Title: *Fire Resistive Materials: Thermal Barriers between Fires and Structures*

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ABSTRACT

Fire resistive materials (FRMs) serve a critical function in insulating (steel) structures to limit steel temperature rise during a fire exposure. This paper provides an overview of FRMs, focusing on the measurement of their thermophysical properties. After a brief review of the standard fire test conventionally used to evaluate the performance of FRM-protected components and systems, the measurement of thermophysical properties at room and elevated temperatures is considered. Standard test methods available for each property measurement are noted and example results for FRM materials are presented. These property values can provide critical inputs for simulations of the thermal performance of components and systems during standard and real world fires.

INTRODUCTION

For over a century, architects and engineers have explicitly considered the exposure of materials and structures to a fire during their intended service life. Particularly after large scale fires in several major U.S. cities during the first decade of the 20th century (such as the conflagration in Baltimore in 1904), new focus on "fireproof" materials of construction as substitutes for wood emerged [1]. Such materials commonly included masonry, iron and brick, and steel and concrete. The application of spray-applied fire resistive materials (SFRMs) as an alternative to concrete for protecting structural steel initiated in the 1940s [2]. The goal of a fire resistive material (FRM) is to significantly slow down the temperature rise of the structural steel that it is protecting during a fire exposure [3]. As such, both the thermophysical and adhesion properties of the FRM are critical to successful performance [4]. Typical FRMs include standard (typical specific gravity of 0.24 to 0.32) and medium (0.32 to 0.40 specific gravity) density spray-applied mineral fiber materials bonded by a small amount of cementitious binder; standard, medium, and

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high (specific gravity of 0.64 to 0.8) density gypsum and portland cement-based spray-applied products containing a lightweight filler such as vermiculite or shredded polystyrene; spray-applied thin-film or epoxy-based intumescent coatings that may expand up to 40x in thickness during a fire exposure; and board products based on gypsum, mineral fibers, or calcium silicates [3,5]. For 90 years, the performance of structural components in a fire has been evaluated using the ASTM E119 standard test method [6,7].

CONVENTIONAL E119 FIRE TESTING

The first edition of ASTM E119 (originally known as C19) was issued in 1918 [7]. The test method provides a standard time-temperature curve (Figure 1) to which materials and components are exposed to evaluate their resistance to fire. Floors, columns, beams, and walls are commonly tested in such a temperature-controlled environment. The test produces an hourly rating (e.g., ½ h, 1 h, 2 h, 4 h), commonly based on the time required for the protected steel to achieve a threshold temperature (538 ºC). These hourly ratings are then utilized to classify components and assemblies for listings in design guides that can be employed by architects and engineers. The chosen time-temperature curve has been the subject of constant scrutiny by the fire research community, but has remained intact to the present date. It must be emphasized that a 2 h rating in no way implies that the rated assembly will last 2 h in a real world fire.

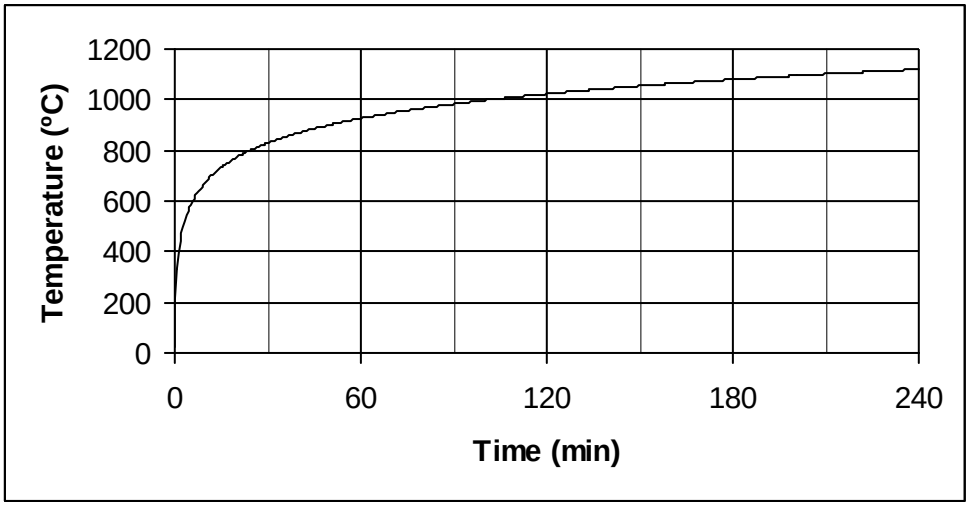

Figure 1. Standard time-temperature curve for an ASTM E119 fire exposure [6].

THERMOPHYSICAL PROPERTY MEASUREMENT: TEST METHODS, EXAMPLE RESULTS, AND STANDARDS

One limitation of the ASTM E119 test is that it typically only provides a pass/fail (time) rating for the material or components being evaluated. As the industry moves towards performance-based design, it would be extremely valuable

to have the capability of predicting (simulating) the performance of a component or a system under real world fire conditions. As was demonstrated during the National Institute of Standards and Technology's (NIST) investigation of the World Trade Center (WTC) collapse, such predictions can only be made when quantitative and reliable data on the thermophysical properties of the materials of construction are available as a function of temperature [8]. Conventionally for FRMs, only room temperature properties for density, thickness, and various bonding and strength parameters are determined [9,10]. Ideally, a better description for thermal modeling would provide the following thermophysical properties as a function of temperature: thermal conductivity, heat capacity, density, heats of reaction and phase changes, and emissivity [11]. Therefore, the measurement of each of these will be discussed next.

Thermal Conductivity

ASTM standard test methods for measuring the thermal properties of insulating materials (such as refractories and building insulation) as a function of temperature have been in place for many years including the hot wire [12] and guarded-hot-plate methods [13]. Generally, it is assumed that the materials being evaluated in these two methods are non-reactive and dimensionally stable during the test period, conditions that are rarely met by FRMs. Thus, recent efforts have focused on developing alternative methods for these reactive and sometimes quite expansive (intumescent) materials. Two such developments will be discussed here: a transient plane source technique and a thermal capacitance (slug) calorimeter. Interestingly, both employ a sandwich construction requiring twin (nominally identical) specimens of the FRM being measured.

The transient plane source (TPS) technique was developed by Gustafsson [14,15] and has been commercialized. In this method, a protected nickel wire spiral probe with a typical radius of tens of millimeters is sandwiched between twin specimens of the FRM being evaluated. A power input is supplied to the probe (0.08 W for 320 s being typical for FRMs) and the thermal response of the material is analyzed to determine both its thermal conductivity and its volumetric heat capacity. By placing the entire measurement setup in a furnace and switching from a polymer-coated probe to a mica-coated one, measurements can be obtained at temperatures up to 700 ºC, or even up to 1000 ºC in a non-oxidizing atmosphere. The technique has not yet been standardized within ASTM, but some efforts for international (ISO) standardization are ongoing.

The thermal capacitance (or slug) calorimeter method was developed at NIST in 2004 [16] and is described in ASTM E2584-07 [17]. In this method, a stainless steel slug with holes for thermocouples is sandwiched between twin specimens of the FRM and its thermal response is monitored during multiple heating/cooling cycles in a furnace. Knowing the surface temperature of the exposed FRM and the temperature of the slug as a function of time, along with the heat capacities and masses of the slug and FRM allows for computation of the apparent thermal conductivity of the FRM as a function of temperature (typically

from room temperature to about 700 ºC). Example results generated using the slug calorimeter at NIST are contrasted against hot wire and transient plane source measurements in Figure 2 for a single FRM material [16]. The three techniques exhibit reasonable agreement for this particular FRM. By comparing the first and second heating cycles for the slug calorimeter technique, the influence of reactions, phase changes, and mass transport of steam can be observed. When intumescents are evaluated using the slug calorimeter, open end plates are utilized to allow for the expansion of the coating during the high temperature exposure. Still, the thickness of the coating as a function of temperature must be measured or estimated, as it is a required input for computing the material's thermal conductivity.

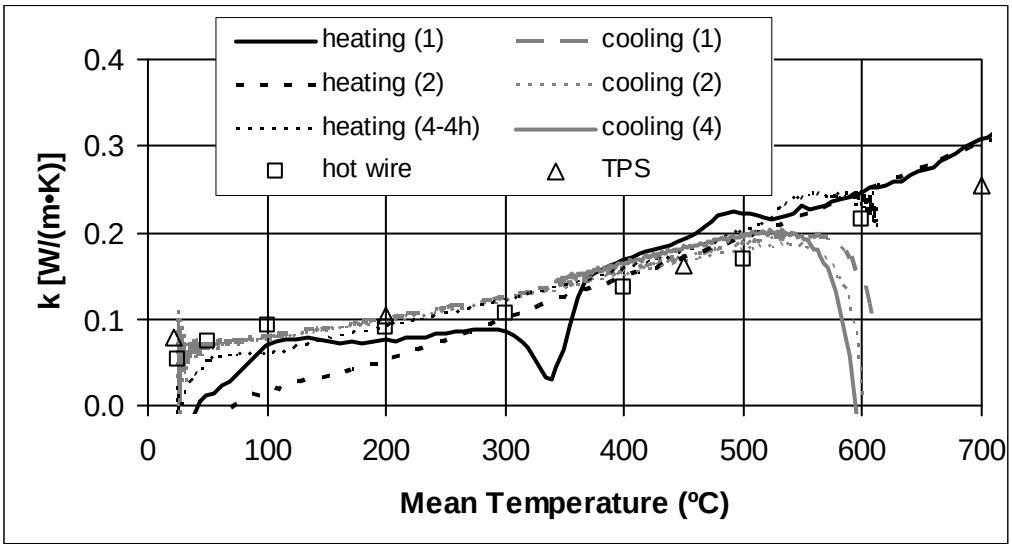

Figure 2. Apparent thermal conductivity of FRM vs. mean specimen temperature for three heating/cooling cycles using the slug calorimeter in comparison to results obtained using the hot wire (ASTM C1113) and transient plane source (TPS) techniques [16].

Heat Capacity

Measuring the heat capacity of FRMs presents its own set of challenges. For many materials, heat capacity as a function of temperature is determined using the ASTM E1269 standard test method [18], typically with sapphire as a reference material to establish the "calorimetric sensitivity". Two challenges for FRMs are their significant mass loss during a high temperature exposure and their relative inhomogeneity, which makes obtaining a small but representative specimen difficult. A typical differential scanning calorimeter (DSC) is only designed to accommodate a sample with a mass of 50 mg to 100 mg. An example data set for a FRM that was obtained using a DSC with gold pans is provided in Figure 3. The endothermic peaks correspond to dehydration and decarbonation reactions for the cementitious binder component of the FRM. For this particular FRM, one could reasonably employ a nominal heat capacity value of 1100 J/(kg·K) for temperatures up to 700 ºC.

If the composition of the FRM is known, the heat capacity can be calculated from the mass-weighted average of the heat capacities of its component materials. Heat capacity can also be assessed using the transient plane source technique described previously for the measurement of thermal conductivity [14,15], assuming that the density of the material as a function of temperature is known in order to convert the provided heat capacity values from a volumetric to a mass basis.

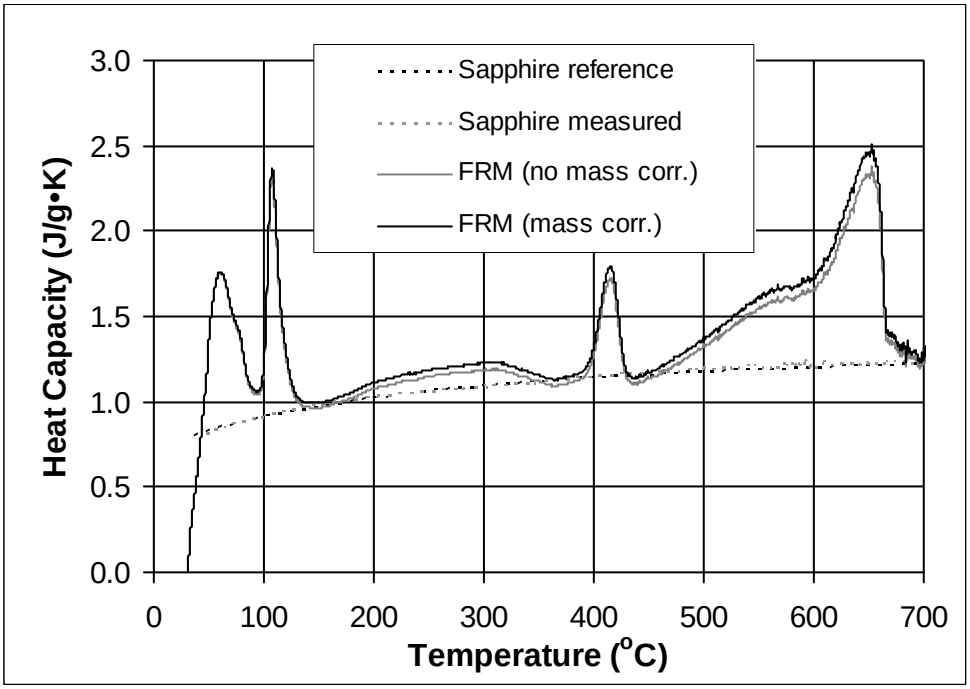

Figure 3. DSC measurement of the heat capacity of a FRM (original and mass corrected) vs. temperature along with reference and measured values for the sapphire reference [11].

From a practical standpoint, when determining thermal conductivities using the slug calorimeter, it may often be sufficient to only measure the room temperature heat capacity of the FRM and use that value in the calculations at all temperatures due to the following two factors: 1) neglecting endothermic and exothermic peaks due to reactions, heat capacity values of common FRMs as a function of temperature typically vary only about ± 20 % from a mean value [11], and 2) due to their low densities, the thermal mass of the FRM is usually minor compared to that of the steel substrate. For example, in the NIST slug calorimeter experimental setup [16], the mass of the stainless steel slug is typically at least 5 times greater than the combined mass of the twin FRM specimens.

Density

Procedures for assessing the density of in-place FRMs applied to structural members are outlined in ASTM E605-93(2006) [9]. Density is evaluated on specimens dried to a constant mass either by a direct measurement of mass, length, width, and thickness on a rectangular prism specimen or by measurement of mass

and volumetric displacement (of either lead shot or expanded polystyrene beads by a known mass of specimen).

In addition to room temperature density, it is also critical to assess the mass loss of the FRM as a function of temperature. This is important both for an accurate assessment of thermal properties such as heat capacity and thermal conductivity and also for computing the heats of reaction and phase changes that will be present during a fire exposure. ASTM E1131-08 [19], while being specific to performing compositional analysis using thermogravimetric analysis (TGA), provides useful general guidelines on executing TGA experiments. As an example, Figure 4 shows a typical mass loss vs. temperature curve for a commercial FRM that loses about 25 % of its initial mass during exposure to a temperature of 800 ºC. Since most analytical TGA instruments may be limited in sample mass to specimens weighing 100 mg or less, an alternative for heterogeneous FRMs would be to conduct manual TGA measurements using crucibles that may easily hold several grams of material, exposed to fixed temperature points in a furnace with manual determinations of remaining mass following each furnace temperature exposure (and cooling).

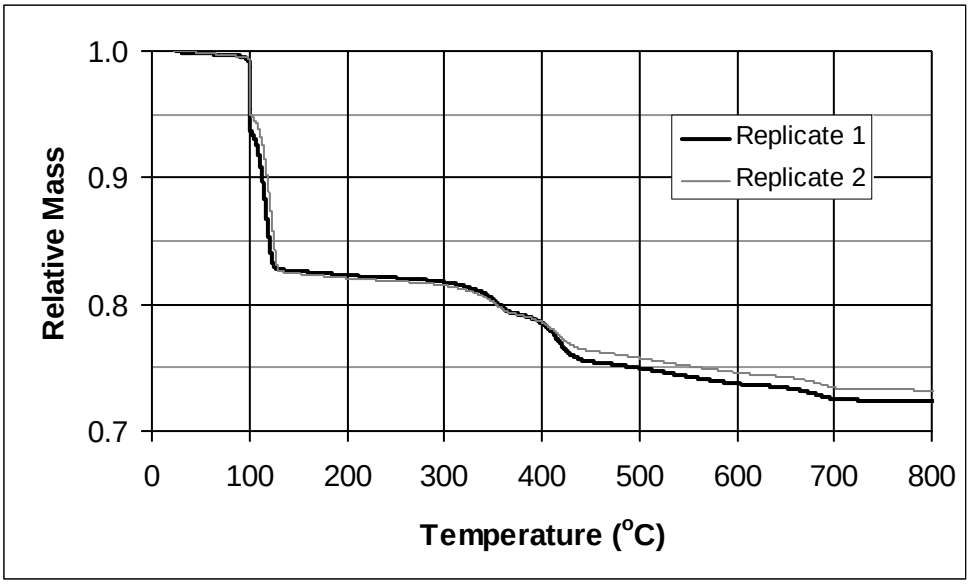

Figure 4. Mass loss vs. temperature for a conventional spray-applied FRM, as determined using a commercial TGA instrument. Replicate specimens provide a measurement of the technique variability.

Heats of Reaction

During a fire exposure, most FRMs undergo one or more chemical reactions including dehydration, decarbonation, or combustion of organic materials such as shredded expanded polystyrene or various components of intumescent coating systems. One approach to quantifying the enthalpies of these reactions is to utilize a differential scanning calorimeter and measure the "area" under each reaction peak, such as those shown in Figure 3. In practice, it is often difficult to obtain reproducible and quantitative results using this approach, due to the small specimen

size, specimen heterogeneity, and variable heating rates. If the chemical composition of the FRM is approximately known, the potential also exists to calculate the enthalpies of reaction from heats of formation and heat capacity data available in the literature [11]. For example, the enthalpies of reaction computed for a variety of dehydration/decarbonation reactions for FRMs containing cementitious or gypsum-based binders are provided in Table 1. The values computed for the two gypsum dehydrations are in reasonable agreement with those recently summarized for gypsum plasterboard by Thomas [20]. It should be noted that in Table 1, the computed enthalpies are expressed in units of kJ per unit mass of "volatiles" (reaction products such as water (gas phase) or carbon dioxide). These are the same volatiles that would normally be measured as a mass loss during a thermogravimetric experiment. To obtain reaction enthalpy values for a specific FRM, one thus only needs to multiply the values in Table 1 by the corresponding measured mass losses (for each assumed temperature range). When a more detailed knowledge of a specific FRM is available, the reactions in Table 1 can be replaced or supplemented by additional ones utilizing the same computational framework.

TABLE 1. COMPUTED ENTHALPIES OF REACTION FOR VARIOUS DEGRADATION REACTIONS OCCURRING IN FRMS.

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	2330 kJ/kg water
Dehydration of "C-S-H" (calcium silicate hydrate gel)	100 °C to 300 °C or 100 °C to 400 °C	125 °C	1440 kJ/kg water
First dehydration of gypsum to hemihydrate	100 °C to 200 °C	150 °C	3010 kJ/kg water
(2^{nd}) dehydration of hemihydrate to anhydrite	200 °C to 450 °C	325 °C	2340 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	3890 kJ/kg CO_2

Emissivity

The emissivity of the FRM influences the radiative heat transfer between a fire (or furnace) and the FRM, and ultimately the temperature rise of the structural steel being protected by the FRM. Measurement of total emittance by portable, inspection-meter instruments is described in ASTM E408-71(2008) [21]. Typically, at room temperature, FRMs are assigned an emissivity value of 0.9, but as shown in Figure 5, this value may decrease substantially at higher temperatures. The data in Figure 5 were obtained by measuring the total reflectance of the FRM at room temperature and at 100 ºC [22,23] and convolving this data with a blackbody

function [24] to obtain the estimated emissivity as a function of temperature. The average expanded uncertainty in the measured total reflectance was 3 %. In a real fire exposure, the FRM will often soon be covered by a high emissivity (absorptivity) layer of soot, so that an emissivity value of 0.9 may be realistic.

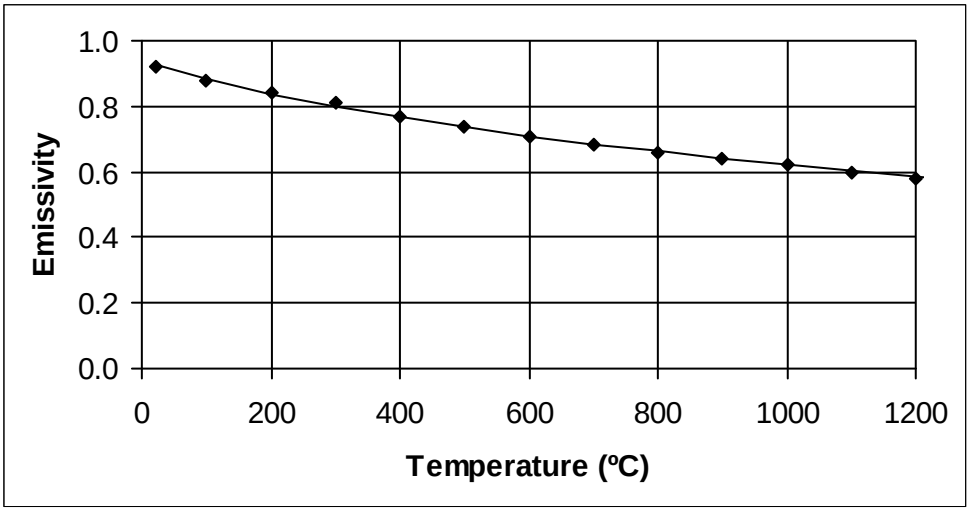

Figure 5. Computed estimated emissivity vs. temperature for a conventional spray-applied FRM.

Durability

Because FRMs must provide protection on demand throughout the life cycle of a building or structure, the changes that occur in thermophysical properties upon aging are as important as their initial property values. These durability issues have received increased recognition in recent years [25], as evidenced by the formation of a task group at Underwriters Laboratories (UL) to develop a durability testing standard test method for spray-applied FRMs. In the new UL 2431 standard "Durability of Spray-Applied Fire Resistive Materials," steel tubes protected with spray-applied FRMs are exposed to various conditioning environments (air erosion, a combination of wet, freeze and dry cycling, humidity, impact resistance, industrial atmosphere, salt spray, temperature stability, ultraviolet light, and vibration), and their subsequent performance in a fire test is compared to that of control tubes that have not been exposed to any aging.

FRM binder materials such as portland cement continue to hydrate and develop strength for many years, but can also be subject to atmospheric attack in the form of carbonation or attack by environmental sulfates. Gypsum-based materials are more susceptible to temperature than portland cement, with measurable dehydration occurring during extended exposure to temperatures as low as 50 ºC to 60 ºC [11]. For these and other reasons (such as susceptibility to moisture), some FRMs are only specified for use in "conditioned interior space." Others, such as intumescents, are employed in severe external environments including chemical plants and offshore oil platforms.

PERFORMANCE PREDICTION

In addition to providing quantitative data for comparing and improving FRMs, data sets of their thermophysical properties provide critical inputs for simulation of the thermal performance of FRM-protected components and systems during a standard or real world fire exposure. Such simulations may provide a framework for true performance-based design, allowing architects and engineers to determine the necessary protection levels for a specific structure for a specific fire scenario.

Numerous authors have applied models of varying complexity for predicting the thermal response (usually in terms of the temperature of the unprotected or protected steel vs. time) of components such as beams, columns, walls, and floors [26-32]. In some cases, a lumped capacity analysis is employed to calculate the change in temperature of the steel as a function of material thermal properties, specimen geometry, and the current temperatures of the furnace/fire and steel [26,32]. Both convective and radiative heat transfer are explicitly considered in such an analysis, and the assignment of appropriate values for the convective heat transfer coefficient (typically on the order of 25 $W/(m^2 \cdot K)$) and the emissivity are critical to making accurate performance predictions. As illustrated by the results of Kirby et al. [27,29], the best-fit emissivity (safety factor) values may be significantly different for exposures in a furnace vs. those in a real world fire. Wong and Ghojel [28,30,31] have implemented several numerical analyses for predicting thermal performance into a spreadsheet software package that is available to the general public [33]. Multi-dimensional modeling can also be conducted using any one of the many commercially available heat transfer analysis packages. Ultimately, the integration of thermal and structural analyses will be required to provide accurate predictions of the real world (structural) performance of FRM-protected steel structures during a fire. Much research and development remains to be completed in this area.

SUMMARY AND PROSPECTUS

The thermophysical properties of FRMs as a function of temperature are critical to their successful performance in insulating structural steel components during a fire exposure. Measurement challenges for these materials include their microstructural heterogeneity, their dimensional instability, a significant mass loss during high temperature exposure, the energy absorbed or generated during high temperature (degradation) reactions, and the mass transport of steam and other hot gases that may accompany this thermal degradation. Advances continue to be made in overcoming these challenges to provide reliable, accurate data sets for critical thermophysical properties including thermal conductivity, heat capacity, density, and emissivity. Concurrently, computational advances are permitting more complex simulations of the thermal (and mechanical) performance of actual three-dimensional components and structures during standard test and real world fire exposures.

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