Computational Materials Techniques for Thermal Protection Solutions: *Materials and Process Design*

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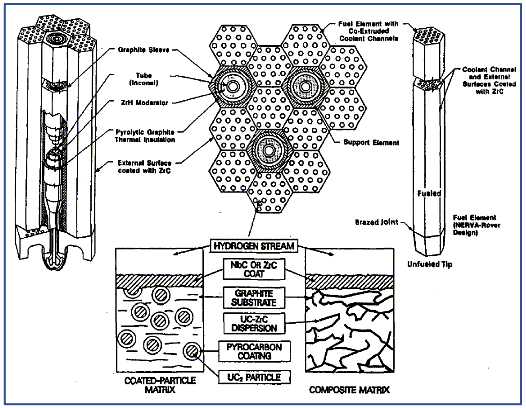

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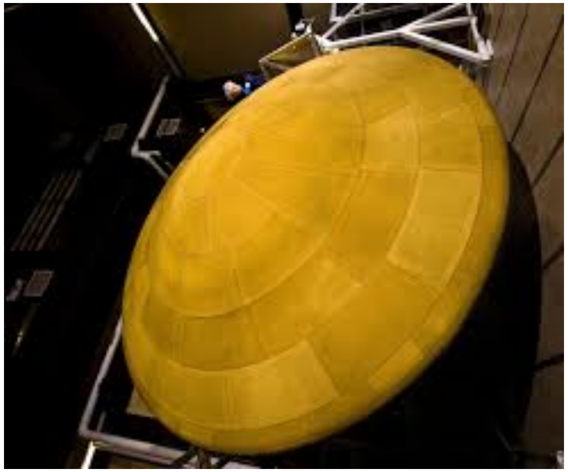
Thermal Protection Materials Branch

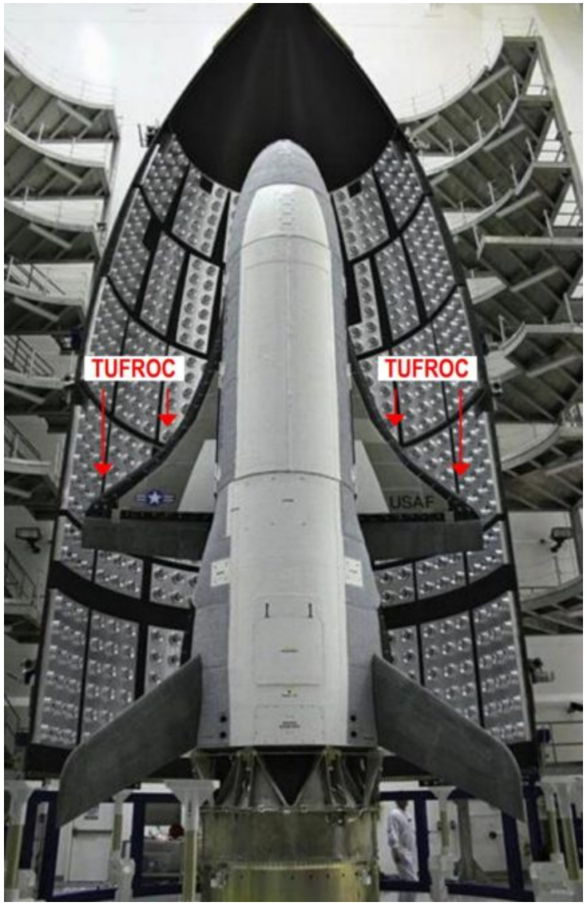
Ablative Heat Shield Composites



PICA

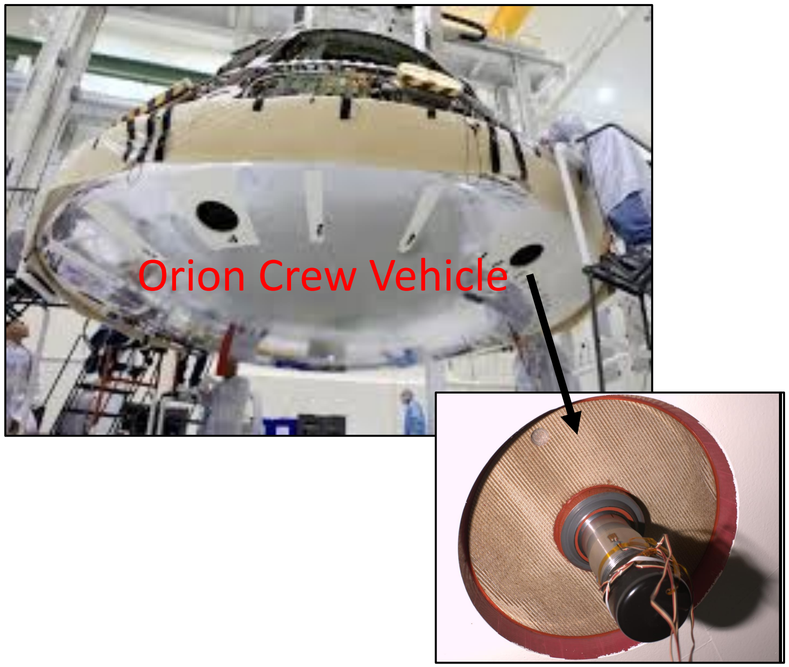
HEEET

Reusable Thermal Protection Coatings

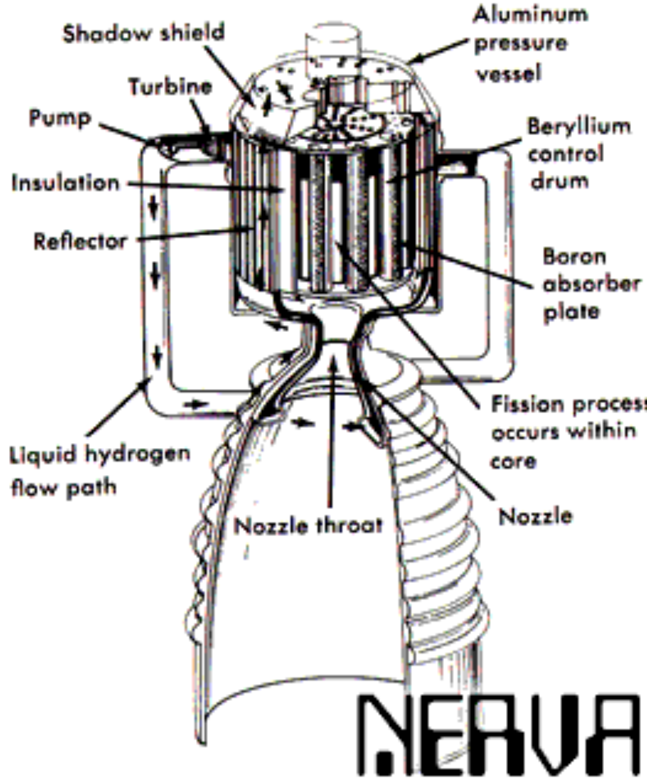


TUFROC (X-37B)

Computational Materials Applications



Compression Pad

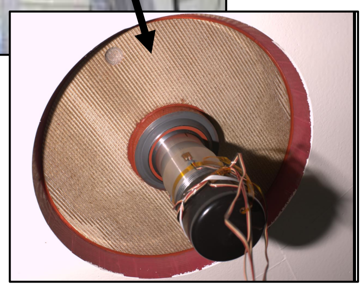


Void Mitigation in Compression Pad Material

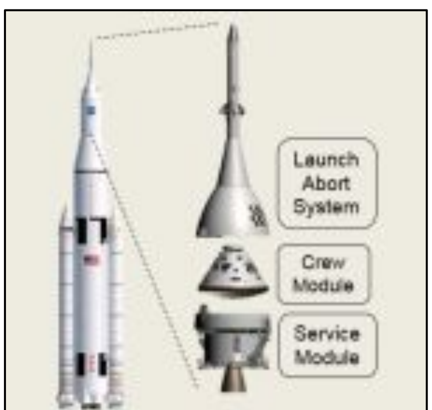
Material Selection for Nuclear Thermal Propulsion

Void Mitigation in Compression Pad Material

Collaborators: Jay Feldman and Peter Gage (NASA ARC)



Compression Pad



Compression Pads – serves as a structural and ablative TPS/separates crew module from the service module

Properties – must withstand mechanical loading during transit and thermal loading during entry

3D-MAT – Three-Dimensional Multi-Functional Ablative Thermal Protection System (woven silica preform infused with resin)

Challenge – void formation during processing (resin curing)

Manufacturing/Integration Process

3D, Woven Quartz Fiber Preform

Resin Infusion

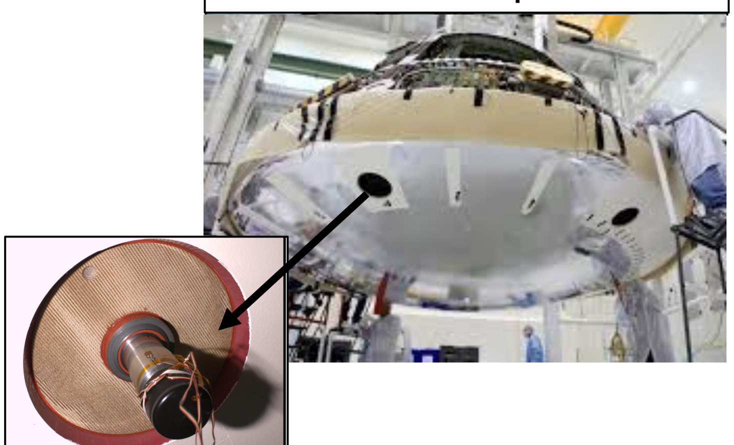
3D Composite Billet

Final Machining

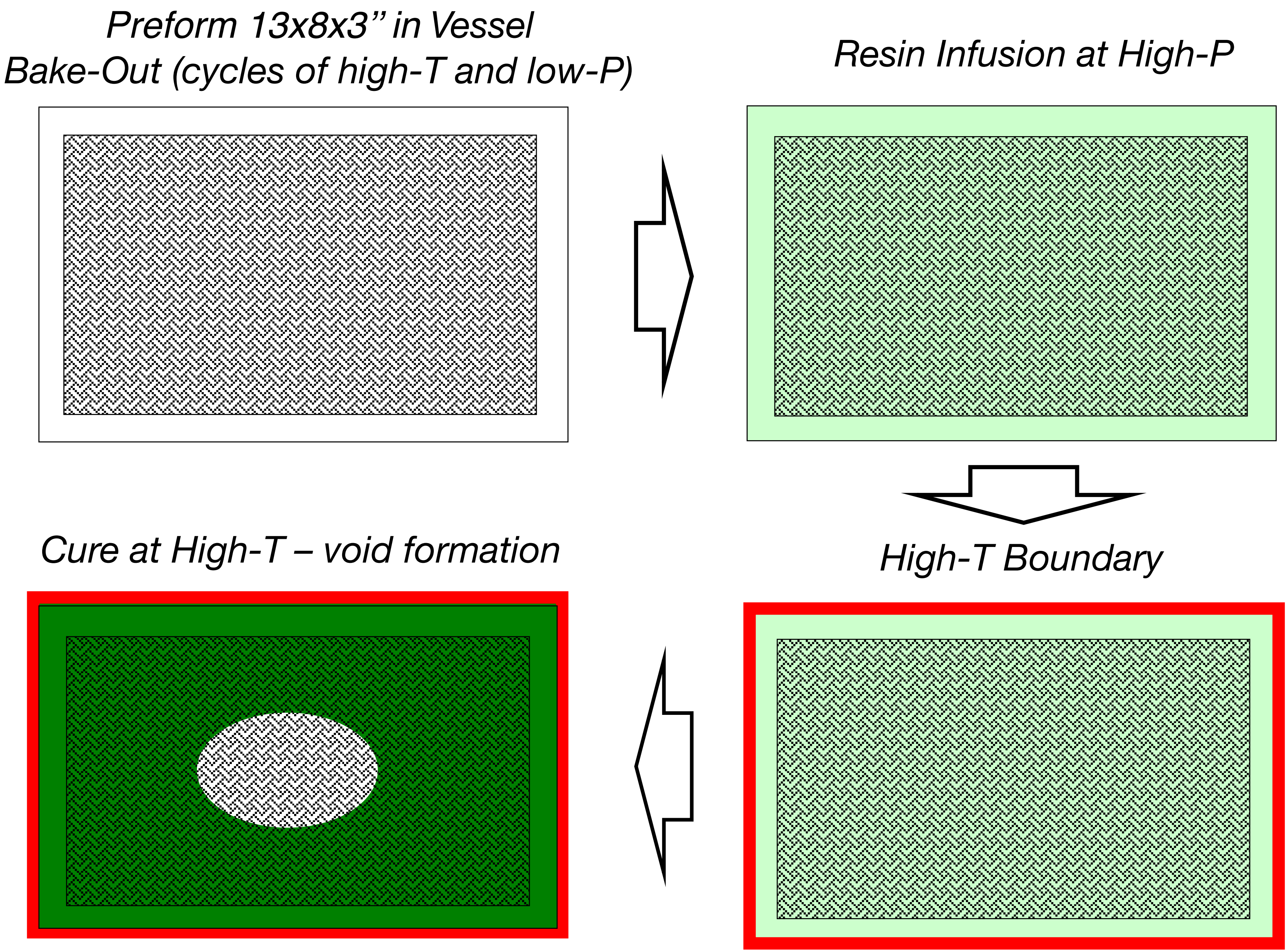
Compression Pad

Incorporation into Heat Shield

Heat Shield with Compression Pads



Manufacturing Process



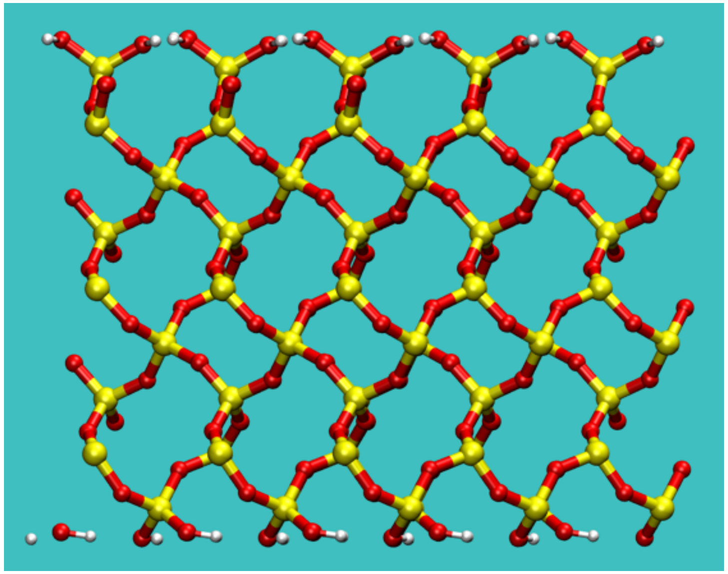
Proposed Void Formation Mechanisms

Gas Adsorption – gaseous species adsorbed on surface and driven to center during infusion and cure

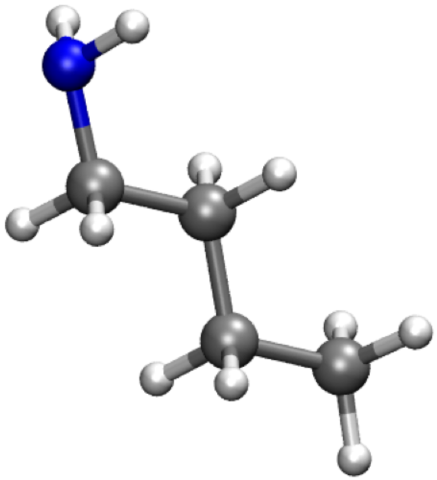
Cure Shrinkage – shrinkage of the resin during the curing reaction

Gas Adsorption: Likely Species?

Silica Fiber



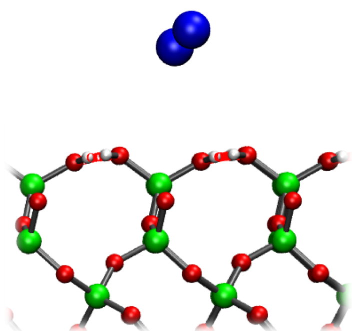
Aminosilane



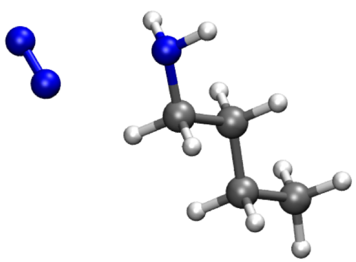
Atomistic models of silica fiber and aminosilane coatings

Gas Adsorption: Likely Species?

Nitrogen

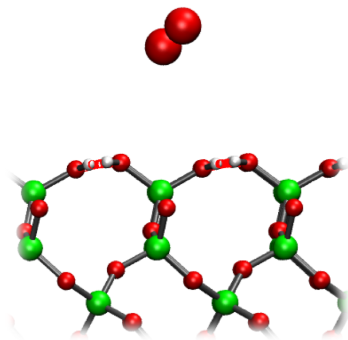


ΔE = -1.3 kJ/mol

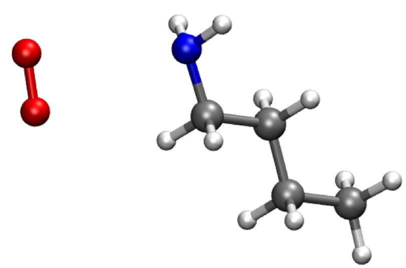


ΔE = -1.3 kJ/mol

Oxygen

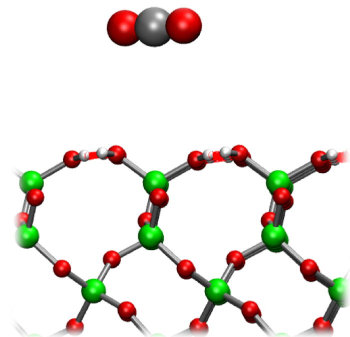


ΔE = -2.2 kJ/mol

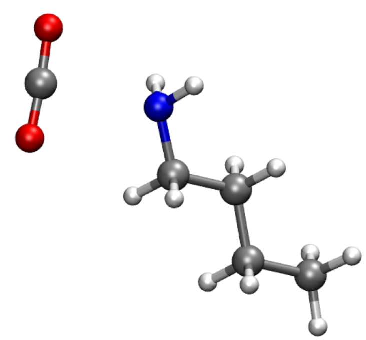


ΔE = -0.9 kJ/mol

Carbon Dioxide

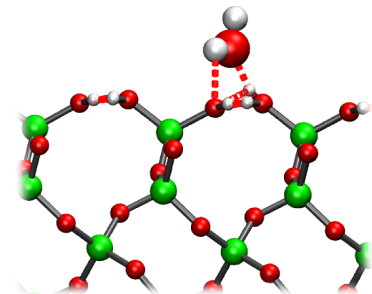


ΔE = -1.1 kJ/mol

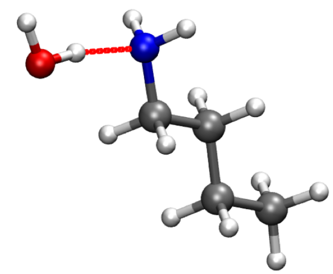


ΔE = -11.3 kJ/mol

Water

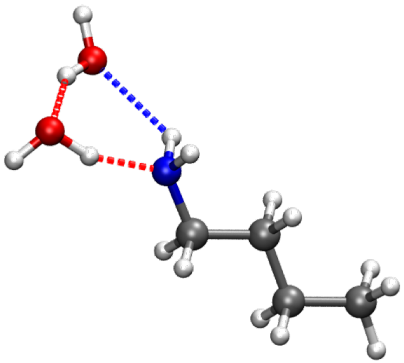


ΔE = -15.6 kJ/mol

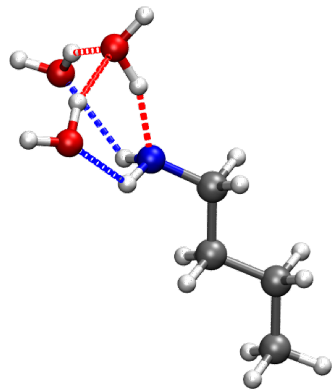


ΔE = -33.7 kJ/mol

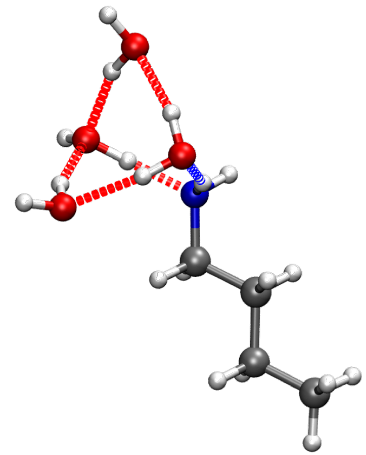
Gas Adsorption: Likely Species?



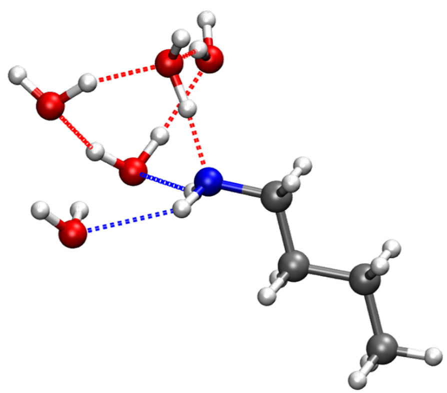
ΔE = -37.5 kJ/mol



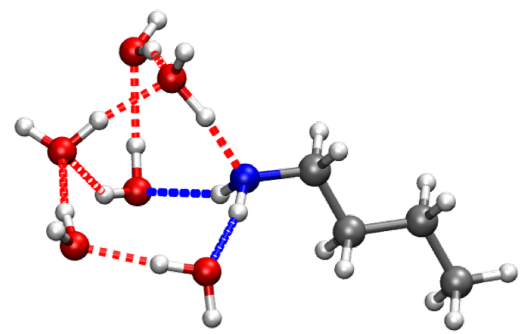
ΔE = -34.8 kJ/mol



ΔE = -39.9 kJ/mol



ΔE = -36.2 kJ/mol

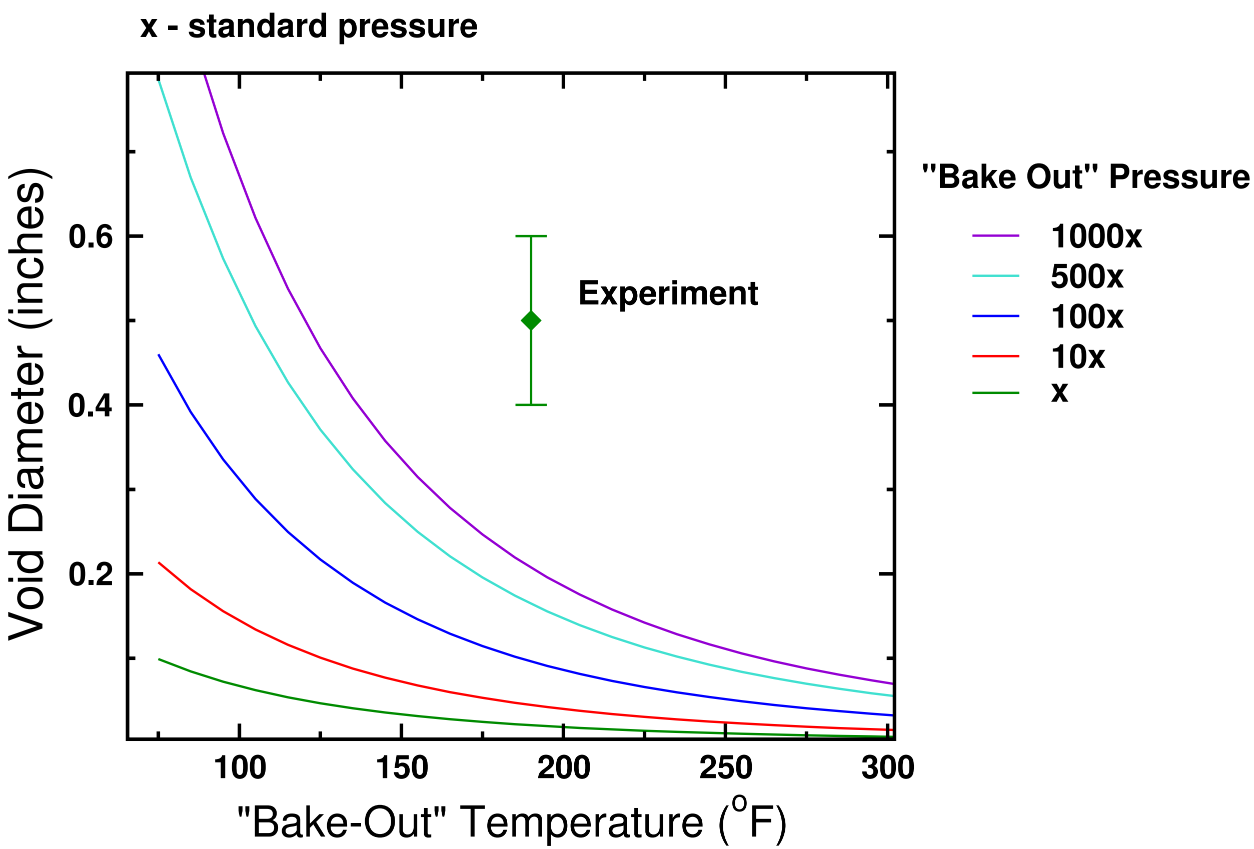


ΔE = -40.2 kJ/mol

Water strongly adsorbs to the aminosilane coating

Gas Adsorption: Gas Quantity?

Lines - BET Adsorption Theory Computations



Significant moisture exists, but not enough to account for voids

Cure Shrinkage

Heat equation

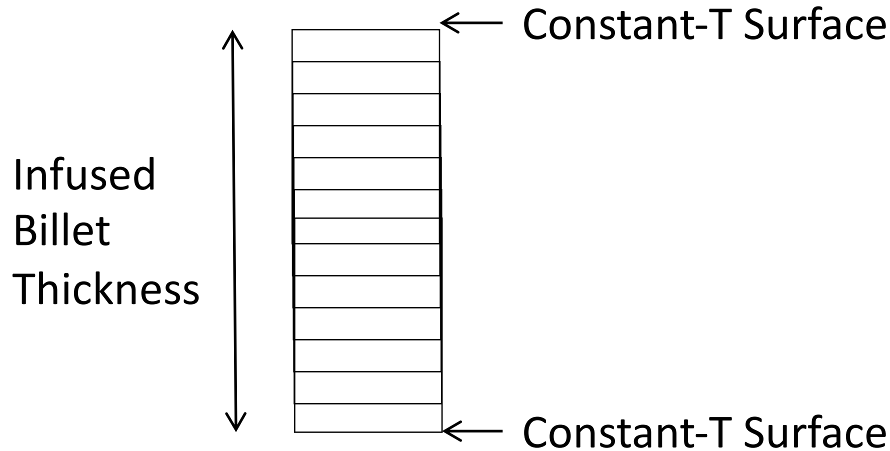
$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2}$$

First order conversion kinetics

$$\frac{\partial a}{\partial t} = Ka$$

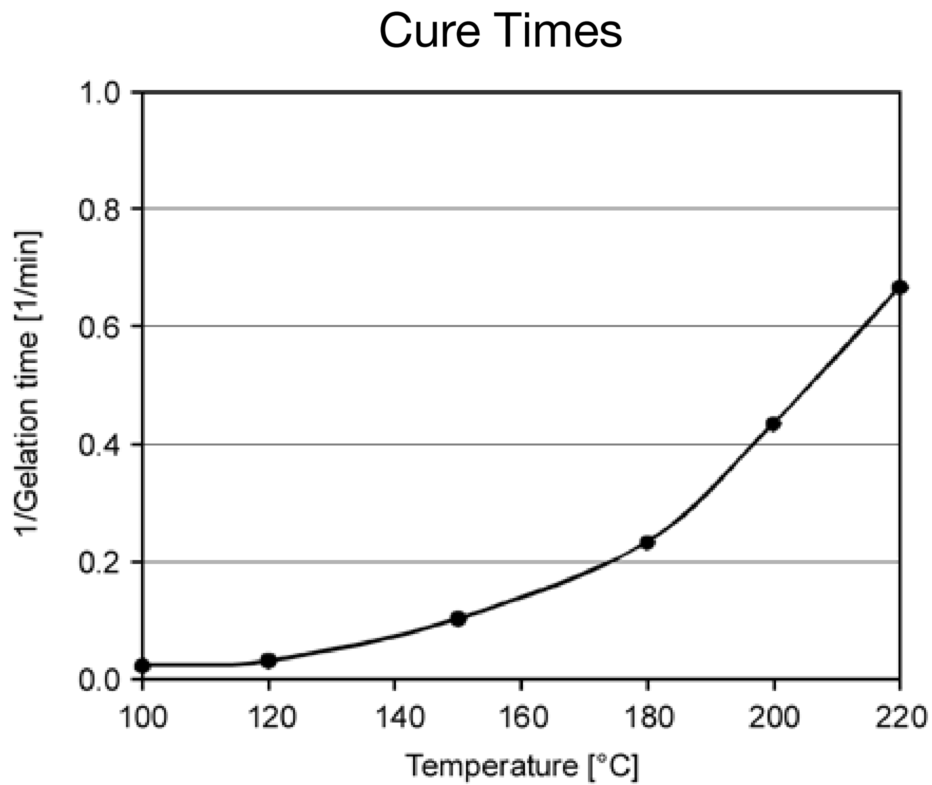
Gradient formula

$$\frac{\partial^2 T}{\partial z^2} = \frac{T_{i-1} - 2T_i - T_{i+1}}{dz^2}$$



1-D finite volume model of heating and cure

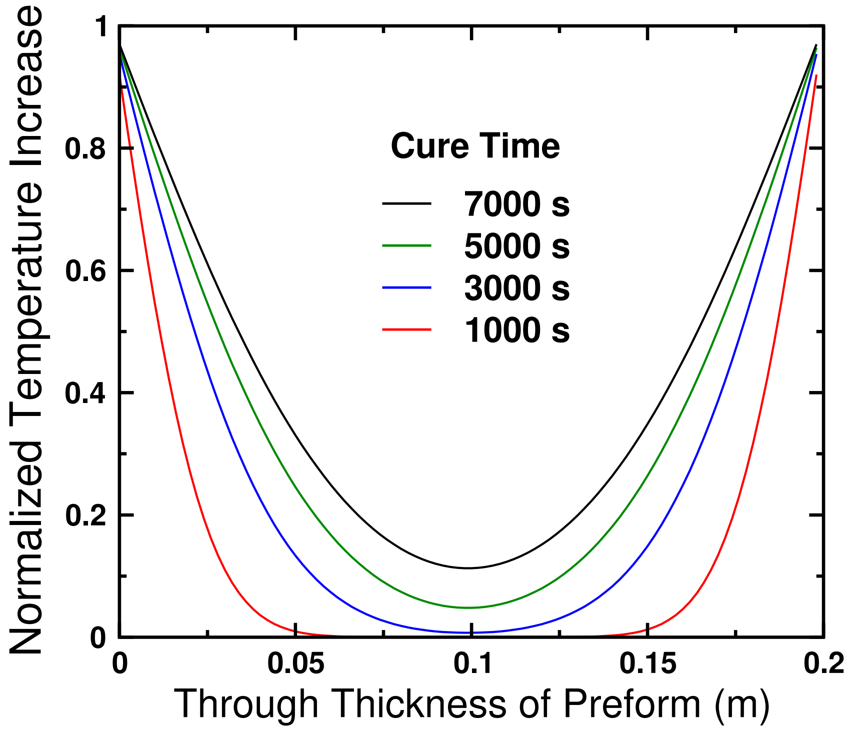
Experimental Cure Data

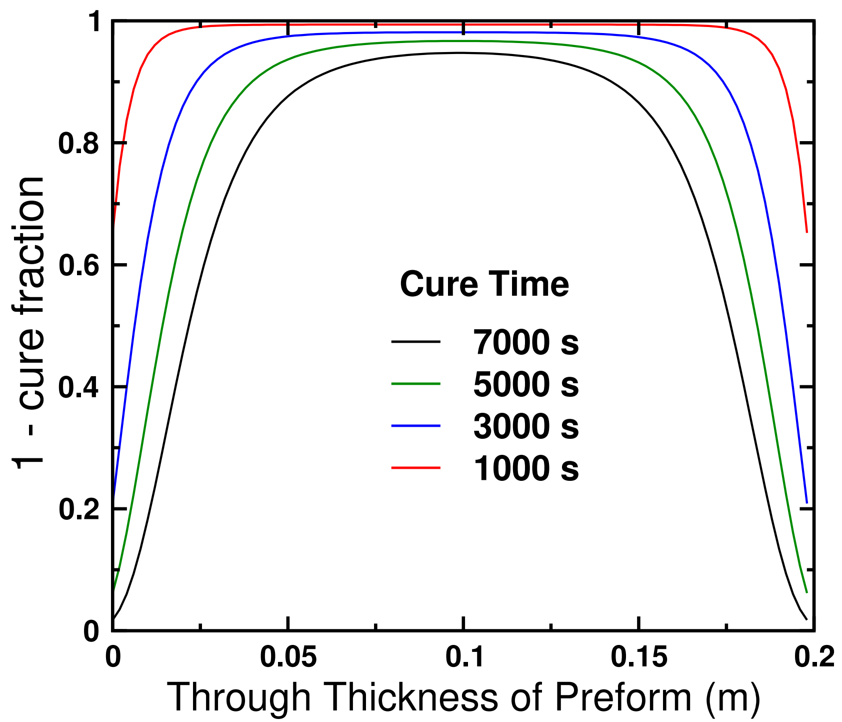


Reaction kinetics parameterized from curing experiments for cyanate ester - Gelation is 60 % conversion (BADcy)

Temperature and Cure Profiles

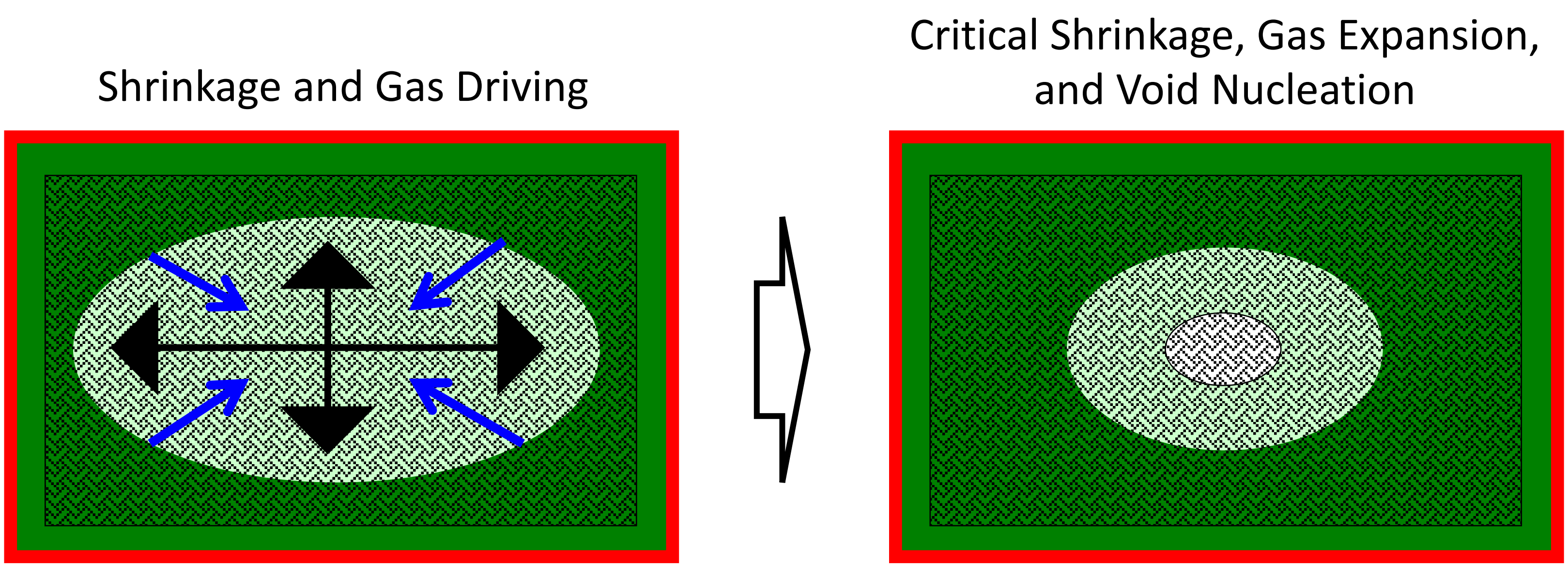
0.2 m inch thick preform; elevated temperature cure

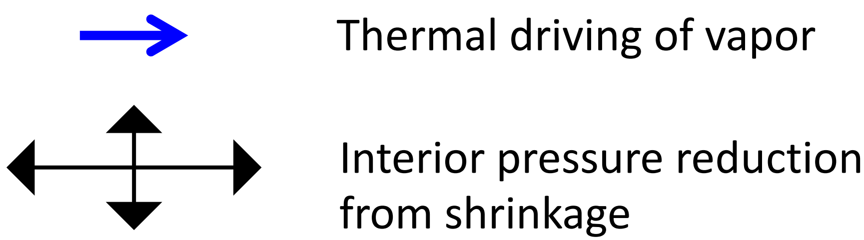




Cure is heterogeneous with the boundaries reaching the gel point first

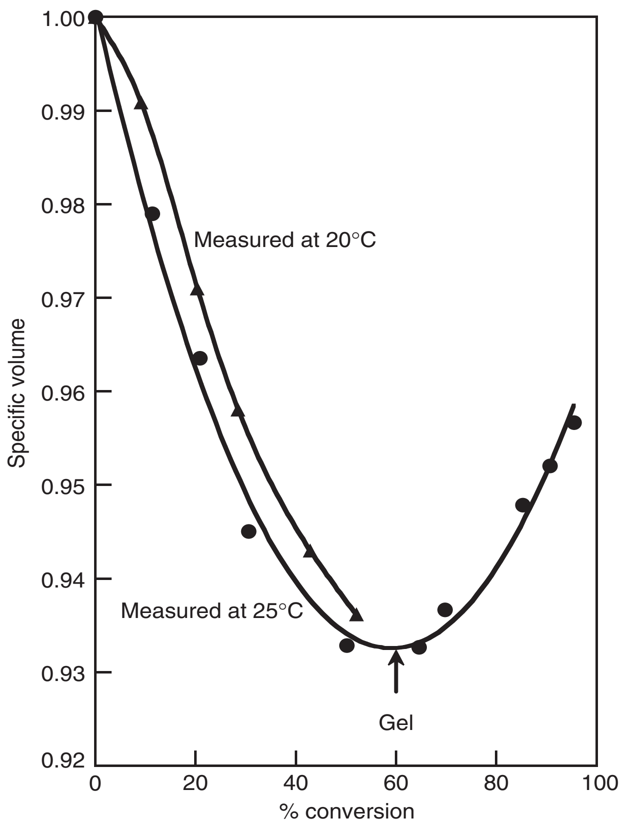
Refined Picture of Void Formation





Cooperative effect of gas adsorption and shrinkage

Cure Shrinkage Profile



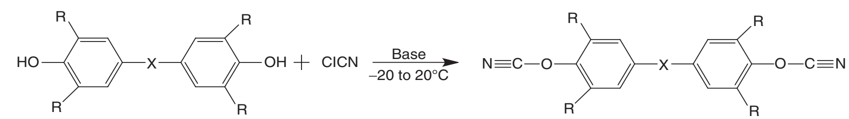
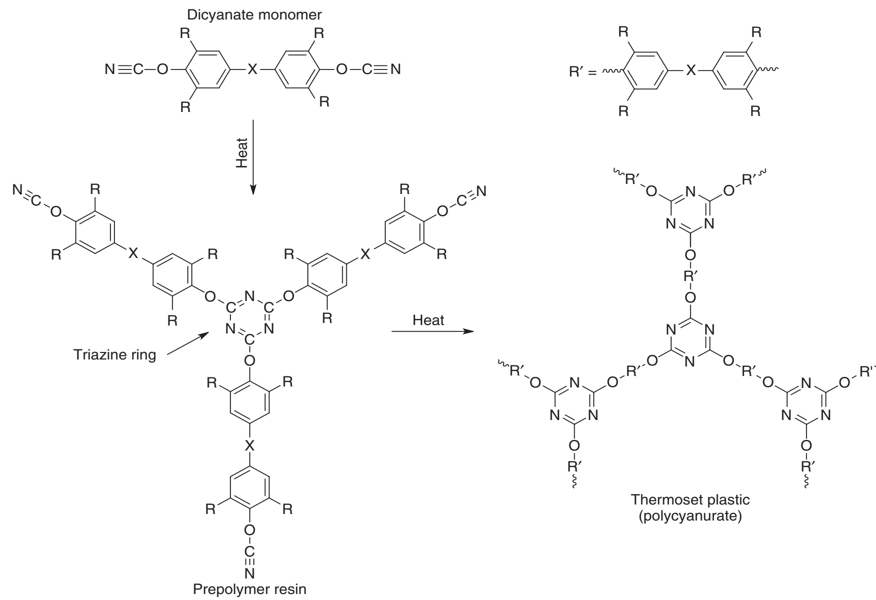
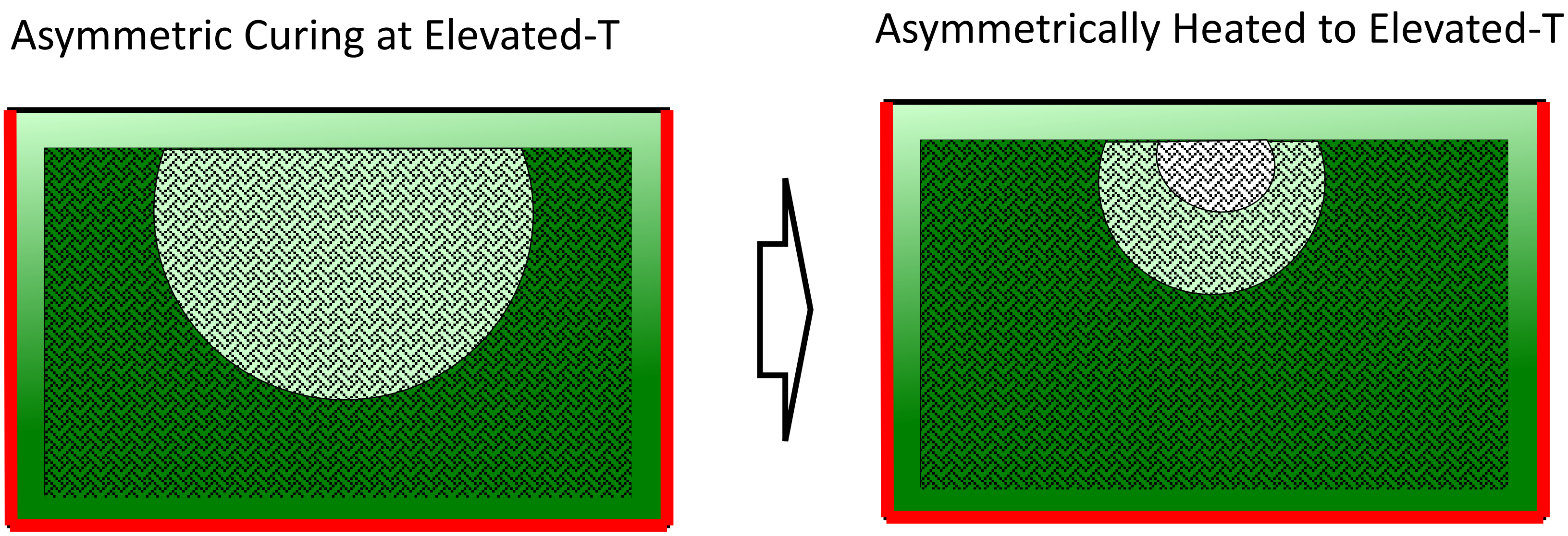


Figure 2. General reaction scheme for monomer synthesis.



Expected cure shrinkage leads to void diameters of 0.5-1.4 inches across potential cure conditions

Void Mitigation: Cure Conditions



Asymmetric curing will mitigate:

- temperature gradient driving of gas to center
- decrease in pressure at the center

Summary

- Water is problematic species on silica/aminosilane
- Symmetric curing can drive gas to center of billet, reduce pressure, and lead to void nucleation
- Asymmetric curing a possible route to void mitigation

Material Selection for Nuclear Thermal Propulsion (NTP)

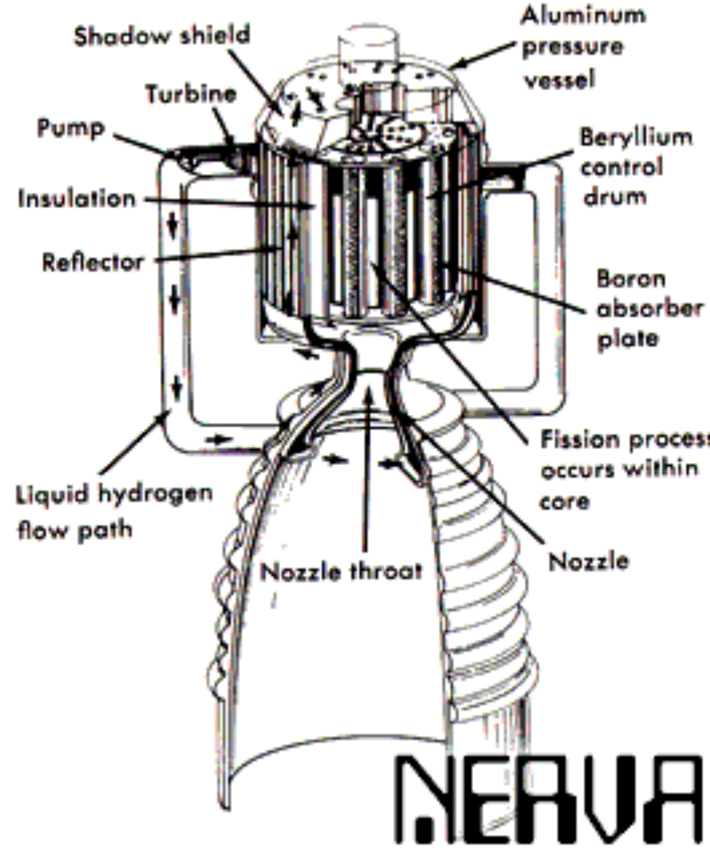
Collaborators: Charles Bauschlicher, Piyas Chowdhury, BJ Tucker (NASA ARC); Dean Cheikh (JPL); Kelsa Benensky (MSFC)

Mechanism – heat hydrogen and exhaust it through a nozzle for propulsion

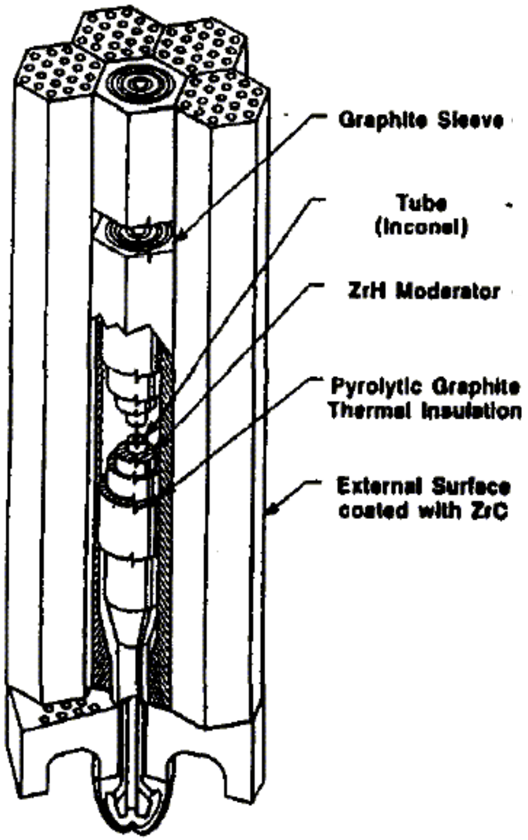
Heat Source – nuclear fission reaction in solid fuel reactor core heats hydrogen

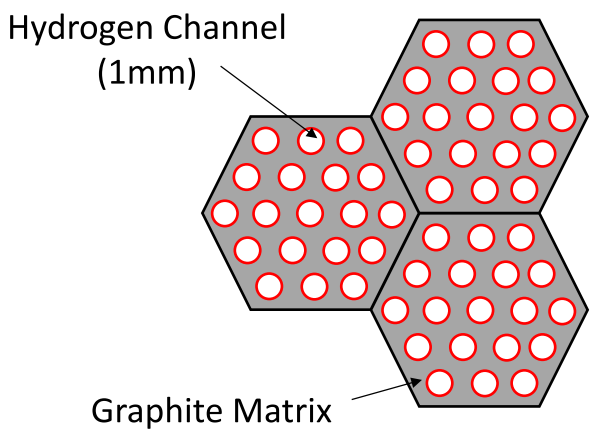
Benefits – I_{sp}~900 s to halve time to Mars

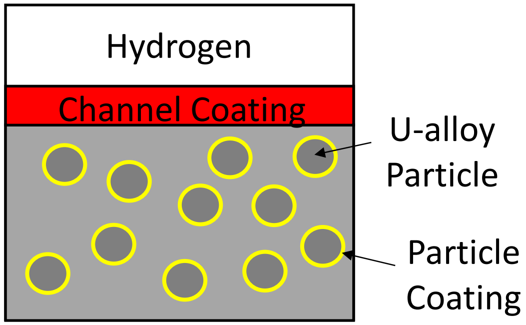
NERVA – last substantial tests of NTP ended in early 70s



Reactor Core



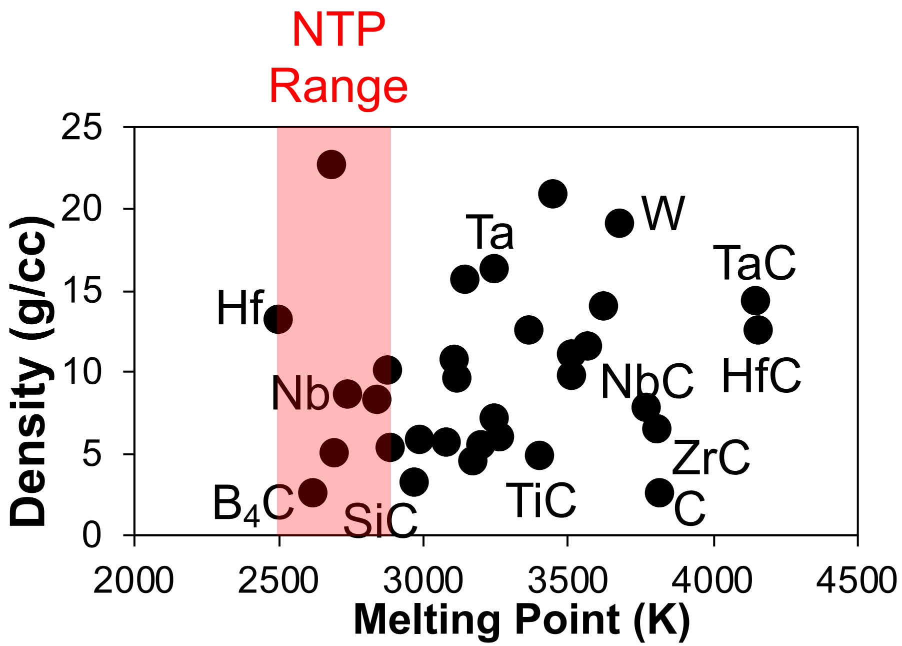


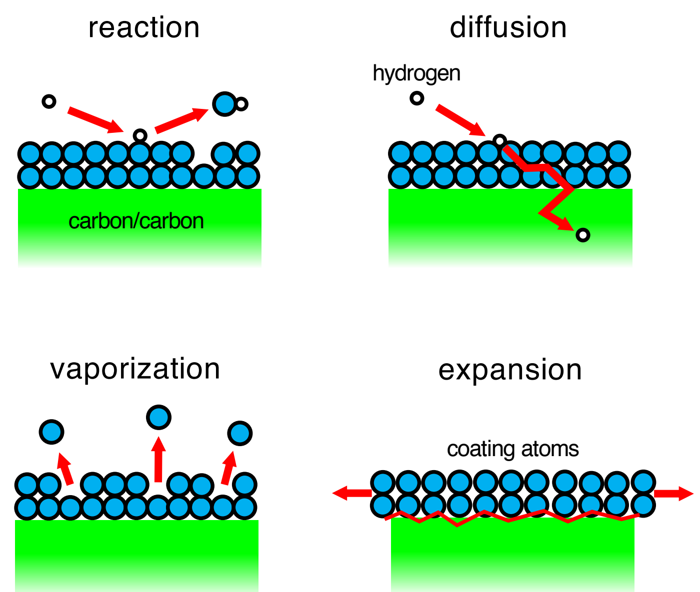


Challenging to find coatings for propellant channels that withstand 2800 K in hot hydrogen for multiple hours

Materials for NTP/STP

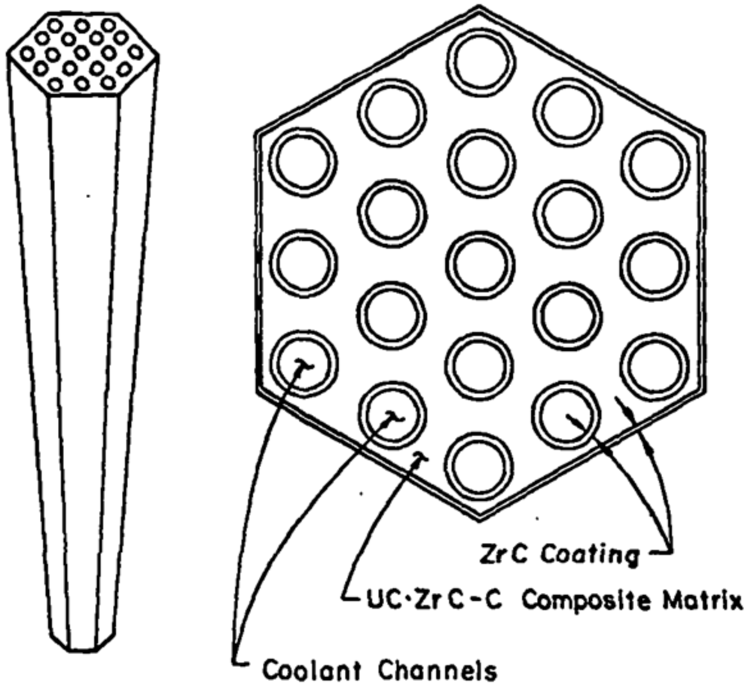
- Coatings must be sized to not react and ablate to failure
- Coatings should restrict hydrogen diffusion to the carbon substrate
- Coatings should be mechanically stable on the carbon substrate



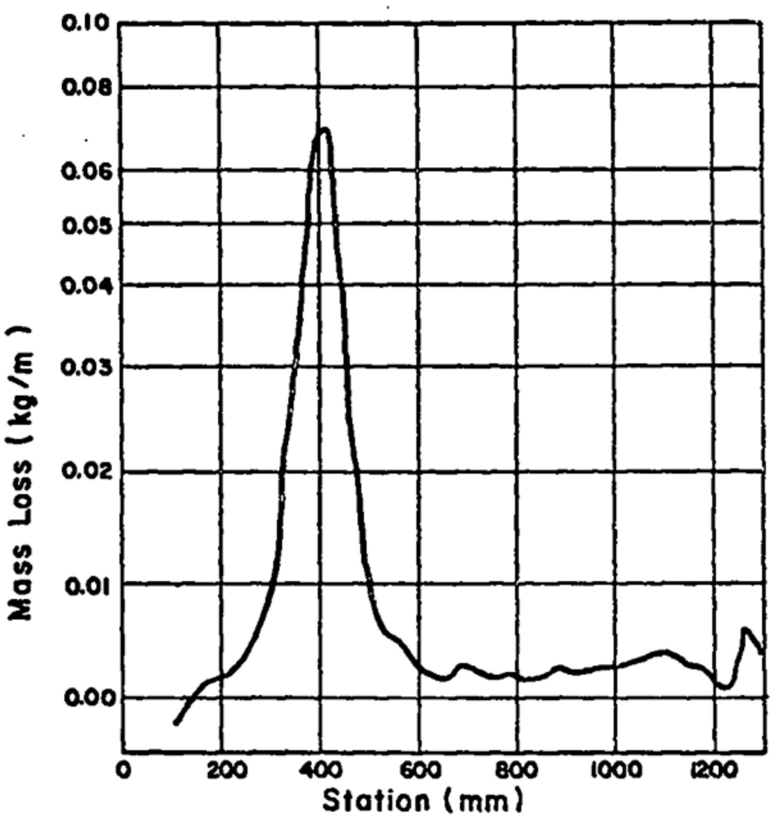


Mid-Range Corrosion

Cold H_2 – Station 0 m

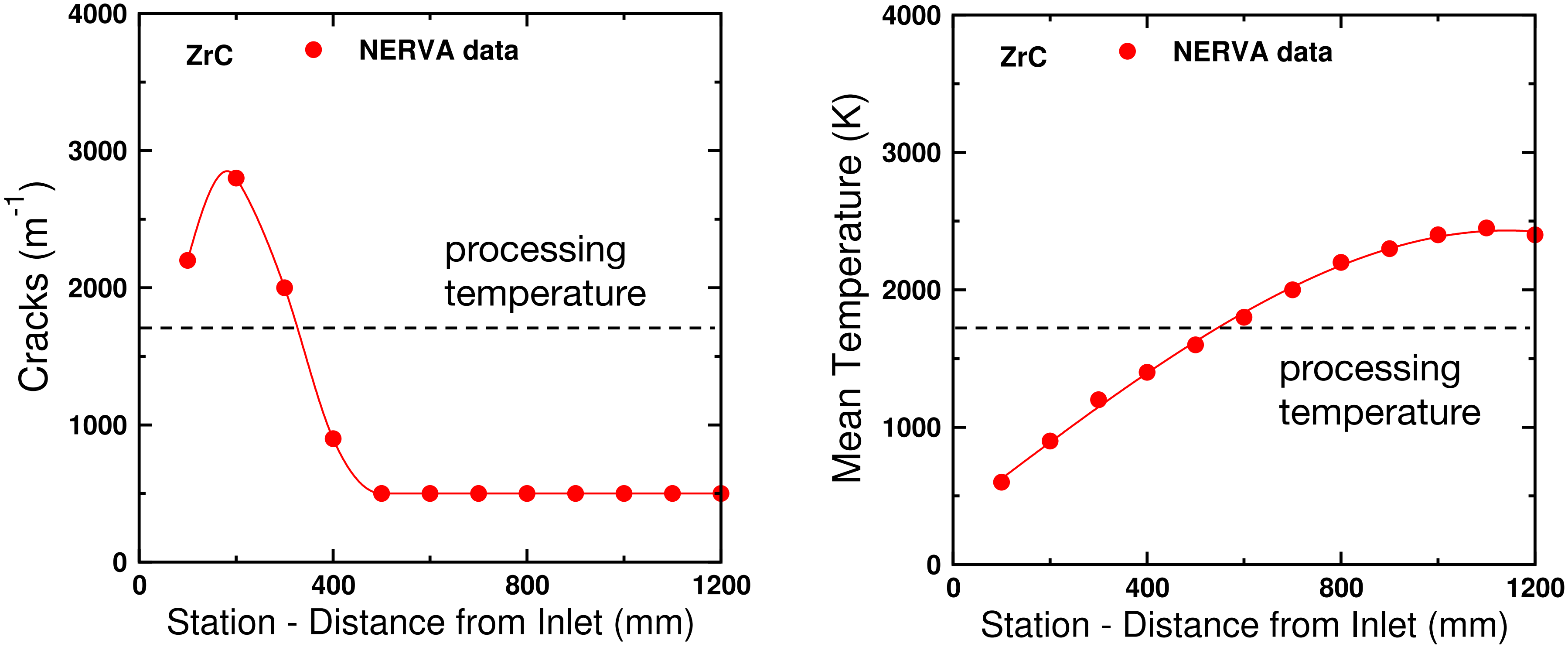


Hot H_2 – Station 1.4 m



Unresolved issues related to non-uniform corrosion of the coatings through the hydrogen channels

Mid-Range Corrosion



Damage dramatically reduced when temperature is above the processing temperature

Initial Approach to Estimate Mass Loss

Key Reaction at Surface:

Reactants	Products	Free Energy (2500 K)
$ZrC(s) + 2H_2$	$Zr(s) + CH_4$	1.96 eV

$$\Delta G_{c,s\rightarrow g} = \Delta E_{c,s\rightarrow g} - TS_g + P_g V_g$$

- Make an equilibrium assumption for surface reaction

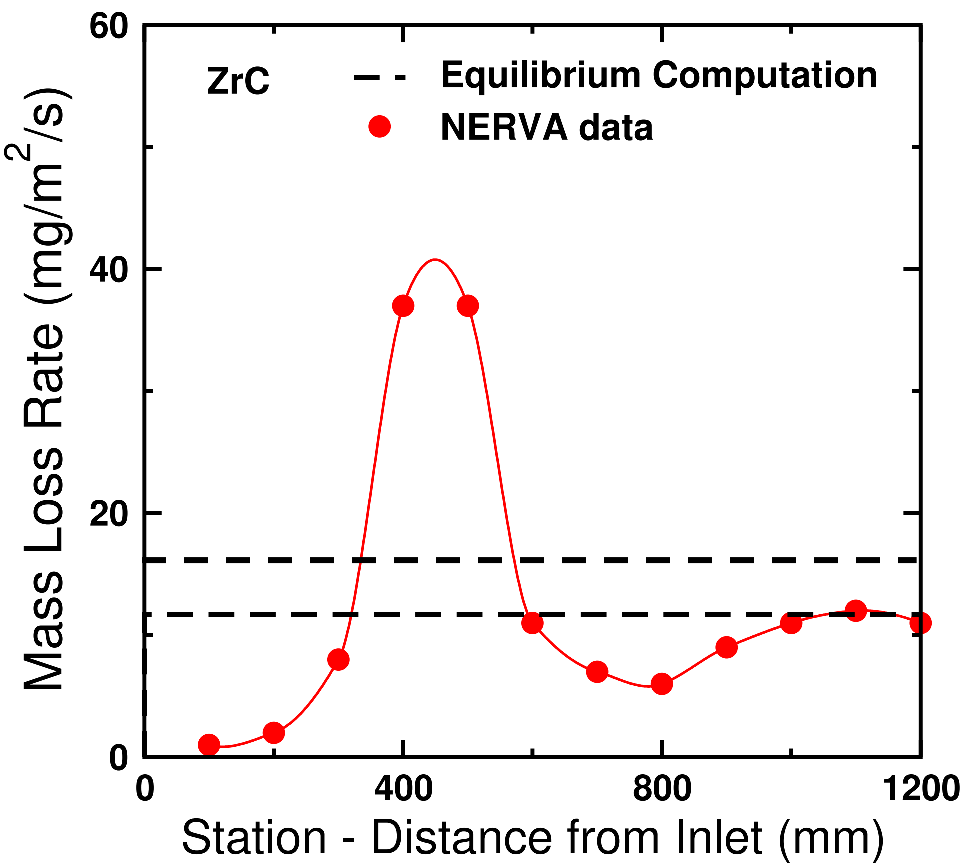
$$\frac{N_{c,g}}{N_{c,s}} = exp(\Delta G_{c,s\rightarrow g}/k_B T)$$

- Use quantum computations to define reaction energetics and solid thermodynamics

$$\frac{\dot{m}_g t}{\rho_g V_g} N_{c,g} = A_c \Delta z_c \rho_c$$

- Compare to original NERVA rocket data (1957-1972) - only at temperature reactor data available

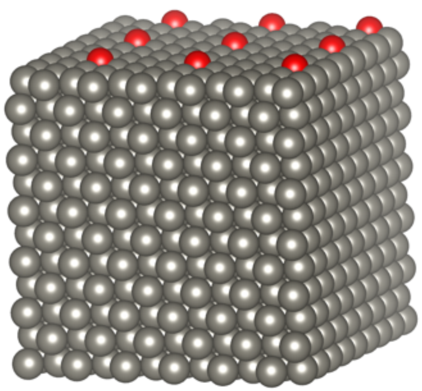
Formulation for Mass Loss Estimates

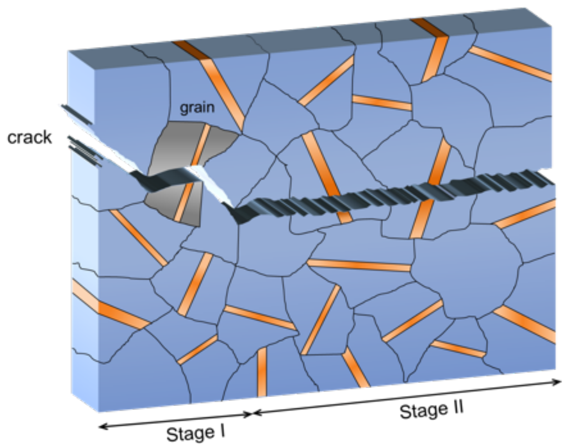


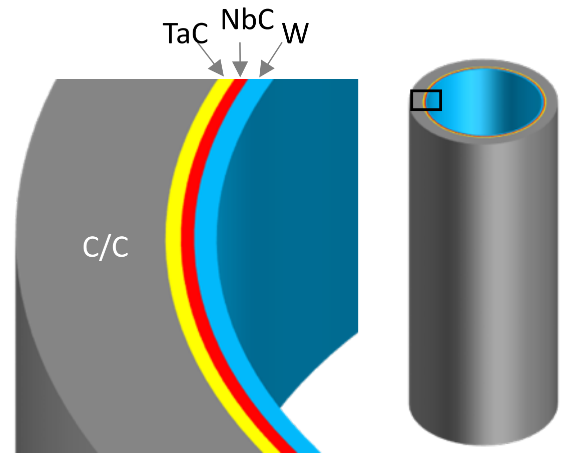
Estimates agree well with heritage data in pristine region of the channel; variability due to material property variances

Multiscale Coating Corrosion and Mechanics

Atomistic | Microscale | Macroscale







-Thermodynamics
-Gas-Surface Interactions
-Transport

-Crack Initiation/Propagation
-Hydrogen Embrittlement
-Mechanical Properties

-Residual Stress
-Delamination
-Net Corrosion Rates

Summary

- NTP presents a highly challenging environment for fuel materials
- Chemical reactions can be characterized to provide a match for corrosion rates in high temperature regime
- Tools developed to understand cracking and erosion

Questions?

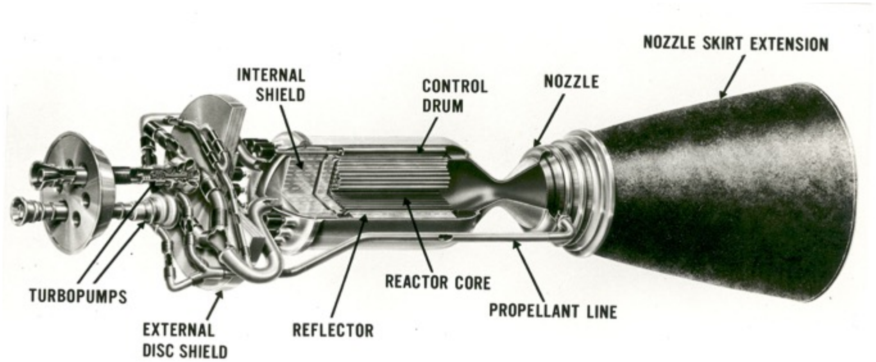
Nuclear Thermal Propulsion

Mechanism – heat hydrogen and exhaust it through a nozzle for propulsion

Heat Source – nuclear fission reaction in solid fuel reactor core heats hydrogen

Benefits – I_{sp}~900 s to halve time to Mars

Challenge – requires coated propellant channels that withstand up to 2800 K in hot hydrogen



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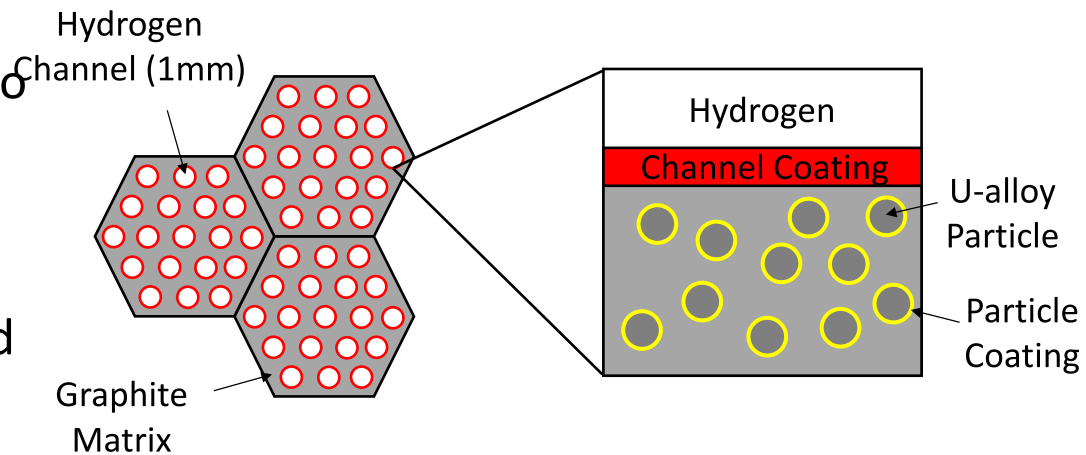
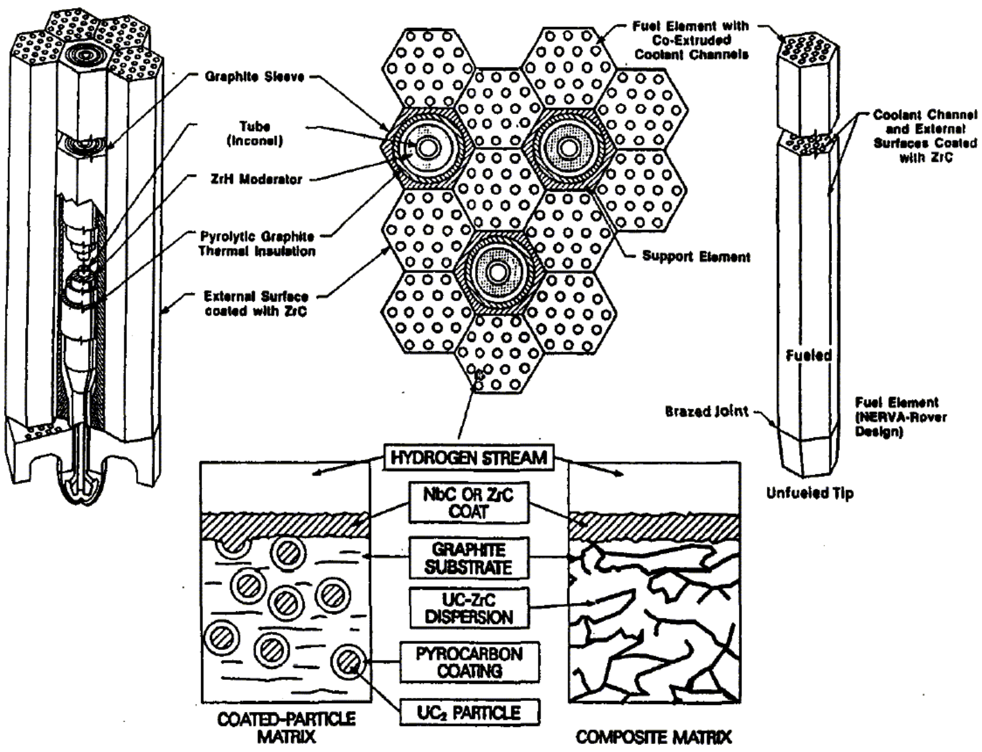
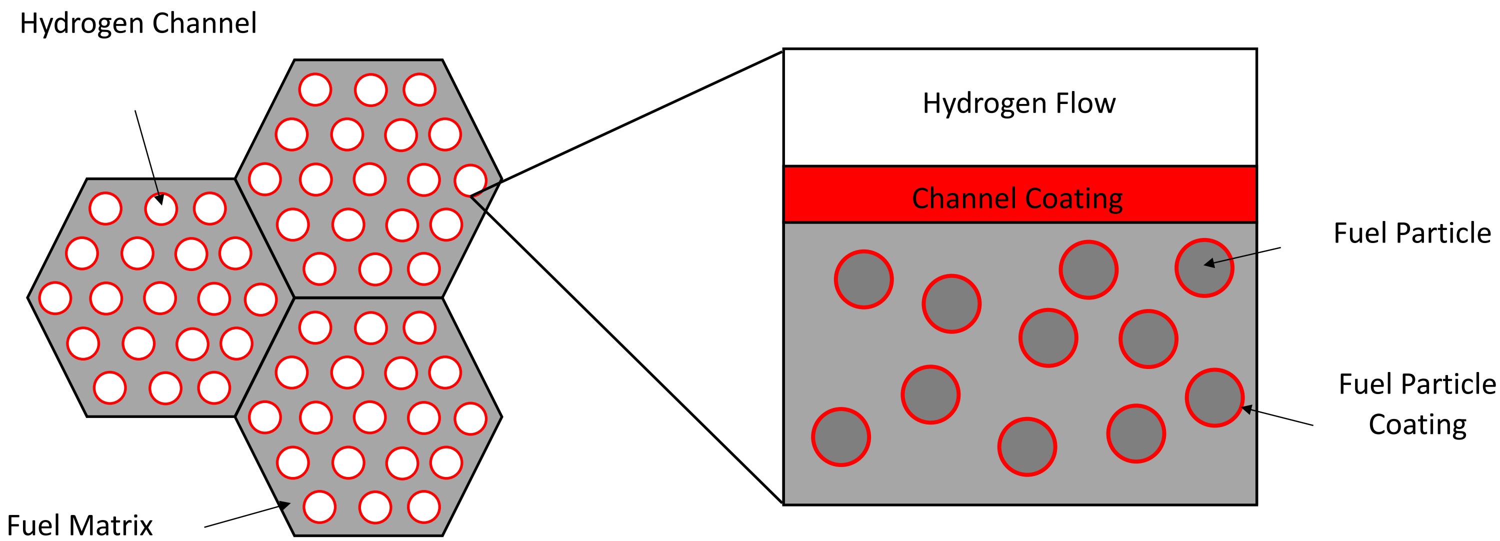


Fuel Element



Fuel Element



If we go with graphite fuel elements:

(1) channel coating needs to be stable to hydrogen and compatible with low expansion graphite

(2) fuel particle coating generally to prevent aggregation, but can utilize tristructural-isotrpic (TRISO) coatings to trap fission products that damage the matrix

Solar Thermal Propulsion

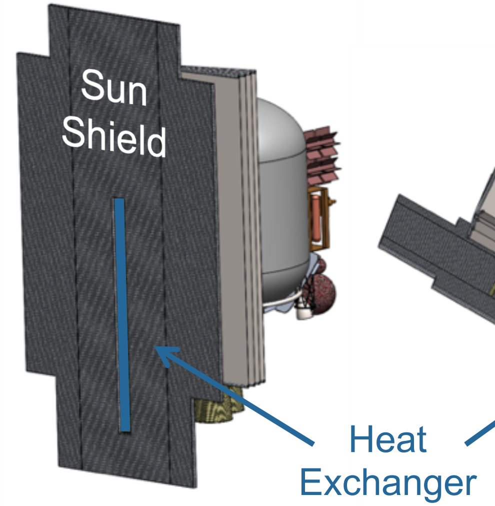
Mechanism – heat hydrogen and exhaust it through a nozzle for propulsion

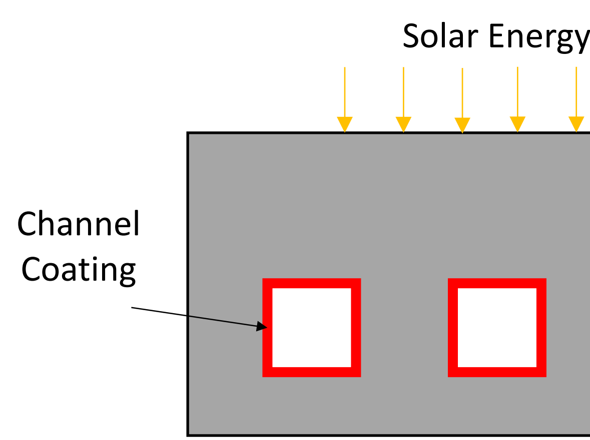
Heat Source – craft closely approaches sun and uses solar energy to heat hydrogen

Benefits – I_{sp}~1200 s for fast travel to the ISM

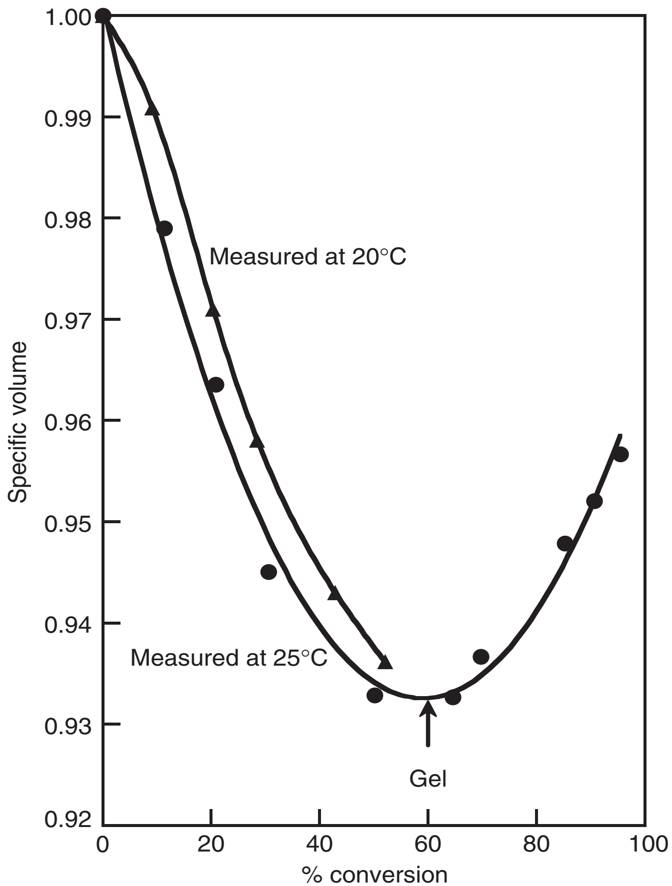
Challenge – requires a coated carbon heat exchanger than can withstand up to 3500 K in hot hydrogen

NASA Partners – JPL (STP project)
GRC (experimental coatings)





Cure Shrinkage



Maximum shrinkage: 4%
Thermal expansion: 3 %
Total Shrinkage: 1 %

Volume in Preform: 3 cubic in.
Diameter: 1.44 in.

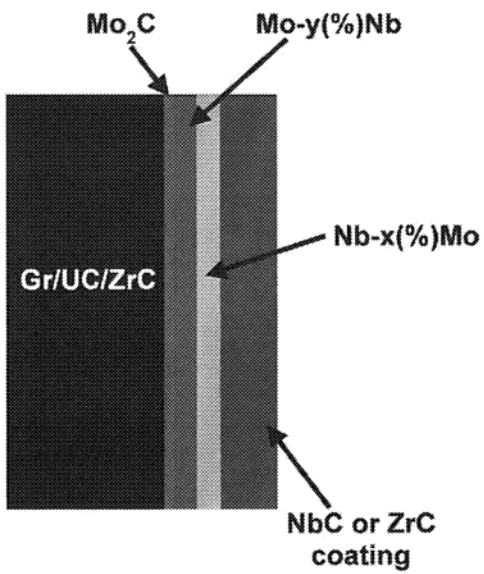
Given a 2 GPa modulus of the resin, final interior pressure falls from 300 psi to a negative value

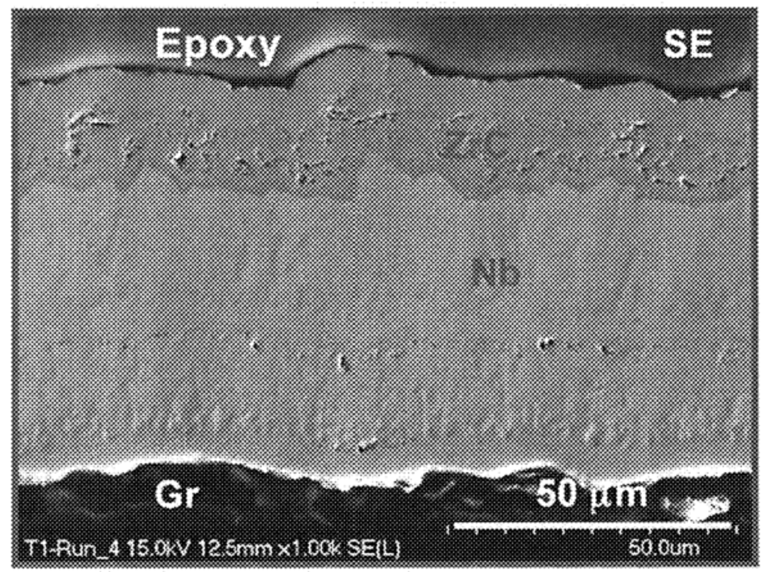
Experimental shrinkage after curing cycle

Channel Coatings

(12) **United States Patent**
Raj et al.

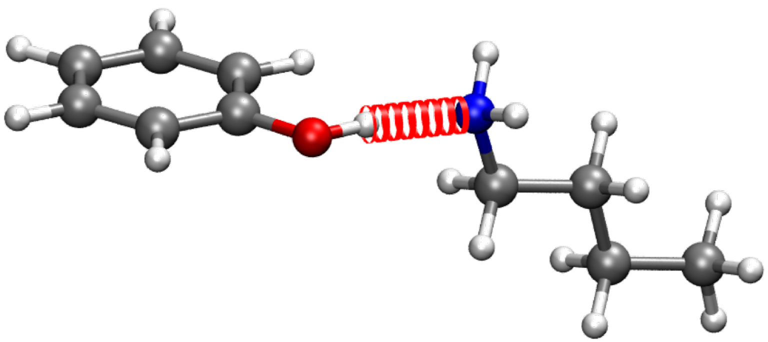
(10) **Patent No.: US 10,068,675 B1**
(45) **Date of Patent: Sep. 4, 2018**



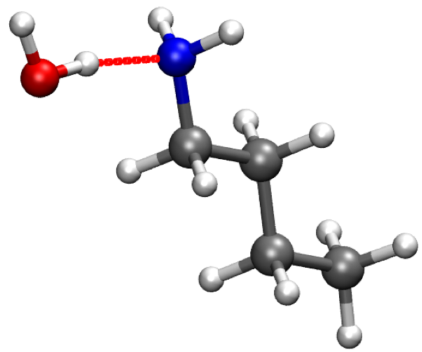


Graded Coatings to Prevent Expansion Mismatch Stress – Sai, et al

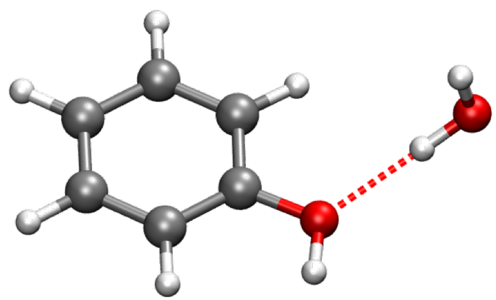
Gas Adsorption: Resin Interactions



ΔE = -41.7 kJ/mol



ΔE = -33.7 kJ/mol



ΔE = -17.8 kJ/mol

Water prefers to interact with aminosilane over resin