Modeling of Polyurethane Foam Thermal Degradation within an Annular Region Subjected to Fire Conditions

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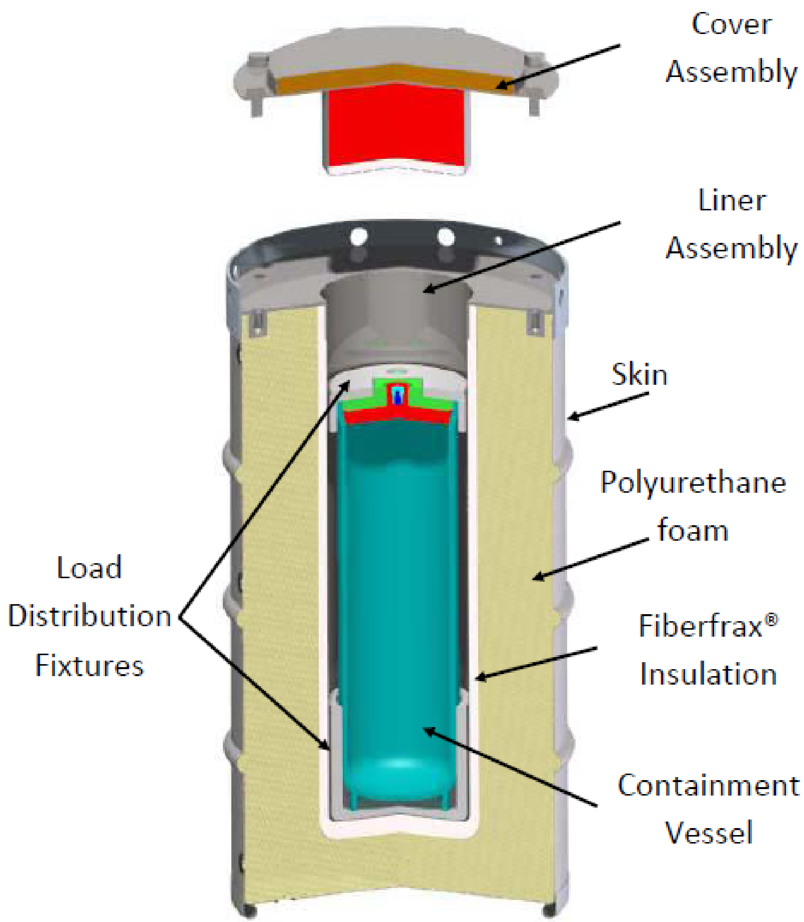
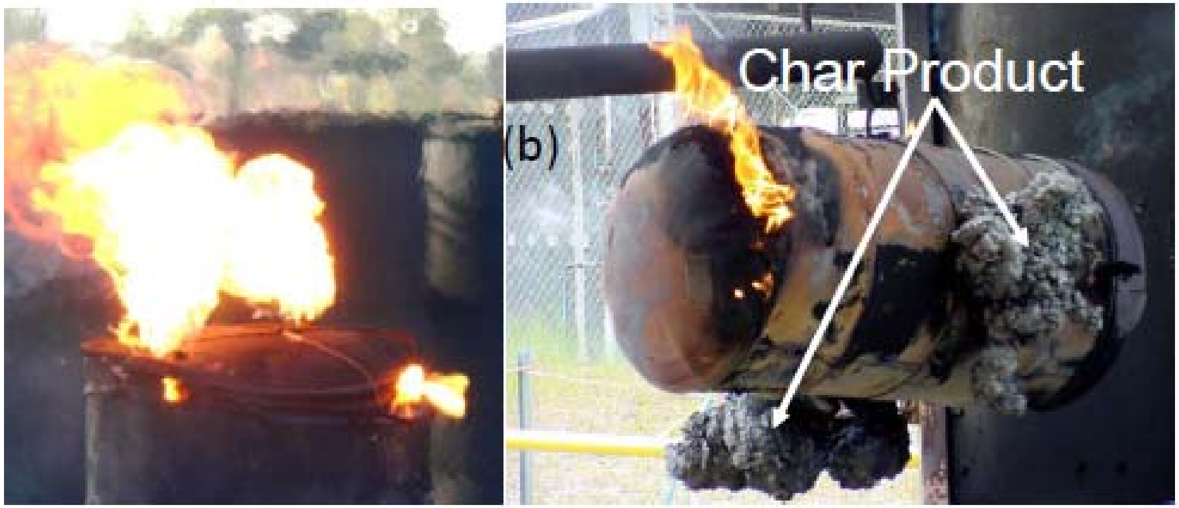
9977 General Purpose Fissile Package



- Containment Vessel within a Stainless Steel and Polyurethane (PU) Foam Overpack
- Must withstand 10CFR71 tests
  - Crush plate drop
  - Puncture bar drop
  - 30-minute, 800°C engulfing fire
- Organic PU foam
  - Provides protection during impact and the fire events
  - At high temp, in the absence of air it reacts endothermically and produces combustible gas and intumescent char
- We wish to understand the high temperature behavior of the PU foam in this package

Outside the Package

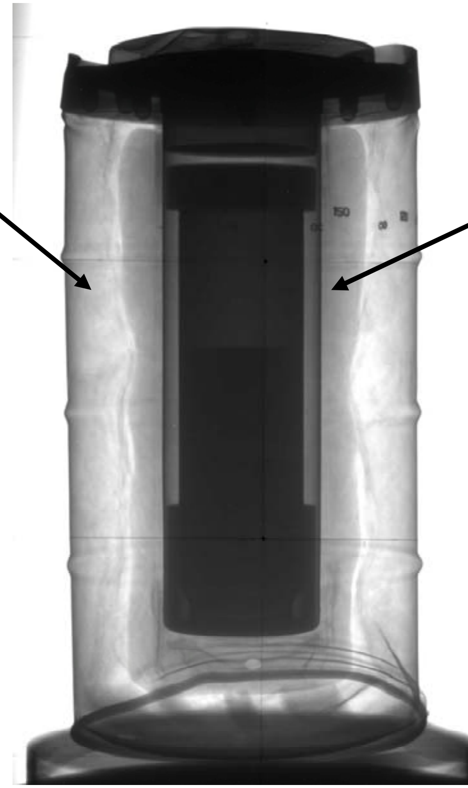


- Combustible product gas jetting out of holes in the skin
- Solid, low density intumescent char product

Inside Package

Low Density Char Product

High Density Un-degraded Foam



- As the outer region of the PU foam is heated, it is replaced by a lower density char and gas products
- The char product is nodular and fragile, and visually opaque
- The outer surface of the un-degraded foam has bubbled and turn orange
- The product gases combust outside the package when they are able to mix with ambient air

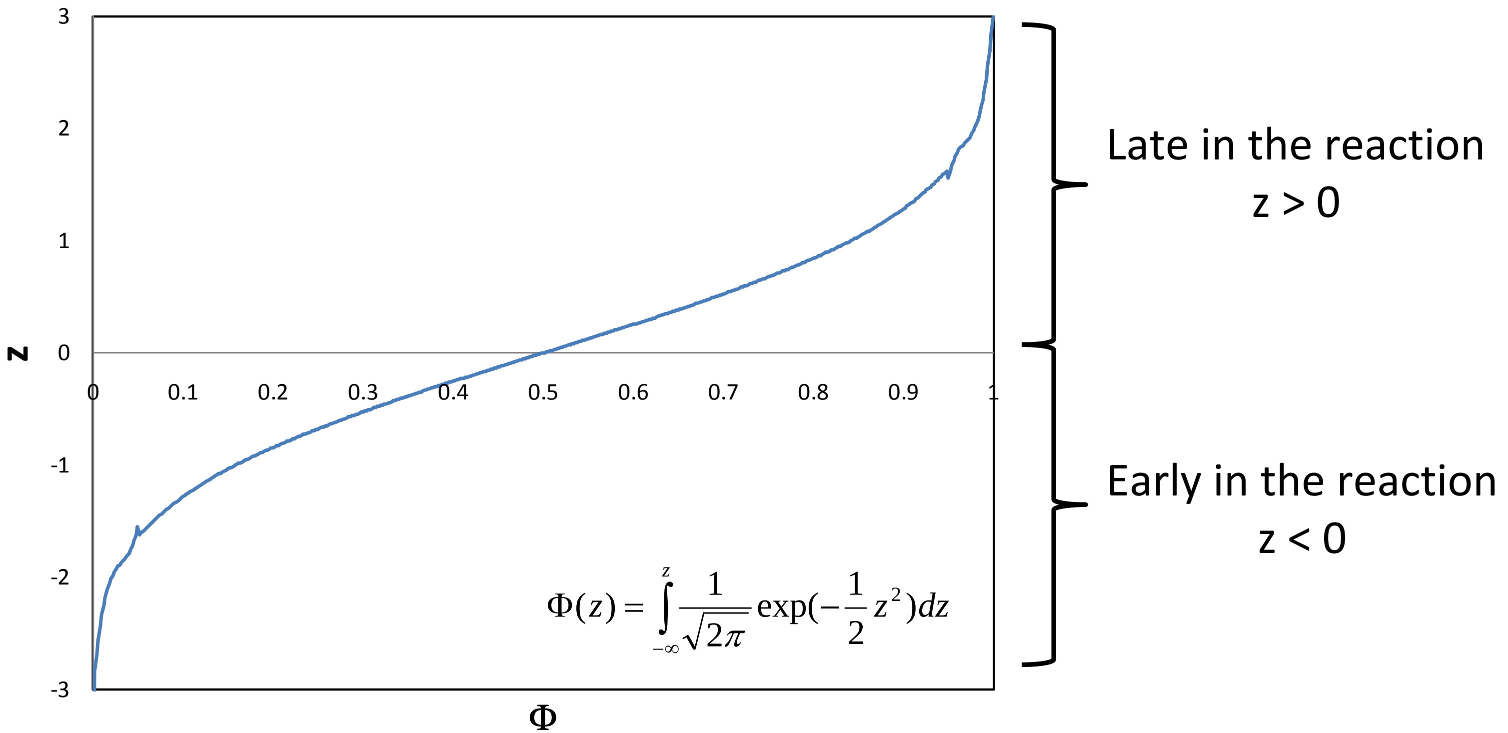
Thermal Degradation of PU Foam

- Hobbs and Lemmon (Sandia 2004) used gravimetric measurements to develop a model of thermal degradation of unconfined PU foam
- They Proposed a two-step degradation process
  - 1 kg (Foam) → 0.7 kg (Primary Gas) + 0.3 kg (Degraded Solid)
    - Reaction rate r_1
  - 1 kg (Degraded Solid) → 1 kg (Secondary Gas)
    - Reaction rate r_2
- Defined mass-based progress variables
  - $F = m_{Foam} / m_{Foam,0}$ (1 to 0)
  - $G_1 = m_{PirmaryGas} / m_{Foam,0}$ (0 to 0.7)
  - $G_2 = m_{SecondaryGas} / m_{Foam,0}$ (0 to 0.3)
  - $S = m_{DegradedSolid} / m_{Foam,0}$ (0 to + to 0)
- Reaction Rates
  - $dF/dt = -r_1$ (always consumed)
  - $dG_1/dt = 0.7r_1$ (always produced)
  - $dG_2/dt = r_2$ (always produced)
  - $dS/dt = 0.3r_1 - r_2$ (produced and then consumed)

Arrhenius Reaction Rates

- $r_1 = F*A*\exp[-E_1/\mathit{R}T]$ $1\ \underline{F} \rightarrow 0.7\ G_1 + 0.3\ S$
- $r_2 = S*A*\exp[-E_2/\mathit{R}T]$ $1\ \underline{S} \rightarrow 1\ G_2$
  - F, S = reactant mass progress variables
  - T = Local temperature
  - *R* = Universal gas constant = 1.9859 cal/mol K
  - Pre-exponential constant A = 10^{13} 1/s
  - Activation Energies:
    - Govern temperature dependence of reaction rate
    - E_1 = 41.4 kcal/mol, E_2 = 45.1 kcal/mol
      - based on measurements

Reaction Rate Reduction due to Damage

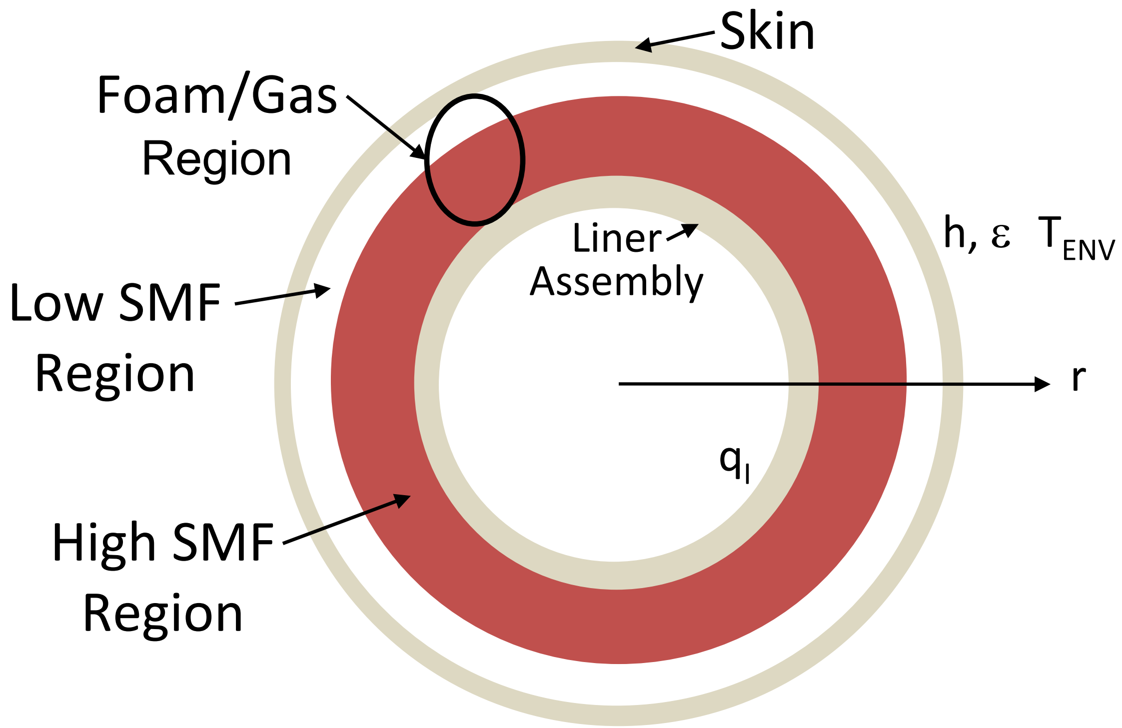


- Physical and chemical damage to the reactants accumulates during the reaction and causes the reaction rate to deceases compared to undamaged reactants
- The accumulation of damage is related to the reaction completions
  - $\Phi_1 = 1 - F$
  - $\Phi_2 = 1 - (F + S)$.
  - $\Phi = 0$ at the beginning of the reaction and 1 at the end
- z = distribution variable affects reaction rate
  - Figure shows $z = z_N(\Phi)$ for a Normally-Distributed reaction
  - z increases as the reaction reaches completion

Reaction Rate Reduction due to Damage

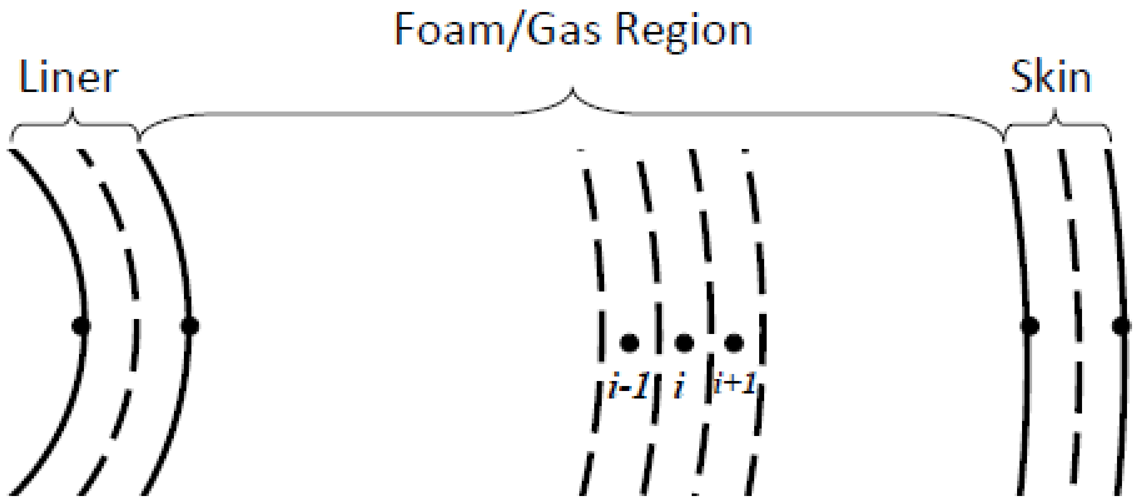
- For a Normally-Distributed activation energy, the reaction rates are
  - $r_1 = F*A*\exp[-(E_1 + \underline{\mathbf{z\sigma_1}})/RT]$
  - $r_2 = S*A*\exp[-(E_2 + \underline{\mathbf{z\sigma_2}})/RT]$
- Hobbs and Lemmon measure distribution parameters
  - σ_1 = 1.08 kcal/mol, σ_2 = 3.14 kcal/mol
- Positive values of z (late in reaction) effectively increase the activation energy, which decreases the reaction rate.

1D Axis-symmetric Computational Domain



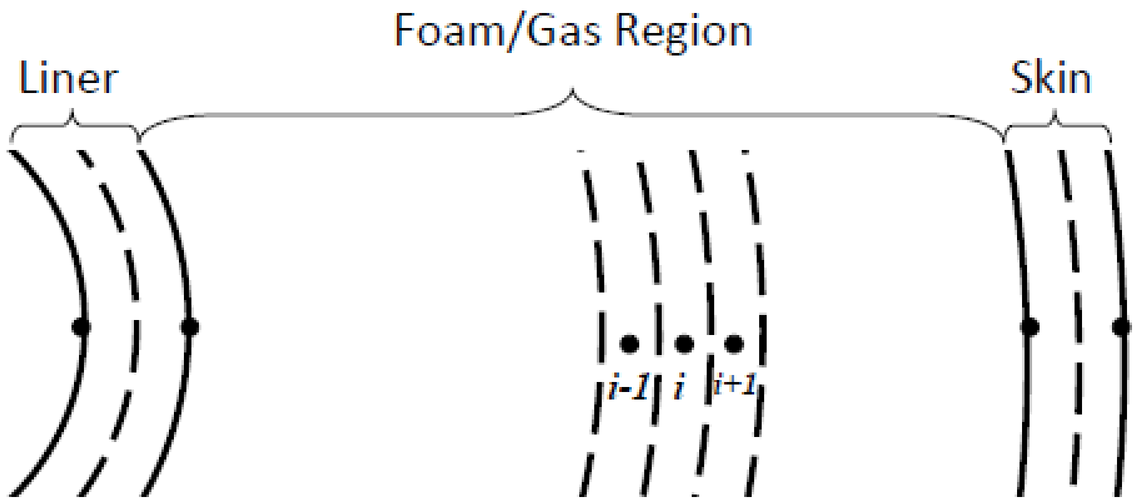
- Geometry
  - R_{INNER} = 10.5 cm, R_{OUTER} = 23 cm, 1.2-mm thick stainless steel skin and liner
- Interior surface heat flux, q_I = 45.8 W/m^2 (19 watt payload)
  - External surface radiation/convection heat transfer
  - h = 5 W/m^{2}K, ε = 0.1
  - T_{ENV} = 38°C (normal) or 800°C (fire)

Finite Difference Formulation



- Two elements in liner and skin
- N = 50 and 100 elements in the Foam/Gas region
- This model does not include flow of gas or degraded solid
  - Total mass in each element is constant
- Species mass conservation:
  - $\dfrac{m_{i,FOAM}^{t+1} - m_{i,FOAM}^{t}}{\Delta t} = V_i(-r_1^t)$, $\dfrac{m_{i,G_1}^{t+1} - m_{i,G_1}^{t}}{\Delta t} = V_i(0.7 r_1^t)$ ....
  - Solid Mass Fraction $SMF_i^t = \dfrac{m_{i,Foam}^t + m_{i,DegradedSolid}^t}{m_{i,Total}}$

Energy Conservation

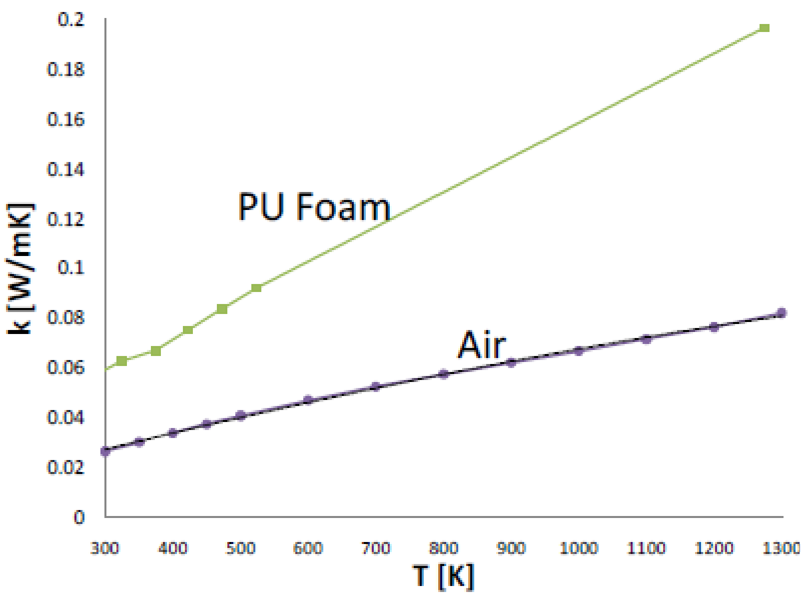


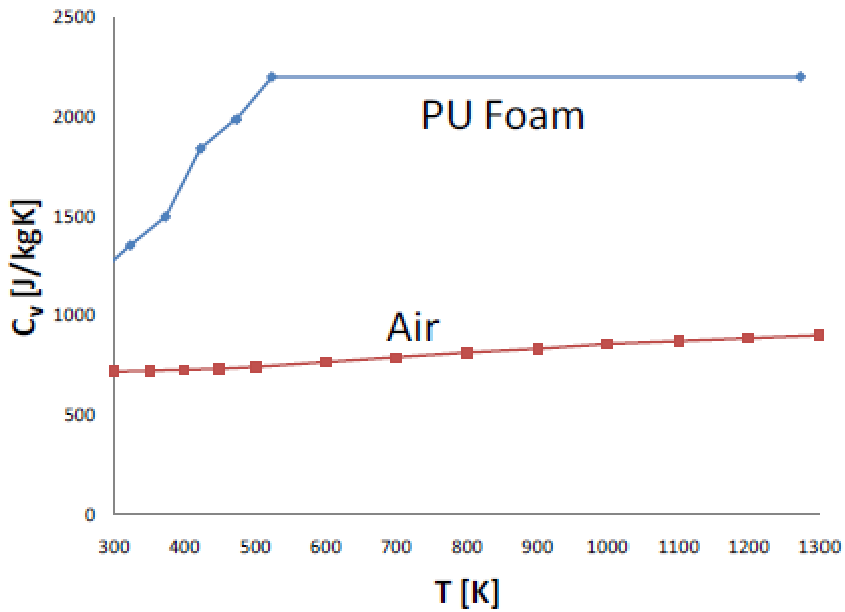
$$(\rho c_v)_i V_i \frac{T_i^{t+1} - T_i^t}{\Delta t} = 2\pi k_{i-1,i} \frac{T_{i-1}^t - T_i^t}{\ln(\frac{R_i}{R_{i-1}})} + 2\pi k_{i,i+1} \frac{T_{i+1}^t - T_i^t}{\ln(\frac{R_{i+1}}{R_i})} + V_i (H_1 r_1^t + H_2 r_2^t) + Q_{Rad}^t$$

Internal Energy Rate of Change | Conduction from Neighboring Elements | Heat from both Reactions | Radiation from Skin

- $H_1 = H_2 = -122\ MJ/m^3$ (endothermic)
- Q_{Rad} = radiation from skin to undegraded foam
  - Only though elements with SMF < 0.038
  - What values should be used for ε_{Skin} and ε_{Foam}?

Material Properties





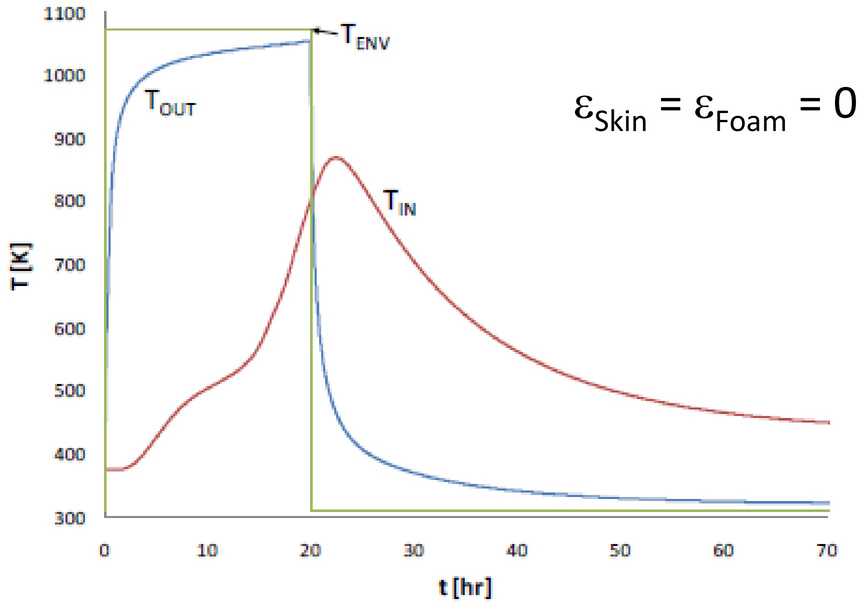
- Use air properties for both product gases
- Use same properties for un-degraded and degraded foam
- Mixture Properties
  - $c_{v,i} = SMF_i \cdot c_{v,PU}(T_i) + (1 - SMF_i) \cdot c_{v,AIR}(T_i)$
  - $k_{i,i+1} = \overline{SVF}_{i,i+1} \cdot k_{PU}(\overline{T}_{i,i+1}) + (1 - \overline{SVF}_{i,i+1}) \cdot k_{AIR}(\overline{T}_{i,i+1})$ (Not fully justified)

Simulations

- Find steady state temperature versus radial location T(r) profile with T_{ENV} = 38°C (311 K) and use it as initial condition
- Perform fire simulations with T_{ENV} = 800°C (1073 K) for durations of either
  - D = 20 hr (reaction front reaches liner) or
  - D = 0.5 hr (regulatory fire duration).
- Perform post-fire simulation using T_{ENV} = 38°C

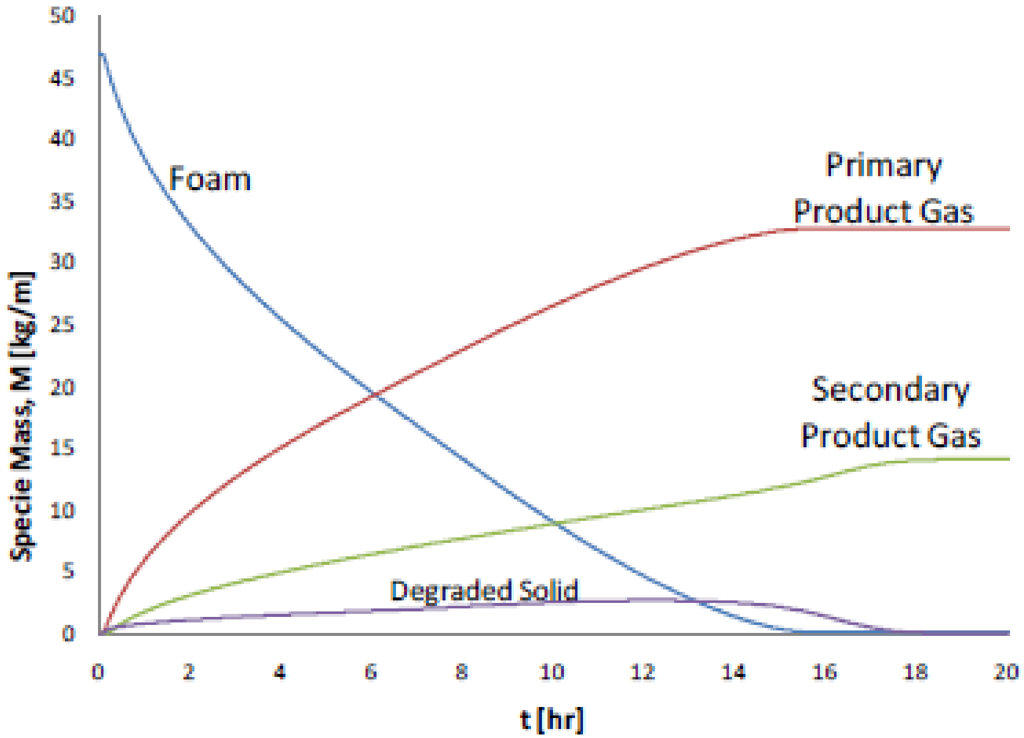
No skin-to-foam Radiation Simulations

Temperature versus Time Results



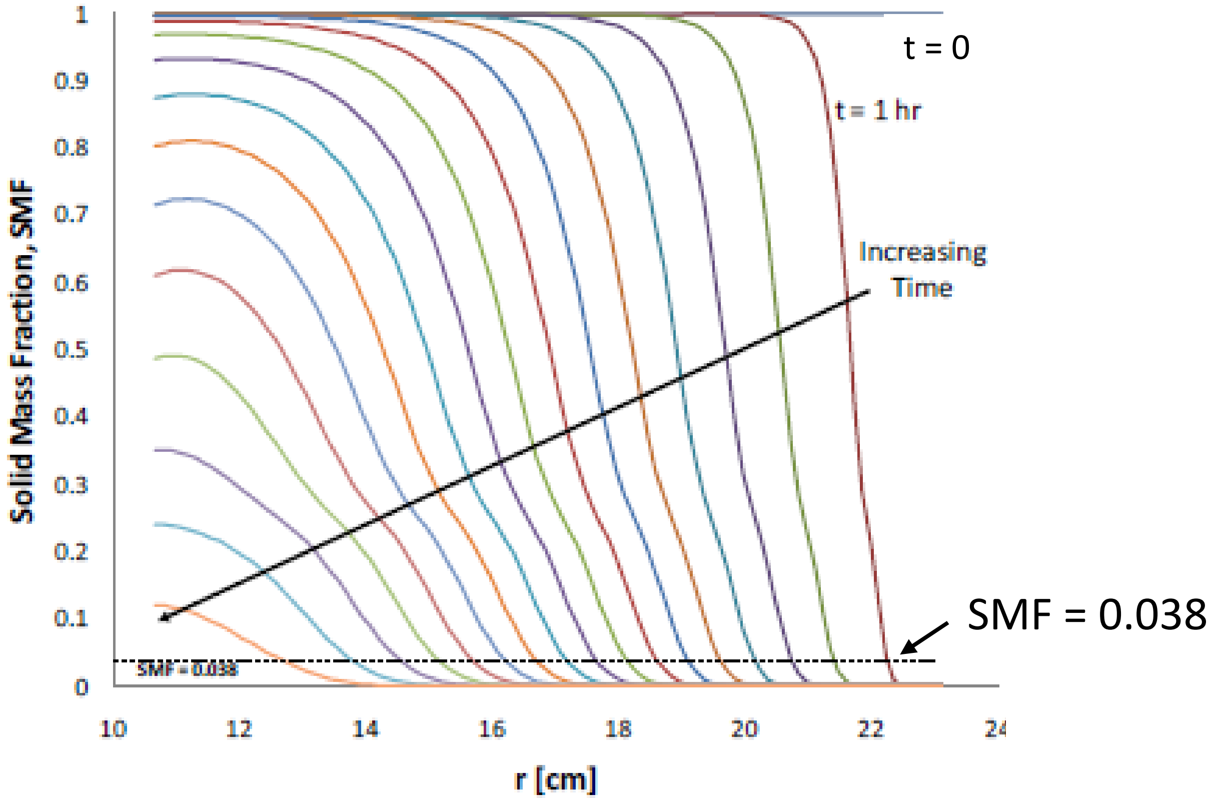
- Environment, and innermost and outermost Foam/Gas temperatures versus time
- Outer temp T_{OUT} approaches fire temp near end of fire
- Inner temperature T_{IN}
  - Is not affected by the fire for nearly two hours.
  - Rate-of-increase decreases from t = 9 to 13 hr
    - While majority of endothermic reaction takes place
  - Continues to increase after fire is extinguished due to heat transfer from hotter outer regions

Total Species Mass versus Time



- Foam produces primary gas and degraded solid and is consumed before t = 16 hr
- Degraded solid produces secondary gas
  - Roughly 3 kg/m accumulates in the system while foam is reaction, but it is consumed before t = 18 hr
- Composition remains constant after t = 18 hr

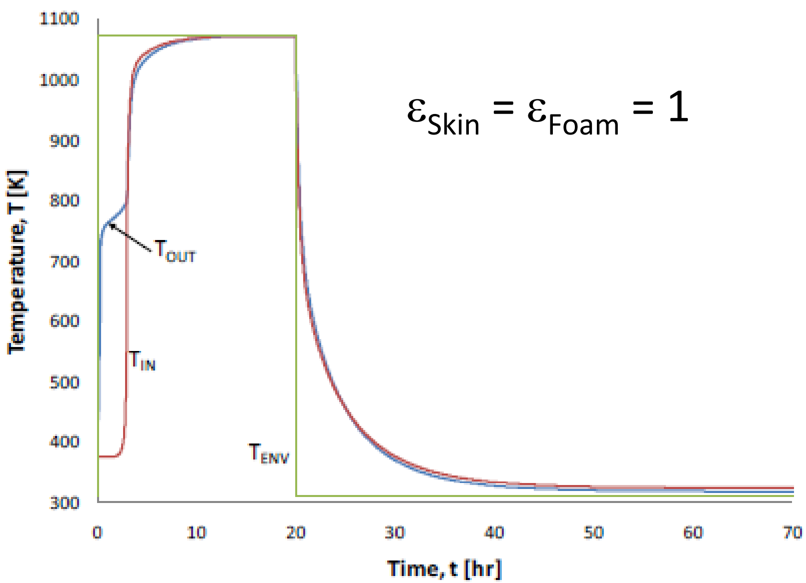
Solid Mass Fraction Profiles

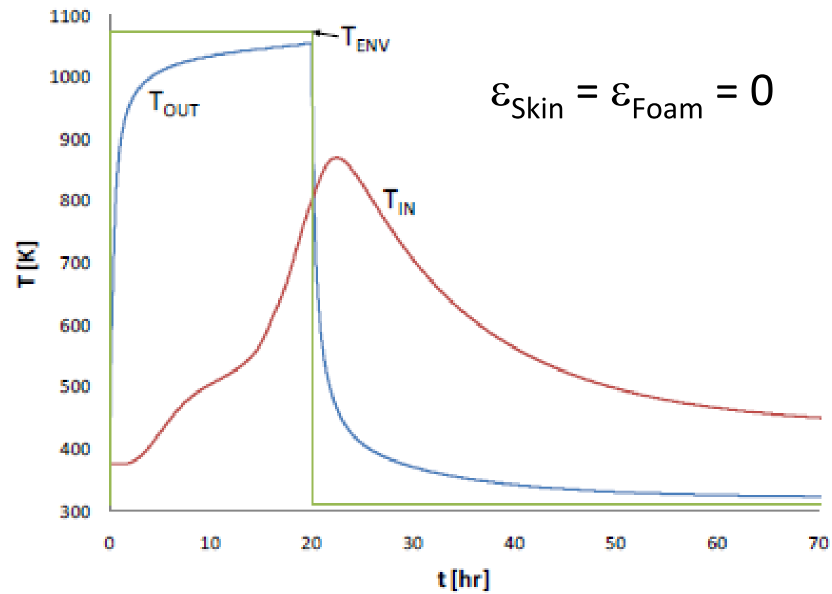


- Foam/gas region is initially completely solid (SMF = 1)
- Reaction consumes the outer layer of foam, replacing it with product gas
- The reaction front moves inward with time
- Regions with SMF < 0.038 are sufficiently clear to allow transmission of thermal radiation from skin to undegraded foam surface
  - However, for this simulation $\varepsilon_{Skin} = \varepsilon_{Foam} = 0$
- Heating by the payload causes reaction of the inner layer

Maximum Skin-to-Foam Radiation Results

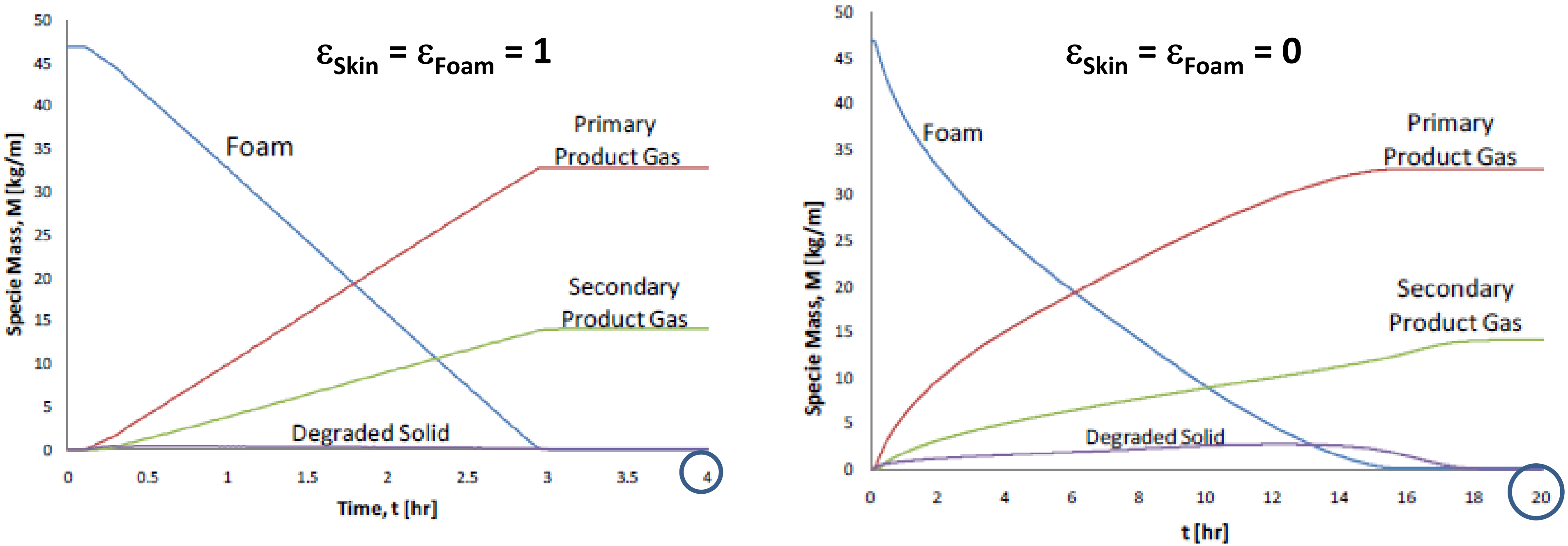
Temp versus Time





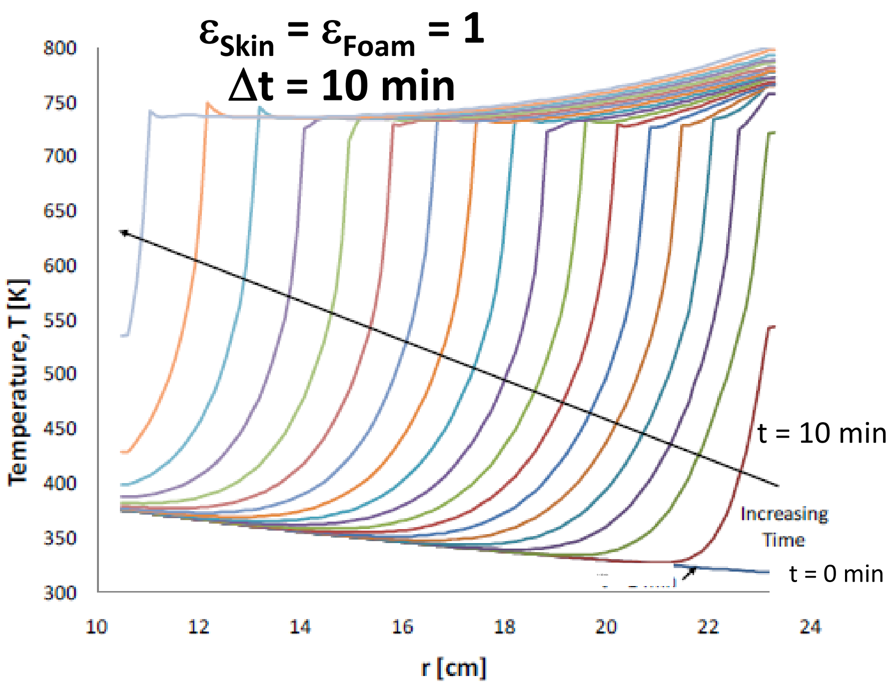
- When the skin-to-foam radiation is maximized the outer temperature rise rate decreases during t = 0.27 to 3 hr, while the foam is reacting
  - T_{OUT} is cooler than for $\varepsilon_{Skin} = \varepsilon_{Foam} = 0$ simulation because radiation puts skin into “direct” thermal contact with foam, which is reacting endothermically
- Once foam is consumed, the inner and outer temperatures are nearly equal due to direct thermal contact.

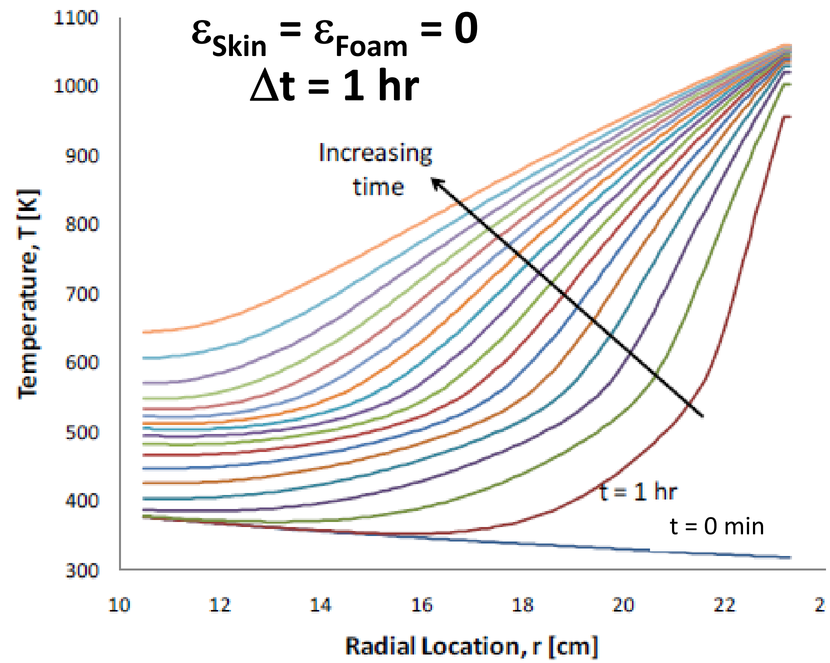
Composition versus Time



- High levels of radiation heat transfer to the foam outer surface causes the foam to be consumed in less than 3 hours (16 hr before)
- Less degraded solid accumulates in this simulation than for the one for $\varepsilon_{Skin} = \varepsilon_{Foam} = 0$

Temperature Profiles in Foam/Gas Region



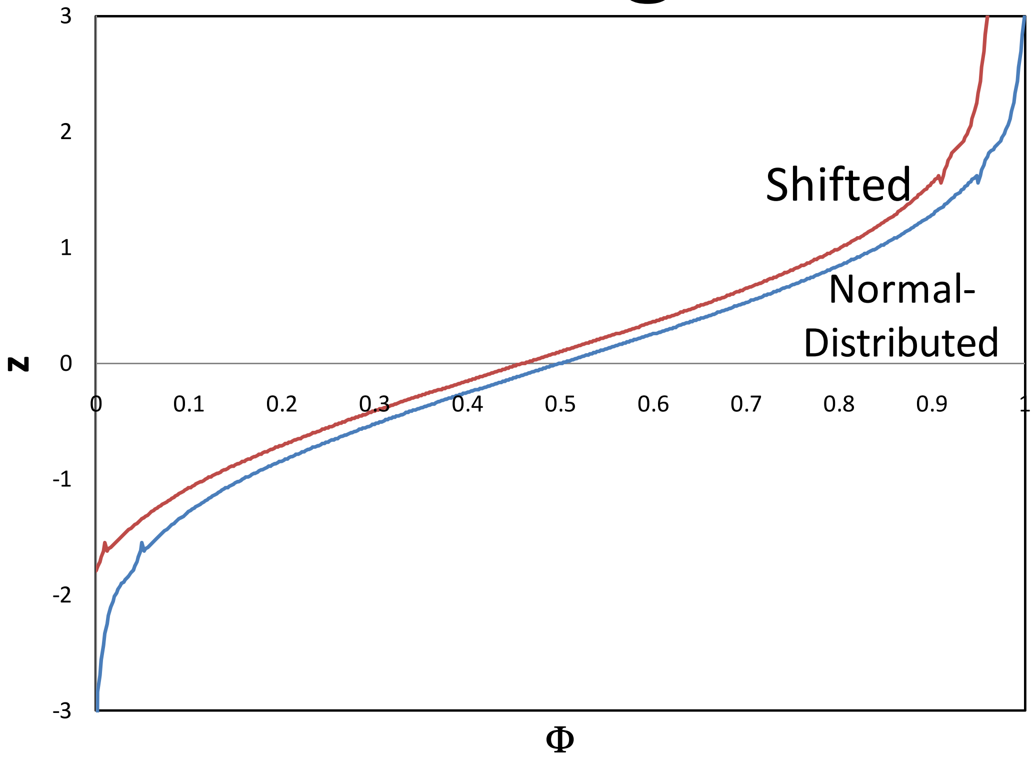


- High levels of skin-to-foam radiation makes the region between those surfaces nearly isothermal
  - The gradient in the foam is much larger
- For $\varepsilon_{Skin} = \varepsilon_{Foam} = 0$ the profiles are smoother and it take longer to affect the inner surface temperature

Normally-Distributed Damage Model

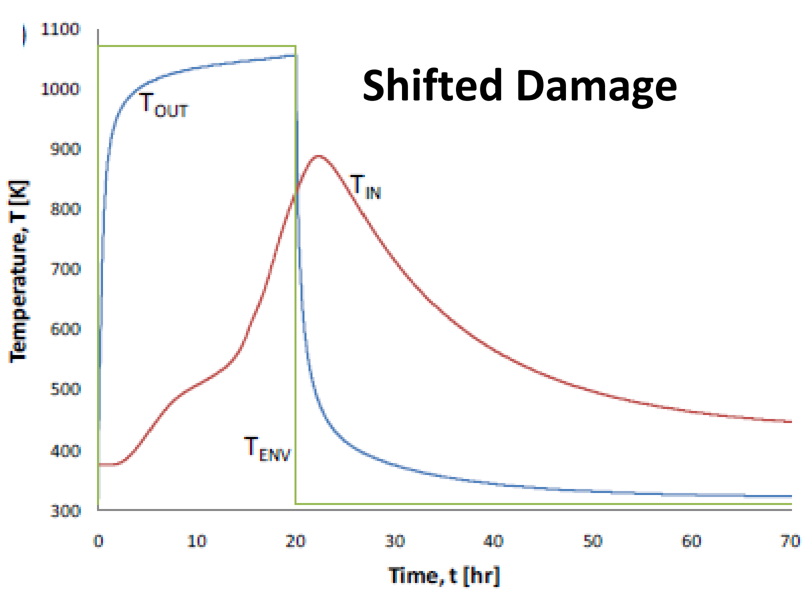
- The normally-distributed damage model decreases the reaction rate when a large fraction of the foam has been consumed
  - The simulations that use it predict that enough foam is consumed after a 20 hour fire that the outer portion of the foam/gas region transmits radiation
- However, the experiments indicate that an optically-opaque layer remains after a fire
  - This suggests that a different damage model must be developed that allows more charred product to remain in the outer portion of the foam/gas region

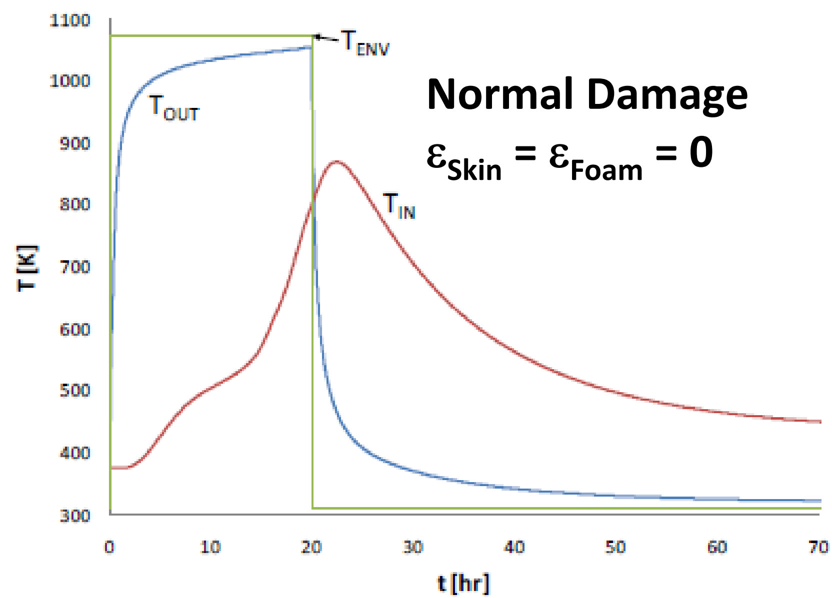
Shifted Damage Model



- The shifted distribution parameter is calculated as $z_S = z_N(\Phi+0.04)$
- Compared to normally-distributed model, this decreases the reaction rate for all Φ and causes the reaction to essentially stop ($z_S \rightarrow \infty$) when $\Phi = 0.96$
  - This correspond to SMF ~ 0.04, which is greater than 0.038, the value that allows transmission of thermal radiation

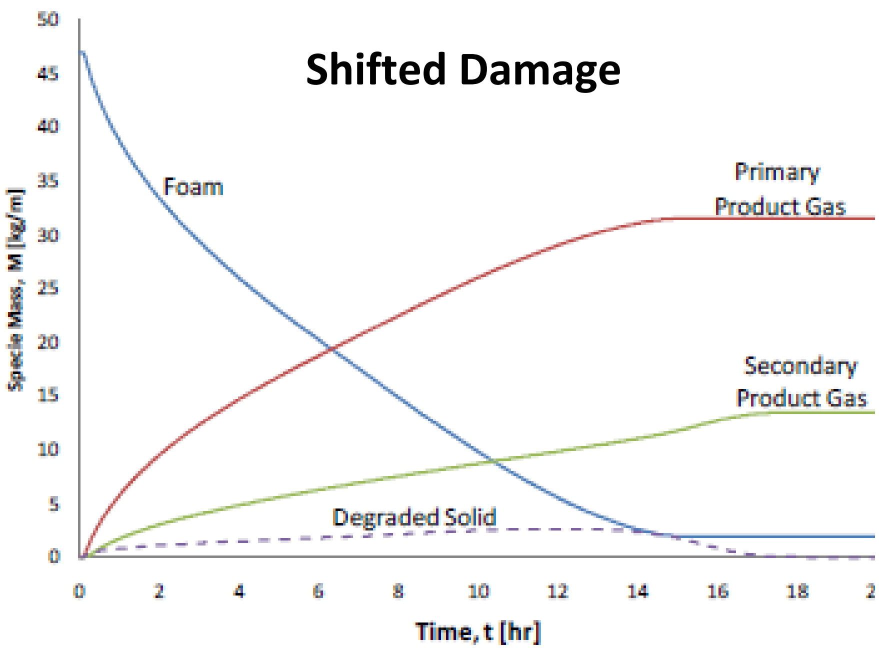
Shifted Damage Model Temp vs Time

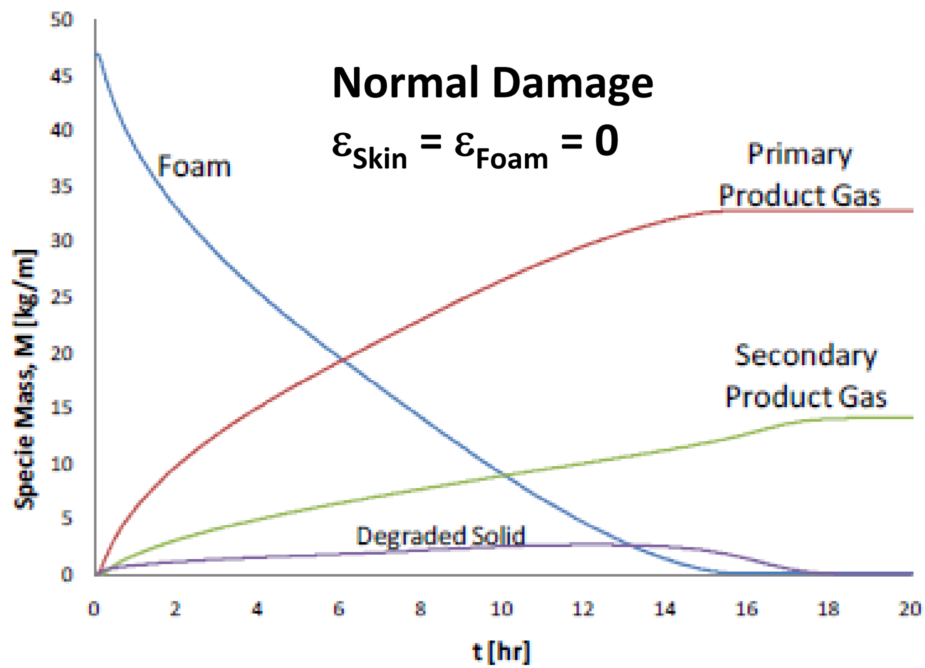




- The shifted damage simulations gives nearly the same T_{IN} and T_{OUT} results as the simulation that used the Normally-Distributed model without surface-to-surface radiation
  - $T_{IN,Peak}$ is 18°C hotter for the shifted model because less foam is able to endothermically react.

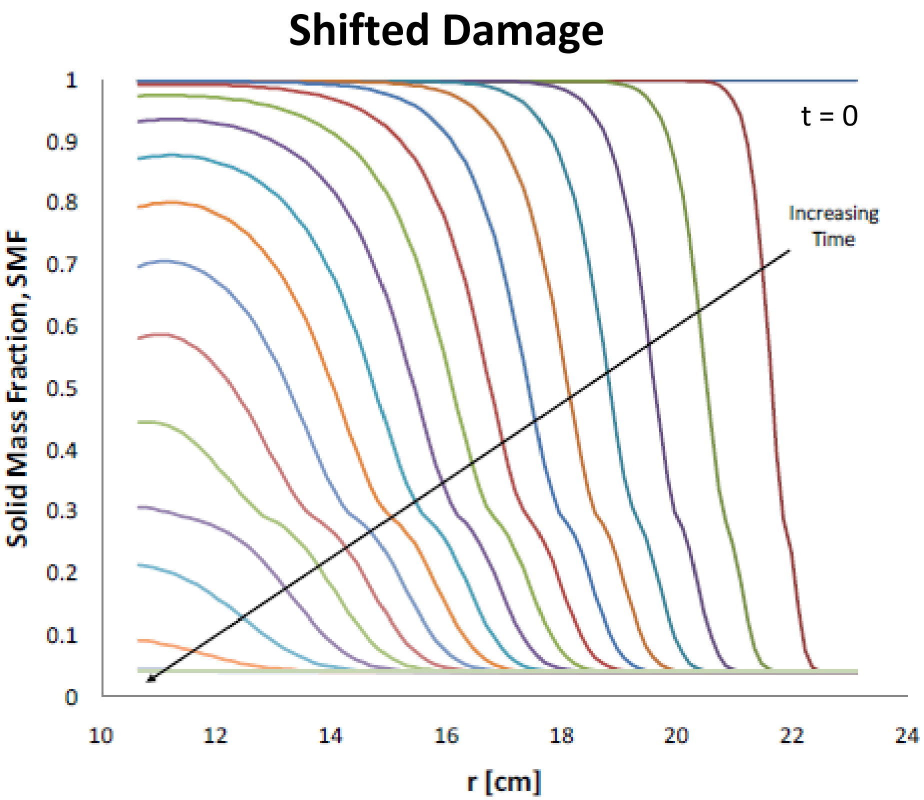
Species Mass versus Time

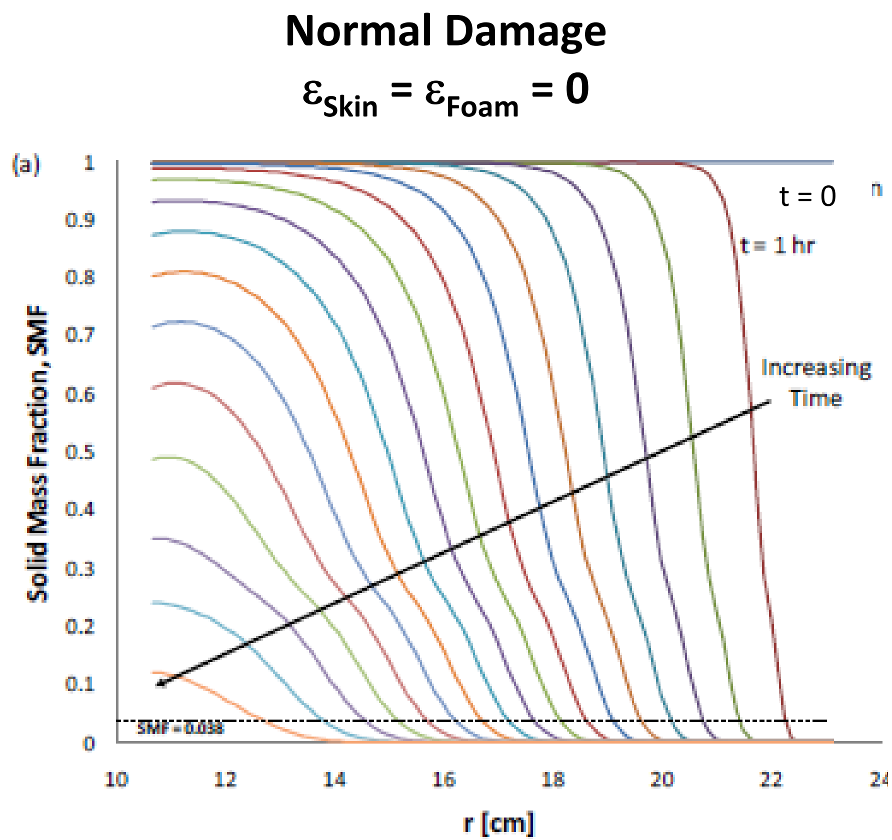




- Some undegraded foam remains after the reaction is complete

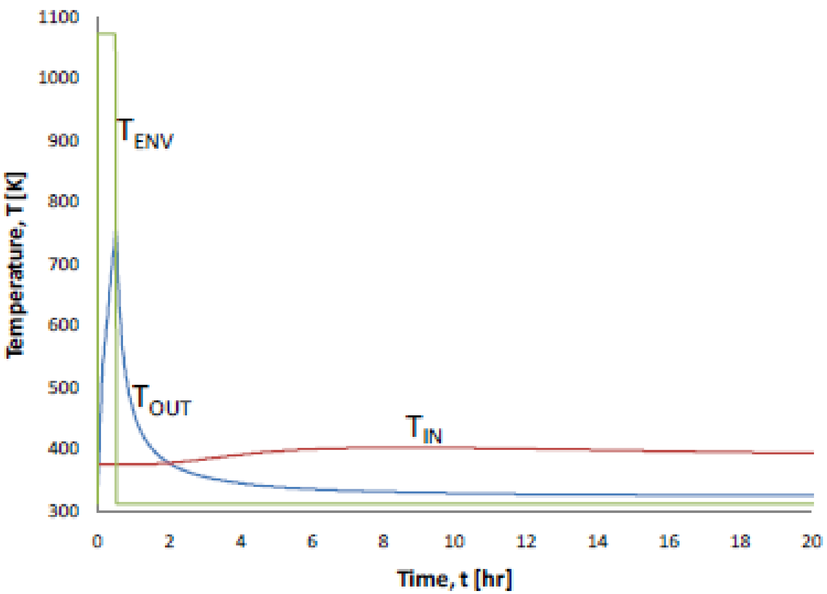
Solid Mass Fraction Profiles

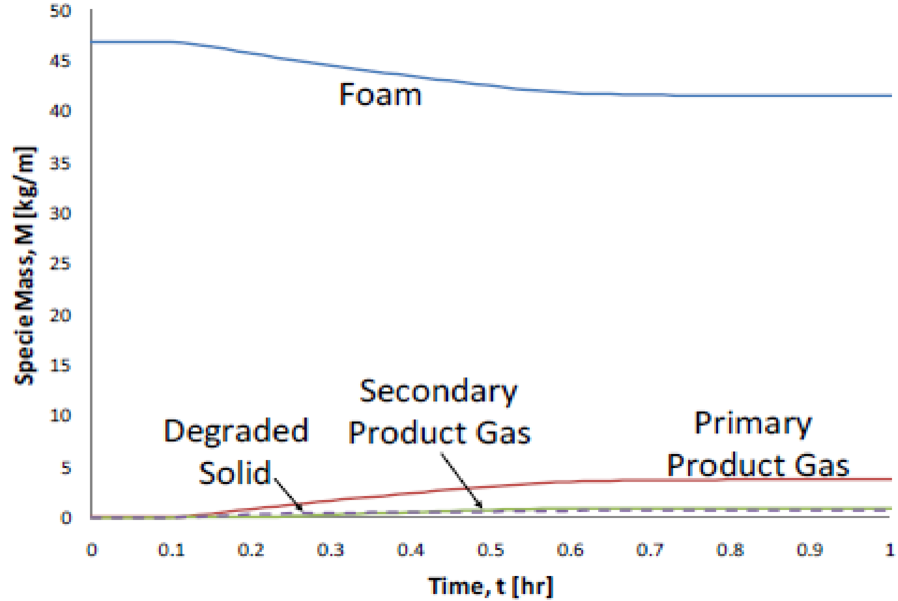




- A layer of low density solid remains in the foam/gas region, which prohibits radiation transmission

Regulatory 30 min Fire





- The peak inner surface temperature is 402 K (129°C), which is below the containment vessel seal limit of 377°C.
- Degraded Solid remains in the system after the fire is extinguished

Summary

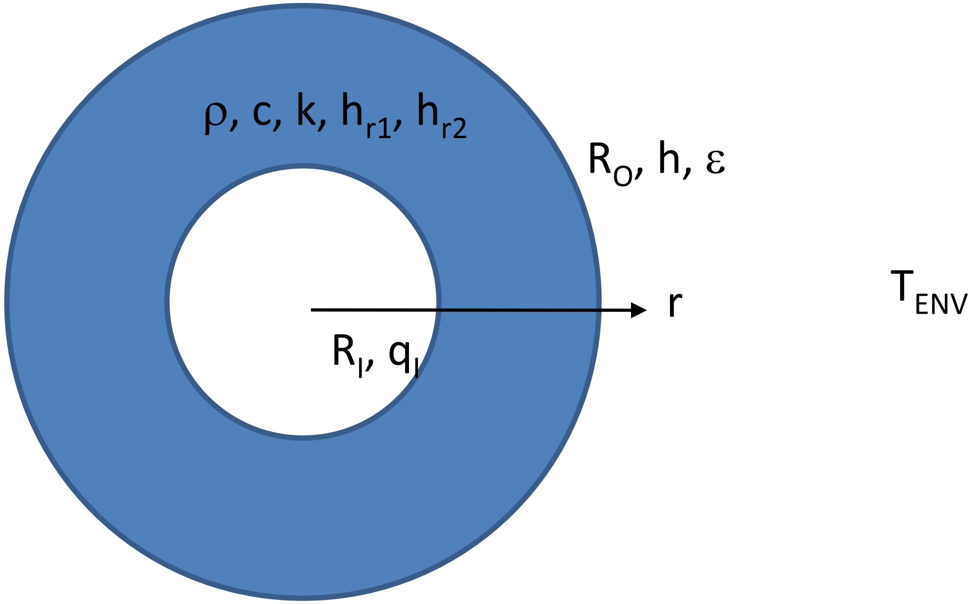
- A one-dimensional axis-symmetric finite-difference model was developed to calculate the temperature and composition within PU foam between the outer skin and liner of a 9977 package, during and after 20-hour-long, 800°C fires
- A Normally-Distributed model as initially used to slow the reaction rate as the foam was damaged during thermal degradation. Those simulations predict that the outer layer of foam is replaced by a gas that allows thermal radiation to be transmitted from the package skin to the un-degraded foam.
  - Depending on the skin and foam surface emissivities, the foam is completely consumed in between 2.9 and 16 hours of fire exposure.
- However, experiments show that an optically opaque layer remains between the un-degraded foam and package skin after a fire.
- A "shifted" damage model was developed in the current work. It essentially stops the thermal degradation reaction when the solid mass fraction is roughly SMF = 0.04.
- Because the solid foam lattice is not completely consumed, there is no direct thermal radiation between the package skin and the reacting zone of the foam
- A simulation using the shifted material-damage model for a 30-min regulatory fire predicts the peak temperature of the inner liner reached 129°C, which is below the short-term fire limit for the 9977 containment vessel seal

Future Work

- Measurements of the density of the char foam that remains in a 9977 package after a fire test will be measured. It will be used as a more rational basis to determine the reaction completion value Φ that stops the thermal degradation reaction.
- Flow of hot gases and degraded foam through the foam/gas region and out of the package skin will be modeled to predict advective thermal transport in the system.
- Once these improvements are made, the model will be used to
  - Predict how long combustible gases will be emitted from the package after it is removed from a fire
  - Design the thickness of PU foam layers used in the outer portion of packages to provide protection during fire accidents
- Additional questions may be address to Miles Greiner
  - greiner@unr.edu

Extra slides

Geometry, BC's and properties

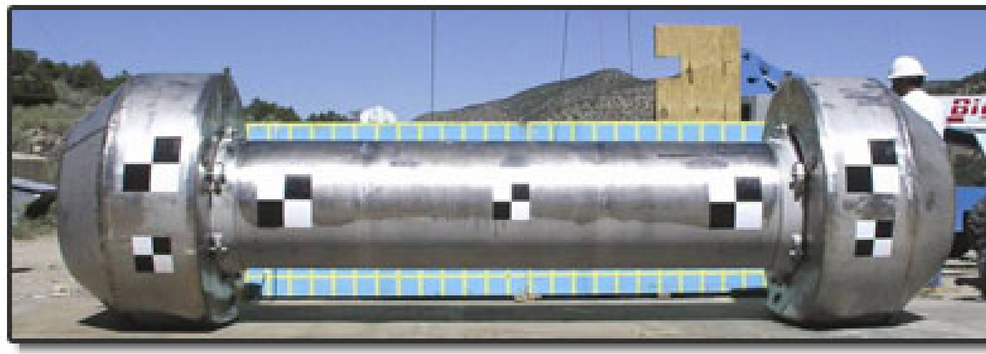


- Based on Hobbs and Lemmon, 2004
  - ρ = 352 kg/m^3, c = 1987 J/kgK k = 0.08368 W/mK
  - $h_{r1} = h_{r2}$ = -122,172,800 J/m^3
- For this problem
  - R_I = 0.1 m, R_O = 0.15 m
  - q_I = 100 W/m^2
  - h = 0.1 W/m^{2}K, ε = 0.1
- For now, temperature independent and $\sigma_1 = \sigma_2 = 0$

Fuel and Fissile Material Packages

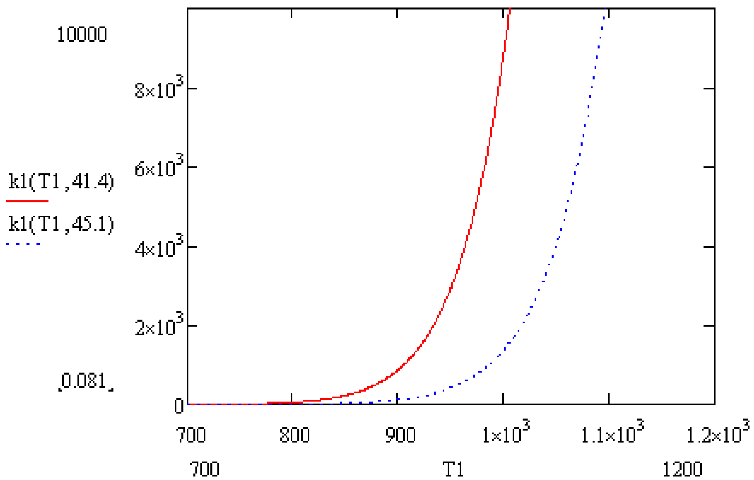
9977 General Purpose
Fissile Package

Hanford Unirradiated
Fuel Package

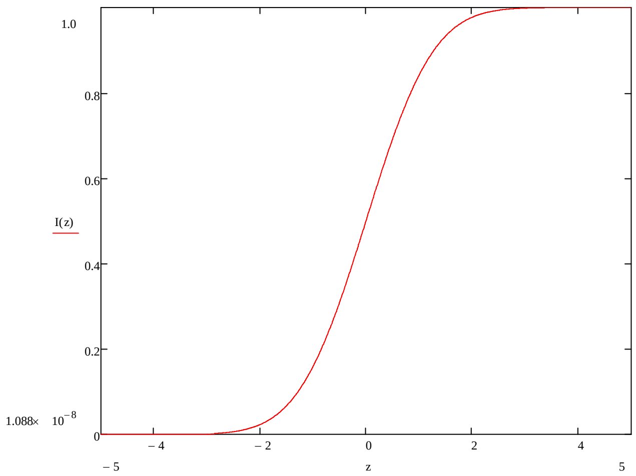


- Polyurethane foam is used in the outer layers or impact limiters of different packages to provide protection during both impact and fire events

Reaction Plots



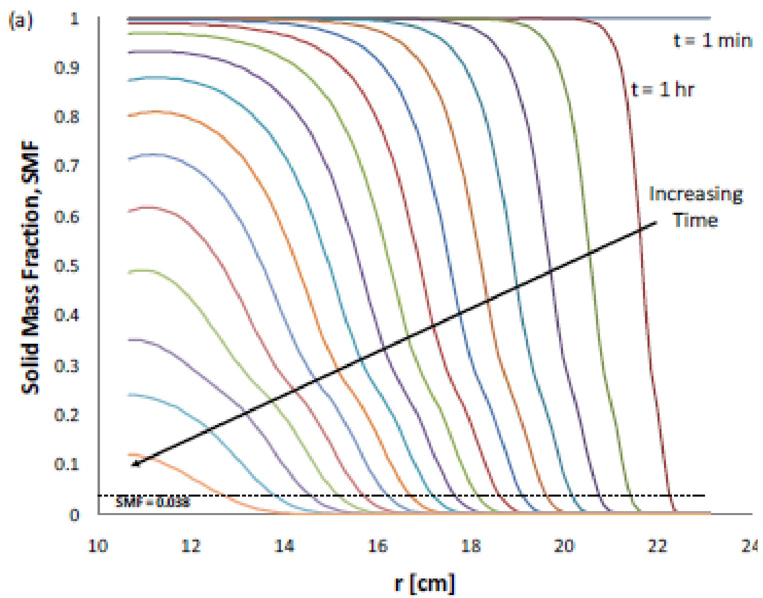
$$k1(T1, E) := 10^{13} \cdot e^{\frac{-E \cdot 1000}{1.9859 \cdot T1}}$$



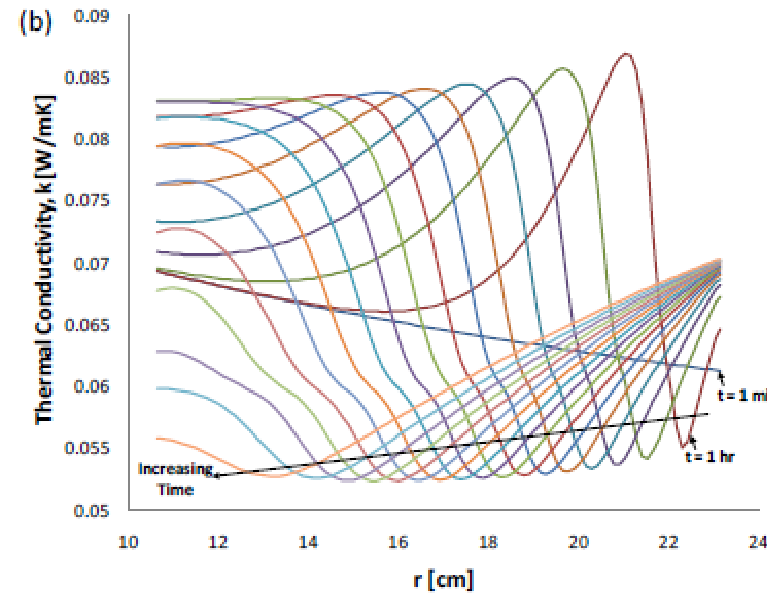
$$1 - S_f = \int_{-\infty}^{z} \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{1}{2} z^2\right) dz$$

Radial Variation of Material Properties

Solid Mass Fraction

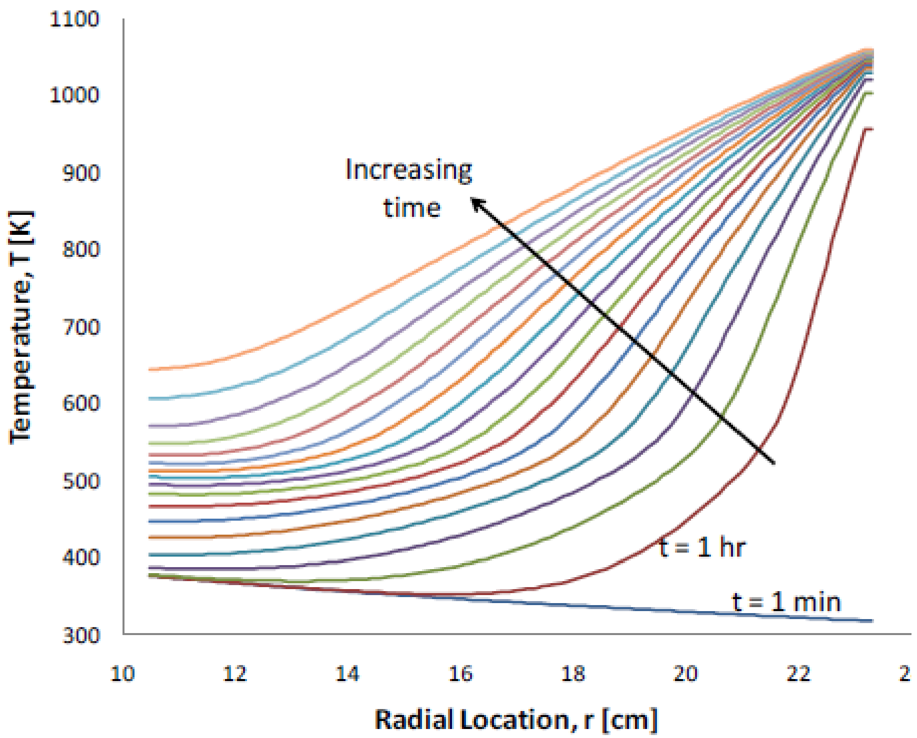


Thermal Conductivity



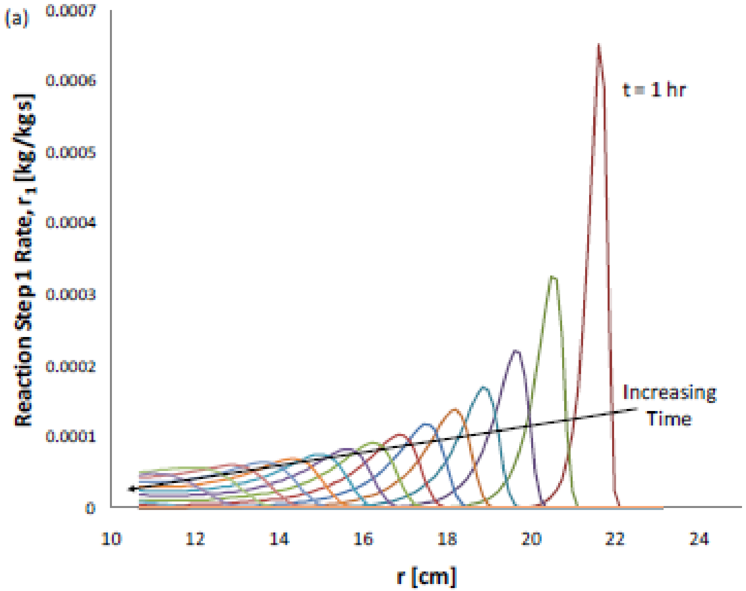
- Initially the foam/gas region is completely solid
- Reaction consumes the outer layer of foam, replacing it with product gas
- The reaction front moves inward with time
- Regions with SMF < 0.038 are assumed to be sufficiently clear to allow transmission of thermal radiation from skin-to-foam surface
  - For this simulation $\varepsilon_{Skin} = \varepsilon_{Foam} = 0$
- thermal Skin to foam surface radiation is assumed to take Surface to surface radition As the outer layers of foam are heated

Temperature Profiles at Different Times



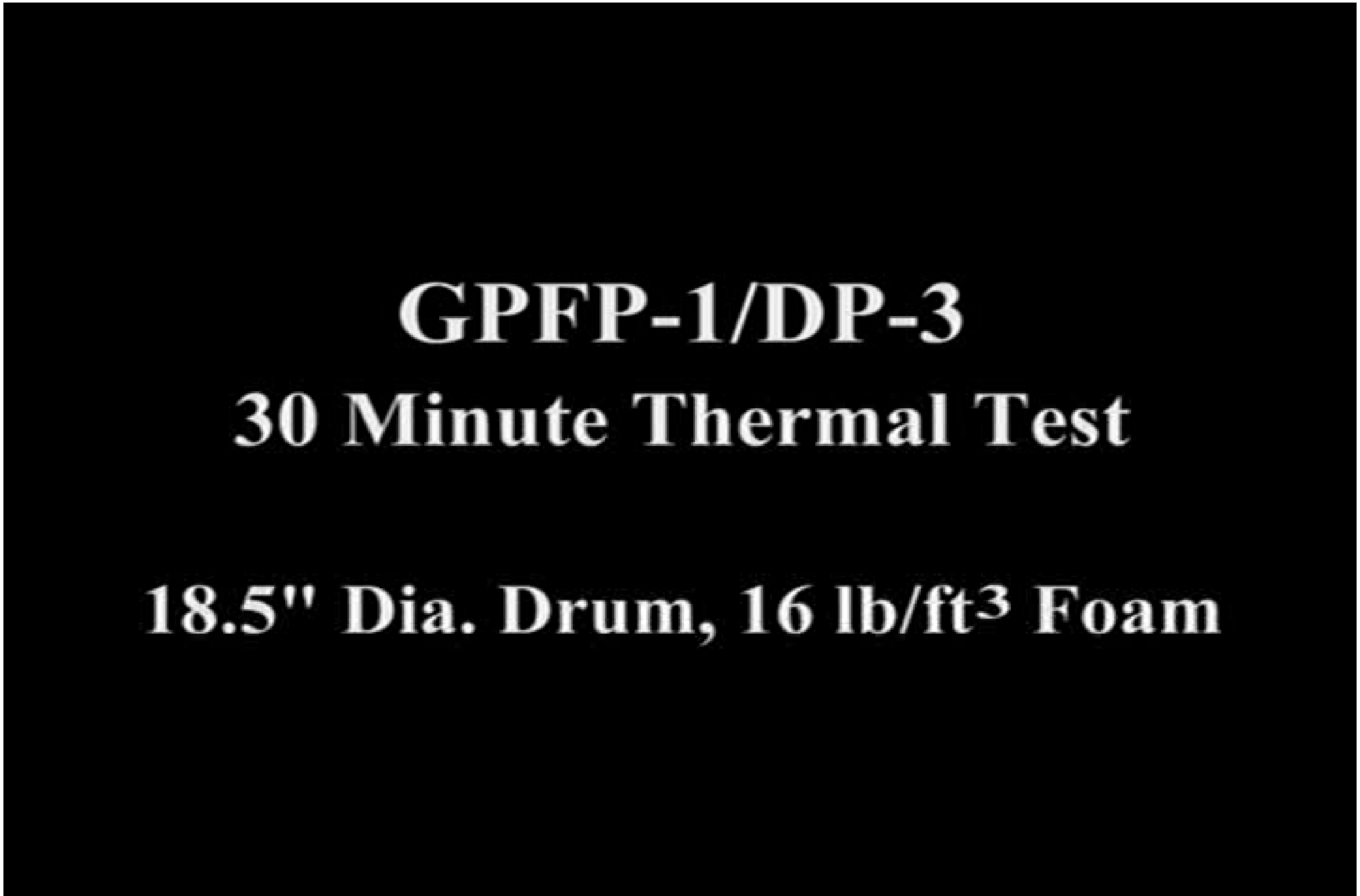
- Before fire temperature profile has a nearly logarithmic shape due to the cylindrical geometry
- Outer temperature rises quickly after fire begins but inner temperature rises more slowly

Primary Reaction Rate Profiles



- At the inner edge of each spike, the reaction rate increases as the temperature increases
- On the outer edge, the reaction rate decreases as the reactant foam is consumed
- The reaction front moves inward with time
- The secondary reaction rate (not shown) is lower than that of the primary reaction

Savannah River National Lab High Temp Tests



- The foam produced combustible gases and low density char product during the fire tests