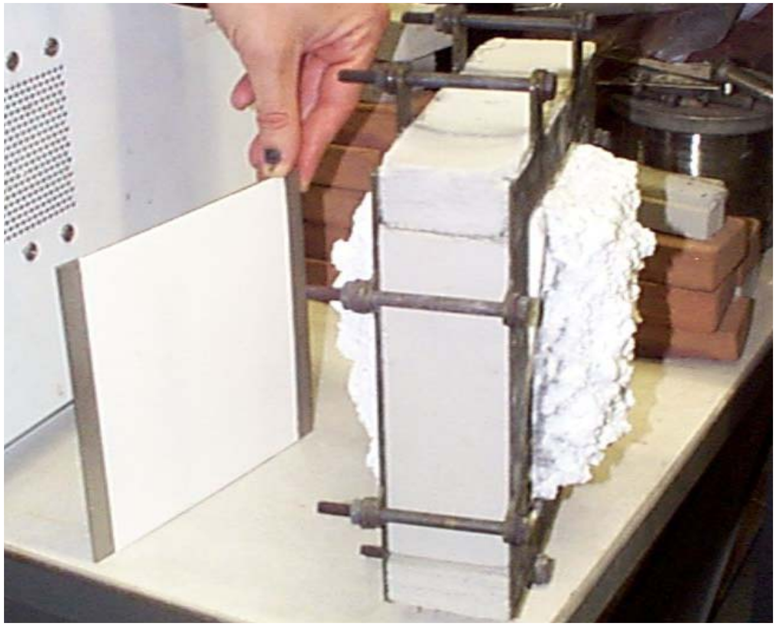
Characterization of Fire Resistive Materials with Respect to Thermal Performance Models



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Technology Administration, U.S. Department of Commerce

Background

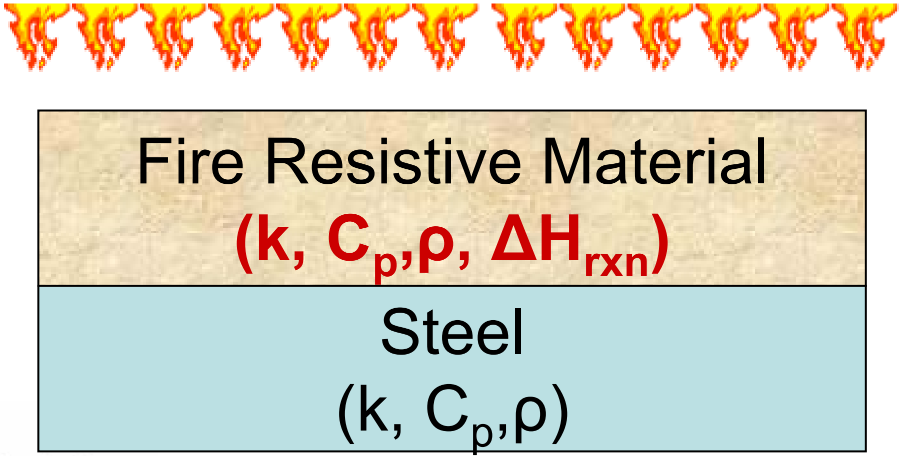
- Events of 9/11 and subsequent WTC investigation have highlighted the importance of fire resistive materials (FRMs) in their role of limiting the temperature rise of structural steel
- WTC investigation demonstrated the possibility to connect fire to structural models via a thermal performance model for the FRM/steel
- R&D project on FRMs included in the Safety of Threatened Buildings program
  - Objective is to apply materials science to understanding and **improving** FRM performance
    - Develop linkages between microstructure and performance properties such as adhesion and thermophysical properties
  - **One activity has been the development of a methodology for characterizing FRMs and (steel) substrates with respect to thermal performance models (inputs needed)**

Outline

- Energy Transfer from Fire to FRM
- Thermophysical Properties of FRM
- Thermal Performance Simulations
  - Slug calorimeter experimental setup

FRMs and Energy Transfer

- FRMs are specified to limit (slow) the energy transfer from a potential fire to the substrate (most often structural steel) that they are protecting
- Energy transfer from fire to substrate controlled by
  - Radiative and convective transfer from the fire to the exposed FRM surface
  - Transfer rate through the FRM
    - Thermal conductivity of FRM
  - Energy absorption/generation of the FRM
    - Heat capacity and density of FRM
    - Enthalpies of phase changes, reactions, etc. within FRM
  - Other concerns
    - Mass transfer (steam, hot reaction gases)
    - Damage/cracking (preferential pathways)
    - Expansion (intumescents)



Fire Resistive Material

$(k, C_p, \rho, \Delta H_{rxn})$

Steel

(k, C_p, ρ)

Energy Transfer from Fire to Surroundings

- Typically characterized by two terms
  - Convection term

    $h(T_{fire}-T_s)$
  - Radiation term

    $\sigma A\varepsilon(T^4_{fire}-T^4_s)$
- Can be simulated in great detail by BFRL Fire Dynamics Simulator (FDS), for example
  - http://www.fire.nist.gov/fds/

Energy Transfer through the FRM

- Basic equation for unsteady-state heat conduction
  - For example, from J.P. Holman, Heat Transfer, McGraw-Hill, New York 1981, **with no reactions**.

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha}\frac{\partial T}{\partial \tau}$$

α indicates the thermal diffusivity and is given by $k/\rho C_p$

Energy Transfer through the FRM

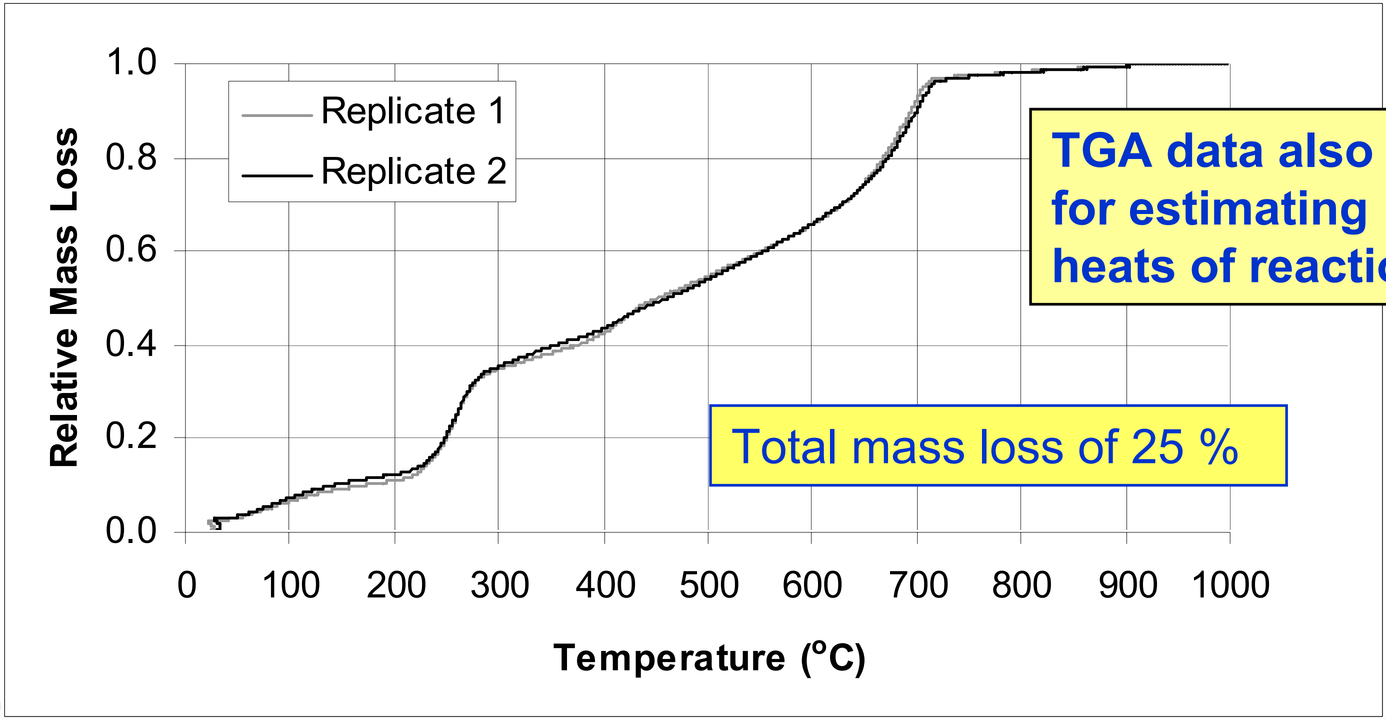
- Equation from the previous slide can be solved, numerically for instance, if:
  - Boundary conditions are known
    - Surface temperature
      - From energy transfer from fire or furnace
    - Interior boundary condition
      - Adiabatic at center line of symmetrical samples, for example
        - Slug calorimeter plate (center)
        - Beam or column (center)
  - **Thermophysical properties are known**
    - **Density**
    - **Thermal conductivity**
    - **Heat capacity**
    - **Heats of reactions and phase changes**

Thermophysical Properties

- Density, heat capacity, heats of reaction/phase changes, and thermal conductivity
- NIST proposed methodology:
  - Bentz, D.P., Prasad, K.R., and Yang, J.C., "Towards a Methodology for the Characterization of Fire Resistive Materials with Respect to Thermal Performance Models," *Fire and Materials*, **30**, 311-321, 2006.
  - Updated recently in: Bentz, D.P., Prasad, K.R., "Thermal Performance of Fire Resistive Materials I. Characterization with Respect to Thermal Performance Models," NISTIR **7401**, U.S. Department of Commerce, 2007.

Thermophysical Properties

- Density
  - Initial mass and mass loss vs. temperature (from TGA)
  - Initial dimensions and expansion factor (for intumescents)



TGA data also critical for estimating heats of reaction

Total mass loss of 25 %

Thermophysical Properties

- Options for heat capacity
  - Direct computation from mixture composition and heat capacities of component materials
  - DSC or STA measurement
    - Small sample size (inhomogeneity, mass change)
  - Transient thermal exposure
    - Thermal diffusivity-type measurement
    - Volumetric heat capacity from transient plane source measurement (e.g., Hot Disk® at NIST)

Thermophysical Properties

- Does one need to characterize heat capacity vs. temperature or does a room temperature measurement suffice?
  - Answer: It depends
    - Purposes and desired level of accuracy
    - For most FRMs, change in C_p from 23 °C to 1000 °C is less than 20 % (and may be less than 10 %)
    - Thermal mass of FRM may be much less than that of the substrate it is protecting
      - For example, in a typical slug calorimeter experiment, mass of slug is more than 5 times greater than the sum of the “twin” FRM specimen masses

Thermophysical Properties

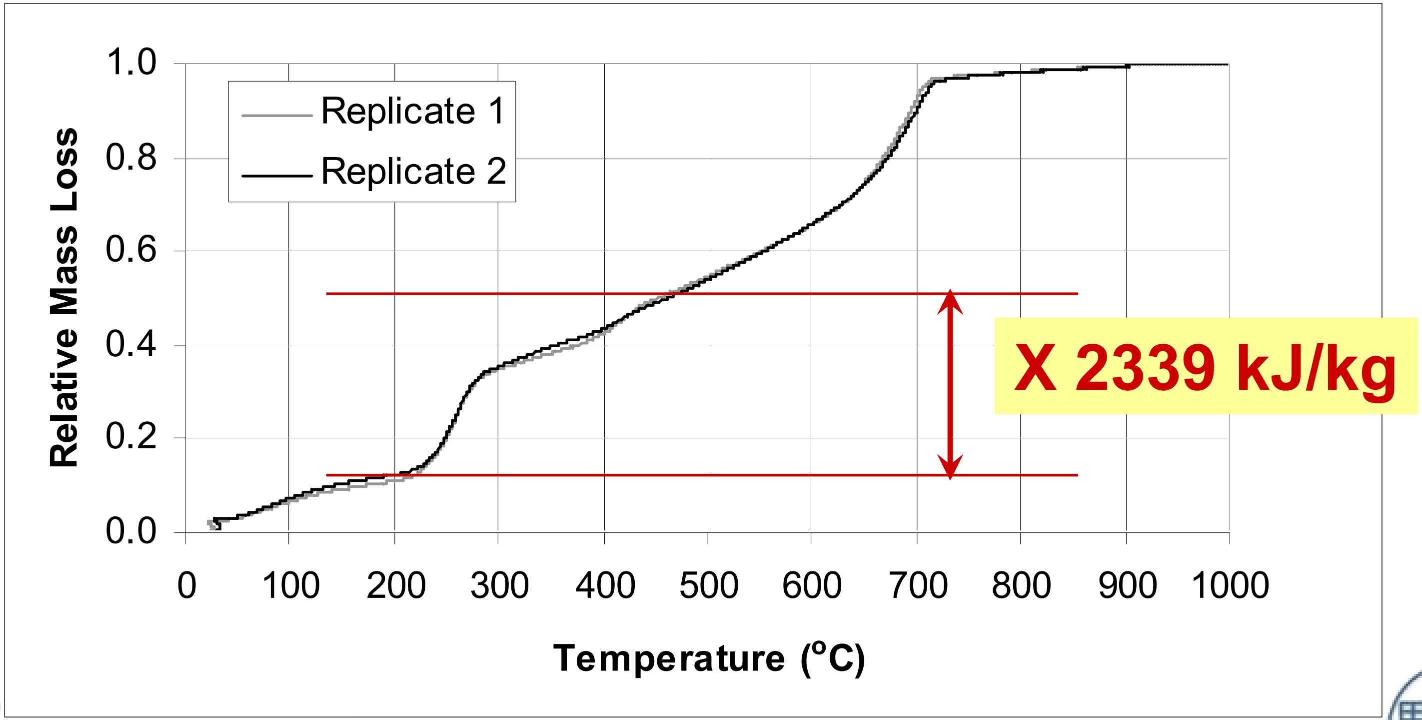
- Heats of Reactions
  - Compute from measured mass loss data (TGA) and theoretical (computed) heats of reaction for **assumed** reactions
    - Evaporation of “free” water
    - Dehydration of gypsum
      - Gypsum → hemihydrate
      - Hemihydrate → anhydrite
    - Dehydration of portland cement
      - Dehydration of C-S-H gel
      - Dehydration of calcium hydroxide
    - Decarbonation

Thermophysical Properties

Reaction	Assumed temperature range for mass loss	Assumed reaction temperature	Computed Enthalpy (kJ/kg product)
Evaporation of free water	25 °C to 100 °C	75 °C	2328 kJ/kg water
Dehydration of "C-S-H"	100 °C to 300 °C or 100 °C to 400 °C	125 °C	1438 kJ/kg water
First dehydration of gypsum to hemihydrate	100 °C to 200 °C	150 °C	3007 kJ/kg water
(2nd) dehydration of hemihydrate to anhydrite	200 °C to 450 °C	325 °C	2339 kJ/kg water
Dehydration of calcium hydroxide	300 °C to 600 °C or 400 °C to 600 °C	450 °C	5660 kJ/kg water
Decarbonation of calcium carbonate	600 °C to 1000 °C or 450 °C to 1000 °C	750 °C	3894 kJ/kg CO_2

Thermophysical Properties

- Heats of reaction
  - Computed enthalpy for reaction multiplied by measured mass loss gives enthalpy change for material



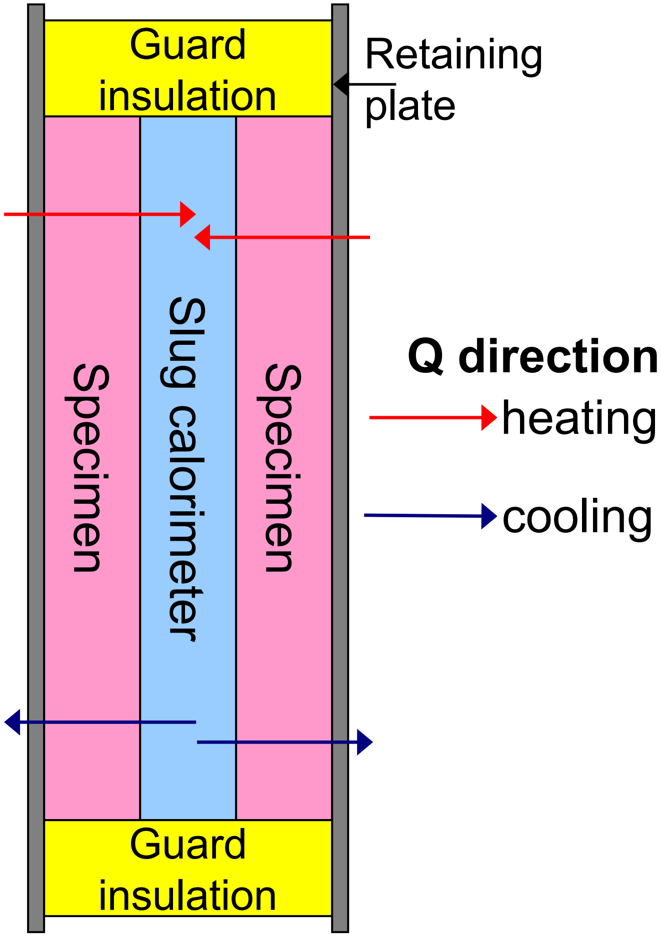
Thermal Conductivity at High Temperatures

- How to measure it?
  - ASTM C1113: Hot wire method
    - Difficult to maintain contact with porous FRM specimens
    - No information on influences of reactions, phase changes, etc.
  - High-temperature guarded hot plate
    - Steady-state method (no info on reactions, etc.)
    - State-of-the art facility under construction in BFRL at NIST
  - Transient plane source method (Hot Disk®)
    - Unit with furnace (test up to 700 ^{o}C) at BFRL
  - **Slug calorimeter** (designed and built at BFRL in 2004 and used extensively since then)
    - Similar in principle to the Cenco-Fitch Apparatus used in ASTM D2214 for estimating the thermal conductivity of leather (first published by Fitch in 1935) and in approach to ASTM E457 for measuring heat-transfer rates using a thermal capacitance transducer
    - Currently being standardized in ASTM E37.05 (Thermophysical Properties) --- submitted to subcommittee ballot in Jan. 2007
    - Using multiple heating/cooling scans provides valuable information on the influences of reactions, phase changes, and mass transfer

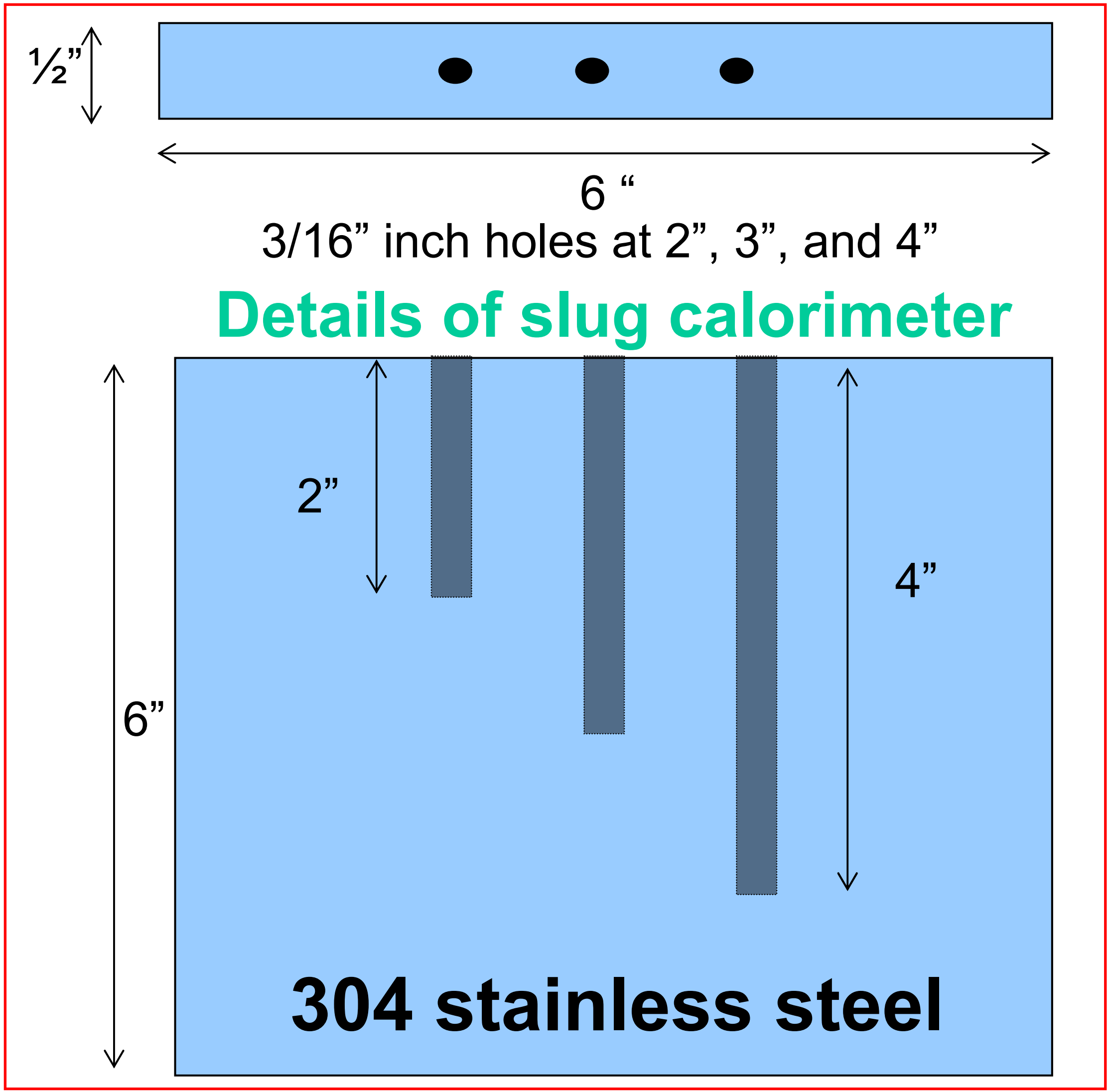
Slug Calorimeter Technique

- Sandwich specimen consisting of two “slabs” of FRM covering two sides of a steel slug of known mass and heat capacity
- Monitor slug temperature change as entire sandwich is exposed to a heating/cooling cycle
- Calculate effective thermal conductivity during **multiple** heating/cooling cycles
- For detailed information see: Bentz, D.P., Flynn, D.R., Kim, J.H., and Zarr, R.R., “A Slug Calorimeter for Evaluating the Thermal Performance of Fire Resistive Materials,” *Fire and Materials*, **30**, 257-270, 2006, available in electronic monograph at http://ciks.cbt.nist.gov/garbocz/slugpaper1.

Slug Calorimeter

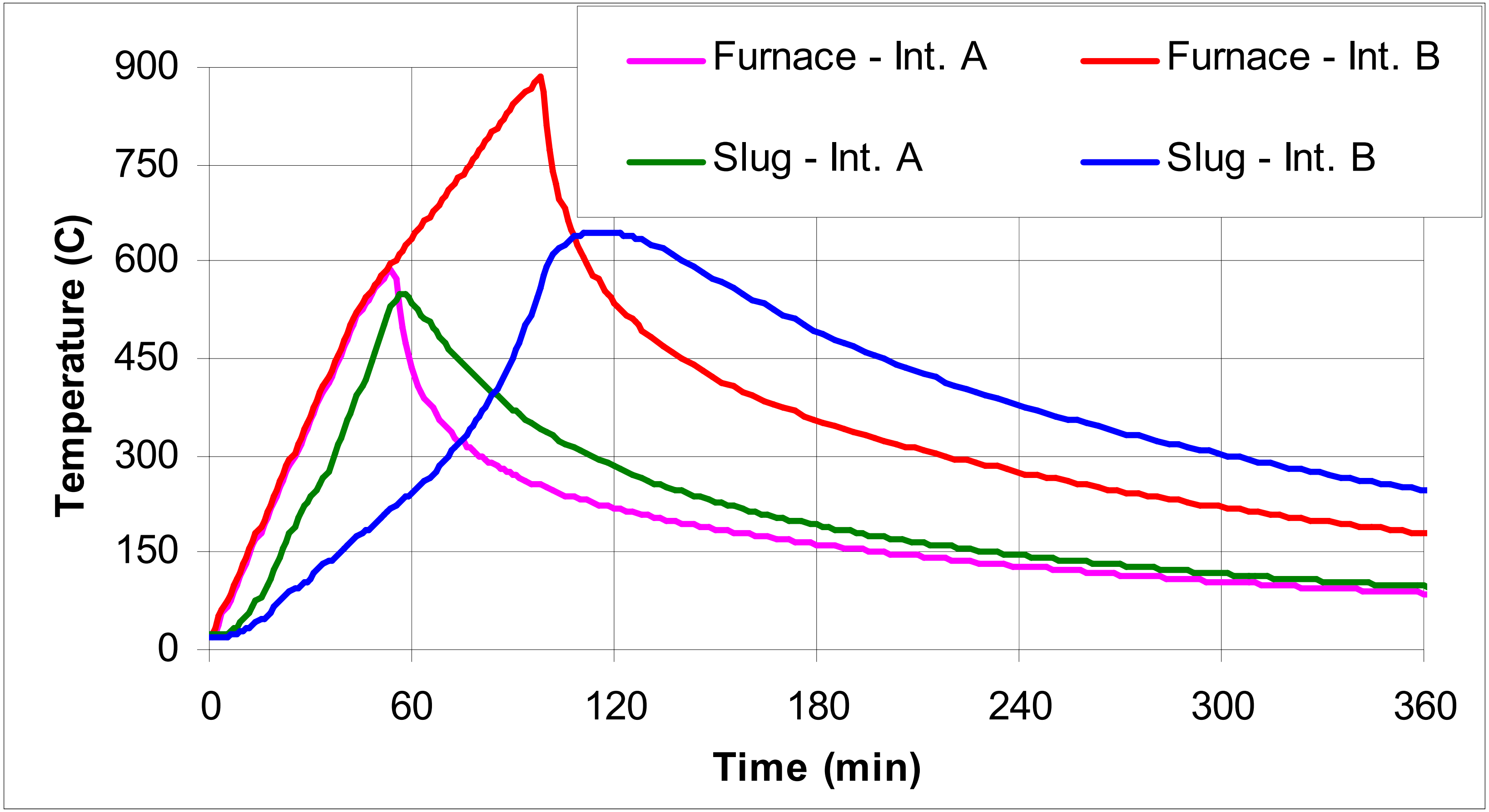


Experimental setup



Details of slug calorimeter

Raw Data for Exposure of Intumescents



Time for central slug to reach 538 °C varied from 52 minutes to 96 minutes for the two different materials

Determination of Effective k

(courtesy of Dan Flynn, BFRL guest researcher)

$$\partial^2 T/\partial z^2 = (1/\alpha)(\partial T/\partial t)$$

With B.C.: $T(0,t)=Ft$, $k(\partial T/\partial z) + H(\partial T/\partial t)=0$

α is the thermal diffusivity

H is the thermal capacity of one half of the slug plate

F is the rate of temperature increase/decrease of the slug

Solution: $T(z,t)=F[t-(H+lC)z/k+Cz^2/(2k)]$

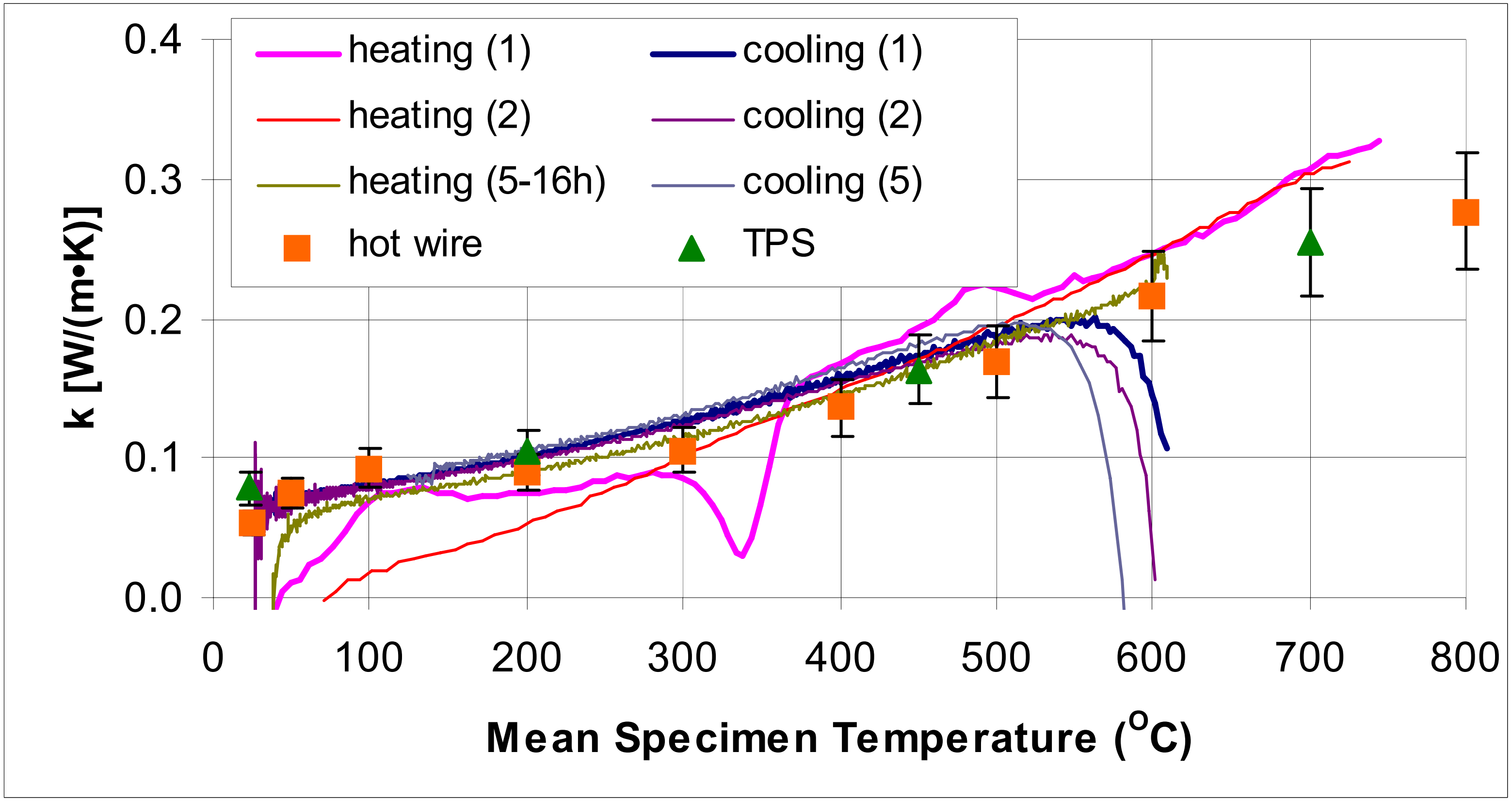
l is the specimen thickness, C its volumetric heat capacity

$$\Delta T = (Fl/k)*[H+lC/2]$$

ΔT is the temperature difference across the specimen

$$k=Fl(H+lC/2)/\Delta T=Fl(M_S c_p^{S}+M_{FRM} c_p^{FRM})/2A\Delta T$$

Slug Calorimeter Results: FRM A

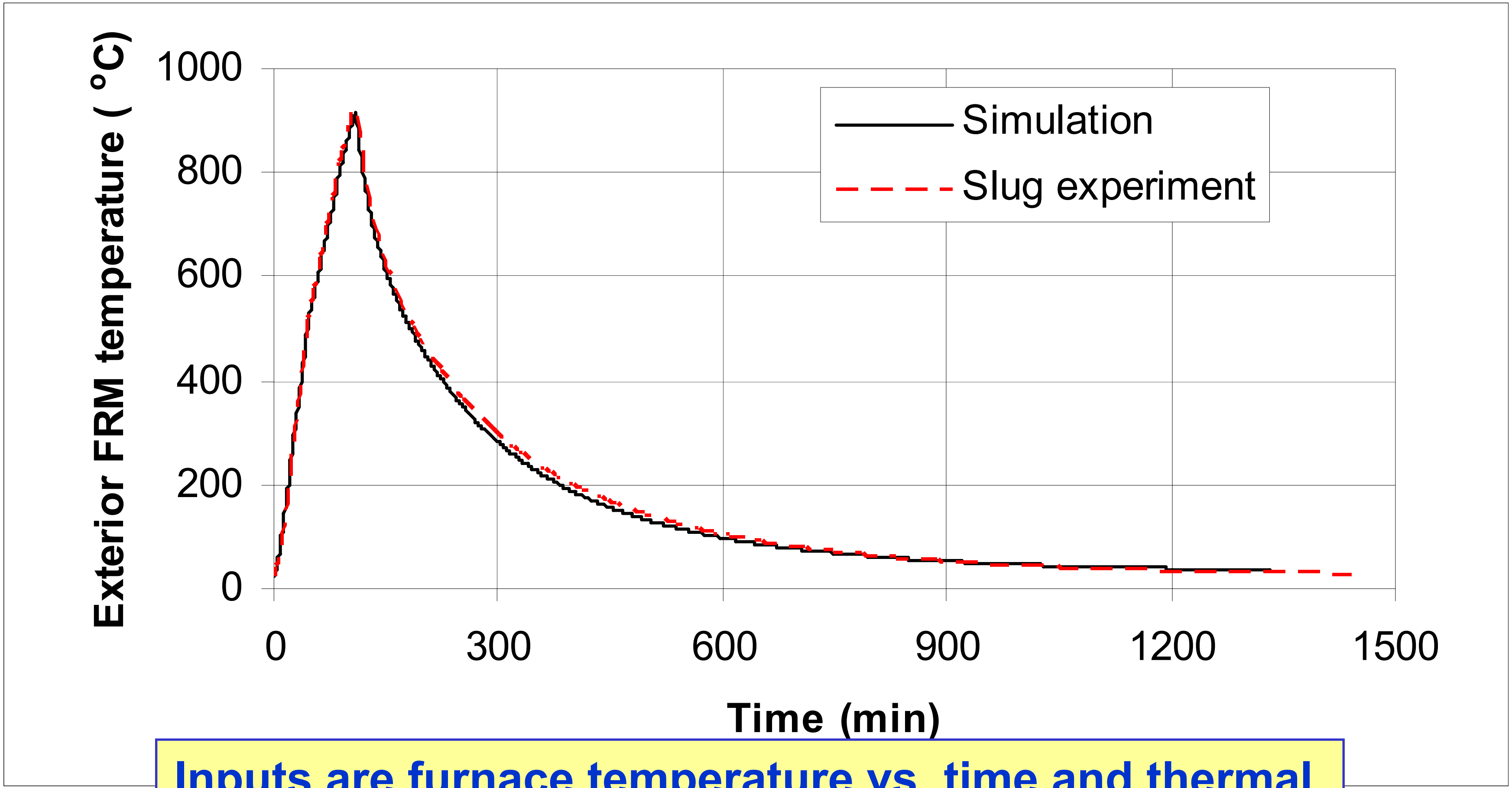


- Good agreement with previously measured values
- Good repeatability in cooling curves for different runs
- Differences between 1st and 2nd heating cycle provide valuable information on influences of endothermic and exothermic events, including reactions, phase changes, and mass transfer

NIST Multi-Layer Fire/Heat Transfer Model

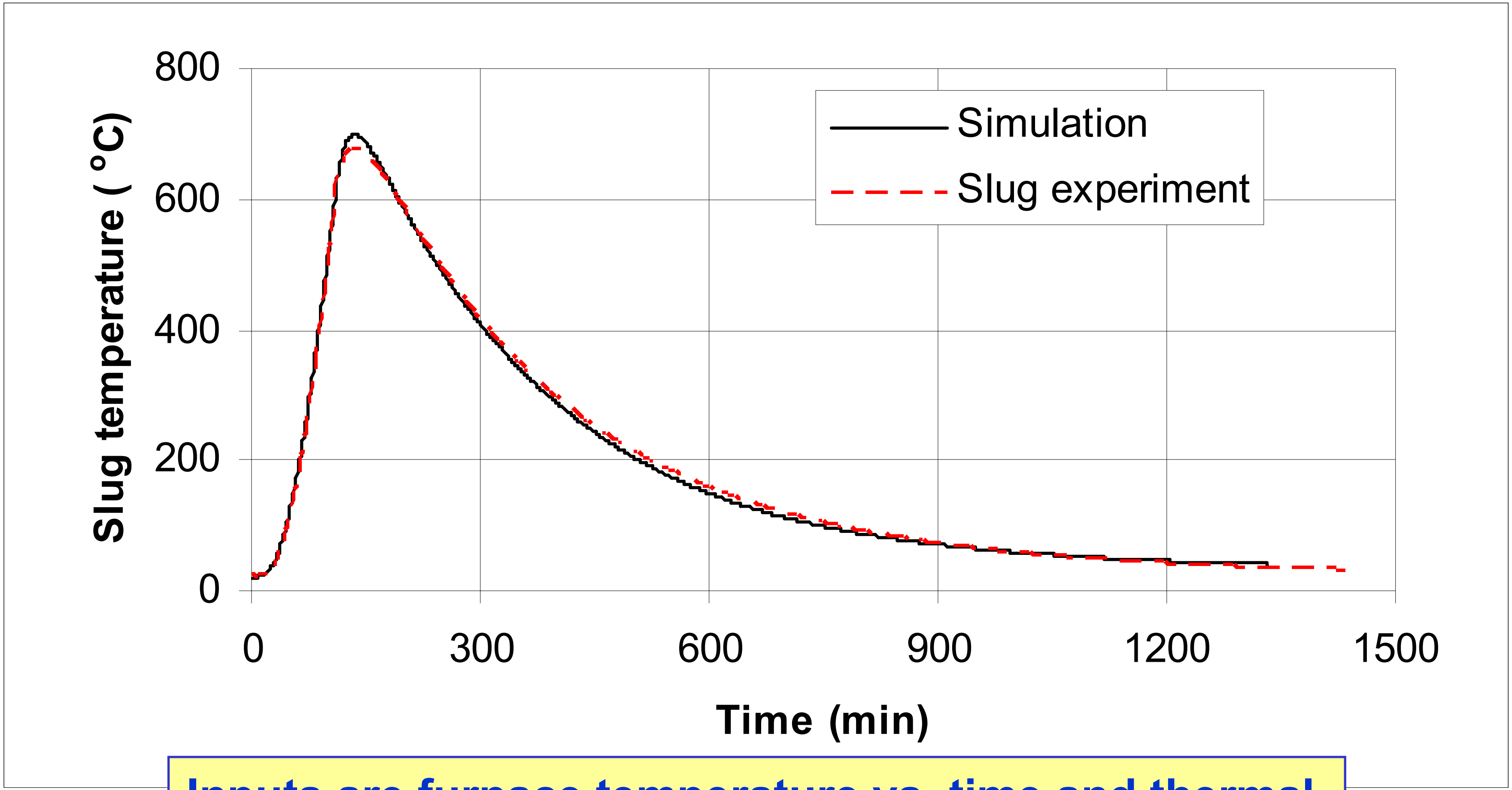
- Developed by Kuldeep Prasad (kuldeep.prasad@nist.gov, x3968)
  - Originally to model performance of layered protective clothing for firefighters (NISTIR 6881, available at BFRL web site)
  - Easily extended to simulating the slug calorimeter experiment
    - Excellent agreement with experiment as illustrated in slides to follow
  - **Can also be applied to simulation of E119 and other fire exposures**

Simulation of Slug Calorimeter Experiment – Exterior FRM Temperature



Inputs are furnace temperature vs. time and thermal properties of AISI 304 stainless steel slug and FRM

Simulation of Slug Calorimeter Experiment – Internal Slug Temperature



Inputs are furnace temperature vs. time and thermal properties of AISI 304 stainless steel slug and FRM

Summary

- Methodology developed and documented for characterizing FRMs with respect to thermal performance models
- Measured properties allow accurate simulation of thermal performance for slug calorimeter experimental setup
- Next steps will be extensions to ASTM E119-type tests and real fires

Outreach and Technology Transfer

- New section of electronic monograph on FRMs
  - http://ciks.cbt.nist.gov/monograph
  - Separate chapters on microstructure, adhesion, and thermophysical properties
- BFRL/industry consortium formed 03/06
  - http://ciks.cbt.nist.gov/~bentz/FRMconsortium.html
  - Seven industrial members each contributing $20 K
  - Initial scope of 2 years
- Standardization
  - Efforts are underway for a slug calorimeter standard practice (in ASTM E37.05 – Thermophysical Properties)
  - Also serving on UL STP 263 where the first of its kind durability standard is being developed for FRMs