SAND2011-7766C

# Phenomena and Modeling of Container Pressurization due to Thermal Decomposition of Polyurethane Foams

**A. B. Dodd, K. L. Erickson, and R. E. Hogan Jr.**

**Sandia National Laboratories**
**Albuquerque, New Mexico, USA**

**6 Laboratory Conference on Engineering and Materials at Extreme Conditions**

**Barcelona, Spain**
**October 23-28, 2011**

**Sandia is a multi program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.**

ASC

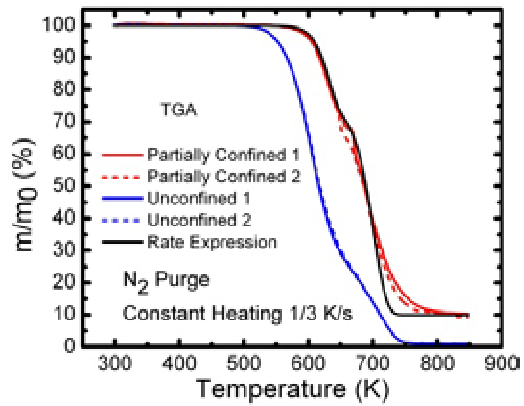
Sandia National Laboratories

# Polymer Foams provide thermal, mechanical, & electrical isolation in engineered systems

- **Systems safety analyses use numerical models to predict heat transfer to encapsulated objects and pressurization/failure of sealed containers**
- **In inert environments, the incident heat flux to a system can cause foams to decompose**
- **Evolved gases can cause pressurization and failure of sealed containers**
- **Container pressurization involves complex physics**
  - Liquefaction/flow introduces convective heat transfer
  - Erosive channeling by hot gases exacerbates liquefaction/flow
  - Pressure depends on rate of gas generation, which depends on temperature history (Heat transfer through foam is very more important)


# Coordinated experiments & analyses are needed to develop models for systems safety analyses

Material properties from independent laboratory experiments



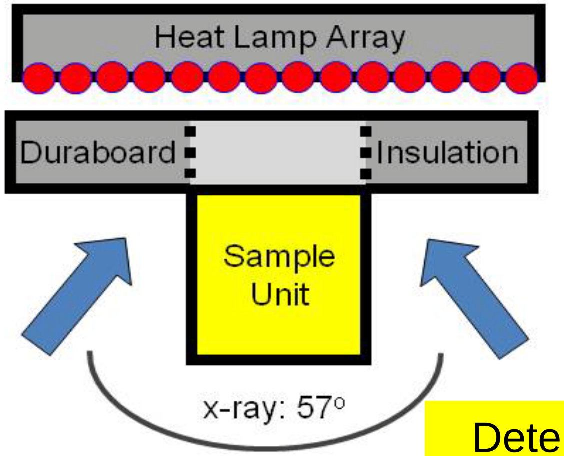

Develop model based on existing radiation-conduction code

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (k + k_e)\nabla T + \sum_i \rho r_i(-\Delta H_i)$$

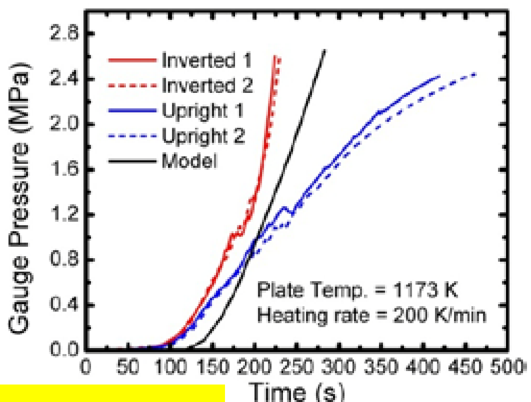
$$P = n_g R \Big/ \int_{V_g} \left( 1/T \right) dV_g$$

*Reaction rate expressions for $r_i$ & $n_g$*

Small container heat transfer and pressurization experiments



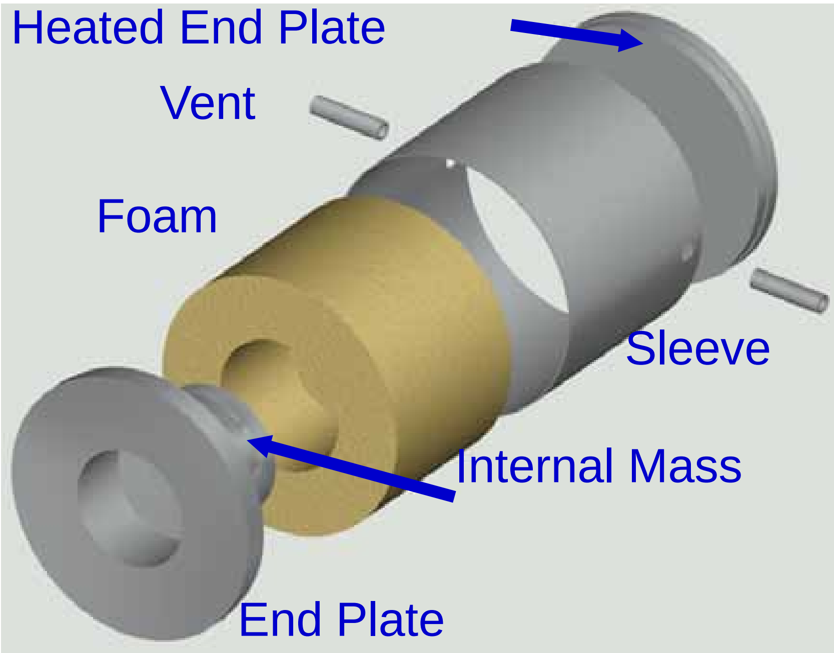

Evaluate models: compare with results from container experiments

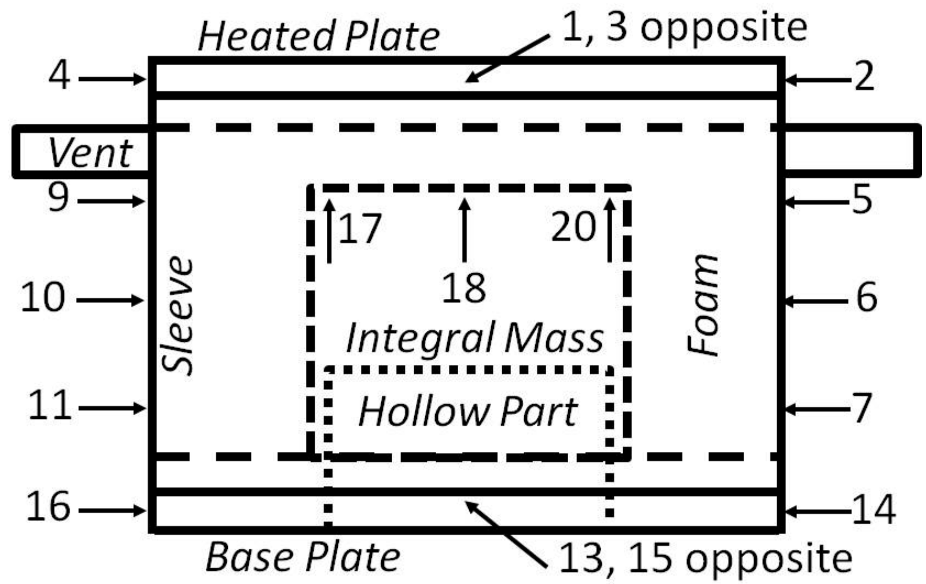


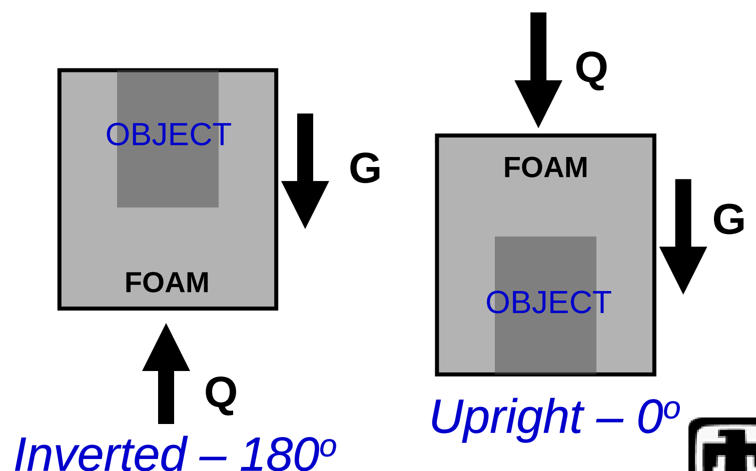

Determine needed experiments and model/code development

# Small container heat transfer & pressurization exp's. provide physical insight and T & P data

TDI-polyester-polyol, rigid, closed cell, polyurethane foam (160 - 720 kg/m$^3$)



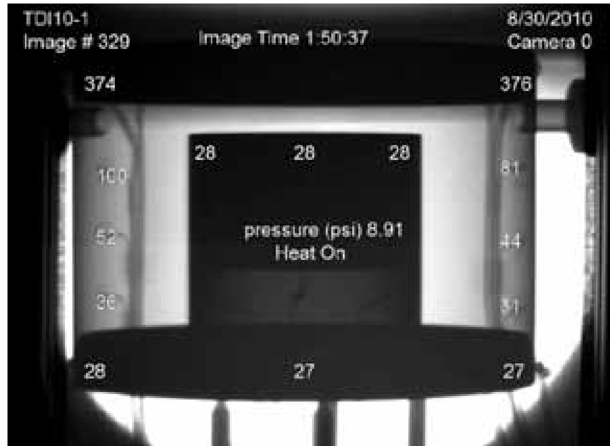



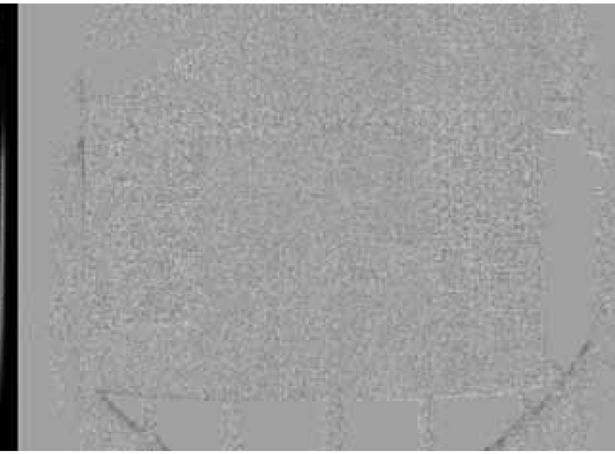

Sample container

- Sleeve 321 SS tubing
  - 8.89-cm OD, 5.40 cm long
  - 0.508-mm wall thickness
- End plates: 0.635-cm thick 304 SS
  - Laser welded to Sleeve

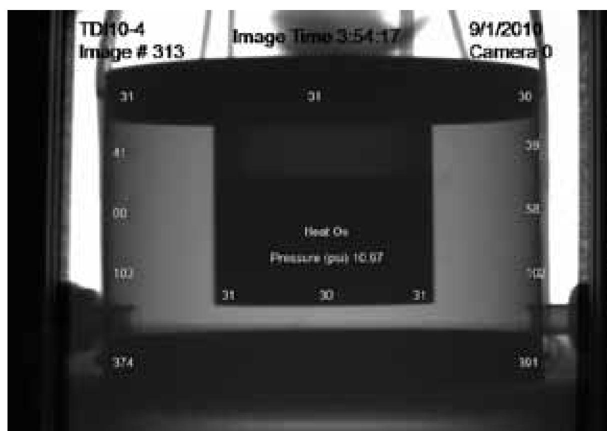
# X-ray images showed liquefaction and flow occurring with lower density TDI-based polyurethane foam

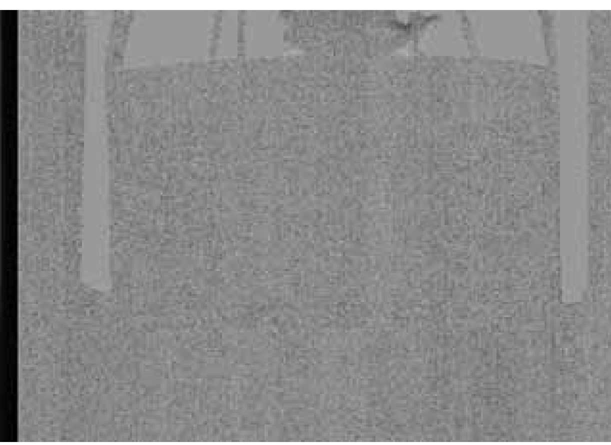
TDI-based foam, 160 kg/m$^3$



↑ Bulk movement was away from the heat source



↑ Bulk movement was toward the heat source

# Laboratory experiments provide material properties*

- **Decomposition rates and evolved gas/vapor products**
  - TGA-FTIR and Pyrolysis-GC-FTIR
- **Specific heat and enthalpy changes**
  - DSC and simultaneous DSC-TGA
- ***Previous joint work between SNL and VNIIA determined mechanisms and kinetics for decomposition of pertinent polyurethane and epoxy materials.****

***V. S. Sirenko, R. A. Koslovskiy, E. I. Popova, S. G. Mulyashow, and K. L. Erickson, "Use of Multiple Experimental Techniques to Study Thermal Decomposition of Polyurethane Foam," Proceedings of SAMPE 2007, Baltimore, MD, June 2007.*

- **Thermal conductivity ($k$) values were taken from literature**
- **Effective radiative conductivity ($k_e$) was determined using an integrating sphere apparatus to measure reflectance and transmittance through un-reacted foam**
- **Scattering ($\sigma_s$) and absorption ($a$) coefficients were calculated using an analytical two-flux representation of radiative transfer**
- $k_e = \dfrac{16\sigma}{3(a+\sigma_s)} T^3$ **or** $k_e = \dfrac{0.005\sigma}{f_{rxn}} T^3$ **W/mK**

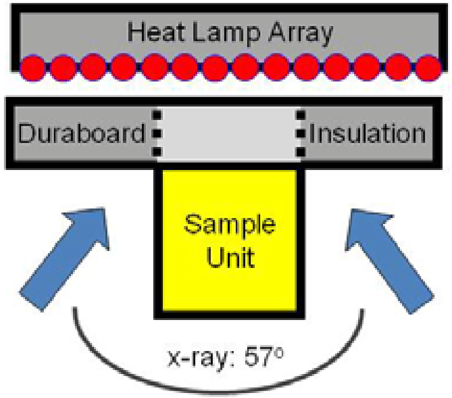
# Modeling approach was based on diffusive approximation for radiant heat transfer

## Energy Balance

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (k + k_e)\nabla T + \sum_i \rho r_i(-\Delta H_i)$$

*Diffusive approximation:*
*Optically thick material*

$$k_e = \frac{16\sigma}{3(a + \sigma_s)} T^3$$




## Decomposition reactions / rates ($r_i$)

$$\text{Polymer} = w_1 A_1 + w_2 A_2 + \cdots$$

$$A_i \xrightarrow{r_i} \xi_{i1} B_{i1} + \xi_{i2} B_{i2} + \cdots$$

$$\frac{dw_{A_i}}{dt} = -k_i w_{A_i} = -r_i \qquad \frac{d\bar{\rho}_{B_{ij}}}{dt} = \rho_B^0 \frac{\xi_{ij} w_i^0}{\bar{M}_{B_{ij}}} k_i w_{A_i}$$

$$k_i = k_i^0 \exp(-Q_i / RT)$$

## Pressure - Assume

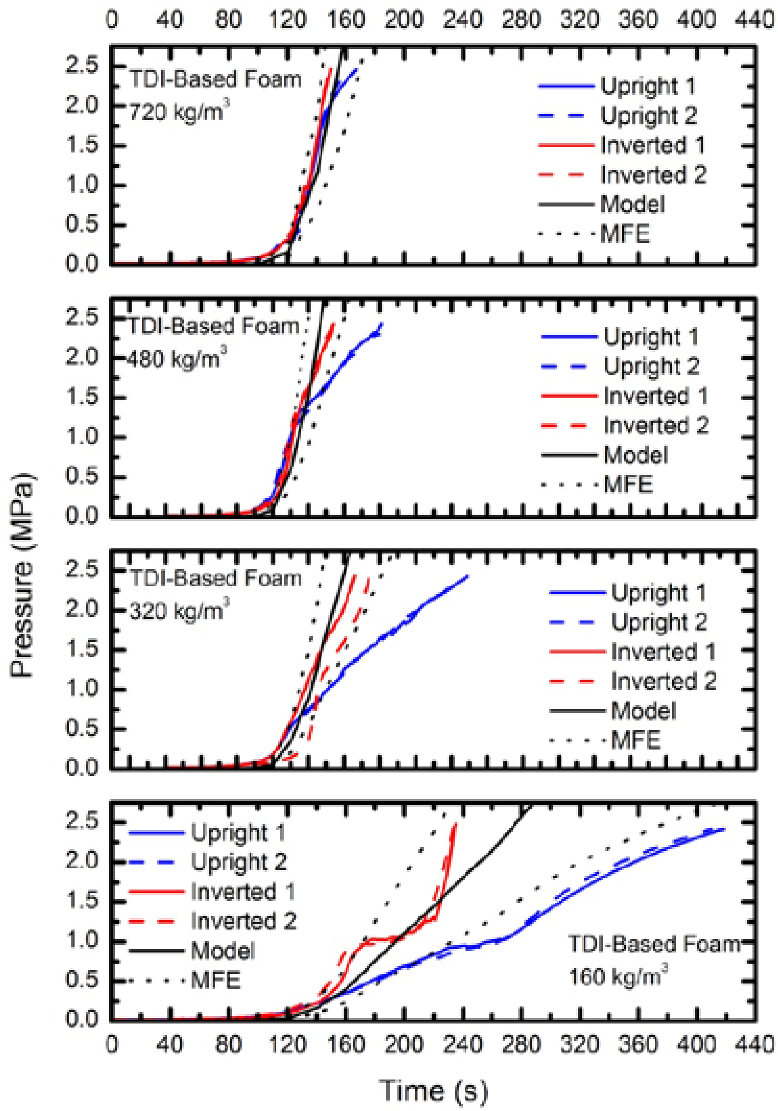
- Gradients relax quickly
- Ideal gas law
- All decomp. prod. ↑
- Gas occupies all free volume

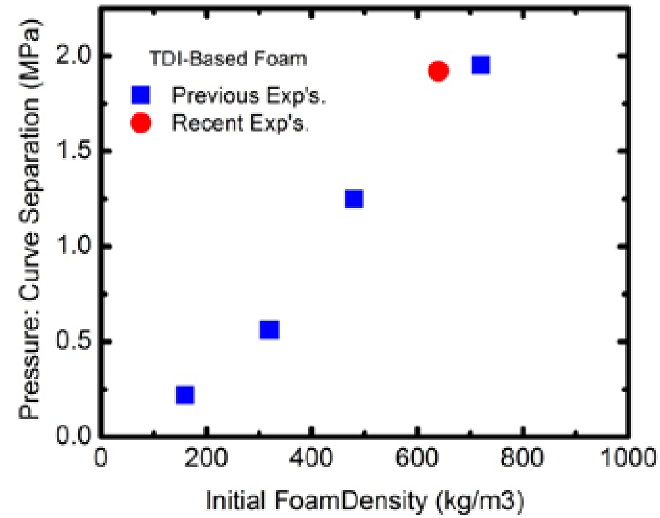
$$P = \frac{n_g R}{\int_{V_g} \frac{1}{T} dV_g}$$

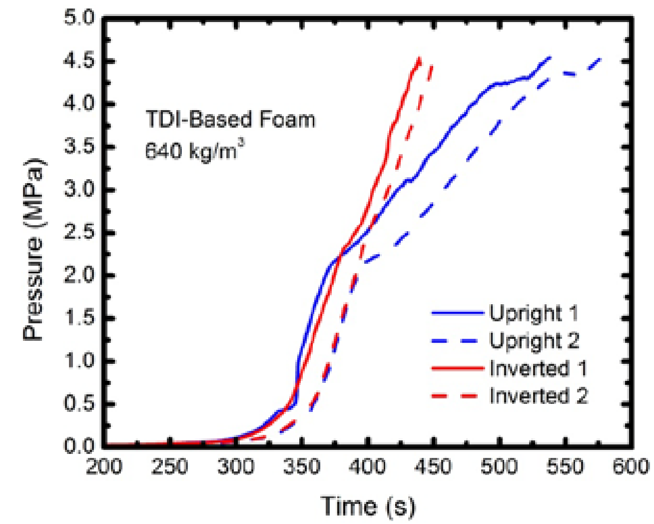


Sandia National Laboratories

# For both RPU foams, time to vent pressure (2.4 MPa) decreased as bulk density of initial foam increased



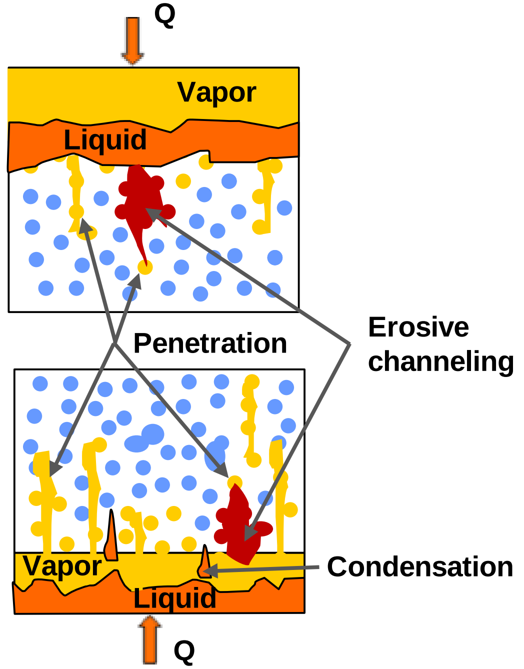



# Foam density and structure determine physical behavior during thermal decomposition

- **Rate of container pressurization depends on physical behavior**
- **Low-density (160 kg/m3) TDI based-foam**
  - Significant convective heat transfer was caused by
    - Liquefaction and flow
    - Penetration and erosive channeling by hot gases
- **In pressure range previously studied (ambient to 2.4 MPa), magnitude of effects decreased as foam density increased**
- **In recent work (ambient to 4.5 MPa), difference between upright and inverted samples increased significantly above ~2.5 Mpa**
- **Sources of Model Form Error (MFE)**
  - Convective heat transfer (gas permeation in pores structure and liquefaction and flow) causes MFE in current model
    - Heat transfer to foam and, therefore, the amount of foam that has decomposed as a function of time
    - Volume that is available to the gas phase as a function of time
  - A related MFE is the distribution of organic decomposition products between condensed and vapor phases

# Future work to reduce model form error and include additional physics

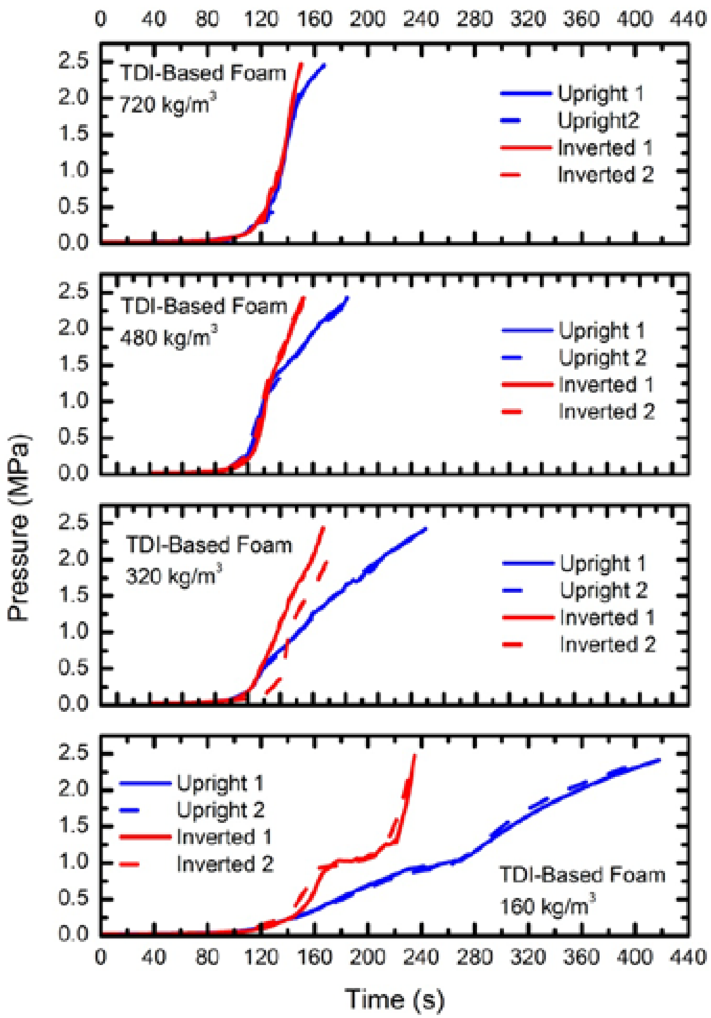
- **Liquefaction and flow of decomposition products**
  - *Significantly impacts heat transfer to foam / rate of gas generation and container pressurization*
- **Gas penetration into pores and erosive channeling by hot gas-phase decomposition products**
- **Vapor-liquid distribution of organic decomposition products**

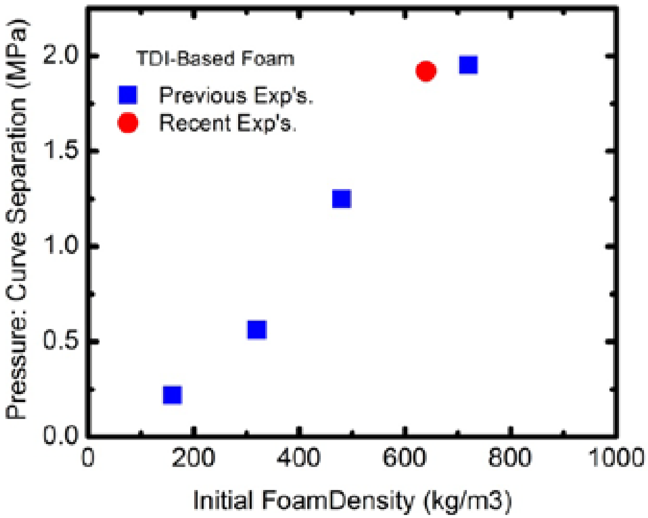


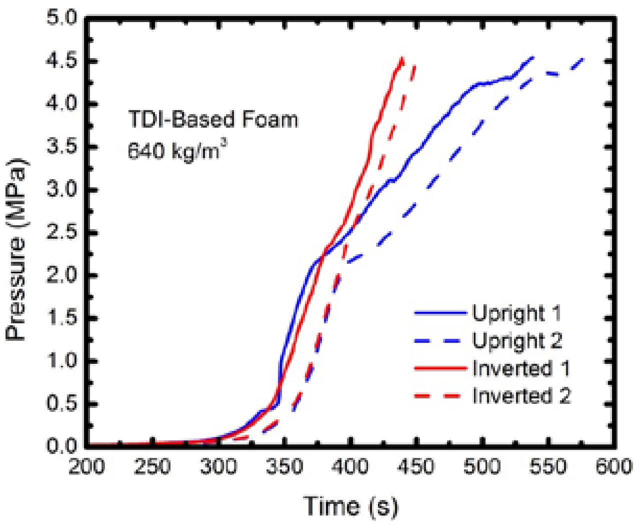

- **Continue collaboration with VNIIA building on previous thermal decomposition and current modeling work**
  - Evaluate and develop advanced computational tools for system-integrated safety analyses requiring approximations to complex phenomena.
  - Continued computational modeling with best available code capabilities at respective labs
  - Explore additional experimental techniques to provide results from variety of physical and thermal boundary conditions and sample geometries

# Backup Slides

# For both RPU foams, time to vent pressure (2.4 MPa) decreased as bulk density of initial foam increased

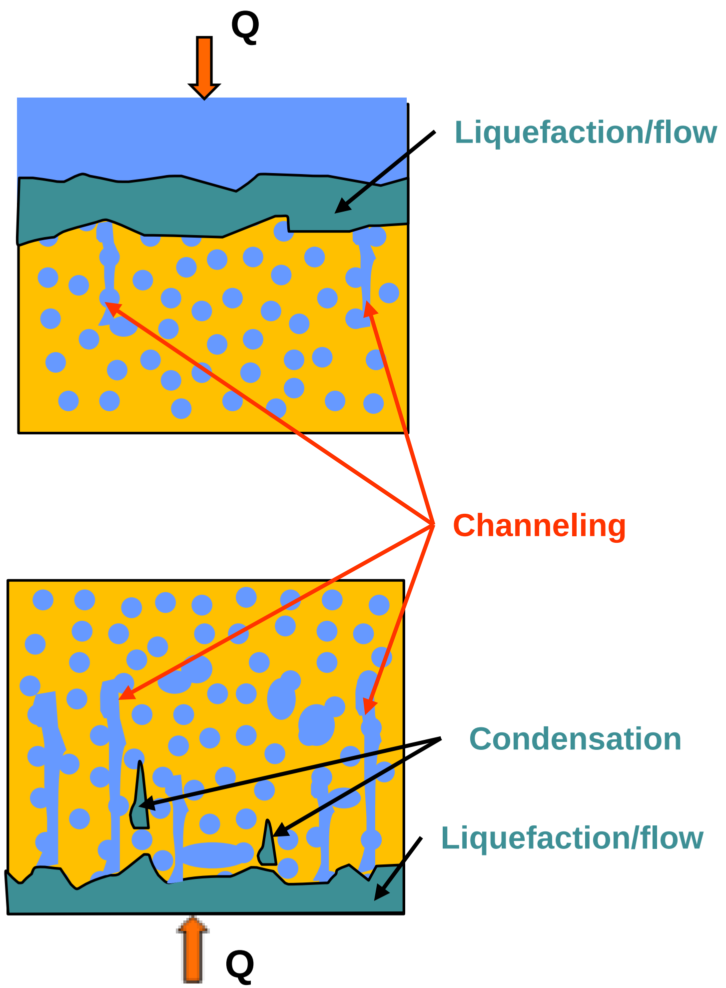


# Path Forward

- **Estimating partial pressure of volatile organic decomposition products**
- **Liquefaction/flow of decomposition products**
  - *Significantly impacts heat transfer to foam / rate of gas generation and container pressurization*
- **Erosive channeling by hot gas-phase decomposition products**



# Postmortem examination of samples also indicates different physical behavior (density = 160 kg/m$^3$)

TDI-Based

Upright

PMDI-based

Inverted

# Larger-scale experiments examined heat transfer to encapsulated objects & pressurization

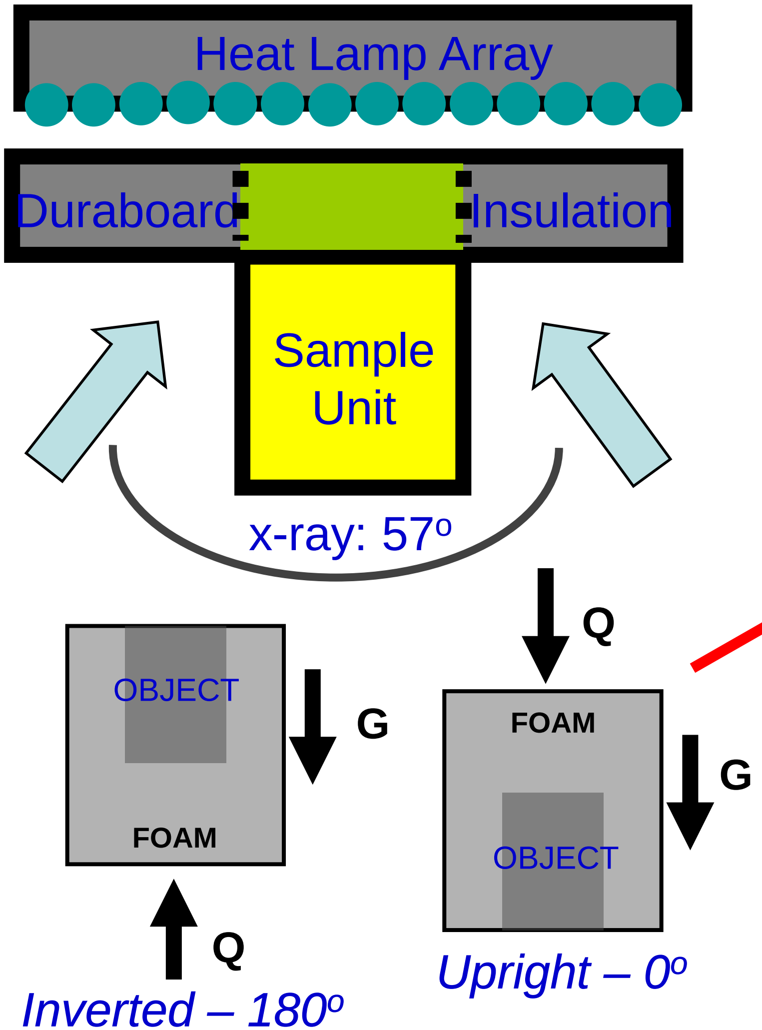
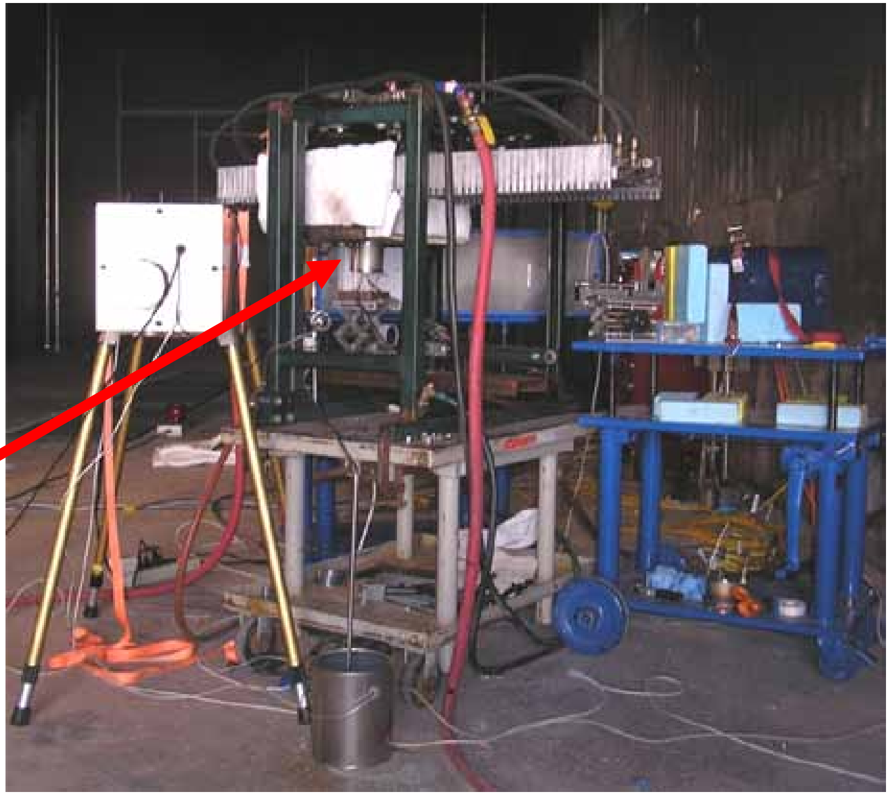
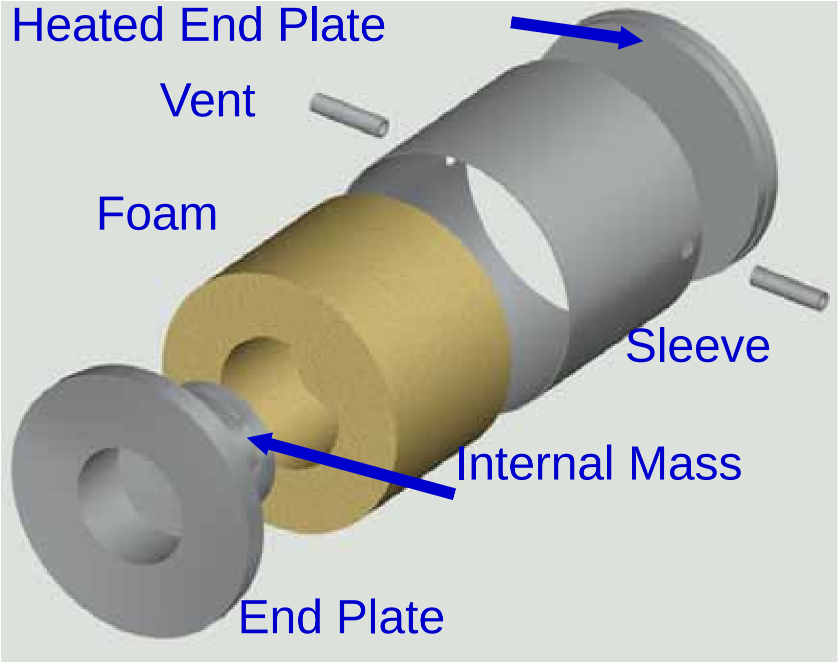


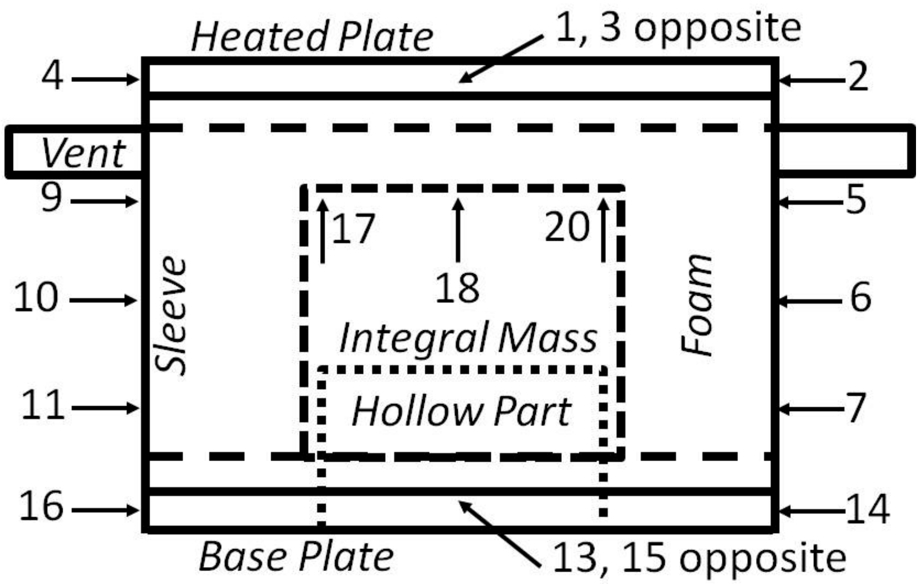

Plate temperature: 1173 K

Foam density = 160 to 720 kg/m$^3$



# Experiments were done using *foam-in-can* (*FIC*) configuration




Sample container

- Sleeve 321 SS tubing
  - 8.89-cm OD, 5.40 cm long
  - 0.508-mm wall thickness
- End plates: 0.635-cm thick 304 SS
  - Laser welded to Sleeve

Rigid, closed cell, polyurethane foams

- TDI-polyester-polyol
  (160 - 720 kg/m$^3$)
- PMDI-polyether-polyol
  - 160 & 320 kg/m$^3$

# Multiple techniques were used to examine decomposition mechanisms and obtain rate data

Decomposition rates and evolved gas/vapor products

- TGA-FTIR
- Pyrolysis-GC-FTIR

Postmortem condensed-phase analyses

- FTIR - ATR

Specific heat and enthalpy changes

- DSC simultaneous DSC-TGA

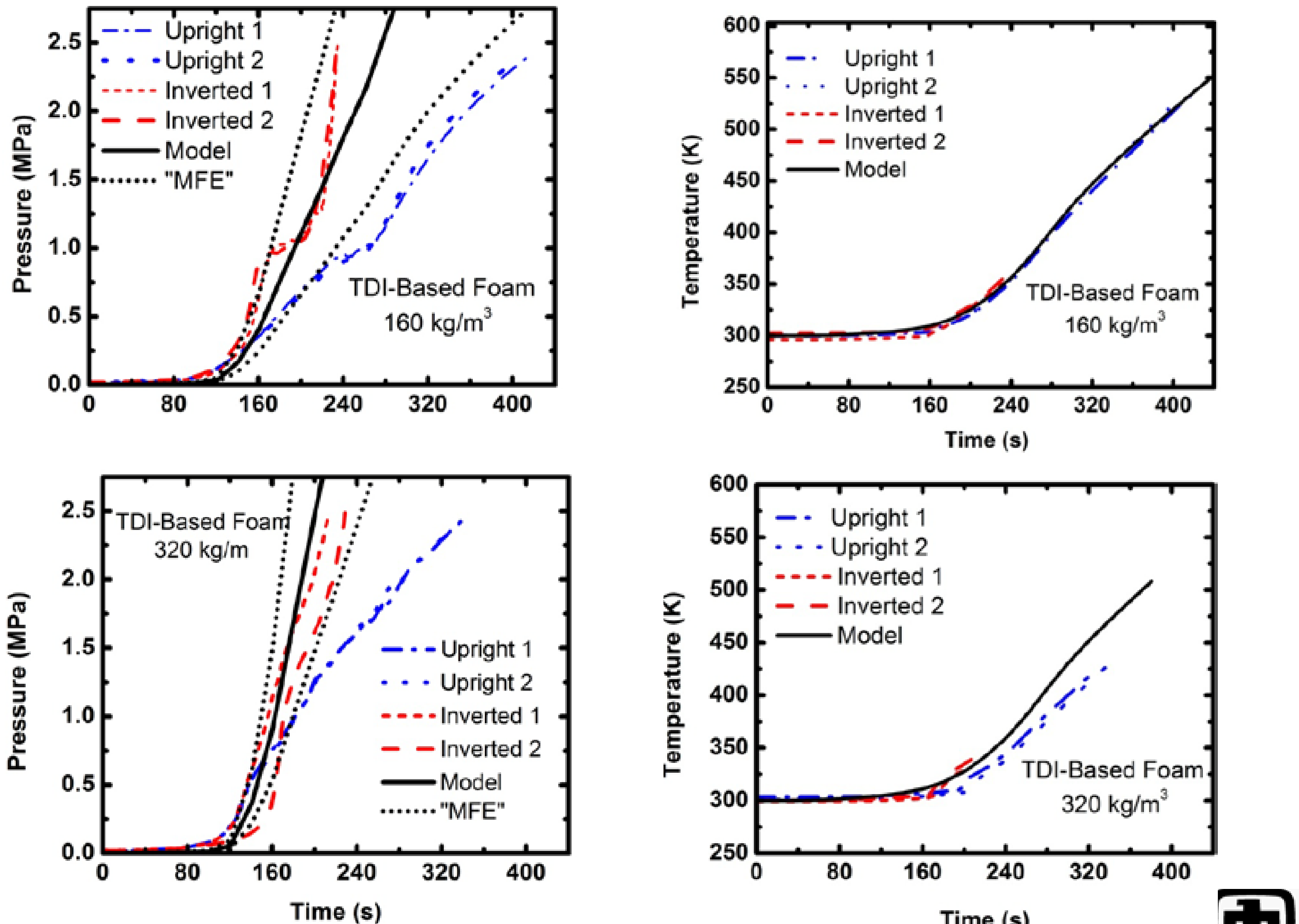
| Initial Foam $w_1^0 A_1 + w_2^0 A_2 + \ldots + w_n^0 A_n$ | Reaction $\longrightarrow$ | Decomposition Products |
|---|---|---|
| ***A*₁** $\boldsymbol{A_1}$ | $r_1$ | $x_{11}B_{11} + x_{12}B_{12} + \mathrm{L} + x_{1m}B_{1m}$ |
| $\boldsymbol{A_2}$ | $r_2$ | |
| … | … | $x_{21}B_{21} + x_{22}B_{12} + \mathrm{L} + x_{2m}B_{2m}$ |
| $\boldsymbol{A_n}$ | $r_n$ | $x_{n1}B_{n1} + x_{n2}B_{n2} + \mathrm{L} + x_{nm}B_{nm}$ |

# Values for ρ, c, k, and ke were obtained from available literature or independent exp's

- **Density was determined by measuring/weighing samples**
- **Heat capacity (c ) values were taken from available literature and were consistent with DSC results**
- **Thermal conductivity (k ) values were taken from available literature**
- **Effective radiative conductivity ke was determined using an integrating sphere apparatus to measure reflectance and transmittance through un-reacted foam**
- **Scattering ($\sigma_s$) and absorption ($a$) coefficients were calculated using an analytical two-flux representation of radiative transfer**

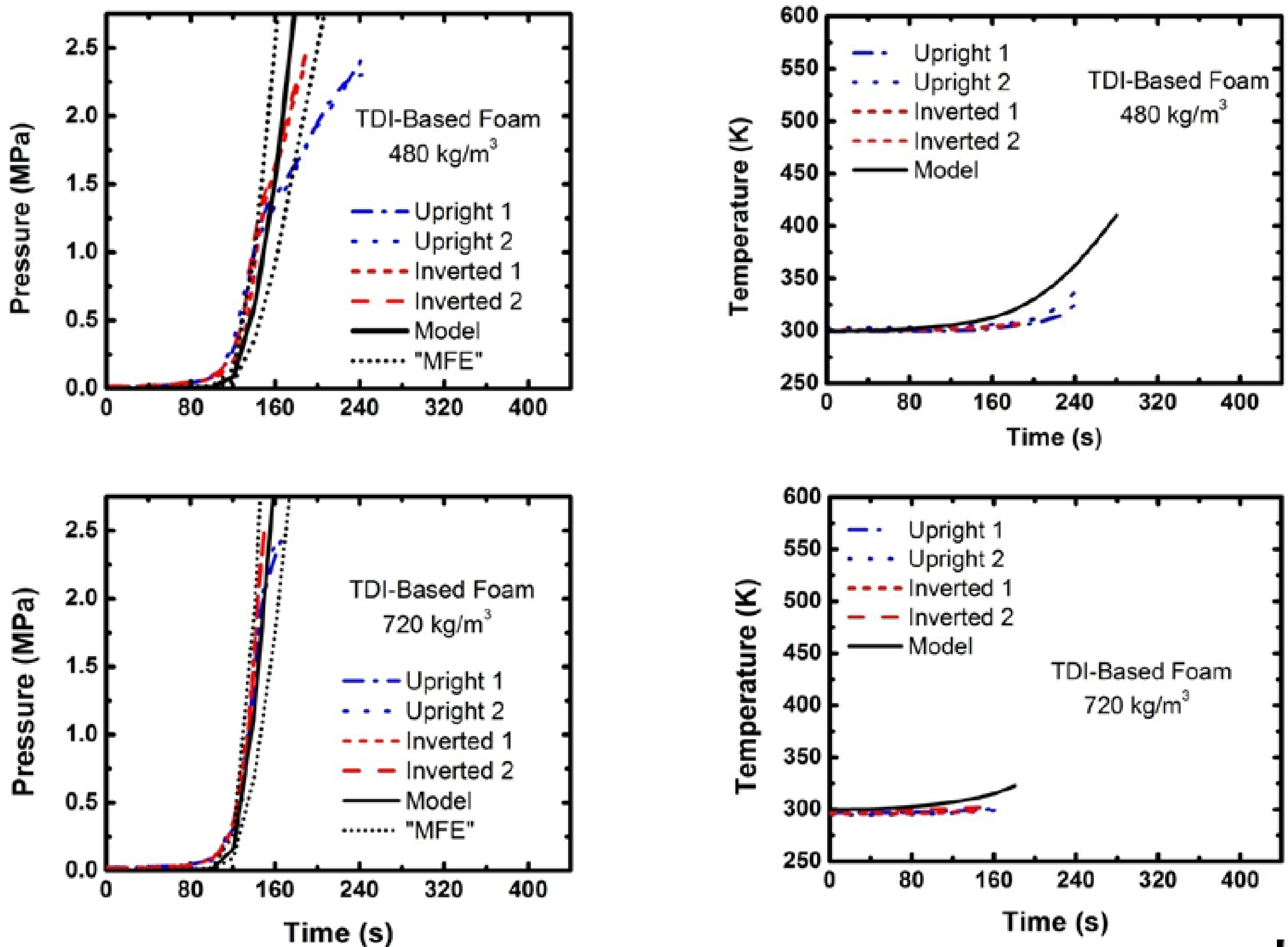
$$k_e = \frac{16\sigma}{3(a+\sigma_s)} T^3 \quad \text{or} \quad k_e = \frac{0.005\sigma}{f_{rxn}} T^3 \quad \text{W/mK}$$

# Current simulations do not account for convective heat transfer by gases or liquids




*MFE is Model Form Error

# Difference between experimental and modeling results is less with higher density TDI-based foams






Sandia National Laboratories

# Similar results were obtained for PMDI-based foams