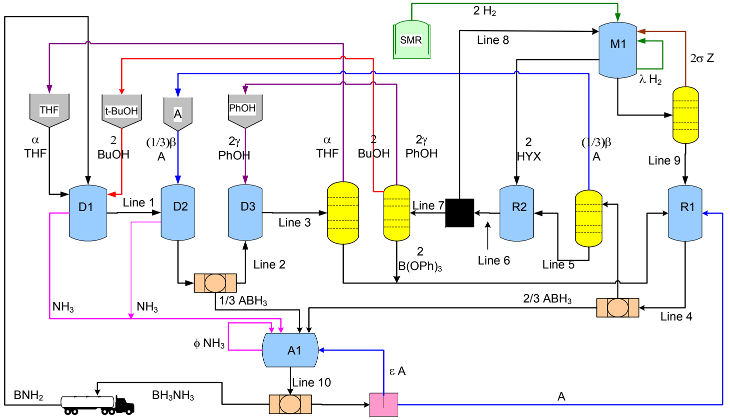
Sensitivity Analysis (LN_2 Cooling Option)

- Need to double the absolute adsorption for 6 wt% and 45 kg/m^3 capacities at 250 bar, 100 K with 50 K temperature swing
  - 50% increase in absolute adsorption for the revised 2015 targets



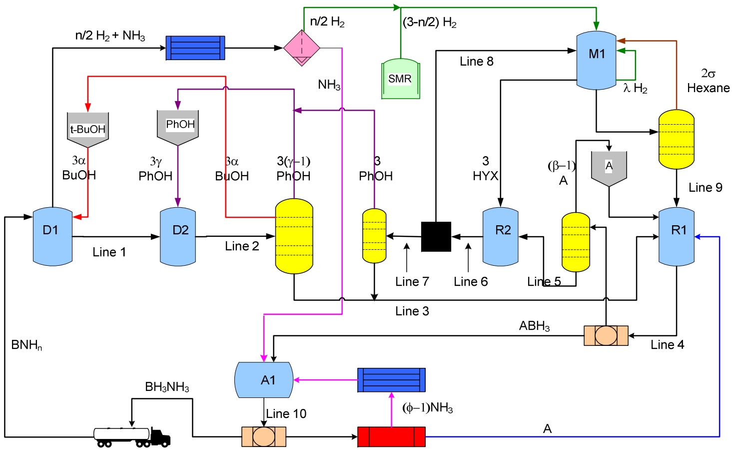
Regeneration of Ammonia Borane (AB) from BNH_2

- Constructed process flowsheets for PNNL regeneration chemistry using concepts of limited reactants and excess reagents
- Digestion of spent fuel with excess t-BuOH in THF (D1); co-product B(O-*t*-Bu)$_3$ reacted with excess PhOH to form $B(OPh)_3$ (D3)
- Reduction of $B(OPh)_3$ with excess MH in an amine medium (R1)
- Add excess NH_3 to form BH_3NH_3 (A1)
- Recover MH from MX salt using excess H_2 in the presence of a base
- Two digestion approaches
  - Preserve BH bond in spent fuel
  - Recover residual H_2



Line 1: $HB(t\text{-}BuO)_2 + \alpha\ THF$
Line 2: $2/3\ B(t\text{-}BuO)_3 + \alpha\ THF + 1/3\ (\beta\text{-}1)A$
Line 3: $2/3\ B(OPh)_3 + 1/3\ (\beta\text{-}1)A + 2\ t\text{-}BuOH + 2(\gamma\text{-}1)PhOH + \alpha\ THF$
Line 4: $2\ MB(OPh)_4 + 2(\delta\text{-}1)Y + (1/3)\beta\ A + 2\ t\text{-}BuOH + 2(\gamma\text{-}1)PhOH + 2/3\ ABH_3$
Line 5: $2\ MB(OPh)_4 + 2(\delta\text{-}1)Y + 2\ t\text{-}BuOH + 2(\gamma\text{-}1)PhOH$

Line 6: $2\ B(OPh)_3 + 2\ MX + 2\delta Y + 2\ t\text{-}BuOH + 2\gamma\ PhOH$
Line 7: $2\ B(OPh)_3 + 2\ t\text{-}BuOH + 2\gamma\ PhOH$
Line 8: $2\ MX + 2\delta Y$
Line 9: $2\ MH + 2(\delta\text{-}1)Y$
Line 10: $BH_3NH_3 + (\varepsilon+1)\ A$



Line 1: $3(\alpha\text{-}1)\ t\text{-}BuOH + B(t\text{-}BuO)_3$
Line 2: $B(OPh)_3 + 3(\alpha-1)\ t\text{-}BuOH + 3(\gamma\text{-}1)PhOH$
Line 3: $4\ B(OPh)_3$
Line 4: $3\ MB(OPh)_4 + ABH_3 + (\beta\text{-}1)A + 3(\delta\text{-}1)Y$
Line 5: $3\ MB(OPh)_4 + 3(\delta\text{-}1)Y$

Line 6: $3\ MX + 3\delta Y + 3\ PhOH + 3\ B(OPh)_3$
Line 7: $3\ PhOH + 3\ B(OPh)_3$
Line 8: $3\ MX + 3\delta Y$
Line 9: $3\ MH + 3(\delta\text{-}1)Y$
Line 10: $BH_3NH_3 + A + \phi NH_3$

Ref: Don Camaioni, Private Communication, PNNL (2008)

Process Energy for Regenerating 1 kg H_2 in AB

- Analysis assumptions
  - 85% thermal efficiency
  - 2 times stoichiometric amount of reagents
  - Reflux ratio of 0.5 in distillation steps
- Recovery of residual H_2 approach requires significantly more energy

BH Bond Preservation Approach

Process	Q, MJ
Digestion	
Distill THF solvent	27.6
Distill t-BuOH	34.5
Distill PhOH	40.8
Reduction	
Distill tertiary/secondary amine	9.9
Distill PhOH	40.8
MH Formation	
Distill hexane solvent	50.8
Total	
0% heat integration	204.4
30% heat integration	143.1

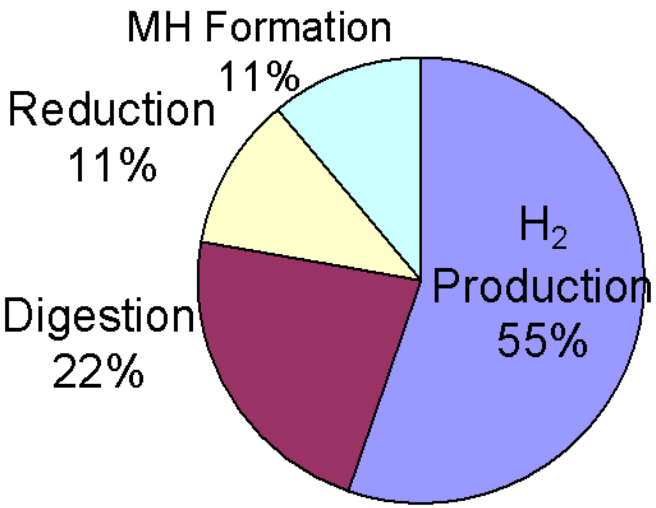
H_2 Recovery approach

Process	Q, MJ	E, kWh
Digestion		
Distill t-BuOH	103.5	
Distill PhOH	61.1	
Reduction		
Distill tertiary/secondary amine	14.9	
Distill PhOH	61.1	
MH Formation		
Distill hexane	76.2	
Ammoniation		
Liquefy NH_3		2.3
Cool H_2		0.1
Total		
0% heat integration	316.8	2.4
30% heat integration	221.8	2.4

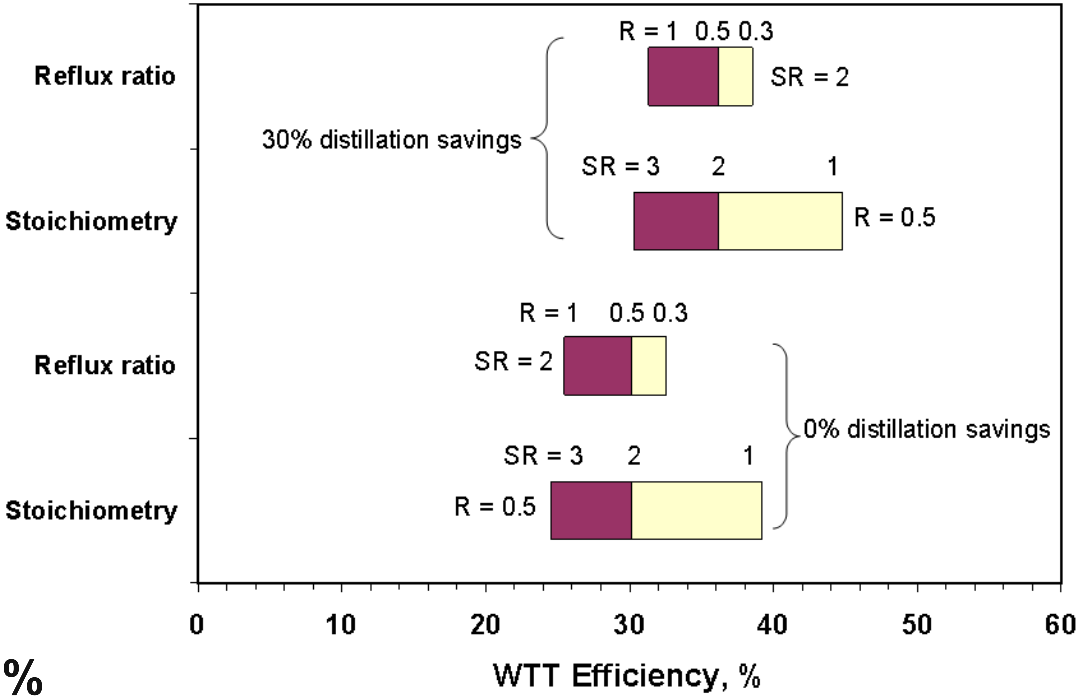
FCHtool Analysis: Primary Energy & WTT Efficiency

- Preliminary estimate of WTT efficiency for spent AB regeneration by PNNL scheme is 25 - 47% (BH bond preserved)
- Recovery of residual H_2 approach lowers WTT efficiency by 5 – 7 percentage points

Primary Energy Consumption



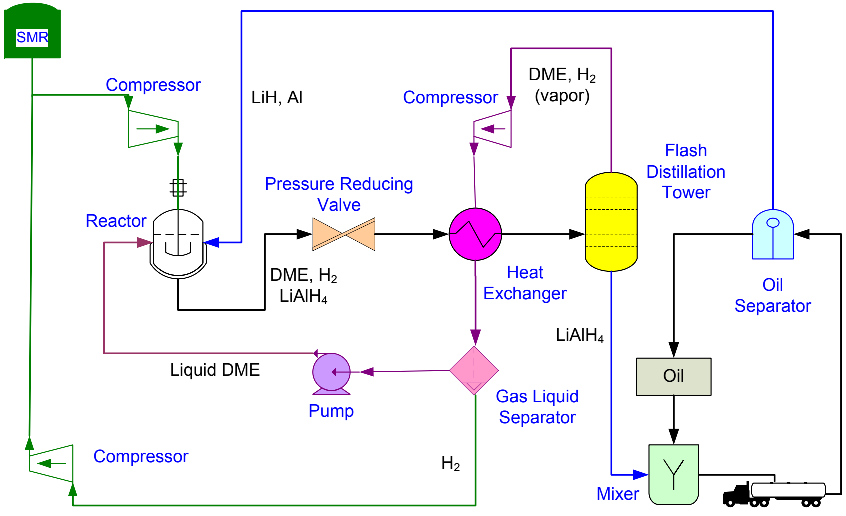
Total = 320 MJ/kg H_2, WTT = 37%

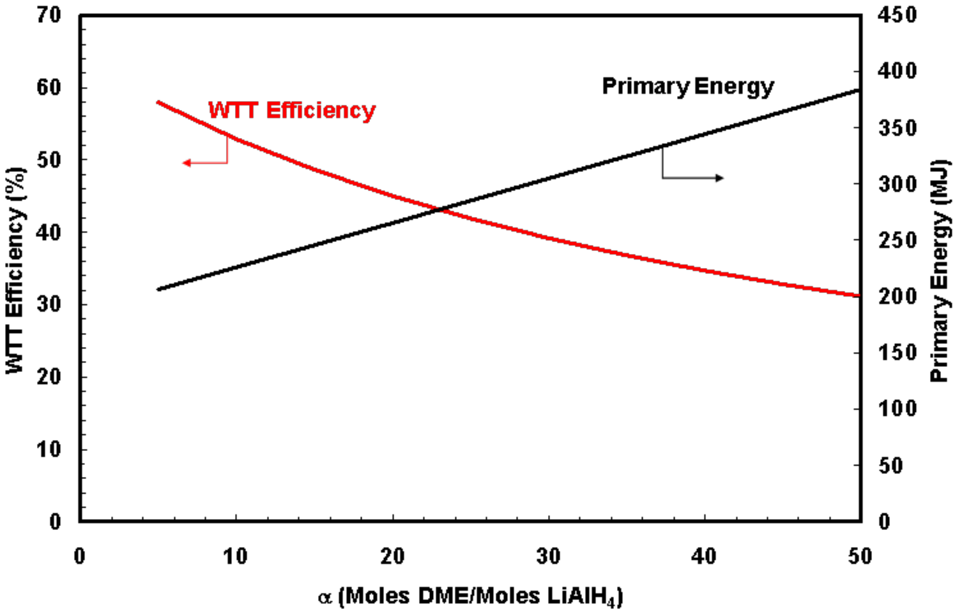


Regeneration of $LiAlH_4$

- UH/UNB scheme for regenerating $LiAlH_4$ from LiH, Al and H_2 in DME solvent at 100 bar and RT

  $3LiH + Al(Ti) + 3/2\ H_2 \rightarrow Li_3AlH_6$
  $Li_3AlH_6 + 2Al(Ti) + 3H_2 \rightarrow 3LiAlH_4$
- Constructed a process flowsheet without depressurizing the reactor
- Energy requirement for regeneration depends on molar ratio (α) of DME to $LiAlH_4$
  - Recent tests at UNB confirm regeneration for α = 5, 58% WTT efficiency
  - Potential to achieve 60% WTT efficiency if α reduced to ~4





Future Work

As lead for Storage System Analysis Working Group, continue to work with DOE contractors and CoEs to model, validate and analyze various developmental hydrogen storage systems.

Metal Hydrides

- On-board storage system for lithium alanate
- Regeneration of $LiAlH_4$ by UH/UNB schemes
- Regeneration of alane by organometallic and electrochemical routes

Sorbent Storage

- On-board system with spillover materials
- Further analysis of MOF system

Chemical Hydrogen

- On-board system for AB class of materials
- Fuel cycle efficiency of candidate materials and processes
- Joint report with TIAX on organic liquid carriers

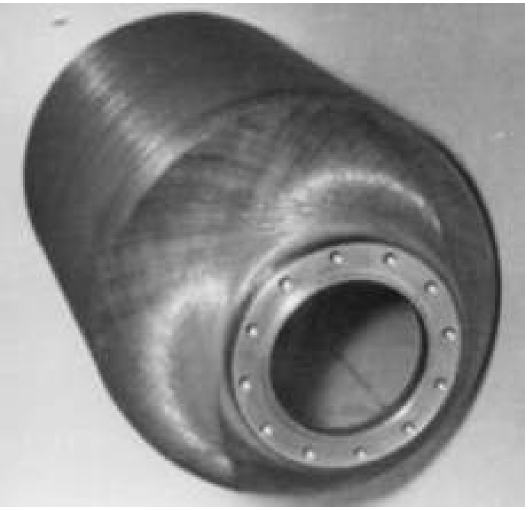
Physical Storage

- Update cryo-compressed storage analysis (LLNL Gen3 system)

BACKUP SLIDES

Carbon Fiber Netting Analysis

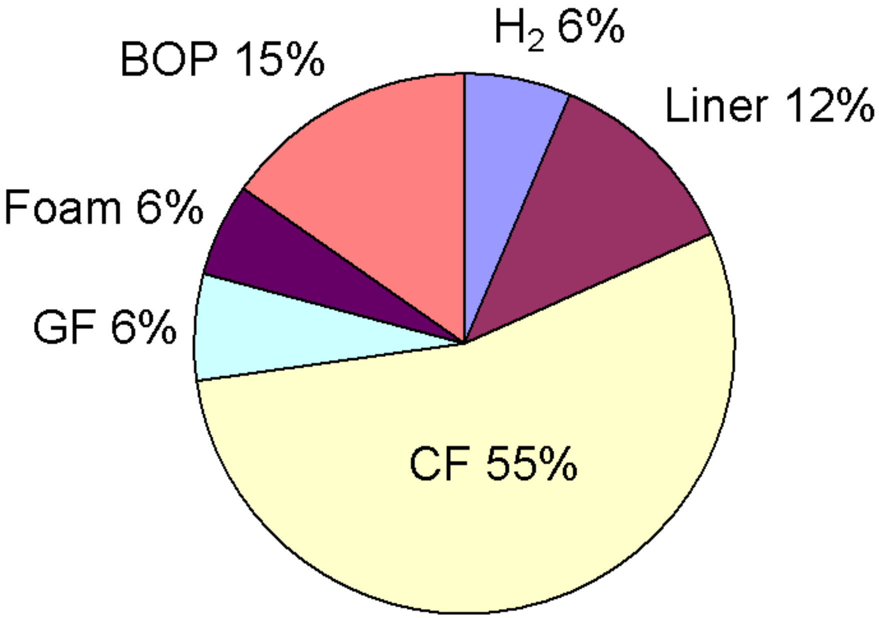
- Benedict-Webb-Rubin equation of state to calculate amount of stored H_2 for 5.6 kg recoverable H_2 and 20-bar minimum pressure
- Carbon fiber translation strength
  - 82.5% for 5,000 psi cH_2
  - 63% for 10,000 psi
- 2.35 safety factor
- 5-mm HDPE liner, 1-mm glass fiber, and 10-mm foam end caps
- Construct optimal dome shape with geodesic winding pattern (i.e., along isotensoids)
- Geodesic and hoop windings in straight cylindrical section
- Iterate for tank diameter, CF thickness (non-uniform in end domes), given L/D
- Commercial data for BOP components



Ref: http://www.adoptech.com/pressure-vessels/main.htm

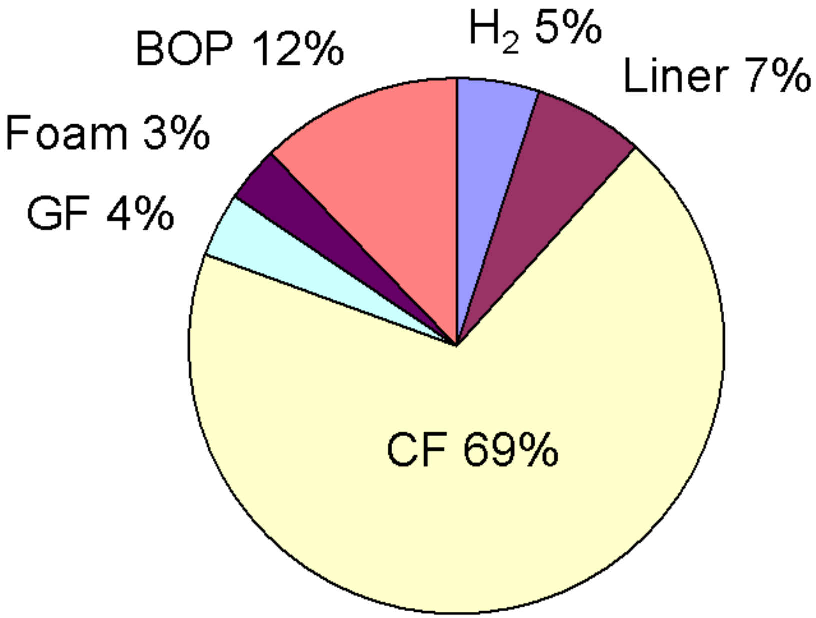
On-board System Gravimetric Capacity

Weight Distribution (%)
5,000 psi, 5.6 kg Usable H_2



System Weight = 95 kg
Gravimetric Capacity = 5.9 wt%

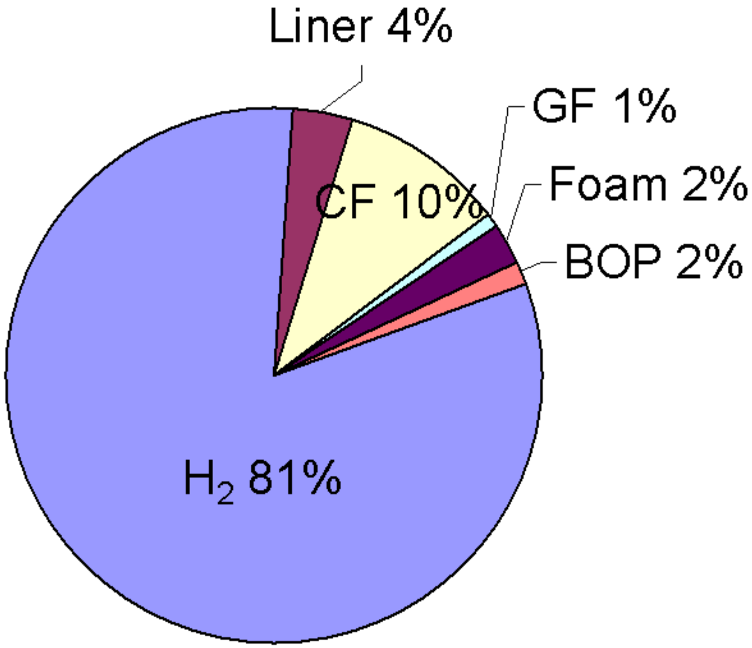
Weight Distribution (%)
10,000 psi, 5.6 kg Usable H_2



System Weight = 119 kg
Gravimetric Capacity = 4.7 wt%

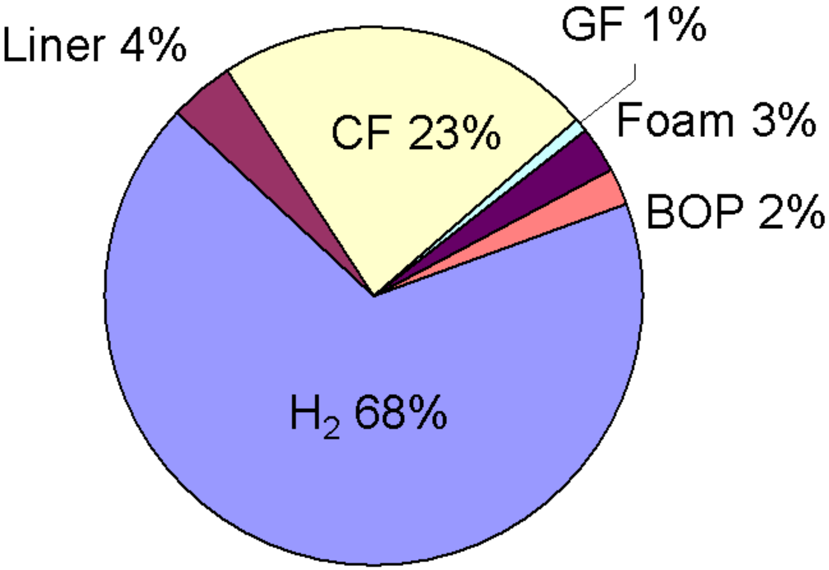
On-board System Volumetric Capacity

Volume Distribution (%)
5,000 psi, 5.6 kg Usable H_2



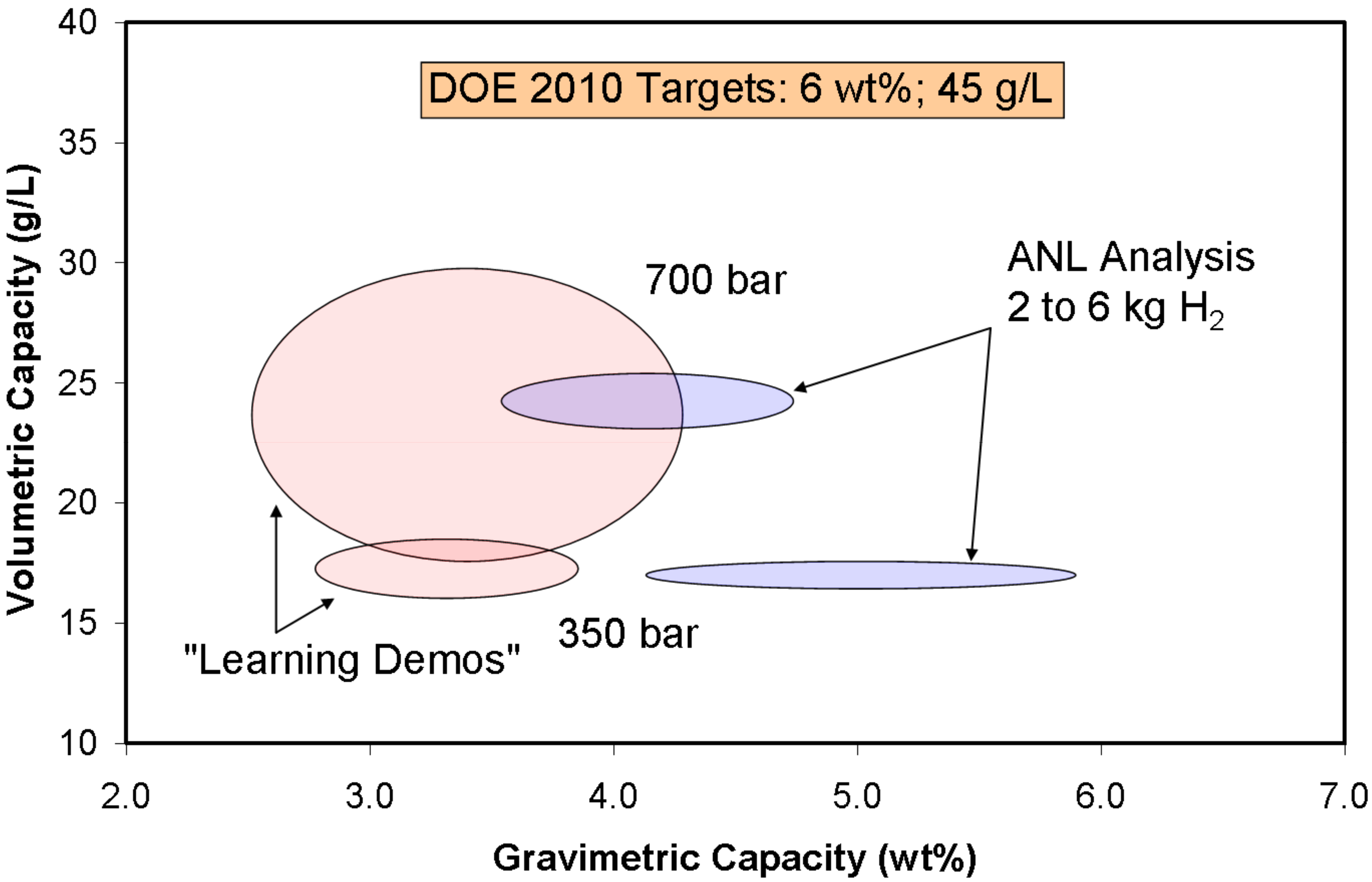
System Volume = 320 L
Volumetric Capacity = 17.5 g H_2/L

Volume Distribution (%)
10,000 psi, 5.6 kg Usable H_2



System Volume = 222 L
Volumetric Capacity = 25.2 g H_2/L

Comparison of ANL Analysis with “Learning Demos”



Electricity Consumption and WTT Efficiency (Pipeline Delivery)

Compression[(a)]		# of Stages	Isentropic efficiency	Electricity (kWh/kg)	WTT efficiency[(b)]	Comments
P_i (bar)	P_f (bar)					
20	70	3	88%	0.6		Central plant, $\Delta P = 50$ bar
20	180	5	65%	1.5	-	Forecourt
180	425	2	65%	0.6	-	Forecourt
180	850	3	65%	1.1	-	Forecourt
20	425	7	65 - 88%	2.7	**58.0%**	5,000 psi on-board storage
20	850	8	65 - 88%	3.3 (c)	**56.1%**	10,000 psi on-board storage

Notes:

a) Compressor mechanical efficiency = 97%, motor efficiency = 90%

b) H_2 produced by SMR central plant, electricity source from U.S. grid 2015, inclusive of 8% transmission loss

c) Includes 0.14 kWh/kg for precooling from 25°C to -40°C

Life Cycle Greenhouse Gas Emissions (Pipeline Delivery, g/kg H_2)

- 5,000 psi on-board storage

	VOC	CO	NO_x	PM_{10}	SO_x	CH_4	N_2O	CO_2	GHGs
H_2 Production	1.55	3.62	7.34	2.20	2.71	29.93	0.06	14,068	14,774
H_2 Storage	0.12	0.35	1.33	1.60	2.91	1.76	0.02	1,259	1,567
H_2 Distribution	0.05	0.26	0.13	0.04	0.05	0.17	0.01	155	497
Total:	1.71	4.23	8.80	3.84	5.68	31.86	0.08	15,482	16,838

- 10,000 psi on-board storage

	VOC	CO	NO_x	PM_{10}	SO_x	CH_4	N_2O	CO_2	GHGs
H_2 Production	1.55	3.62	7.34	2.20	2.71	29.93	0.06	14,068	14,774
H_2 Storage	0.19	0.57	2.17	2.62	4.76	2.87	0.03	2,056	1,953
H_2 Distribution	0.05	0.26	0.13	0.04	0.05	0.17	0.01	155	579
Total:	1.79	4.45	9.64	4.85	7.53	32.98	0.10	16,279	17,306

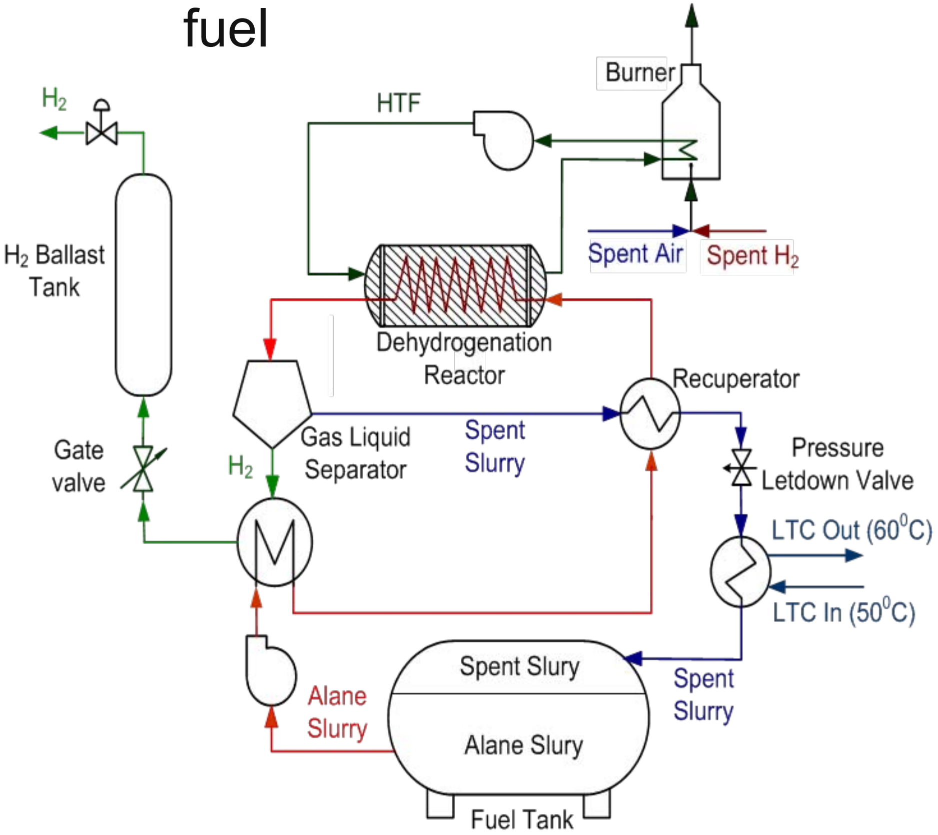
Summary

- Dome shape and carbon fiber thickness were determined by netting analysis
- Minimum tank pressure affects system gravimetric and volumetric capacities while tank geometry (L/D) affects only gravimetric capacity
- WTT efficiency is within six percentage points of DOE target of 60%
- For 5.6 kg recoverable H_2 and L/D = 3

H_2 Tank Pressure (bar)	Minimum Pressure (bar)	Gravimetric Capacity (wt%)	Volumetric Capacity (g/L)	Electricity (kWh/kg)	WTT Efficiency (%)
350	20	5.9	17.5	2.7	58.0
350	4	6.2	18.5	2.7	58.0
700	20	4.7	25.2	3.3	56.1
700	4	4.8	26.0	3.3	56.1

H_2 Storage as Alane Slurry

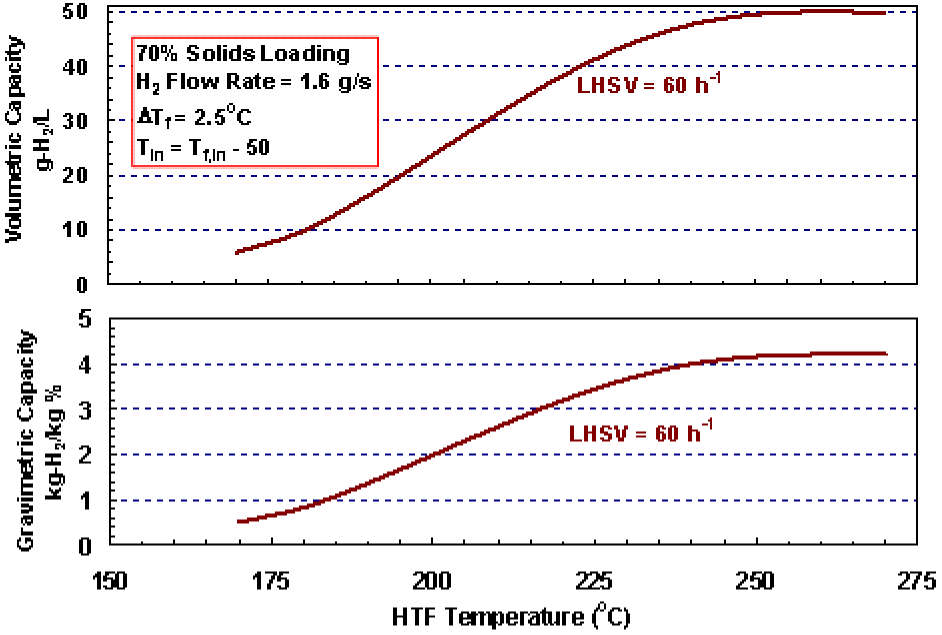
- Investigated several methods of storing alane in powder and liquid forms and selected slurry for initial evaluation
- Pros and cons of storing alane as slurry
  - Pros: heat transfer, easier refueling, liquid infrastructure, practical
  - Cons: reduced material capacity, added difficulty in recycling spent fuel



Component	Key Assumptions
Fuel Tank	Volume-exchange concept, 10% ullage, 5.6 kg usable H_2
AlH_3 Slurry	70 wt% AlH_3 in light mineral oil
Heat Transfer Fluid	XCELTHERM ®
Dehydrogenation Reactor	Slurry on tube side, HTF on shell side, s/d=1.1, slurry at 100 bar, HTF at 3 bar, 1.6 g/s peak H_2 consumption in FCS
AlH_3 Dehydrogenation Kinetics	Avrami-Erofeyev rate expression
HEX Burner	50 kWt, non-catalytic, HTF pumped to stack P, 100°C approach T, 5% excess air
H_2 Ballast Tank	100 bar, 75°C, AL-2219-T81 alloy tank, 2.25 SF
Recuperator, H_2 Cooler, Spent Slurry Cooler	5 - 50°C approach T

Assessment of Results

- Under optimum conditions, ~80% of H_2 stored in slurry is available for use in fuel cell system.
- Usable gravimetric capacity <4.25 wt% H_2, ~75% gravimetric efficiency
- Usable volumetric capacity ~50 g-H_2/l, 73% volumetric efficiency



Data Needs

- Preparation of 70-wt% AlH_3 slurry, effect of particle size distribution, surfactants, etc
- DeH$_2$ kinetics of AlH_3 slurry, fluid dynamics of slurry in micro-channel HX
- H_2 recovery from fuel tank

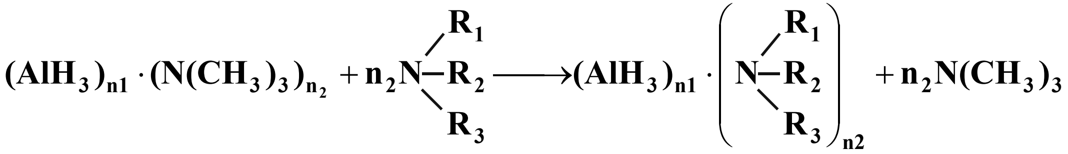
	Value	Units	Range
Intrinsic Material Capacity	10.0	g-H_2/g-AlH_3, %	Variable T_{HTF}, Fixed LHSV
H_2 Capacity in Slurry	7.0	g-H_2/g-slurry, %	
Recoverable H_2 Capacity	6.9	g-H_2/g-slurry, %	θ: 11.3-97.9%
Available H_2 Capacity	6.3	g-H_2/g-slurry, %	η_{DC}: 82.8-93.1%
Usable H_2 Capacity	5.6	g-H_2/g-slurry, %	η_{SU}: 84.7-91.3%
Usable Gravimetric Capacity	4.2	g-H_2/g-system, %	0.5-4.2
Usable Volumetric Capacity	49.8	g-H_2/L-system	5.9-50.0
Peak H_2 Loss at 25°C	0.3	g-H_2/h	0-0.3
Peak H_2 Loss at 50°C	7.7	g-H_2/h	0-7.7

Regeneration of Alane - ANL Reference Flowsheet

- Form AlH_3 as adduct to TMA in ether in the presence of $LiAlH_4$.

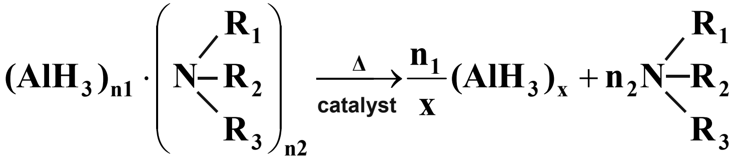
$$n_1 Al + \frac{3n_1}{2} H_2 + n_2 N(CH_3)_3 \xrightarrow[\text{catalyst}]{\Delta\text{-pres.}} (AlH_3)_{n1} \cdot (N(CH_3)_3)_{n2}$$

- Displace TMA from TMAA in ether by TEA (transamination).



$$(AlH_3)_{n1} \cdot (N(CH_3)_3)_{n_2} + n_2 \underset{R_3}{\overset{R_1}{N-R_2}} \longrightarrow (AlH_3)_{n1} \cdot \left(\underset{R_3}{\overset{R_1}{N-R_2}} \right)_{n2} + n_2 N(CH_3)_3$$

- Decompose TEAA in presence of $LiAlH_4$ (thermal decomposition)



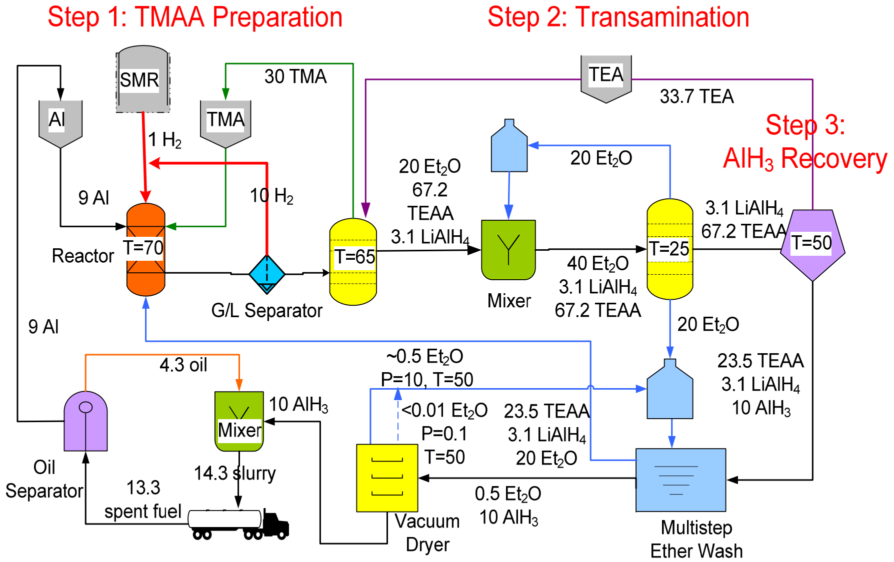
$$(AlH_3)_{n1} \cdot \left(\underset{R_3}{\overset{R_1}{N-R_2}} \right)_{n2} \xrightarrow[\text{catalyst}]{\Delta} \frac{n_1}{x} (AlH_3)_x + n_2 \underset{R_3}{\overset{R_1}{N-R_2}}$$

- For high conversion, use excess amounts of reagents.

  H_2 Stoichiometry: Φ_{H2}

  TMA Stoichiometry: Φ_{TMA}

  TEA Stoichiometry: Φ_{TEA}



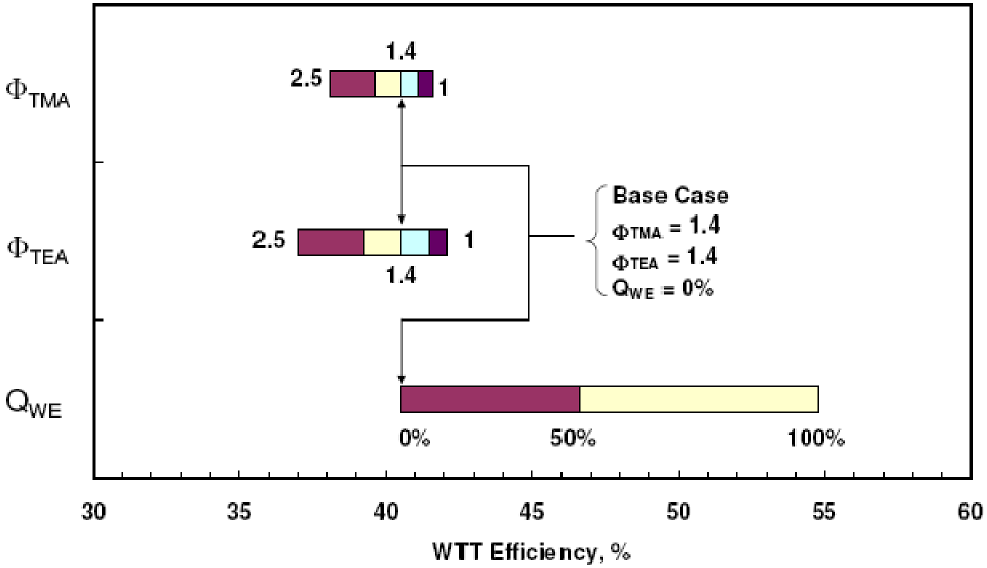
Ref: Murib and Horvitz, U.S. Patent 3,642,853 (1972)

FCHtool Analysis: Preliminary WTT Efficiency

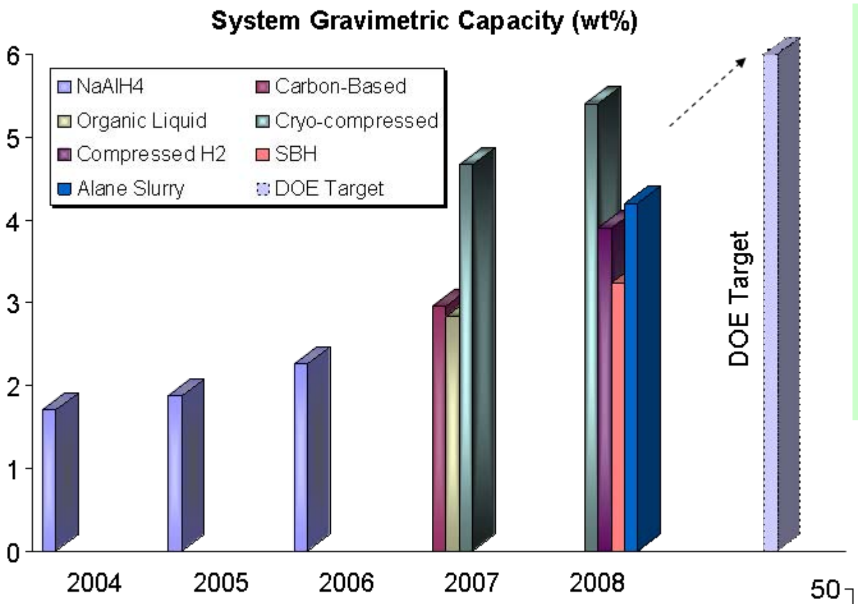
- Without credit for availability of low-grade heat, the WTT efficiency is 40.5% (Φ_{H2}=10, Φ_{TMA}=1.4, Φ_{TEA}=1.4).
  - Q: 71.9 MJ/kg-H_2, E: 3.6 kWh/kg-H_2
- A single-variable parametric analysis indicates that WTT efficiency is most sensitive to the availability of low-grade waste heat.
- We are working with BNL to verify the process steps and determine the operating conditions.

Q: MJ/kg-H_2, E: kWh/kg-H_2

Process	T °C	P bar	Q MJ	E kWh
Compress H_2 from SMR	70	30		0.3
Compress circulating H_2	70	30		0.6
Distill TMA	65	5	28.6	
Distill ether	25	0.3	22.9	1.1
Decompose TEAA	50	0.2	20.2	1.4
Vacuum dry AlH_3	50	$<10^{-1}$	0.2	0.2
Total			71.9	3.6

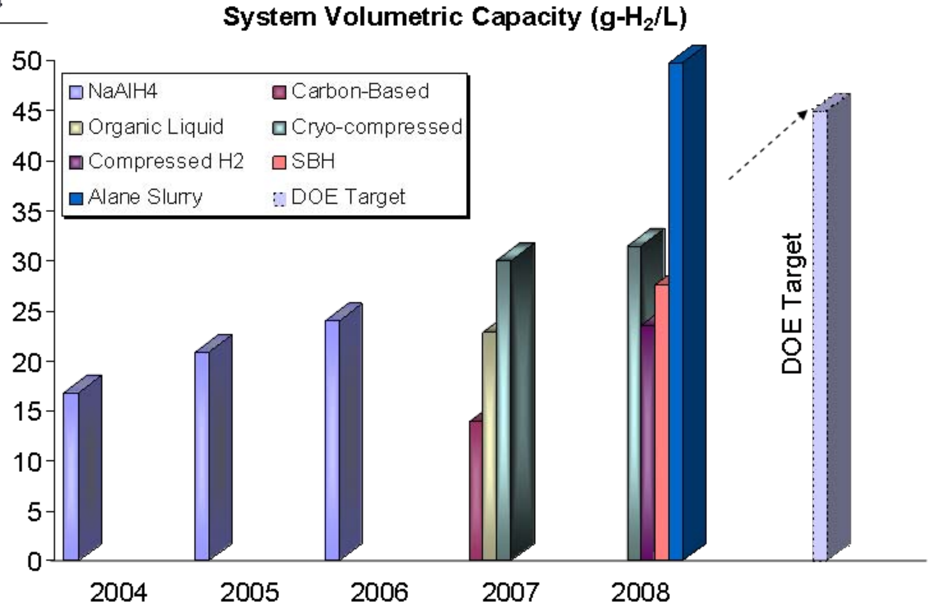


Hydrogen Storage Capacities

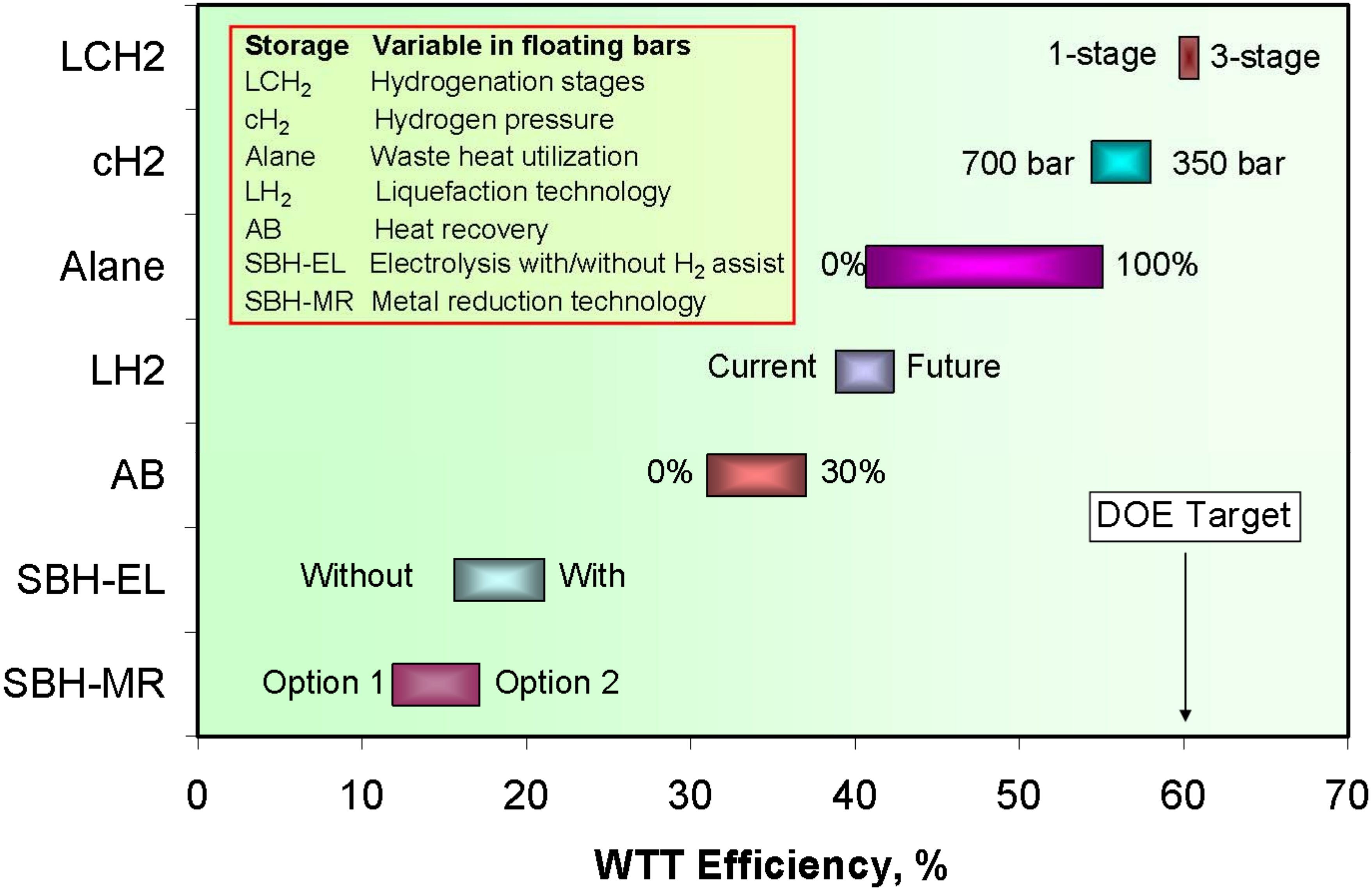


- Cryo-compressed option with AL shell can meet the gravimetric target (but not volumetric)
- Alane slurry option may meet the volumetric target (but not gravimetric)

- ANL modeling results for various hydrogen storage systems
- System capacities based on recoverable H_2 delivered to fuel cell



Well-To-Tank Efficiency



Storage	Variable in floating bars
LCH_2	Hydrogenation stages
cH_2	Hydrogen pressure
Alane	Waste heat utilization
LH_2	Liquefaction technology
AB	Heat recovery
SBH-EL	Electrolysis with/without H_2 assist
SBH-MR	Metal reduction technology