Hydrogen Storage Materials and Systems Development

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Savannah River National Laboratory
May 16, 2007

Project ID#: STP-37

This presentation does not contain proprietary or confidential information

Overview

Timeline

- Start: 10/1/05
- End: 9/30/10
- Percent complete: 25%

Budget

- Funding received in FY06
  - $200k
- Funding for FY07
  - $300k

Barriers Addressed

- System Gravimetric Density
- System Volumetric Density
- Charging/discharging Rates
- Safety

Partners

- Dr. A. Lutz, Sandia National Labs
- Dr. R. Bowman and J. Reiter, Jet Propulsion Lab
- Dr. D. Mosher, United Technologies Res. Ctr.

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Objectives

- Evaluate materials for use as hybrid storage vessels
  - Determine gravimetric and volumetric densities of pressure vessels composed of different materials for:
    - Pressures up to 800 bar
    - Range of recoverable hydrogen, based on hydride weight percent
- Improve criteria for optimized design of composite pressure vessels
  - Develop design formulas for fiber winding criteria and wall thickness
- Identify and evaluate concepts for advanced cooling systems
  - Develop model for heat and mass transfer that is sufficiently complete to serve as a design tool and assess the viability of proposed system for practical use
  - Identify cooling systems that enable the storage system to meet the DOE criteria for:
    - Refueling time
    - Hydrogen capacity
    - Mass and volume

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Summary

- Composite fiber vessels are best choice for hybrid storage tanks. Vessels composed of IM6 graphite fiber and epoxy were found to closely approach their maximum gravimetric and volumetric H_2 storage density over broad ranges of pressure.
- Improved design formulas for the optimized fiber winding angle and wall thickness of composite pressure vessels were developed. These formulas better address material properties and failure criteria for fiber composite tanks than those currently available.
- Three advanced heat exchange designs: permeation cooling, two phase cooling and micro-channel heat exchangers identified for controlling the temperature of the hydride bed. A modeling tool for evaluation and design of these systems was formulated and is in the process of numerical implementation.

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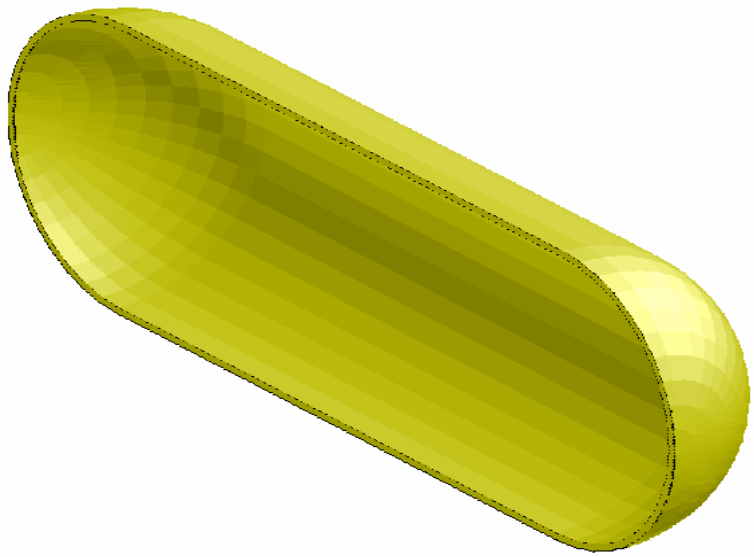
Hybrid Storage Vessels Analysis



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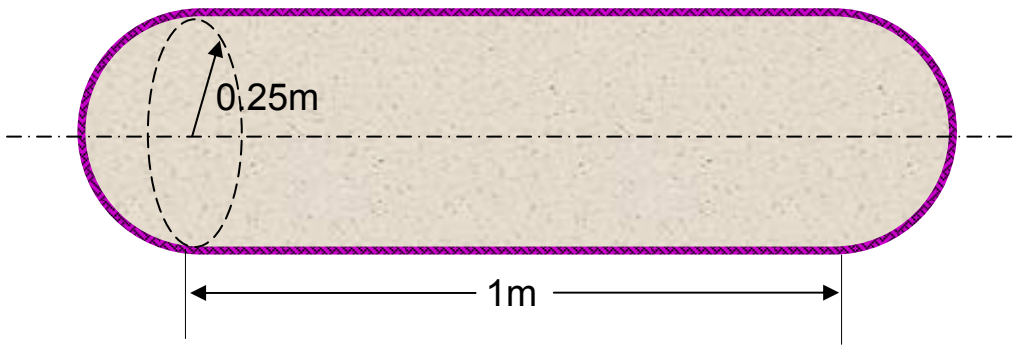
Hybrid Tank Concept

- Combined High Pressure and Solid State Hydride Designs to make maximum utilization of total tank internal volume.
- Assumptions:
  - Most simple geometric design considered with no heat exchange or gas coolant outlets to minimize influence of engineering design and determine maximum densities.
  - 1m long x 0.5m dia. cylindrical section having hemispherical ends (V_0 = 261.8 liter) fabricated from either 316 stainless steel, A92014-T76 Al, and IM6 carbon fiber- epoxy composite (GREC)
  - Pressure range: 50-800 bar (735-11,760psi)
  - Wall stresses for metal vessels meet ASME Sch. 8 Pressure Vessel Code
  - For composite tanks, the design criterion developed in the following section was used to estimate wall thickness & vessel mass



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Description of Analysis

- Performed structural analysis to determine dependence of wall thickness, total mass and total volume of hybrid storage vessel on pressure (from the design criterion developed in the following section)
  - Tank contents:
    - Empty
    - Filled with *$NaAlH_4$-like* metal hydride having:
      - 2, 4, 6 and 8 wt% of recoverable H_2
      - Interparticle void fractions of 0.4, 0.5 and 0.6
      - Media density of 1.3 g/cc
  - Redlich-Kwong approximation of H_2 non-ideal gas behavior used.
- Expressed results in terms of gravimetric and volumetric recoverable H_2 storage density vs. pressure

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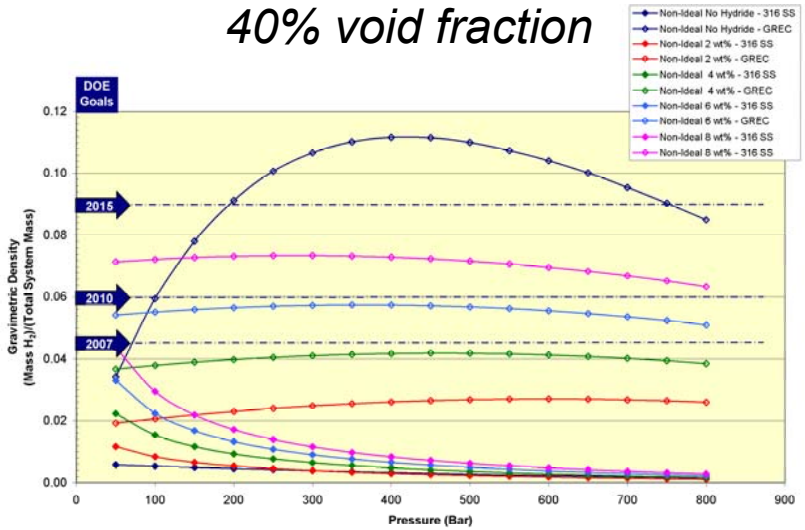
Gravimetric Density

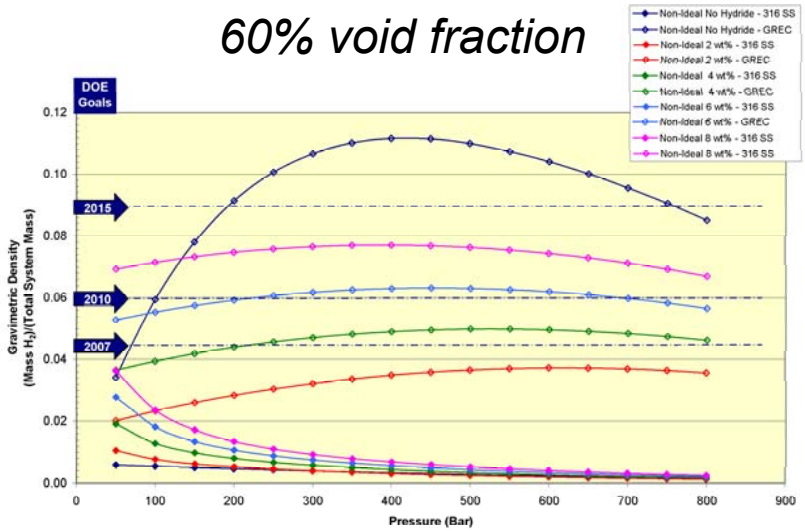
Comparison of Hybrid Tank Gravimetric Density vs Pressure as a function of:

- H_2 wt% media
- Tank materials of construction GREC vs. Stainless Steel
- Media Void Fraction

40% void fraction



60% void fraction



- ***Idealized model of 400bar compressed H_2 tank surpasses DOE 2015 goal***
- ***Increasing porosity fraction increases optimum pressure range for gravimetric density***
- ***Idealized model 6wt% media at 300 bar utilizing GREC at 60% porosity meets DOE 2010 goal***
- ***Stainless steel tanks meet DOE 2007 goals for 8wt% media at 40% void fraction at 50 bar.***

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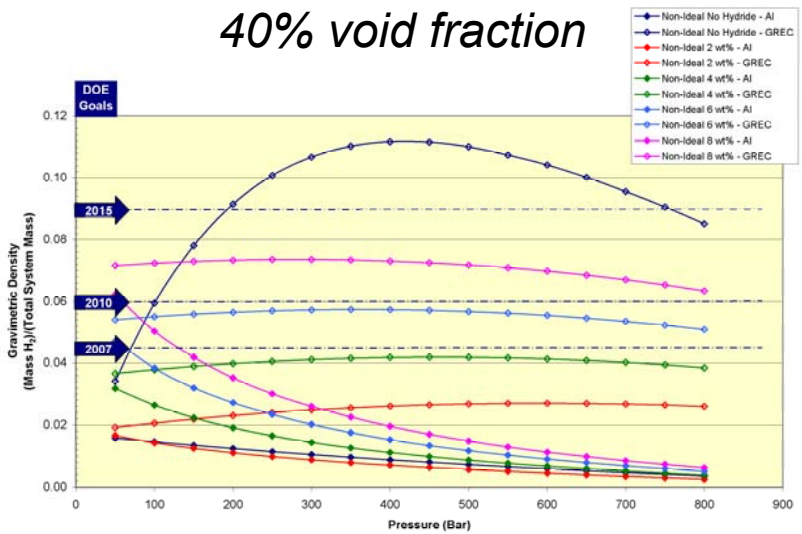
Gravimetric Density

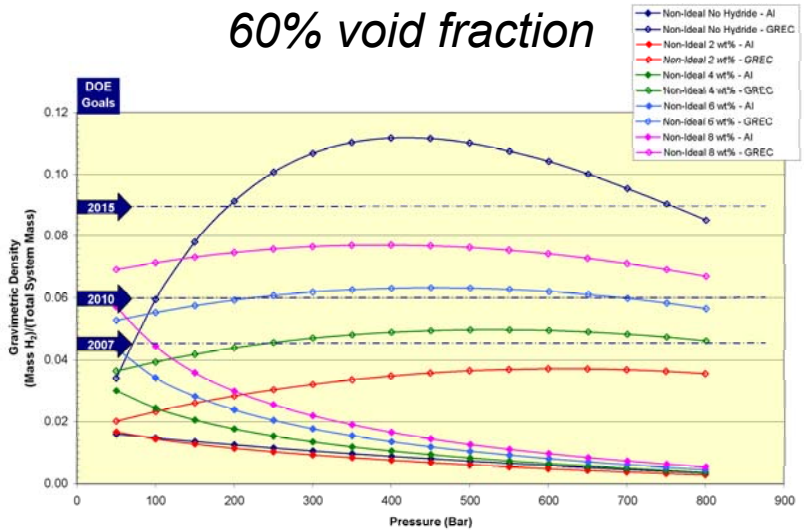
Comparison of Hybrid Tank Gravimetric Density vs Pressure as a function of:

- H_2 wt% media
- Tank materials of construction GREC vs. Aluminum
- Media Void Fraction

40% void fraction



60% void fraction



- ***Gravimetric Densities for Aluminum tanks are superior to stainless steel tanks but far inferior to GREC.***
- ***Idealized model of aluminum tanks meet DOE 2010 goals for 8 wt% media having 40% void space at 50 bar operating pressure.***

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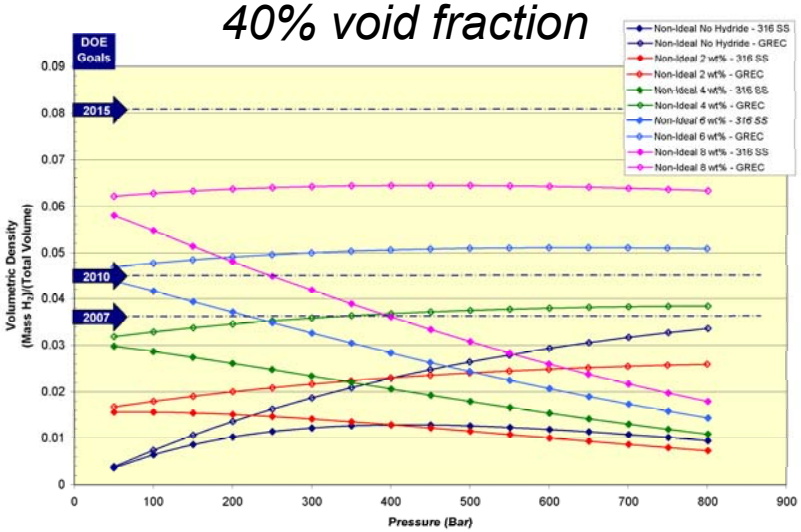
Volumetric Density

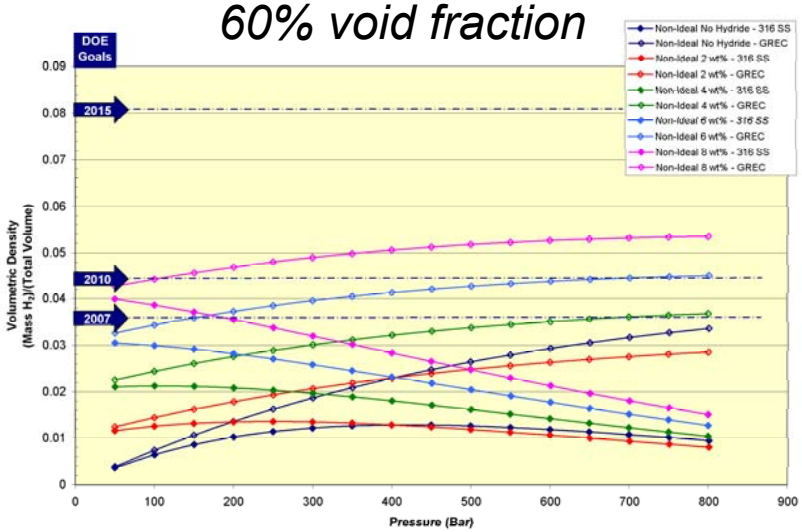
Comparison of Hybrid Tank Gravimetric Density vs Pressure as a function of:

- H_2 wt% media
- Tank materials of construction GREC vs. Stainless Steel
- Media Void Fraction

40% void fraction



60% void fraction



- ***Idealized model of 400bar compressed GREC H_2 tank only 50% of DOE 2007 goal and approaches 2007 only at 800bar***
- ***Idealized model of 6wt% media at 50 bar utilizing GREC at 40% porosity meets DOE 2010 goal***
- ***Idealized model of stainless steel tanks meet DOE 2010 goals for 8wt% media at 40% void fraction at 275 bar.***

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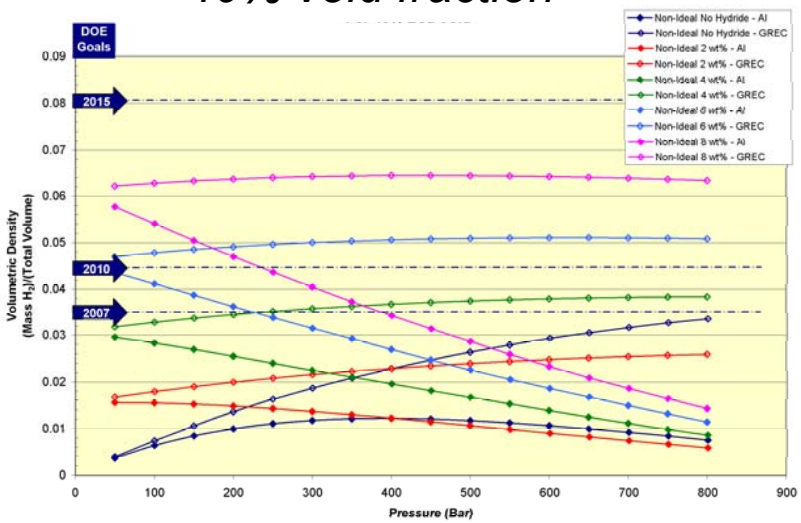
Volumetric Density

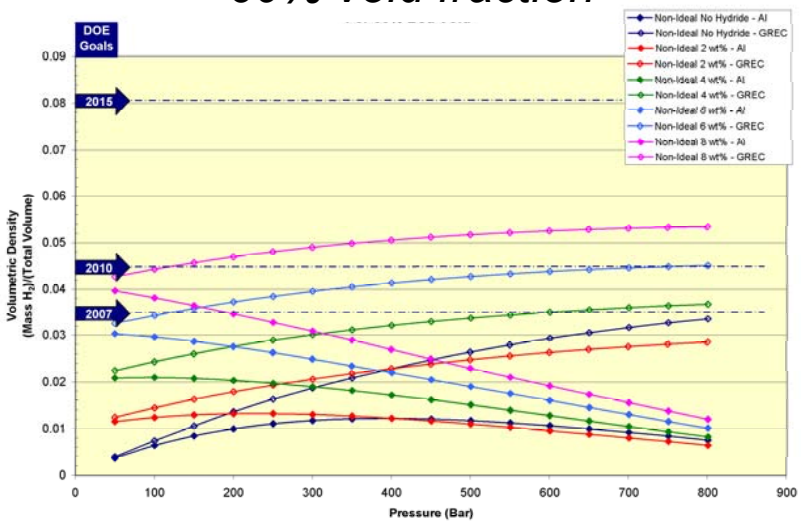
Comparison of Hybrid Tank Gravimetric Density vs Pressure as a function of:

- H_2 wt% media
- Tank materials of construction GREC vs. Aluminum
- Media Void Fraction

40% void fraction



60% void fraction



- ***Volumetric Densities for aluminum tanks are comparable to stainless steel tanks.***
- ***Idealized model of aluminum tanks meet DOE 2010 goals for 8 wt% media having 40% void space at 250 bar operating pressure.***

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Summary

- Demonstrated that graphite composite vessel has superior weight and volume characteristics
- For Graphite Reinforced Epoxy Composite (GREC) vessels containing metal hydride, having void fractions between 40 and 60%, it was found that:
  - Gravimetric H_2 densities depend weakly on the void fraction
  - Volumetric H_2 densities demonstrate stronger dependence on the void fraction
- For composite vessels that contain hydride, the gravimetric and volumetric densities are close to their maximum values over a broad range of pressures
- No hybrid combination analyzed thus far approaches DOE 2015 goals for volumetric density.

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Future Work

- Better identify maxima of gravimetric and volumetric H_2 storage density for graphite reinforced composite vessels
- Consider different fiber and epoxy composite formulations
- Investigate vessel shapes that conform to the body of vehicle and minimize adverse effects on vehicle handling
- Examine structural effects of fixtures that couple the pressure vessel to the vehicle and refueling system
- Consider the durability of the tanks in the event of a credible hypothetical accident

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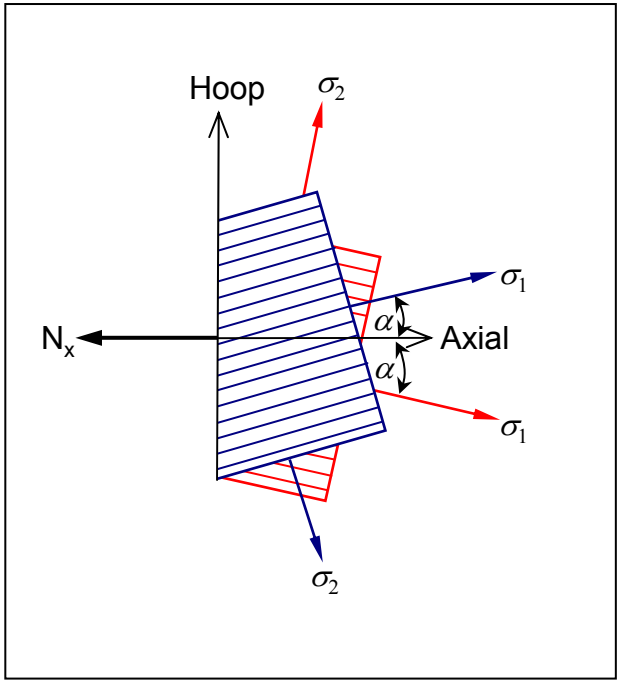
Design Criteria for Graphite Fiber Reinforced Epoxy Composite (GREC) Pressure Vessels



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Discovered Need for Optimization Criterion for Graphite Reinforced Epoxy Composite Pressure Vessels

- Need design criterion for rapid assessment of design prototypes
  - Final design is investigated with more accurate, but expensive, numerical analyses
- Design formulas for steel pressure vessels are given in Section VIII and Section III of the ASME Boiler and Pressure Vessel Code
- Similar codes and standards are not available for composite pressure vessels, only design criterion is in Military Handbook
  - This design formula has two major shortcomings:
    - Stresses are assumed to be carried only by the fibers, the effect of epoxy is not considered
    - Failure criterion is the ultimate tensile strength in fibers. However, a vessel may also fail when the distortion energy reaches the critical value, (the widely used Tsai-Wu failure criterion)

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Basis of Design Criterion

- Developed improved design criterion for GREC Pressure Vessels
  - Which determines optimum fiber winding angle and vessel wall thickness based on:
    - Effects of both the fibers and the epoxy on the determination of the optimized fiber winding angle
    - Three failure criteria:
      - The maximum tensile strength of fiber
      - The maximum tensile strength of epoxy
      - The maximum distortion energy

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Design Criterion

- ***Expressions for the winding angle and wall thickness were obtained from the laminate force equations in global coordinates.***
- ***The expression for the stress reduction factor was obtained from the Tsai-Wu failure criterion for composite materials & the laminate force equations.***

Optimum Winding Angle, θ

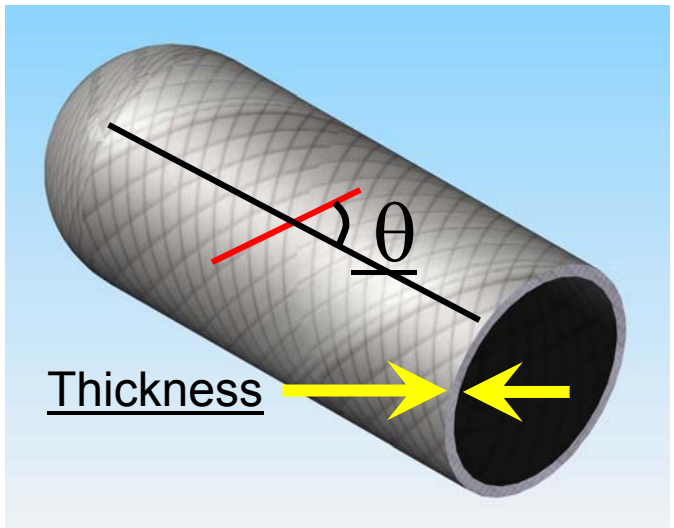
$$\tan^2\theta = \frac{2\sigma_1^T - \sigma_2^T}{\sigma_1^T - 2\sigma_2^T}$$

Wall Thickness, t

$$t = \frac{pr}{2\alpha\left(\sigma_1^T \cos^2\theta + \sigma_2^T \sin^2\theta\right)}$$

Stress Reduction Factor, α

$$\left(2 + \frac{\sigma_1^T}{\sigma_1^C} + \frac{\sigma_2^T}{\sigma_2^C}\right)\alpha - \left[\frac{\sigma_1^T}{\sigma_1^C} + \frac{\sigma_2^T}{\sigma_2^C} + \sqrt{\left(\frac{\sigma_1^T}{\sigma_1^C}\right)\left(\frac{\sigma_2^T}{\sigma_2^C}\right)}\right]\alpha^2 = 1$$



Cut-Away Sketch of Filament-Wound Hydrogen Storage Vessel

Design criterion used to calculate GREC pressure vessel wall thickness and volume is in the form of equations that give the optimum winding angle and wall thickness

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Future Work

- Compare design criterion to detailed structural model
- Application to other design concepts for hybrid storage tanks composed of graphite reinforced composite material
- Incorporate into ASME Boiler and Pressure Vessel Code

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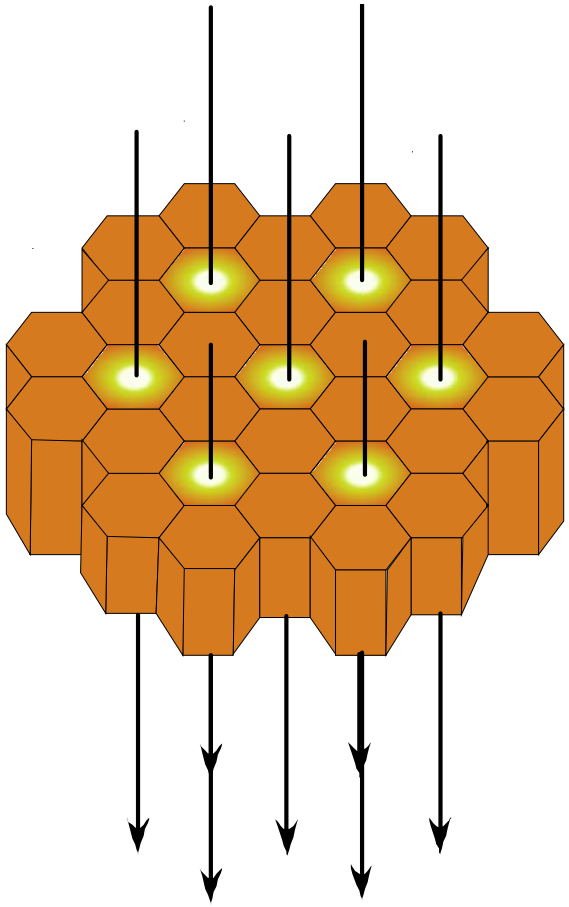
Advanced Heat Exchange Systems



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Approach

- Develop mathematical model that couples:
  - Heat transfer via conduction and convection
  - Temperature dependent chemical reaction kinetics
  - Rate of heat generation due to hydride formation
  - Hydrodynamics for H_2 and coolant flow
- Identify advanced concepts for heat removal from bed during H_2 uptake
  - Must balance hydride particle size requirements for rapid kinetics and bed flow resistance
  - Ensure sufficient heat transfer rates to control temperature dependent reaction kinetics
- Use model to assess integrated operational characteristics

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Equations for Bed Model

Mass action equations

$$\underbrace{NaAlH_4}_{\text{Species1}} \underbrace{\leftrightarrow}_{\text{Reaction1}} \underbrace{\frac{1}{3}Na_3AlH_6}_{\text{Species2}} + \frac{2}{3}Al + H_2 \underbrace{\leftrightarrow}_{\text{Reaction2}} \underbrace{NaH}_{\text{Species3}} + Al + \frac{3}{2}H_2$$

Backward and forward rate equations

$$r_{1a} = k_{1a}C_2\left(\frac{P - P_{eq_1}}{P_0}\right)\exp\left[-\frac{E_{1a}}{RT}\right] = \left.\frac{\partial C_{NaAlH_4}}{\partial t}\right|_{H_2\ \text{absorption}}$$

$$r_{1d} = k_{1d}C_1\left(\frac{P_{eq_1} - P}{P_0}\right)\exp\left[-\frac{E_{1d}}{RT}\right] = \left.\frac{\partial C_{NaAlH_4}}{\partial t}\right|_{H_2\ \text{desorption}}$$

$$r_{2a} = k_{2a}C_3\left(\frac{P - P_{eq_2}}{P_0}\right)\exp\left[-\frac{E_{2a}}{RT}\right] = \left.\frac{\partial C_{NaH}}{\partial t}\right|_{H_2\ \text{absorption}}$$

$$r_{2d} = k_{2d}C_2\left(\frac{P_{eq_2} - P}{P_0}\right)\exp\left[-\frac{E_{2d}}{RT}\right] = \left.\frac{\partial C_{NaH}}{\partial t}\right|_{H_2\ \text{desorption}}$$

The net rates of formation of species 1-3 are

$$\frac{\partial C_1}{\partial t} = r_{1a} - r_{1d}$$

$$\frac{\partial C_3}{\partial t} = 3(r_{2d} - r_{2a})$$

$$\frac{\partial C_2}{\partial t} = (r_{2a} - r_{2d}) + \frac{1}{3}(r_{1d} - r_{1a})$$

Equilibrium hydrogen pressures are given by the van't Hoff equation as

$$P_{eq_1} = P_0 \exp\left[\frac{\Delta H_1}{RT} + \frac{\Delta S_1}{R}\right]$$

$$P_{eq_2} = P_0 \exp\left[\frac{\Delta H_2}{RT} + \frac{\Delta S_2}{R}\right]$$

The heat conduction equation is

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = -\nabla^2 T + \frac{\partial C_1}{\partial t}\Delta H_1 - \frac{1}{2}\frac{\partial C_3}{\partial t}\Delta H_2$$

Idealized chemical kinetics used to date. Actual chemical kinetics developed by UTRC for catalyzed $NaAlH_4$ to be implemented 1st Q FY'07

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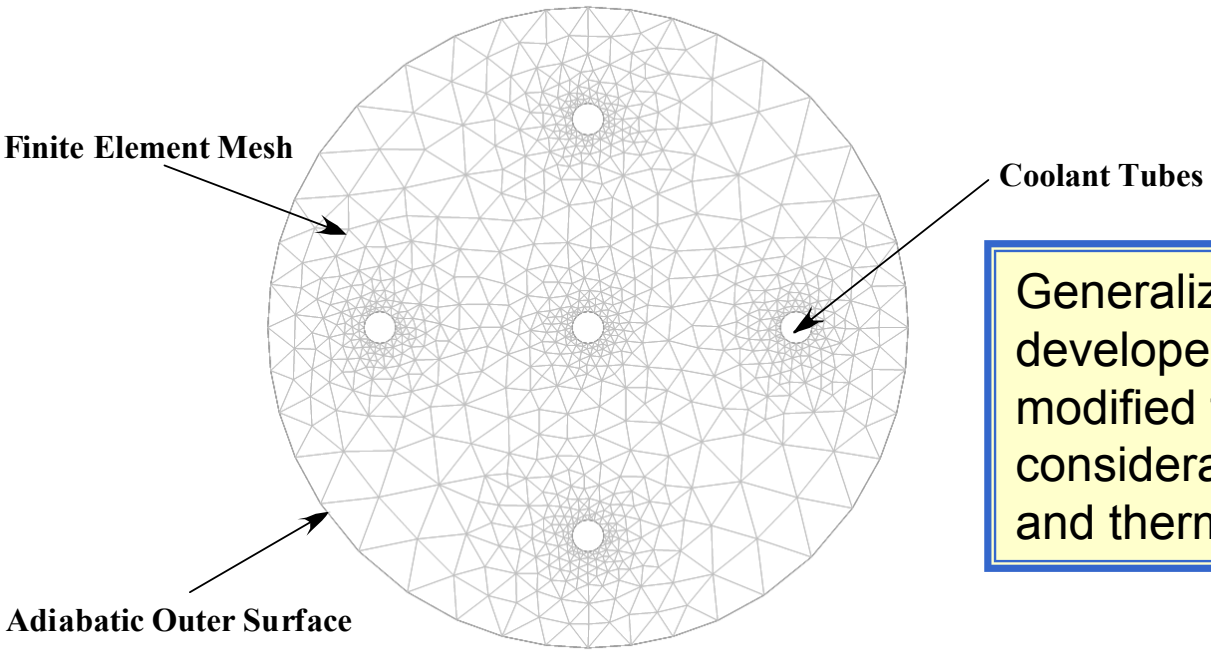
Parameters and Geometry for Shell & Tube Model



Generalized FEM model developed which can be modified to take into consideration any geometry and thermal properties.

Bed Diameter 16 in
Coolant Tube Diameter 0.8 in
Initial Bed Temperature 27°C
Coolant Temperature 27°C
Convection Heat Transfer Coefficient 100W/m^2°C
Bed Thermal Conductivity 10W/m°C

Initial Concentrations:

$NaAlH_4$ = 0 mol/m^3
Na_3ALH_6 = 0 mol/m^3
NaH = 25 mol/m^3

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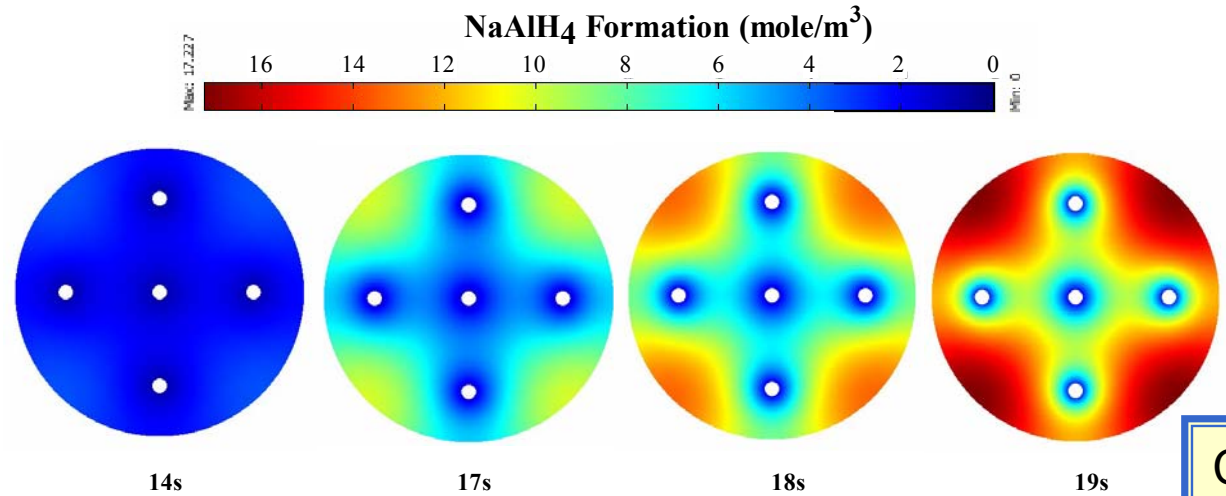
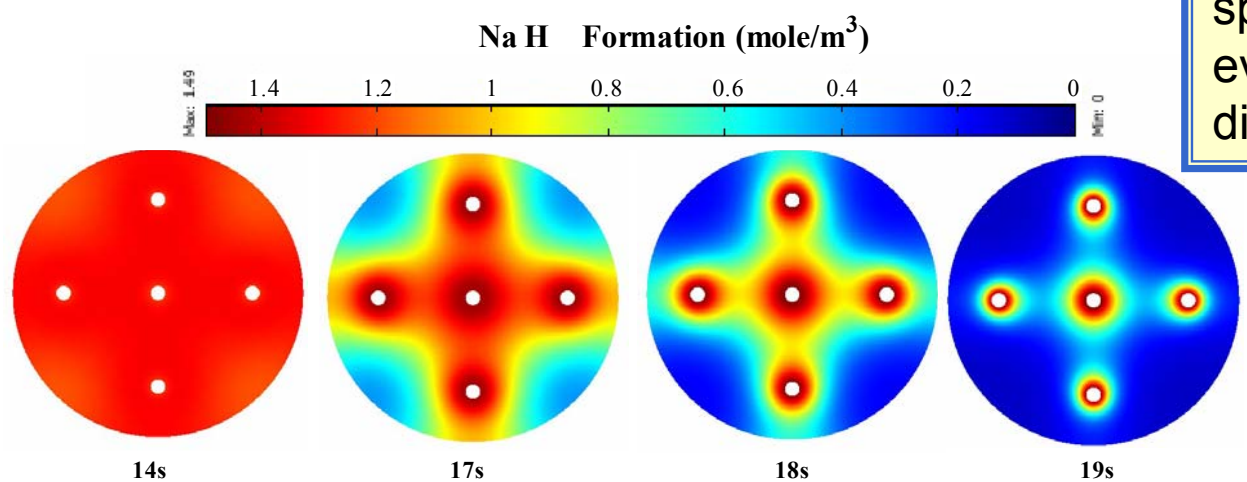
Rate of Hydride Formation





Chemical composition spatially and temporally evaluated in two dimensional FEM model.

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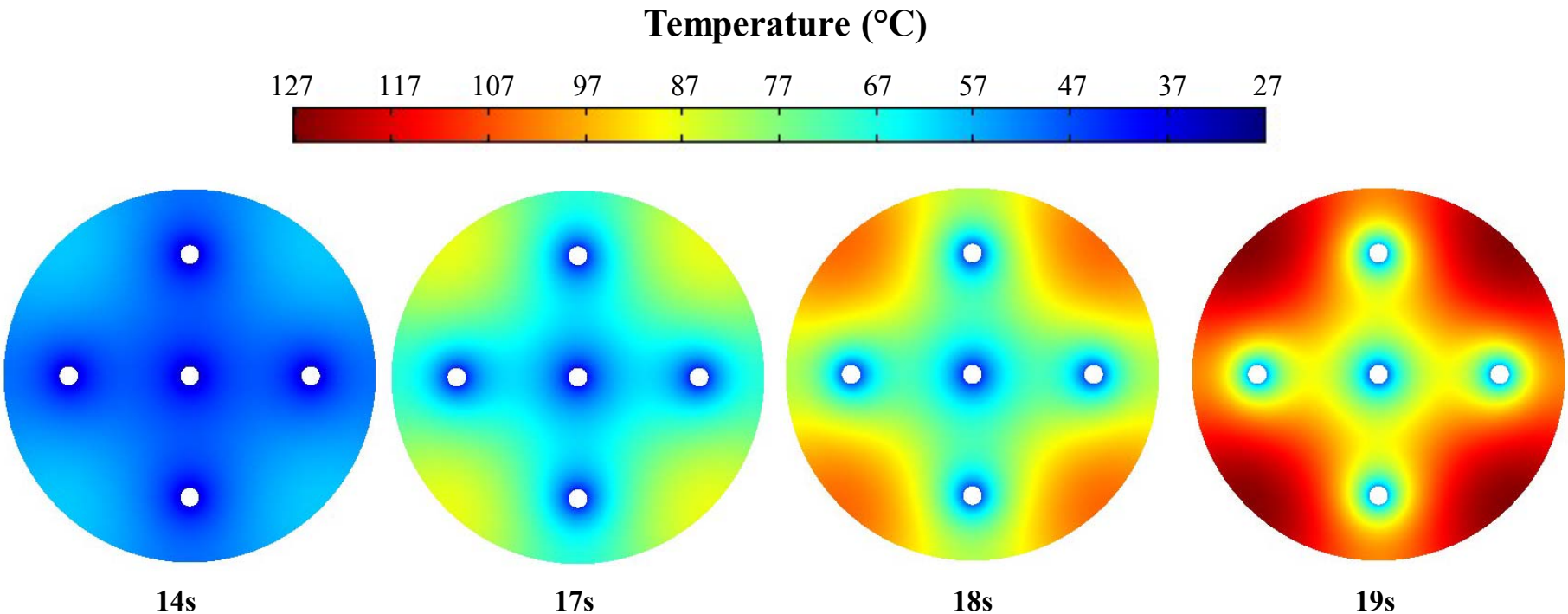
Transient Temperatures



- Thermal distribution spatially and temporally evaluated in two dimensional FEM model.
- Work needs to be extended from convention shell/tube to permeation cooling which will eliminate coolant and tubes.

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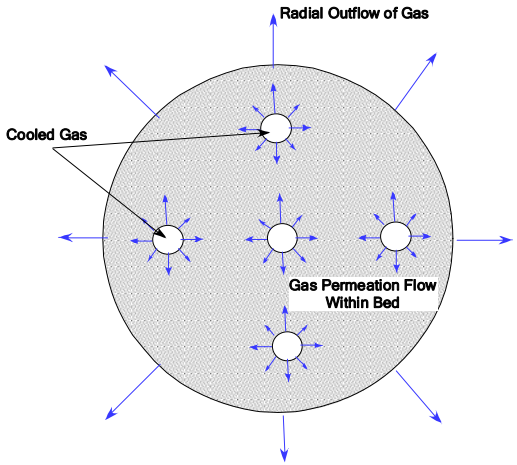
Advanced Cooling Design Concepts

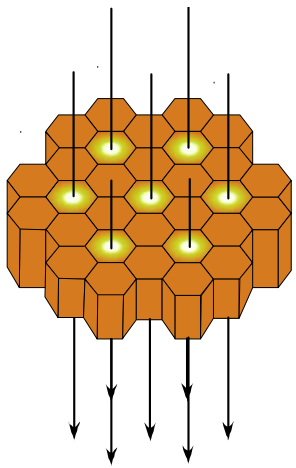
Prior Work

- Shell and tube with metal foam
- Shell and tube with fins

Advanced Methods for Heat Removal

- Permeation cooling
  - Uses H_2 and/or carrier gas to cool bed during refueling
- Microchannel heat exchanger
  - Acts as structured foam
- Modified hydride particles
  - Control size to balance flow, heat and mass transfer
  - Alloy with thermally conductive metal
- Two-phase cooling
  - Used in conjunction with systems above





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Future Work

- Acquire necessary data for the models
  - Constitutive properties of bed
  - Hydride particle sizes, total void fraction
  - Kinetics data
  - Heat transfer correlation data
- Apply model to conceptual cooling systems
  - Implement model equations numerically
    - Develop specific models each system
  - Identify ability to meet the DOE 2010 and 2015 goals for recharging the bed
  - Use model to optimize acceptable candidate systems

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