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Fire Hardening Assessment (FHA) Technology For Composite Systems

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This report describes the application of a Fire Hardening Assessment (FHA) methodology to five composite materials. The results are compared to eight materials previously evaluated under Army contract and also materials examined for the U.S. Navy. The FHA Methodology consists for four tests: 1) ignition, 2) combustion, 3) fire propagation, and 4) flame extinction. The tests are performed in a Flammability Apparatus designed to perform such tests. The test data was used to establish the Critical Heat Flux, Thermal Response Parameter, Fire Propagation Index, Heat Release Rate, Product Generation Parameter, Smoke Damage Parameter, Corrosion Index and Flame Extinction using Halon. The application of these composite materials is primarily for Army armored combat vehicle.

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ABSTRACT

This report describes the application of Fire Hardening Assessment (FHA) Technology to five composite systems examined in this study and eight composite systems examined by FMRC in two previous studies for the U.S.Army. The results are compared with testing results for 24 composite systems, with and without fire barriers, examined by the U.S. Navy and six general composite systems examined in Europe.

FHA Technology consists of performing four types of tests: 1) ignition, 2) combustion, 3) fire propagation, and 4) flame extinction. The tests, performed in a Flammability Apparatus, determine if the following fire hardening criteria are satisfied by the composite systems: 1) Critical Heat Flux (CHF) ≥ 20 kW/m^2; 2) Thermal Response Parameter (TRP) ≥ 650 kW-s$^{1/2}$/m^2; 3) Fire Propagation Index (FPI) ≤ 7; 4) Heat Release Parameter (HRP) < 4;, 5) Product Generation Parameter (PGP)[1]; 6) Smoke Damage Parameter (SDP) ≤ 5 mg/kJ; 7) Corrosion Index (CI) < 0.25 [(Å/min)/(g/m^3)]; and 8) Flame Extinction[1].

The current and the previous two studies performed for the U.S.Army show that: 1) five out of 13 composite systems satisfy the CHF and TRP criteria; 2) six out of 13 composite systems satisfy the FPI criterion; 3) seven out of 13 composite systems satisfy the HRP criterion; 4) three out of 13 composite systems satisfy the SDP criterion; 5) three out of five composite systems satisfy the CI criterion.

Flame extinction for all 13 composite systems was achieved by using 3.0 to 4.5% of Halon 1301. The predicted concentrations for flame extinction by Halon alternates, which can be used in normally occupied areas, for the 13 composite systems were: 1) FE232 (HCFC-22, Du Pont): 12 to 18%; 2) FM 200 (HFC-227a, Great Lakes): 6 to 10%; and 3) PFC 614 (FC-5-1-14, 3M): 6 to 9%.

Utilization of the recently developed Fire Spread and Growth (FSG) model at the Factory Mutual Research Corporation for the FHA Technology is recommended.

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[1] Criterion has not yet been defined.

DEDICATION

The Army Research Laboratory Materials Directorate has been the pioneer of the development and demonstration of composite materials for structural armor applications. Prototype hatches, turrets and vehicles have been designed, fabricated and tested under Materials Directorate guidance and control. The understanding of the flammability characteristics of organic materials in combat vehicles was vital to the success of this program. Program Managers Mr. William E. Haskell III and Mr. Gordon R. Parsons from the ARL/MD Composites Development Branch depended on the late Mr. Dom Macaione to head this technical area. Mr. Macaione was a member of the ARL/MD Polymer Research Branch.

The author wishes to dedicate this report to the memory of the late Dominique Macaione, who introduced the author to the world of composite materials, continued his interest and provided valuable technical input towards the development of the Fire Hardening Assessment (FHA) Technology for composite systems presented in this report.

I

INTRODUCTION

Composite systems consist of about 60 to 80% by weight of lightweight high strength-high modulus reinforcing fibers and about 20 to 40% by weight of specialty resin systems. They have excellent mechanical properties, high strength-to-weight ratios, and resistance to ballistic penetration by munition fragments. Composite systems thus are very attractive for use in combat vehicles as a means of decreasing weight and enhancing survivability, without reducing personnel safety. The U.S. Army Research Laboratory (ARL) has examined several composite systems and has successfully demonstrated that a ground vehicle turret could be fabricated from these systems; since then the technology has been applied to the fabrication of a composite vehicle hull[1].

Although composite systems are very serviceable, there is always a fire safety concern, as the resins generate heat and various combustion products as they burn. Generation of heat creates a thermal hazard, whereas generation of combustion products creates a nonthermal hazard due to toxic and corrosive environments with reduced visibility[2]. Thus there is a great emphasis on the reduction of thermal and nonthermal hazards by fire hardening composite systems. Several avenues are being explored: for example, increase in the fiber content and decrease in the resin content of the composite systems within the limits of the end-use compatibility of the systems, increase in the fire retardant treatment of the resins, use of advanced polymers as resins, etc. New technologies are also being introduced to assess the degree of fire hardening of various composite systems.

Most of these assessment technologies deal with increased resistance to ignition and fire propagation and reduced rates of generation of heat, smoke, toxic, and corrosive products. One of the new technologies has been developed by the U.S.Army Research Laboratory (ARL), Watertown, MA, in collaboration with Factory Mutual Research Corporation (FMRC)[3-10]. This technology is defined as the Fire Hardening Assessment (FHA) Technology .

The FHA Technology uses the Flammability Apparatus, shown in Figs. A-1 and A-2 in Appendix A. Four types of tests are performed in the Apparatus: 1) ignition, 2) combustion, 3) fire propagation, and 4) flame extinction. The FHA test procedures for the composite systems are described in Chapter II. Detailed descriptions of the Apparatus, fundamental concepts used in the FHA Technology and test results are described in Appendices A to F.

This report describes the results for five composite systems using the FHA Technology. The results are compared with those obtained for: 1) eight composite systems in our previous two studies for ARL[7,9] 2) 24 composite systems, with and without fire barriers, used by the U.S. Navy[11] and 3) six general composite systems[12]. Results of these studies are shown in Tables B-1, B-2, C-2, C-3 and C-4, Appendices B and C.

II

THE FIRE HARDENING ASSESSMENT (FHA) TECHNOLOGY FOR COMPOSITE SYSTEMS

2.1 TEST APPARATUS

The test apparatus used is the FMRC Flammability Apparatus, described and illustrated in Appendix A.

2.2 SAMPLE SIZE

Two sets of samples are used:

1) *Ignition, Pyrolysis, Combustion, and Flame Extinction Tests*

Samples (100 x 100 mm) contained in a thin walled aluminum dish, in horizontal configuration, were tested with natural air flow.

2) *Fire Propagation Tests*

Samples (600 mm long and 100 mm wide) attached to a ladder-like holder, in a vertical configuration were used. The back of the sample was covered tightly with a heavy duty aluminum foil, and the sides with a 3 mm thick ceramic paper. The vertical samples were used inside a 162 mm diameter and 432 mm long air tight quartz tube with a 162 mm diameter and 260 mm quartz tube extension.

The samples used in this study are listed in Appendix B, Table B-1.

2.3 TESTS

The tests consist of the following: 1) ignition test; 2) combustion test; 3) fire propagation test, and 4) flame extinction test. The tests are described in Appendix A.

2.3.1 Ignition Test

The ignition concept used in the FHA Technology test is described in Appendix C, and the test procedure is described in Appendix A. The ignition test is performed to determine the degree of fire hardening of the composite systems in terms of the resistance to ignition and fire propagation. In the test, the *Critical Heat Flux (CHF)* and the *Thermal Response Parameter (TRP)* values are determined by measuring the time to ignition at various external heat flux values in the range of 10 to 65 kW/m^2. CHF is the minimum heat flux at or below which there is no sustained ignition. TRP expresses the time delay in generating flammable vapor-air mixture for a composite system exposed to external heat flux above the CHF value. The higher the CHF and TRP values, the higher the degree of fire hardening.

The degree of fire hardening of a composite system for higher resistance to ignition and fire propagation is judged by the magnitudes of the CHF and TRP values.

2.3.2 Combustion Test

The combustion concept used in the FHA Technology test is described in Appendix C and the combustion test procedure is described in Subsection A.2.2 of Appendix A. The combustion test is performed to determine the degree of fire hardening in terms of reduced rates of release of heat and toxic and corrosive fire products and smoke. The composite systems are burned in normal air at various external heat flux values in the range of 10 to 65 kW/m^2. The lower the rates, the higher the degree of fire hardening.

The degree of fire hardening of a composite system for reduced rates of release of heat and toxic and corrosive fire products and smoke is expressed in terms of the reduced values of the *Heat Release Parameter (HRP), Product Generation Parameter (PGP), Product Damage Parameter (PDP)*, and *Corrosion Index (CI)*. These parameters are defined in Subsections D.1.5, D-3, and D-4 of Appendix D.

2.3.3 Fire Propagation Test

The fire propagation concept used in the in the FHA Technology test is described in Appendix E and the fire propagation test procedure is described in Subsection A.2.3 of Appendix A. The fire propagation test is performed to determine the degree of fire hardening of the composite systems to the extent that there is no fire propagation beyond the ignition zone and the *Fire Propagation Index (FPI)* ≤ 7.

2.3.4 Flame Extinction Test

The flame extinction concept used in the FHA Technology test is described in Appendix F and the flame extinction test procedure is described in Subsection A.2.4 in Appendix A. The flame extinction test is performed to determine the concentration of a gaseous agent required for extinction of a turbulent flame of the composite systems representative of large-scale fire conditions.

The increase in the degree of fire hardening of a composite system, *defined as increased passive fire protection*, is judged by the reduction in the concentrations of the agents required for flame extinction.

III

RESULTS

In the FHA Technology for the composite systems, the critical values of 8 parameters must be satisfied for the proper fire hardening of the composite systems. The parameters and their critical values are listed in Table 1.

Table 1
Parameters and Their Critical Values Used in the
FHA Technology for Composite Systems

Need	Parameter	Test	Critical Value Requirement
To define ignition resistance (Appendix C)	1. Critical Heat Flux (CHF) 2. Thermal Response Parameter (TRP)	Ignition	≥ 20 kW/m^2 ≥ 650 kW-s$^{1/2}$/m^2
To define non-propagating fire behavior (Appendix E)	3. Fire Propagation Index (FPI)	Fire Propagation	≤ 7
To define reduction in fire intensity (Appendix D)	4. Heat Release Parameter (HRP)	Combustion	HRP < 4
To define reduction in generation rates of fire products (Appendix D)	5. Product Generation Parameter (PGP)	Combustion	NYD
To define extent of smoke damage (Appendix D)	6. Smoke Damage Parameter (SDP)	Fire Propagation	≤ 5 mg/kJ
To define extent of corrosion damage (Appendix D)	7. Corrosion Index (CI)	Fire Propagation	< 0.25 (Å/min)/(g/m^3)
To define concentration of an agent for flame extinction (Appendix F)	8. Flame Extinction	Combustion	NYD

NYD: not yet defined.

3. CRITICAL VALUE REQUIREMENTS FOR THE FHA TECHNOLOGY

3.1 Ignition Resistance

The increased resistance to ignition is reflected in higher values of the *Critical Heat Flux (CHF)* and the *Thermal Response Parameter (TRP).*

3.1.1 Critical Heat Flux (CHF)

The CHF values of materials belong to one of the three ranges:

1) *First Range*: CHF values $\leq$ 10 to 20 kW/m^2. This is the lowest range of CHF values, mainly for ordinary combustibles;

2) *Second Range*: CHF values > 20 and < 30 kW/m^2. This is the intermediate range of CHF values. Fire retarded materials and materials with inerts belong to this range; and

3) *Third Range*: CHF values $\geq$ 30 kW/m^2. This is the highest range of CHF values. Highly fire retarded and halogenated materials belong to this range. These materials have the highest fire hardening characteristics in terms of high heat flux requirement to initiate a fire.

The CHF values for the thirteen composite systems examined by us for the U.S.Army are listed in Table C-1 in Appendix C. The CHF values for the 12 composite systems belong to the first range, while the CHF value for the graphite/epoxy (#13) composite system is in the second range.

The CHF values indicate that it would be possible to start a fire with a heat flux exposure between 10 to 20 kW/m^2, which corresponds to a small heat source, for most of the composite systems examined in our three studies.

3.1.2 Thermal Response Parameter (TRP)

Generally materials with TRP values $\leq$ 450 kW-s$^{1/2}$/m^2 have lower resistance and materials with TRP values > 450 kW-s$^{1/2}$/m^2 have higher resistance to ignition, and fire propagation. Materials with TRP values > 650 kW-s$^{1/2}$/m^2 have the highest resistance to ignition, and fire propagation beyond the ignition zone is generally difficult.

The TRP values are listed in Tables C-1 to C-5 in Appendix C. The TRP values for the thirteen composite systems examined by us for the U.S.Army are listed in Table C-1 and shown in Fig. C-2. The TRP values for the 24 composite systems, with and without fire barriers, derived from the test results reported by the U.S.Navy[11] are listed in Table C-2 and C-3. The TRP values derived from the results for the composite systems examined in Europe[12] are listed in Table C-4. A comparison of the TRP values for the common composite systems of interest to the U.S.Army, U.S.Navy, and in Europe is listed in Table C-5.

Higher CHF and TRP values lead to a higher degree of fire hardening. The TRP values listed in Tables C-1 to C-5 show an increase with increase in the fiber content, decrease in the resin content and in the presence of fire barriers. The generic nature of the fiber, the resin and fire retardant treatment of the resin may also have an effect on the TRP values.

The TRP values show that the composite systems examined in this study are greater than 650 kW-$s^{1/2}/m^2$ and thus have a higher degrees of fire hardening than the systems examined in the previous two studies for the U.S.Army (Table C-1 and Fig. C-2)[7,9], by the U.S. Navy and in Europe (Table C-5). Fire barriers appear to be effective in increasing the TRP values of the composite systems beyond 650 kW-$s^{1/2}/m^2$ (Table C-3).

3.1.3 Relationship Between the Structural Performance, Strength and the Thermal Response Parameter

The structural performance and strength of composite systems is important for the survivability and damage control during and after the fire[11]. The Dynamic Mechanical Thermal Analysis (DMTA) and Residual Flexural Strength Retained (RFSR) and temperature-time-thickness profile during heat flux exposure are considered for composite structural performance at elevated temperatures by the U.S.Navy[11].

The data for the Residual Flexural Strength Retained (RFSR) for various composite systems exposed to 20 kW/m^2 for 20 minutes as reported by the U.S.Navy[11] are listed in Tables C-2 and C-3. The data in Table C-2 show that the RFSR value is highest for the graphite/PEEK-26 (75%), followed by graphite/phenolic-20 (53%), and glass/polyimide-23 (45%) composite systems. Graphite/epoxy-5 composite system delaminates. The TRP values for these composite systems are greater than 526 kW-$s^{1/2}/m^2$. Fire barriers applied to surface of the composite systems as ceramic coating, intumescent coating and a hybrid ceramic-intumescent coating increase the RFSR as well as the TRP values (Table C-3).

The higher the TRP value, the lower the interior and surface temperature of the composite system; and as one would expect, the higher the RFSR value, leading to better structural performance. *It thus appears that the relationship between RFSR and TRP values needs to be* *explored. The relationship would suggest that it is possible to simultaneously fire harden the composite systems and increase their structural performance.*

3.2 Non-Propagating Fire Behavior

Increased resistance to fire propagation is reflected in the decrease in the *Fire Propagation Index (FPI)* value. The fire hardening of the composite systems is considered to be adequate when the value of FPI ≤ 7.

The FPI values as functions of time for the five composite systems examined in this study are shown in Fig. E-1 and the peak values are listed in Table E-1 in Appendix E. The FPI values do not exceed 5, these composite systems thus are classified as non-propagating. For comparison, peak FPI values for the composite systems examined in the previous two studies[7,9] are also listed in Table E-1.

The data for the thirteen composite systems examined by us for the U.S.Army show that the composite system based on kevlar and glass fibers (< 70% by weight) need modifications of the resin for fire hardening (Table E-1 and Fig. C-3). Composite systems based on graphite fibers (> 60% by weight) provide adequate fire hardening (Table E-1 and Fig. C-3). Use of boron, beryllium, aluminum oxide (sapphire), boron nitride, silicone carbide and nitride etc. would further enhance fire hardening.

3.3 Reduction in Fire Intensity, Smoke and Corrosion Damage

Four parameters have been identified to assess the fire hardening of the composite systems for reduction in fire intensity, smoke and corrosion damage: 1) *Heat Release Parameter (HRP)*- to assess reduction in the heat release rate, 2) *Product Generation Parameter (PGP)*- to assess reduction in the generation rates of the products, 3) *Smoke Damage Parameter (SDP)*- to assess the nonthermal damage expected from smoke, and 4) *Corrosion Index (CI)*- to assess the nonthermal damage expected from corrosive products.

3.3.1 Heat Release Parameter (HRP)

For a fire scenario, the lower the HRP value, the lower the chemical heat release rate and the higher the degree of fire hardening.

The HRP values for the 13 composite examined by us for the U.S. Army, HRP values derived from the results reported by the U.S.Navy for 24 composite systems[11] and six general composite systems examined in Europe[12] are listed in Tables D-2 in Appendix D and in Tables C-2, C-3, and C-4 in Appendix respectively. The data in the these tables and in Table E-1 for the FPI values indicate that for composite systems with non- propagating fire behavior, HRP ≤ 4.0.

3.3.2 Product Generation Parameter (PGP)

The lower the PGP value, the lower the generation rate of the product and the higher the degree of fire hardening. The PGP values for the composite systems examined for the U.S. Army in our studies (this study and Refs. 7 and 9) are listed in Table D-4.

3.3.3 Smoke Damage Parameter (SDP)

Table D-5 in Appendix D lists the data for the parameter for the composite systems and ordinary combustibles, which have been tentatively classified into five groups. The *SDP* values used for classification are: Group 1, SDP ≤ 1.4 mg/kJ; Group 2, 1.5 ≤ SDP≤ 5.4 mg/kJ; Group 3, 5.5 ≤ SDP≤ 10.4 mg/kJ; Group 4, 10.5 ≤ SDP ≤ 14.4 mg/kJ; Group 5 , SDP > 14.5 mg/kJ. The smoke damage expected in fires involving the Group 1, Group 2 , Group 3, Group 4 and Group 5 materials are low, medium, medium-high, high, and very high.

The data in combination with the FPI value suggest that the fires of composite systems examined in this study have medium smoke damage potential.

3.3.4 Corrosion Index (CI)

The higher the Corrosion Index (CI) value, the higher the damage due to corrosion. The CI values are shown in Fig. D-11 in Appendix D. The CI values for the composite systems examined in this study are negligibly small compared to the value for PVC, except for the graphite/cyanate composite system (#10).

The CI values in combination with the FPI values suggest that the corrosion damage from the products of the composite systems examined in this study is expected to be of minor importance.

3.4 Flame Extinction by Halon 1301/Alternates

Flame extinction is defined in terms of volume percent of an agent required for flame extinction of a composite system burning in air with an external heat flux exposure of 60 kW/m^2. Figure F-1 in Appendix F shows that the concentration of Halon 1301 required for flame extinction varies between 3.0 to 4.5%.

Table F-1 in Appendix F lists the concentrations of Halon 1301 and alternates required for flame extinction in the cup burner[24]. Concentrations of the alternates relative to Halon 1301 are also listed in the table. FE232 (HCFC-22, Du Pont), FM 200 (HFC-227a, Great Lakes), and PFC 614 (FC-5-1-14, 3M) are acceptable as total flooding agents in occupied areas[23]. From the relative concentrations in Table F-1 in Appendix F and concentrations of Halon 1301 required for flame extinction of the composite systems (Fig. F-1 in Appendix F), the following concentrations are estimated for the alternates for flame extinction of composite systems:

1) FE232: 12 to 18%; 2) FM 200: 6 to 10%; and 3) PFC 614: 6 to 9%.

IV

SUMMARY

1. The five composite systems examined in this study are found to have strong resistance to ignition and are not expected to have self-sustained fire propagation beyond the ignition zone;

2. Of the 12 composite systems which have been examined by FMRC for the U.S. Army in this and two previous studies, six composite systems were found to have propagating fire behavior and six non-propagating fire behavior;

3. The heat release parameter suggested the fires of the composite systems with FPI ≤ 7 are low intensity fires with low thermal damage expectancy;

4. The smoke damage parameter in combination with the Fire Propagation Index (FPI) suggested that the smoke damage would be medium from the fires of the composite systems with FPI ≤ 7;

5. With the exception of the graphite/cyanate, the corrosion damage from the four composite systems examined in the current study was found to be negligible compared to the corrosion from PVC;

6. The concentration of Halon 1301 required for flame extinction of the 13 composite systems examined in FMRC studies for the U.S. Army was between 3.0 to 4.5%. Concentrations of the three alternates required for flame extinction of the 13 composite systems were estimated to be : 12 to 18% for FE232, 6 to 10% for FM200 and 6 to 9% for PFC614.

V

RECOMMENDATION

It is recommended that the Fire Hardening Assessment (FHA) Technology developed by the Army Research Laboratory in collaboration with the Factory Mutual Research Corporation and presented in this report be adopted for the composite systems for combat vehicle hull structures using the criteria listed in Table 1.

A new computer-based model has been developed at Factory Mutual Research Corporation to predict the fire propagation rate and heat release rate (product generation rate is to be implemented). The model is identified as the Fire Spread and Growth (FSG) model. The FSG model has been incorporated into the FMRC Flammability Apparatus. The model uses the data being acquired in a test and at the end of the test predicts the fire propagation rate and heat release rate. It is strongly recommended that the FSG model be used in the FHA technology.

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VII

NOMENCLATURE

A	total exposed surface area of the material (m^2)
$\dot{C}''_o$	mass consumption rate of oxygen (g/m^2-s)
c_p	specific heat (kJ/g-K)
CDG	Carbon Dioxide Generation Calorimetry
CHF	Critical Heat Flux (kW/m^2)
CI	Corrosion Index (corrosion rate)/(mass loss rate/volumetric flow rate of product-air mixture) [(Å/min)/(g/m^3)]
D	optical density $[\{\ln (I_0 / I)\}/ l]$ (1/m)
E_i	total amount of heat generated in the combustion of a material (kJ)
f_j	volume fraction of a product (-)
FPI	Fire Propagation Index 1000 $[0.40\ \dot{Q}''_{ch})^{1/3}$ / TRP
FHA	Fire Hardening Assessment
$\dot{G}''_j$	mass generation rate of product j (g/m^2-s)
ΔH_i	heat of combustion per unit mass of fuel vaporized (kJ/g)
ΔH_{co}	heat of complete combustion of CO (10 kJ/g)
ΔH_g	heat of gasification at ambient temperature (kJ/g)
ΔH^*_{co}	net heat of complete combustion per unit mass of CO generated (kJ/g)
ΔH^*_{co2}	net heat of complete combustion per unit mass of CO_2 generated (kJ/g)
ΔH^*_o	net heat of complete combustion per unit mass of oxygen consumed (kJ/g)
HRP	heat release parameter (heat of combustion/heat of gasification)
I/ I_0	fraction of light transmitted through smoke (-)
k	thermal conductivity (kW/m-K)
l	optical path length (m)
$\dot{m}''$	mass loss rate (g/ m^2-s)
OC	Oxygen Consumption Calorimetry
PGP	Product Generation Parameter (mg/kJ) [product yield /heat of gasification]
$\dot{q}''_e$	external heat flux (kW/m^2)
$\dot{q}''_f$	flame heat flux (kW/m^2)

$\dot{Q}''_j$	heat release rate per unit sample surface area ($\dot{m}'' \Delta H_i$) (kW/m^2)
$\dot{Q}'_j$	heat release rate per unit sample width (kW/m)
r_{corr}	Corrosion rate (Å/min)
SDP	Smoke Damage Parameter (smoke generation rate/heat release rate)
t_{ig}	time to ignition (s)
ΔTig	ignition temperature above ambient (K)
TRP	Thermal Response Parameter [$\Delta T_{ig} (k\rho c_p)^{1/2}$] (kW-s$^{1/2}$/m^2)
u	fire propagation rate [dX_p / dt] (mm/s or m/s)
$\dot{V}$	total volumetric flow rate of fire product-air mixture (m^3/s)
$\dot{W}$	total mass flow rate of the fire product-air mixture (g/s)
W_f	total mass of the material lost in the flaming and nonflaming fire (g)
W_j	total mass of product j generated in the flaming and nonflaming fire (g)
y_j	yield of product j ($\dot{G}''_j$ / $\dot{m}''$)

Greek

χ_{ch}	combustion efficiency [$\dot{Q}''_{ch} / \dot{m}'' \Delta H_T$] (-)
λ	wavelength of light (μm)
σ	Stefan-Boltzmann constant (56.7×10^{-12} kW/m^2-K^4)
ρ	density (g/m^3)

Subscript

a	air or ambient
ch	chemical
cr	critical
e	external
f	flame
g	gas
i	chemical, convective, radiative
ig	ignition
j	fire product
n	net

o	initial
rr	surface re-radiation
s	surface

Superscripts

.	per unit time (s^{-1})
'	per unit width (m^{-1})
"	per unit area (m^{-2})

Definitions

Chemical Heat of Combustion	calorific energy generated in chemical reactions leading to varying degrees of incomplete combustion per unit fuel mass consumed
Corrosion Index	rate of corrosion of a metal per unit concentration of the material vapors
Heat of Gasification	energy absorbed to vaporize a unit mass of fuel originally at ambient temperature
Heat Release Parameter	calorific energy generated per unit amount of calorific energy absorbed by the material
Product Generation Parameter (PGP)	amount of a product generated per unit amount of energy absorbed by the material
Net Heat of Complete Combustion	calorific energy generated in chemical reactions leading to complete combustion with water as a gas per unit fuel mass consumed
Smoke Damage Parameter	amount of smoke generated per unit amount of energy released in a fire

APPENDIX A

THE FHA TECHNOLOGY TEST APPARATUS
FOR THE COMPOSITE SYSTEMS

A.1 THE FLAMMABILITY APPARATUS

The Flammability Apparatus is used for the ignition, pyrolysis, combustion, and flame extinction tests (Fig. A-1) and for the fire propagation test (Fig. A-2). It consists of a lower and an upper section. The lower section is used for the measurements of time to ignition, mass loss rate, pyrolysis and flame heights, and flame spread rate, and concentrations of gaseous agents required for flame extinction. The upper section is used to measure the heat release rate, generation rates of products, optical transmission through the products and corrosive nature of the products.

A.1.1 Lower Section of the Flammability Apparatus

The sample is located in this section in a horizontal or a vertical configuration. the horizontal configuration is used for the ignition, pyrolysis, combustion, and flame extinction tests, and the vertical configuration is used for the fire propagation test.

For the horizontal configuration, a rectangular sample (about 100 x 100 mm) up to 100 mm thick, contained in a thin walled aluminum dish, is used at the location shown in Fig. A-1. For the vertical configuration, about 600 mm long and 100 mm wide, a sample, with its back covered tightly with heavy duty aluminum foil and the sides with 3 mm thick ceramic paper, is used. The sample is attached to a thin steel ladder-like holder, at the location shown in Fig. A-2. In this arrangement, flame spread is restricted to a single surface.

The ignition test is performed in the open under natural flow condition, and the combustion, flame extinction, and fire propagation tests are performed inside a quartz tube under co-flow condition. For the co-flow condition, the sample is kept inside an airtight quartz tube, 162 mm in diameter and 432 mm in length with a 260 mm long quartz tube extension. A gas distribution section is located at the bottom of the quartz tube. Air or a mixture of air and oxygen, or air and the flame extinguishing agent is introduced into the air distribution section, through several downward facing holes, beneath a bed of screens, to achieve a uniform flow

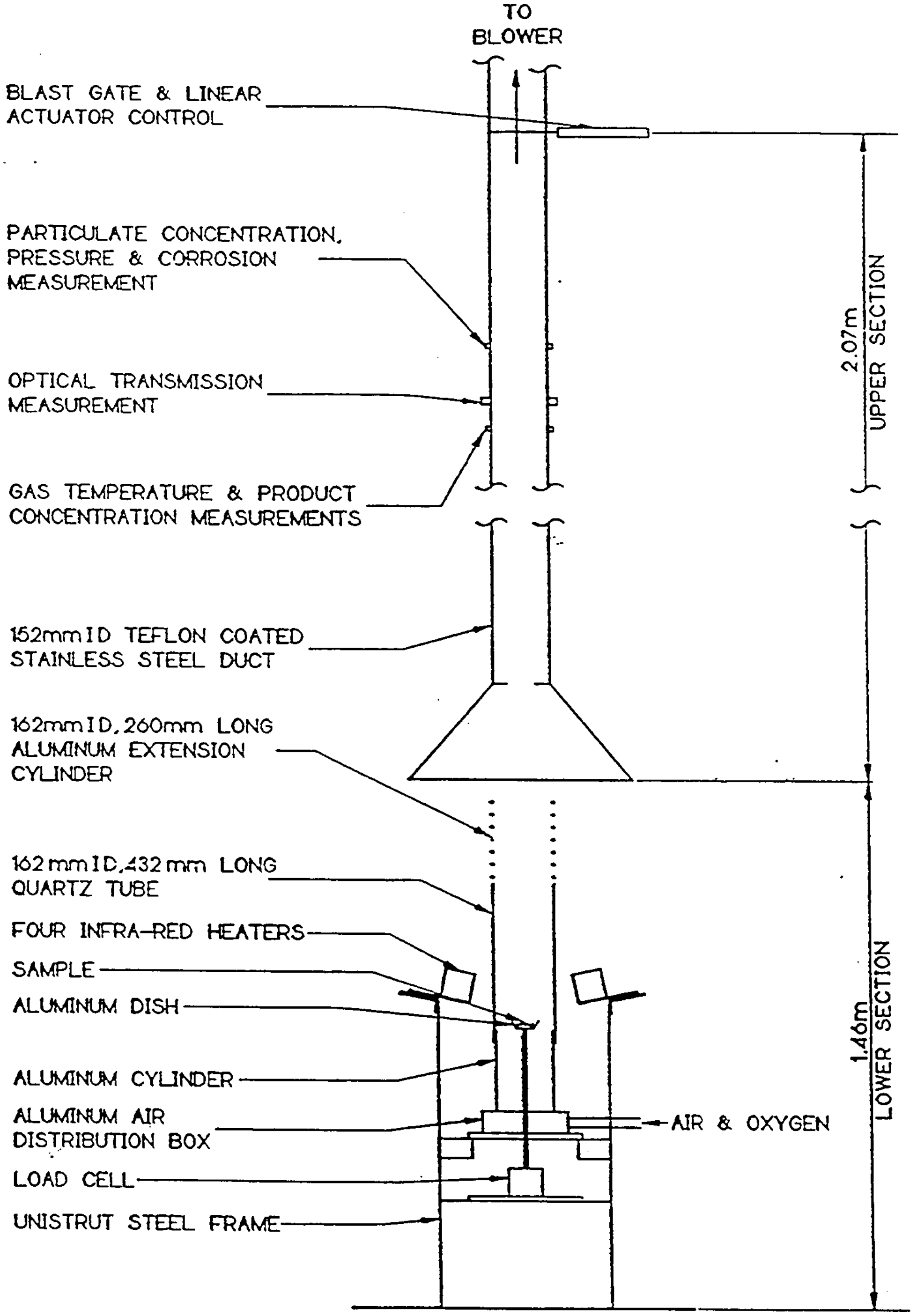

Figure A-1. The Flammability Apparatus for the Ignition, Combustion, and Flame Extinction Tests for the Composite Systems.

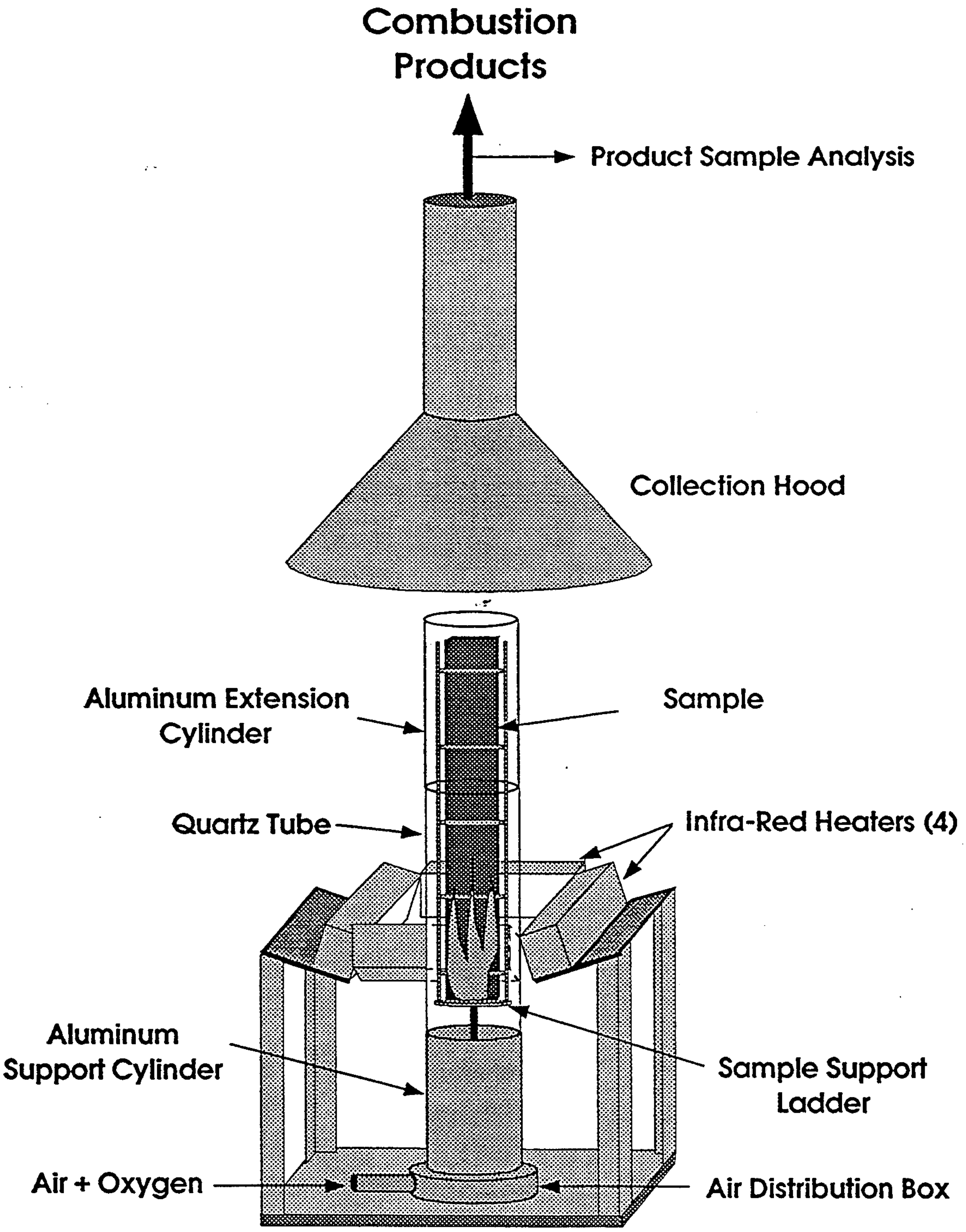

Figure A-2. The Flammability Apparatus for the Fire Propagation Test for the Composite Systems.

across the tube. The flow rate and oxygen concentration of the inlet air or air-oxygen or air-flame extinguishing agent mixture are measured every second. The flow rate (velocity) is set at 3 x 10^{-3} m^3/s (0.16 m/s). For the fire propagation test, oxygen concentration is set at 40% by volume. A Beckman 755 paramagnetic analyzer is used for the measurement of the oxygen concentration. For the flame extinction test, the concentration of the flame extinguishing agent is varied until flame extinction is achieved.

For the application of the external heat flux to the sample, four water and air cooled, tungsten-quartz radiant heaters are used. A controller is used to vary the power to the radiant heaters. The heat flux to the surface of the sample, in the open or inside the quartz tube, is calibrated by placing a heat flux gauge at several locations, within the sample dimensions of about 100 x 100 x 100 mm, and averaging the data for each controller setting. The entire surface of the horizontal sample and the bottom 125 mm of the vertical sample are exposed to the external heat flux values of up to a maximum of 65 kW/m^2. In each test, a constant specified value of external heat flux is used.

For the ignition of the flammable-vapor air mixture created by exposing the sample to the external heat flux, a 10 mm long premixed ethylene-air pilot flame, located about 10 mm from the sample surface, is used. For the measurement of the mass loss rate, the sample is placed on a platform attached to a load cell. The output from the load cell is recorded every second.

A.1.2 Upper Section of the Flammability Apparatus

All the products generated in the ignition, pyrolysis, combustion, and fire propagation are captured, along with ambient air in the sampling duct. Measurements are made in the duct, about six diameters downstream, where all the temperature and concentration profiles are almost flat. The location is used for the measurements of gas temperature, mass and volumetric flow rates of product-air mixture through the duct at the gas temperature, and volume fractions of CO, CO_2, hydrocarbons, O_2, smoke, and water. A Concurrent Model 5550 computer with a DADiSP software recorded the data at one-second intervals. The data are analyzed by an Xess spreadsheet and plotted by a Grafit software on a SUN workstation.

The volume or mass fractions of the products are measured by: 1) flowing reference Beckman 865 infrared analyzers for CO and CO_2; 2) a Siemen's Oxymat II flowing reference paramagnetic analyzer for oxygen, 3) a Beckman 400 flame ionization analyzer for the low molecular weight gaseous mixtures of hydrocarbons, 4) an FMRC-designed triple beam turbidimeter and a Rupprecht & Patashnick TEOM Series 1200 Ambient Particulate Monitor for smoke, 5) a Vaisala HMP135Y water sensor, and a 6) a Rohrback Cosasco 2500 Å high sensitivity atmospheric corrosion probe (designed for the FMRC Apparatus, shown in Fig. A-3). The output of the probe is monitored by a Rohrback Cosasco 4208 Corrosometer. The volume or mass fraction measurement accuracy in the FMRC Flammability Apparatus is about ± 5%.

The generation rates of the gaseous products are calculated using Eq. D-12 in Appendix D. The generation rate of smoke is calculated from Eqs. D-18 to D-20 in Appendix D. The chemical heat release rate is calculated from Eqs. D-2 and D-5 in Appendix D. The yields of fire products and chemical heat of combustion are calculated from Eqs. D-23 and D-10 in Appendix D.

A.2 THE FIRE HARDENING ASSESSMENT (FHA) TECHNOLOGY TEST PROCEDURES

The FHA technology utilizes four types of tests in the Flammability Apparatus: 1) ignition test; 2) combustion test; 3) fire propagation test; and 4) flame extinction test.

A.2.1 Ignition Test

The ignition concepts used in the tests are described in Appendix C. Ignition tests are performed to determine the *Critical Heat Flux (CHF)* and the *Thermal Response Parameter (TRP),* defined in Appendix C.

In the ignition test, a square sample (about 100 x 100 mm), up to a thickness of about 25 mm is used. The sample is placed inside a heavy duty aluminum dish and the surface is coated with a thin layer of 50:50% by volume of Fisherbrand activated carbon 50-200 mesh and Cabot Corporation's carbon black to reduce errors due to differences in the surface absorptivity.

The sample contained in the dish is placed on top of the platform (Fig. A-1) and the 10 mm long premixed ethylene-air pilot flame, located about 10 mm from the sample surface, is ignited. The water-cooled shield is raised up to prevent the initial heat flux exposure of the sample. The radiant heaters are turned on by manually setting the controller dial for the desired heat flux at the sample surface. For the manual setting, a calibration curve of controller dial setting versus the average external heat flux within 100 x 100 x 100 mm of sample dimension is used.

At 60 seconds, a time used to stabilize the test condition, the water-cooled shield is dropped down instantaneously and the sample surface is exposed to the desired external heat flux. The time at which the sample is exposed to the external heat flux is recorded using a stop watch. The surface and the times for the initiation of vapor formation and ignition are recorded by a stop watch. This procedure is repeated five to six times using various external heat flux values ranging from 10 to 65 kW/m^2. The external heat flux value at which there is no ignition for 15 minutes is defined as the *Critical Heat Flux* (CHF).

At the completion of the ignition test series, the time to ignition versus external heat flux data are entered into the Grafit software on the SUN work station and the square root of the inverse of time to ignition is plotted against the external heat flux (Eq. C-1). The TRP value is calculated, by the Grafit software on the SUN System, from the inverse of the slope of straight line, away from the CHF value.

The ignition test provides the values of the *Critical heat Flux (CHF)* and the *Thermal Response Parameter (TRP)*.

A.2.2 Combustion Test

The combustion concepts used in the test are described in Appendix D. The combustion test is performed to determine the chemical heat release rate, generation rates of fire products, heat of combustion, yields of the products, and corrosive nature of the products, using one to four external heat flux values.

In the test, a square sample (about 100 x 100 mm) with a thickness up to 25 mm is used in a horizontal configuration inside the quartz tube under co-flow condition. The sample is placed on top of the platform attached to the load cell (Fig. A-1). The quartz tube is placed around an aluminum cylinder with rubber gaskets, which is part of the air distribution section. The quartz tube extension is placed on top of the main quartz tube surrounding the sample. The gas sampling lines connected to the analyzers, particulate filter paper, water condenser, and drying agent are checked and replaced as needed.

The pilot flame, inlet air pump in the lower section of the Apparatus and the blower for the sampling section in the upper section of the Apparatus are started. The gas analyzers are checked for their output by introducing gases of known concentrations directly into the gas sampling lines connected to the analyzers. The outputs of the load cell, turbidimeter, thermocouple, flow sensor, water sensor, and the gas phase corrosion probe are checked and corrected as needed.

After the calibration of the Apparatus, the data acquisition system is first turned on for 30 seconds to obtain background readings. Then the water-cooled shield is raised up to prevent any initial heat flux exposure of the sample; then radiant heaters are turned on by manually setting the controller dial for the desired heat flux at the sample surface. At 120 seconds, the water-cooled shield is dropped down instantaneously to expose the sample surface to the desired external heat flux.

During the combustion test, observations are made for times to initiation of sample vaporization and ignition. The physical condition of the sample and flame heights and other pertinent observations are made at various times throughout the test. The test is continued until there is no release of vapor. The Apparatus is allowed to cool down and the sample residue and the particulate filter paper in the gas sampling line are taken out and weighed to determine the weight of smoke and residue respectively.

Hard copies of the data in the form of DADiSP plots, Xess spreadsheets and Grafit plots are analyzed to derive the pertinent information from the test. The above procedure is repeated for each external heat flux value in the range of 10 to 65 kW/m^2.

The combustion test provides the values for the chemical heat release rate, generation rates of fire products, light obscuration and corrosion, chemical heat of combustion, yields of the fire products, and *Corrosion Index (CI)*, which is the corrosion rate per unit concentration of the vapors of the composite system.

A.2.3 Fire Propagation Test

The fire propagation concept used in the test is described in Appendix E. The fire propagation test is performed to determine if there is propagation beyond the ignition zone, and, if so, the self-sustained fire propagation characteristics. Since it is a small-scale test, it is performed under conditions which simulate large-scale flame radiation feedback. The effect of large-scale flame radiation feedback is simulated by increasing the oxygen concentration of inlet co-flowing air to 40% by volume. This enhanced oxygen significantly increases the flame radiation.

In the test, a sample of the composite system, about 600 mm long and 100 mm wide, is used in a vertical configuration under co-flowing mixture of air and oxygen with an oxygen concentration of 40% by volume. The back of the sample is tightly covered by a heavy duty aluminum foil, and the sides are protected by a 3 mm thick ceramic paper. The sample is attached to a thin steel ladder-like holder. The sample attached to the holder is placed inside the airtight quartz tube around the aluminum cylinder, which is part of the air distribution section (Fig. A-2 in Appendix A) with rubber gaskets. The quartz tube extension is placed on top of the main quartz tube surrounding the sample. The gas sampling lines connected to the analyzers, particulate filter paper, water condenser, and drying agent are checked and replaced as needed.

The pilot flame located at the bottom of the sample, inlet air pump in the lower section of the Apparatus and the blower for the sampling section in the upper section of the Apparatus are started. The gas analyzers are checked for their output by introducing gases of known concentrations directly into the gas sampling lines connected to the analyzers. The outputs of the load cell, turbidimeter, thermocouple, flow sensor, water sensor, and the gas phase corrosion probe are checked and corrected as needed.

After the calibration of the Apparatus, the data acquisition system is turned on for background readings and then, 30 seconds later, the radiant heaters are turned on by manually setting the controller dial to expose the bottom 125 mm of the sample to a heat flux of 50 kW/m^2; a pilot flame is located close to the sample surface.

During the fire propagation test, observations are made of the time to ignition, pyrolysis front location, flame height, physical condition of the sample surface, color of the smoke at various times throughout the test. The test is continued until there is no release of vapors. The Apparatus is allowed to cool down and the sample residue and the particulate filter paper in the gas sampling line are taken out and weighed to determine the weight of the residue and smoke.

Hard copies of the data in the form of DADiSP plots, Xess spreadsheets and Grafit plots are examined to derive pertinent information for the test. The fire propagation test provides the *Fire Propagation Index (FPI)* value as a function of time. Composite systems with FPI values ≤ 7 are considered as non-propagating and composite systems with FPI ≥ 8 are considered as propagating. The fire propagation behavior of composite systems with $7 \geq$ FPI≤ 8 is uncertain; these systems need to be examined in the large-scale fire propagation tests to judge their fire propagation behavior.

A.2.4 Flame Extinction Test

The flame extinction concept used in the test is described in Appendix F. The flame extinction test is performed to determine the concentration of an agent of interest required for flame extinction. A gas flow line with a pressure regulator and a calibrated flow meter is available in the FMRC Flammability Apparatus for introducing gaseous extinguishing agents. The gaseous extinguishing agent flow line is attached to the inlet air flow line, both of which enter the air distribution section and are well mixed. In the flame extinction test, a co-flow condition is used for the mixture of the extinguishing agent and air.

In the test, a horizontal square sample (about 100 x 100 mm and up to 25 mm thick) is used under co-flow conditions. The sample is placed on top of the platform attached to the load cell (Fig. A-1). The quartz tube is placed around the aluminum cylinder with rubber gaskets, which is part of the air distribution section. The quartz tube extension is placed on top of the main quartz tube surrounding the sample. The gas sampling lines connected to the analyzers, particulate filter paper, water condenser, and drying agent are checked and replaced as needed.

The pilot flame, inlet air pump in the lower section of the Apparatus and the blower for the sampling section in the upper section of the Apparatus are started. The gas analyzers are checked for their output by introducing gases of known concentrations directly into the gas sampling lines connected to the analyzers. The outputs of the load cell, turbidimeter, thermocouple, flow sensor, water sensor, and the gas phase corrosion probe are checked and corrected as needed.

After the calibration of the Apparatus, the data acquisition system is turned on for background readings and at 30 seconds the water-cooled shield is raised up to prevent the initial heat flux exposure of the sample. The radiant heaters are turned on by manually setting the controller dial to achieve a heat flux exposure of 60 kW/m^2 at the sample surface. At 120 seconds, the water-cooled shield is dropped down instantaneously and the sample surface is exposed to the desired external heat flux. The combustion test results are used to determine the time to introduce the agent. The extinguishing agent flow meter is turned on 10 to 20 seconds before the peak heat release rate is expected to be achieved. The flow meter is set to provide a concentration of 2.5% by volume. The concentration of the agent is increased in increments of 0.5% every 20 to 60 seconds, depending on the total duration of the test, until a concentration is reached at which flame is extinguished[2]. For a sample with a short combustion time, several tests are performed to determine the agent concentration for flame extinction.

During the test, observations are made for times to sample vaporization and ignition. Physical condition of the sample, color of smoke, flame height and other pertinent observations are made at various times throughout the test. The Apparatus is allowed to cool down and the sample residue and the particulate filter paper in the gas sampling line are taken out and weighed to determine the weight of the residue and smoke.

Hard copies of the data in the form of DADiSP plots, Xess spreadsheets and Grafit plots are examined to derive the pertinent information for the test.

The flame extinction test provides the data for the concentration of extinguishing agents required for flame extinction for 0.009 m^2 samples of composite systems burning under a heat flux exposure of 60 kW/m^2 in air.

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[2] For composite systems, this procedure needs to be modified. Concentration of an agent required to completely suppress ignition needs to be explored.

APPENDIX B

COMPOSITE SYSTEMS EXAMINED IN THIS STUDY AND TWO PREVIOUS STUDIES

The samples examined in this study are listed in Table B-1. The samples examined in the last two studies [7 and 9] and this study are listed in Table B-2.

Table B-1

Samples of the Composite Systems for the Combat Vehicle Hull Structures Examined in The Study

Sample No.	Composite System	Fiber /Resin (weight %)	Description
#9	S2 Glass/Epoxy	76/24	Shell 862 Epoxy; curing agent W Owens-Corning S-2 Fabric; resin transfer molded
#10	Graphite/Cyanate	73/27	YLA Incorporated prepeg polycyanate (250°F Cure); G30-500 5HS fabric vacuum bag molded
#11	S-2 Glass/PPS	84/16	Polyphenylene sulfide (PPS) thermoplastic resin; unidirectional S-2 glass fiber Quadrax QLG4368
#12	Glass/Epoxy/phenolic sandwich panel	82/18	4 plies S-2/phenolic; 7 plies E glass/epoxy; 4 plies S-2/phenolic
#13	AS4 Graphite/epoxy	71/29	Shell 862 epoxy resin; Shell curing agent W; Hercules CBX 0800 AS4 fabric with polyester stitching resin transfer molded

Table B-2

Composite Systems for the Combat Vehicle Hull Structures
Examined in the Current Study and the Two Previous Studies

Sample No.	Composite Systems	Glass/Resin (weight %)	Description
#1	S2 Glass/Polyester	70/30	1-E-701 Baseline
#2	S2 Glass/Polyester	70/30	1-Owens-Corning
#3	S2 Glass/Polyester	70/30	1-American-Cyanamide
#4	Kevlar/Phenolic-PVB	84/16	1-Russell Corp
#5	S2 Glass/Phenolic	80/20	1-Owens-Corning
#6	S2 Glass/Epoxy	65/35	2-Ferro Corp
#7	S2 Glass/Epoxy	65/35	2-ICI-Fiberite
#8	S2 Glass/Epoxy	65/35	2-American Cyanamide
#9	S2 Glass/Epoxy	76/24	3-Shell/Owens-Corning
#10	Graphite/Cyanate	73/27	3-YLA Inc.
#11	S2 Glass/PPS	84/16	3-Quadrax
#12	Glass/Epoxy/Phenolic	82/18	3-Lewcott/Ferro
#13	As4 Graphite/Epoxy	71/29	3-Shell/Hercules

[a]: Batch 1: Contract DAAL04-87-0078 (Ref. 7);
Batch 2: Contract DAAL04-90-M-0746 (Ref. 9);
Batch 3: Contract DAAL01-93-M-S403 (this study).

APPENDIX C

IGNITION

C-1 CRITICAL HEAT FLUX AND THERMAL RESPONSE PARAMETER

Ignition is a process where a material is gasified by heating its surface. The gasified material mixes with air, forms a flammable mixture, comes in contact with a flame, ignites and a fire is initiated. The region where the material is heated by internal or external heat sources and the flammable mixture is generated, resulting in fire initiation, is defined as the *ignition zone*. Minimum heat flux at or below which a material cannot generate the flammable mixture is defined as the *Critical Heat Flux (CHF)*[3,6-10,13-17]. The resistance of a material to generate flammable vapors is defined as the *Thermal Response Parameter (TRP)*[3,6-10,13-17] as reflected in the times to ignition at various imposed heat fluxes.

The higher the CHF and TRP values, the longer it takes for the material to heat up, ignite and initiate a fire, and the slower the fire propagation. For thermally thick materials, away from the *CHF* value, the time to ignition satisfies the following linear relationship[3,6-10,13-17]:

$$\sqrt{\frac{1}{t_{ig}}} = \frac{\sqrt{4/\pi}\,(\dot{q}''_e - \dot{q}''_{cr})}{\Delta T_{ig}\sqrt{k\rho c_p}} \qquad \text{(C-1)}$$

where t_{ig} is the time to ignition (s), $\dot{q}''_e$ is the external heat flux (kW/m^2), $\dot{q}''_{cr}$ is the critical heat flux (kW/m^2), ΔT_{ig} is the ignition temperature above ambient (K), k is the thermal conductivity of the solid material (kW/m-K), ρ is the density of the solid material (g/m^3), c_P is the specific heat of the solid material (kJ/g-K). $\Delta T_{ig}\ (k\rho c_P)^{1/2}$ is defined as the *Thermal Response Parameter (TRP),* which has the units of kW-s$^{1/2}$/m^2.

Figure C-1 shows the ignition data for the glass/epoxy/phenolic sandwich panel. The CHF value is indicated on the figure. The TRP value is obtained from the inverse of the slope of the line away from the CHF value, as indicated in the figure. The CHF and TRP values obtained in this fashion for the composite systems for the combat vehicle hull structures are listed in Table C-1 and shown by the bars in Fig. C-2. The TRP values for the 24 composite systems obtained in this fashion from the data reported by the U.S. Navy[11] are listed in Tables C-2 and C-3, and from the data for composite systems examined in Europe in Table C-4. TRP values for

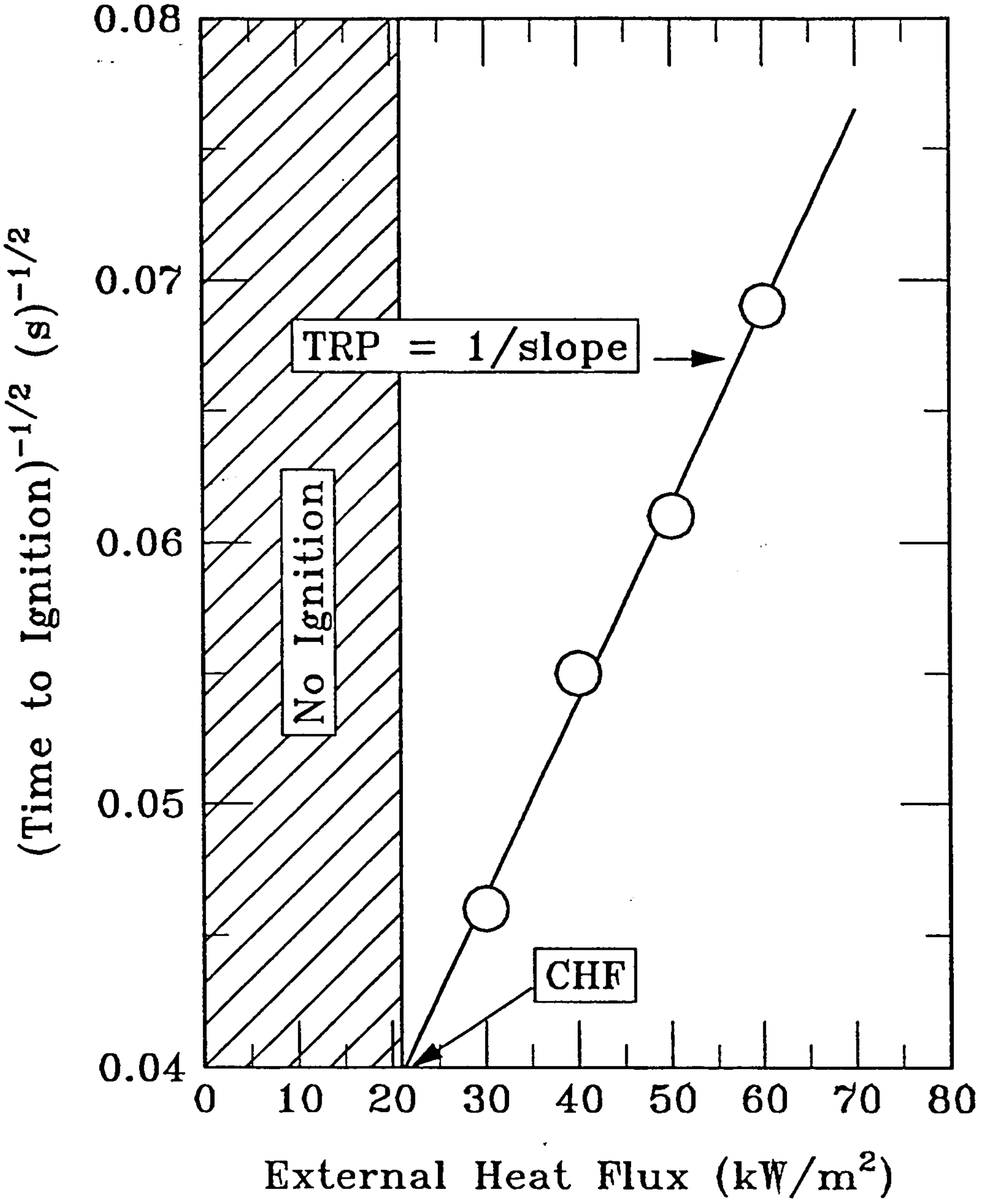

Figure C-1. Piloted Ignition Data for Glass/Epoxy/Phenolic Sandwich Panel.

similar composite systems examined for the U.S. Army by FMRC, by the U.S. Navy, and in Europe are listed in Table C-5.

The higher the CHF and TRP, the higher the degree of fire hardening. The TRP values in Tables C-1 to C-5 show that the degree of fire hardening depends on the fire barriers (Table C-3), generic nature of the fiber and the resin and fire retardant treatment of the resin (glass/PPS in Table C-5; sample #11 of the U.S. Army appears to have higher fire retardant treatment than the sample examined by the U.S. Navy). The TRP value increases with fire barrier and with increase in the fiber content and decrease in the resin content.

The TRP values show that the present composite systems have a higher degree of fire hardening than the systems examined in the previous two studies for the U.S. Army (Table C-1 and Fig. C-2)[7,9], by the U.S. Navy and in Europe (Table C-5). Fire barriers increase the TRP values (Table C-3).

The increase in the TRP value due to fire barriers and increases in the fiber content and type and fire retardant treatment, and decrease in the resin content and type could be due to increase in the density, thermal conductivity, specific heat, and the ignition temperature.

Figure C-3 shows a plot of the TRP values versus the resin fraction in the composite systems examined in the current study and the previous two studies[7,9] and from the U.S.Nav[11] and European study[12]. The TRP values increase with decrease in the resin content and increase in the fiber content. TRP values are highest for the graphite fiber systems, intermediate for the glass fiber systems and lowest for the kevlar fiber systems. Moderate variations in the densities and ignition temperatures of the composite systems have small effect on the TRP values. The specific heats of the fibers do not show much variation either. Thus the thermal conductivity appears to have a dominant effect on the TRP value. The thermal conductivity values for some materials, taken from the Handbook of Physics and Chemistry, as possible reinforcing fibers for the composite systems, are listed in Table C-6.

Table C-1

Critical Heat Flux and Thermal Response Parameter for Composite Systems for the Combat Vehicle Hull Structures (U.S. Army)

Sample No.	Composite Systems	Fiber/Resin (weight%)	Critical Heat Flux (kW/m^2)	Thermal Response Parameter (kW-s$^{1/2}$/m^2)
#1[a]	S2 Glass/Polyester	70/30	10	382
#2[a]	S2 Glass/Polyester	70/30	15	406
#3[a]	S2 Glass/Polyester	70/30	10	338
#4[a]	Kevlar/Phenolic-PVB	84/16	15	403
#5[a]	S2 Glass/Phenolic	80/20	20	610
#6[b]	S2 Glass/Epoxy	65/35	10	420
#7[b]	S2 Glass/Epoxy	5/35	10	410
#8[b]	S2 Glass/Epoxy	65/35	10	400
#9[c]	S2 Glass/Epoxy	76/24	15	667
#10[c]	Graphite/Cyanate	73/27	20	1000
#11[c]	S2 Glass/PPS	84/16	20	909
#12[c]	Glass/Epoxy/Phenolic	82/18	20	1250
#13[c]	As4 Graphite/Epoxy	71/29	24	667

[a]: Batch 1:Ref. 7;
[b]: Batch 2: Ref. 9;
[c]: Batch 3: This study.

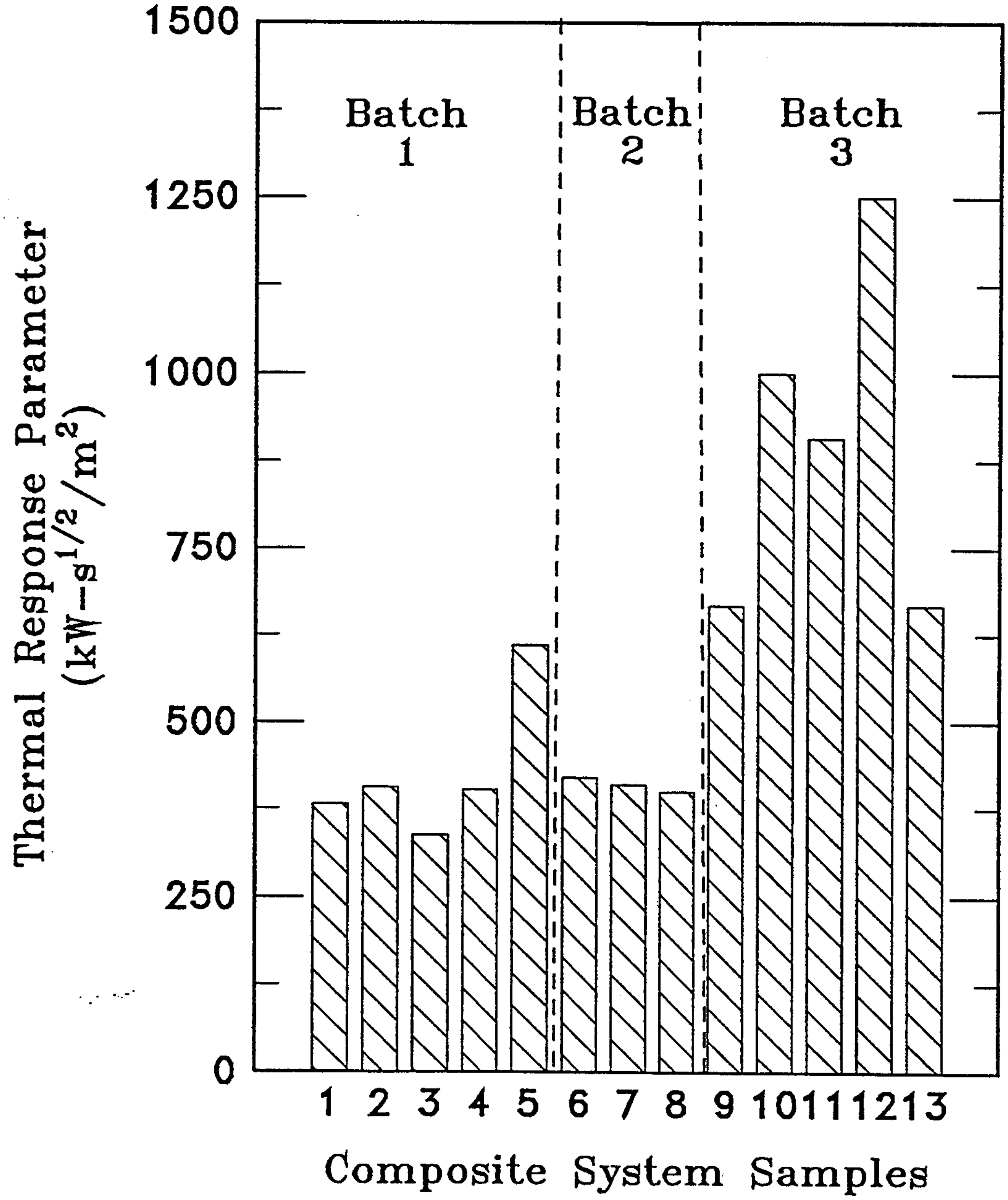

Figure C-2. Thermal Reponse Parameter Values for the Composite Sytems for Combat Vehicle Hull Structures. Batch 1: Ref. 7; Batch 2: Ref. 9; Batch 3: This Study.

Table C-2

Thermal Response Parameter, Heat Release Parameter, Residual Flexural Strength Retained for the Composite Systems (U.S. Navy)

Composite System	TRP ($kW\text{-}s^{1/2}/m^2$)[a]	HRP[a]	RFSR (%)[b]
Glass/Vinyl ester -1	312	3.4	32
Glass/Vinyl ester -2	526	2.5	14
Glass/Epoxy-3	667	2.4	5
Graphite/Epoxy-5	476	3.0	0
Graphite/Epoxy-6	500	1.6	-
Graphite/Bismaleimide-9	526	1.9	4
Glass/Bismaleimide-10	625	2.2	21
Graphite/Bismaleimide-11	588	3.6	16
Graphite/Bismaleimide-12	526	1.4	-
Graphite/Bismaleimide-13	526	1.8	14
Glass/Phenolic-14	417	1.6	-
Glass/Phenolic-16	556	-	-
Glass/Phenolic-17	476	0.8	-
Glass/Phenolic-18	769	2.8	-
Glass/Phenolic-19A	345	2.2	-
Glass/Phenolic-19B	385	1.2	-
Graphite/Phenolic-20	714	2.3	53
Graphite/Phenolic-21	400	2.8	30
Glass/Polyimide-23	833	1.1	45
Glass/PPS-24	588	2.4	36
Graphite/PPS-25	333	1.9	41
Graphite/PEEK-26	526	1.1	75
Graphite/Polyaryl sulfone-27	357	0.8	36

[a] TRP and HRP values calculated from the data reported in Ref. 11;

[b] RFSR: Residual Flexural Strength Retained from Ref. 11 for a 25 kW/m^2 heat flux exposure for 20 min

Table C-3

Thermal Response Parameter, Heat Release Parameter, Residual Flexural Strength Retained for the Composite Systems with Fire Barriers (U.S. Navy)[a]

Composite System	Fire Barrier	TRP (kW-$s^{1/2}/m^2$)	HRP	RFSR (%)[b]
Glass/Vinyl ester	None	281	2.36	14
	CC	676	2.80	26
	IC	1471	0.92	28
	H-CC/IC	1923	2.96	46
Graphite/Epoxy	None	481	1.76	0.5
	CC	2273	1.60	13
	IC	962	1.80	77
	H-CC/IC	1786	1.52	14
Graphite/Bismaleimide	None	610	-	-
	CC	1786	1.40	-
	IC	1563	1.28	-
	H-CC/IC	2500	1.60	-
Graphite-Phenol	CC	807	1.36	
	IC	1563	1.28	
	H-CC/IC	-	1.64	
Graphite/PPS	None	329	1.20	-
Glass/PPS	None	431	1.32	-

[a] CC: ceramic coating; IC: intumescent coating; H-CC/IC: hybrid ceramic-intumescent coating; TRP (Thermal Response Parameter) and HRP (Heat Release Parameter) values calculated from the data reported in Ref. 11;

[b] RFSR: Residual Flexural Strength Retained from Ref. 11 for 25 kW/m^2 of heat flux exposure for 20 minutes.

Table C-4

Thermal Response Parameter and Heat Release Parameter
Composite Systems Examined in Europe[a]

Composite System	Fiber/Resin (weight%)	TRP ($kW\text{-}s^{1/2}/m^2$)	HRP
Glass/Polyester	30/70	256	6.4
Glass/Polyether ether ketone (PEEK)	30/70	301	2.6
Glass/Isophthalic polyester (IPES) (non-fire retarded)	0/100	296	6.2
	30/70	426	1.1
Glass/Vinyl ester (non-fire retarded)	100	263	13.1
	69/31	444	2.30
Glass/Epoxy (non-fire retarded	100	257	10.5
	69/31	388	2.05
Glass/Phenolic	45/55	683	1.2

[a] TRP: (Thermal Response Parameter) and HRP (Heat Release Parameter) values calculated from the data reported in Ref. 12;

Table C-5

Thermal Response Parameter for Common Composite Systems Examined by the U.S.Army, the U.S.Navy and In Europe

Composite System	Fiber/Resin (weight %)	TRP ($kW\text{-}s^{1/2}/m^2$)		
		U.S. Army[a]	U.S. Navy[b]	Europe[c]
Glass/Polyester	30/70	-	-	256
	70/30	382 (#1)	-	-
	70/30	406 (#2)	-	-
	70/30	338 (#3)	-	-
Glass/Phenolic	45/55	-	-	683
	80/20	610 (#5)	-	-
	-	-	345	-
	-	-	385	-
	-	-	417	-
	-	-	476	-
	-	-	556	-
	-	-	769	-
Glass/Vinyl ester	0/100	-	-	263
	62/38	-	312	-
	66/34	-	526	-
	69/31	-	-	444
Glass/Epoxy	0/100	-	-	257
	65/35	420 (#6)	-	-
	65/35	410 (#7)	-	-
	65/35	400 (#8)	-	-
	69/31	-	-	388
	76/24	667 (#9)	-	-
	81/19	-	667	-
Glass/PPS	84/16	909 (#11)	588	-
Graphite/Epoxy	71/29	667 (#13)	500	-
	81/19	-	476	-

[a] From this study and older studies[7,9];
[b] Calculated from the data reported in Ref. 11;
[c] Calculated from the data reported in Ref. 12.

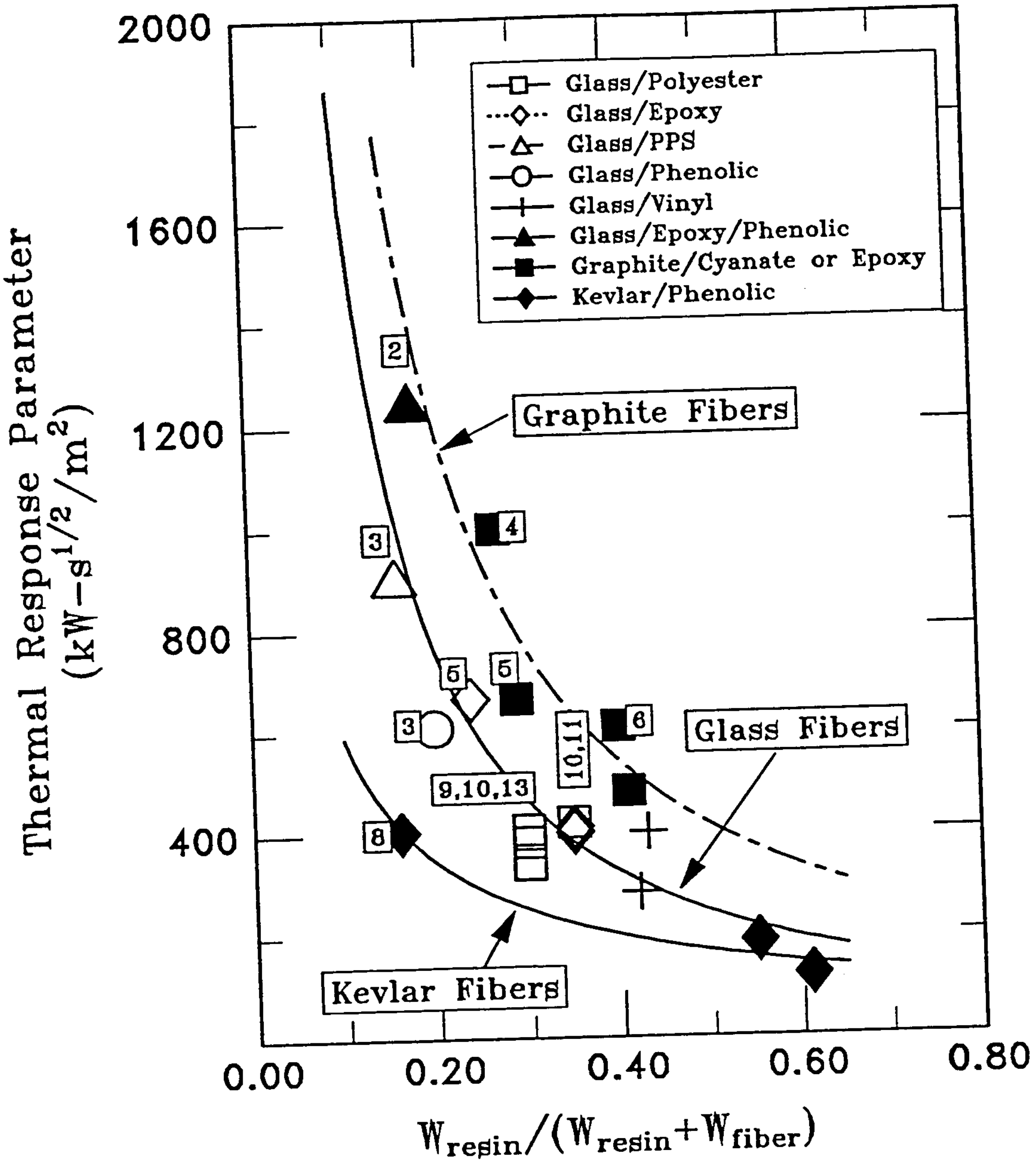

Figure C-3. Thermal Response Parameter Versus Resin Fraction of Composite Systems. Numbers Less than 7 Indicate No Fire Propagation. Numbers Greater than or Equal to 8 Indicate Fire Propagation

Table C-6

Thermal Conductivity of Materials
from the Handbook of Chemistry and Physics

Material	Thermal Conductivity (kW/m-K) x 10^3
Kevlar	0.200
Glass	1.05
Quartz	1.72
Graphite	5.02
Sapphire (Aluminum oxide)	24.0
Silicone carbide	85.0

The trends in the thermal conductivities in Table C-6 are: silicone carbide >> sapphire>> graphite > glass > kevlar. The TRP values of the composite systems listed in Table C-1 appear to follow these trends in the thermal conductivity values, which is expected, because for higher thermal conductivity systems, the time taken to bring the surface to the ignition temperature is longer than for the systems with low thermal conductivities.

The ignition data suggest that further fire hardening of composite systems could be achieved by using high thermal conductivity fibers such as boron, beryllium, sapphire (aluminum oxide), boron carbide, silicon carbide and nitride, and others. The restraining factor for the use of these fibers would be their end-use compatibility and the cost of the composite systems.

C.2 STRUCTURAL PERFORMANCE AND STRENGTH AND THERMAL RESPONSE PARAMETER

The structural performance and strength of composite systems is very important for survivability and damage control during and after a fire[11]. The U.S. Navy has been assessing the structural performance and strength of composite systems from the inter-relationship of temperature, mechanical property and time[11]. For such an assessment measurements are made for[11]: 1) the Dynamic Mechanical Thermal Analysis (DMTA) and Residual Flexural Strength

Retained (RFSR) after heat flux exposure; 2) temperature-time-thickness profile during heat flux exposure, and 3) reduction in the flexural modulus with increase in temperature.

The data for the Residual Flexural Strength Retained (RFSR) for various composite systems exposed to 20 kW/m^2 for 20 minutes as reported by the U.S. Navy[11] are listed in Tables C-2 and C-3. RFSR has been selected to characterize the residual mechanical integrity of composite systems after fire exposure[11]. In Table C-2, the RFSR value is highest for the graphite/PEEK-26 composite system (75%), followed by graphite/phenolic-20 (53%), and glass/polyimide-23 (45%) composite systems. Graphite/epoxy-5 composite system delaminates. The TRP values for these composite systems are greater than 526 kW-s$^{1/2}$/m^2. Fire barriers applied to the surfaces of the composite systems as ceramic coating, intumescent coating and a hybrid ceramic-intumescent coating increase the RFSR as well as the TRP values..

The smaller the time-temperature-thickness profile for a composite system, the higher the RFSR value and the higher the composite structural performance at elevated temperatures in fires. The Time-temperature-thickness profile is a strong function of the TRP value of the composite system. Thus the higher the TRP value, the shallower the time-temperature-thickness profile, the higher the structural performance and resistance to ignition and fire propagation of the composite system. *There appears to be a relationship between the RFSR and TRP values, which needs to be explored.*

APPENDIX D

COMBUSTION

Combustion is a process where the gasified material reacts with oxygen from air, burns and releases heat and products of complete and incomplete combustion. The heat release rate in a fire is defined as the *chemical heat release rate*[6-10,13-21] and is responsible for thermal damage[2]. The release of the products in a fire is responsible for nonthermal damage due to smoke damage and reduced visibility, toxicity, and corrosivity[2].

The heat transfer per unit area from the flame back to the surface is defined as the *flame heat flux*. The hot surface loses heat to the environment in the form of radiation and is defined as the *surface re-radiation loss*. If there are external sources near the burning material, there is an additional heat flux transferred from the external sources to the surface of the burning material, which is defined as the *external heat flux*. The rate at which the material loses mass is defined as the *mass loss rate*. The mass loss rate determines the rate at which the vapors of the material are fed to the flame. The mass loss rate is expressed as the heat balance between the heat flux transferred and heat lost from the surface and heat required to gasify a unit mass of the material, defined as the *heat of gasification*[13,18]:

$$\dot{m}'' = (\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) / \Delta H_g \qquad \text{(D-1)}$$

where $\dot{m}''$ is the mass loss rate per unit surface area of the sample (g/m^2-s), $\dot{q}''_e$ is the external heat flux per unit surface area of the sample (kW/m^2), $\dot{q}''_f$ is the flame heat flux per unit surface area of the sample (kW/m^2) $\dot{q}''_{rr}$ is the surface re-radiation loss per unit surface area of the sample (kW/m^2), and ΔH_g is the heat of gasification (kJ/g).

D.1 HEAT RELEASE RATE

The chemical heat release rate is determined from the *Carbon Dioxide Generation (CDG)* and Oxygen Consumption (OC) Calorimetries[13,18].

D.1.1 The CDG Calorimetry

The chemical heat release rate is determined from the following relationships[18]:

$$\dot{Q}''_{ch} = \Delta H^*_{CO_2}\dot{G}''_{CO_2} + \Delta H^*_{CO}\dot{G}''_{CO} \tag{D-2}$$

$$\Delta H^*_{CO_2} = \Delta H_{CO_2}/\Psi_{CO_2} \tag{D-3}$$

$$\Delta H^*_{CO} = (\Delta H_T - \Delta H_{CO}\Psi_{CO})/\Psi_{CO} \tag{D-4}$$

where $\dot{Q}''_{ch}$ is the chemical heat release rate (kW/m^2), ΔH^*_{co2} is the net heat of complete combustion per unit mass of CO_2 generated (kJ/g), ΔH^*_{co} is the net heat of complete combustion per unit mass of CO generated (kJ/g), ΔH_T is the net heat of complete combustion per unit mass of fuel consumed (kJ/g), Ψ_{co2} is the stoichiometric yield for the maximum conversion of fuel to CO_2 (g/g), Ψ_{co} is the stoichiometric yield for the maximum conversion of fuel to CO (g/g), $\dot{G}''_{co2}$ mass generation rate of CO_2 (g/m^2-s) and $\dot{G}''_{co}$ the mass generation rate of CO (g/m^2-s).

For the determination of the chemical heat release rate, mass generation rates of CO_2 and CO are measured and multiplied by the average values of the net heat of complete combustion per unit mass of CO_2 and CO generated, which are 13.3 kJ/g ± 11% and 11.1 kJ/g ± 18% , respectively[18].

D.1.2 The OC Calorimetry

The chemical heat release rate is determined from the following relationship[18]:

$$\dot{Q}''_{ch} = \Delta H^*_{O}\dot{C}''_{O} \tag{D-5}$$

$$\Delta H^*_{O} = \Delta H_{O}/\Psi_{O} \tag{D-6}$$

where ΔH^*_o is the net heat of complete combustion per unit mass of oxygen consumed (kJ/g), $\dot{C}''_o$ is the mass consumption rate of oxygen (g/m^2-s) and Ψ_o is the stoichiometric mass-oxygen-to-fuel ratio (g/g). For the determination of the chemical heat release rate, mass consumption rates of O_2 is measured and multiplied by the average value of the net heat of complete combustion per unit mass of O_2 consumed, which is 12.8 kJ/g ± 7%[18].

Figure D-1 shows examples of the applications of Eqs. D-2 and D-5.

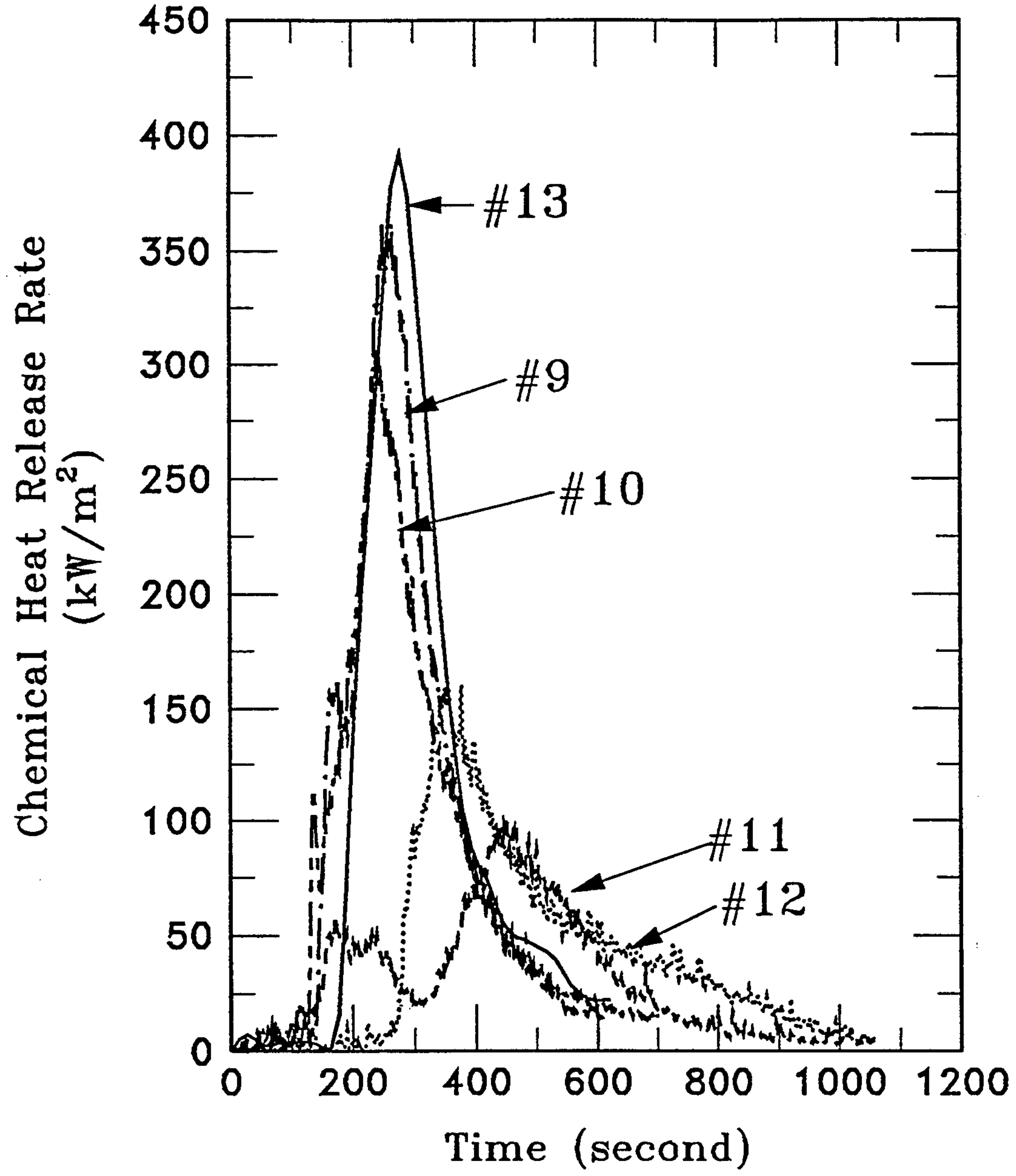

Figure D-1. Chemical Heat Release Rate for Composite Systems Burning at an External Heat Flux Exposure of 60 kW/m^2 with a Surface Area of 0.008 m^2.

D.1.3 Energy Released in a Fire

The total amount of heat generated as a result of chemical reactions in the combustion of a material is defined as the chemical energy. The chemical energy is calculated by the summation of the respective heat release rates :

$$E_{ch} = A \sum_{n=t_{ig}}^{n=t_{ex}} \dot{Q}''_{ch}(t_n)\,\Delta t_n \qquad \text{(D-7)}$$

where E_{ch} is the chemical energy (kJ), A is the total surface area of the material burning (m2), t_{ig} is the ignition time (s), and t_{ex} is the flame extinction time (s). The total mass of the material lost during combustion is measured directly from the initial and final mass and is calculated by the summation of the mass loss rate:

$$W_f = A \sum_{n=t_{ig}}^{n=t_{ex}} \dot{m}''(t_n)\,\Delta t_n \qquad \text{(D-8)}$$

where W_f is the total mass of the material lost in the combustion (g).

D.1.4 Heat of Combustion

Heat release rate is the product of the mass loss rate and the heat of combustion[6-16]:

$$\dot{Q}''_{ch} = \Delta H_{ch}\dot{m}'' \qquad \text{(D-9)}$$

where ΔH_{ch} is the chemical heat of combustion (kJ/g). The average chemical heat of combustion is calculated from the relationship based on Eqs. D-7 to D-9:

$$\Delta \overline{H_{ch}} = E_{ch}/W_f \qquad \text{(D-10)}$$

where $\Delta \bar{H}_{ch}/\Delta H_g$ is the average chemical heat of combustion (kJ/g). An example of the application of Eq. D-10 is shown in Fig. D-2 for the graphite/cyanate (#10) composite system. The chemical heats of combustion obtained in this fashion for the composite systems examined in this study and in the previous two studies[7,9] are listed in Table D-1 and shown as bars in Fig. D-3; dashed lines in the figure represent chemical heats of combustion of ordinary combustibles.

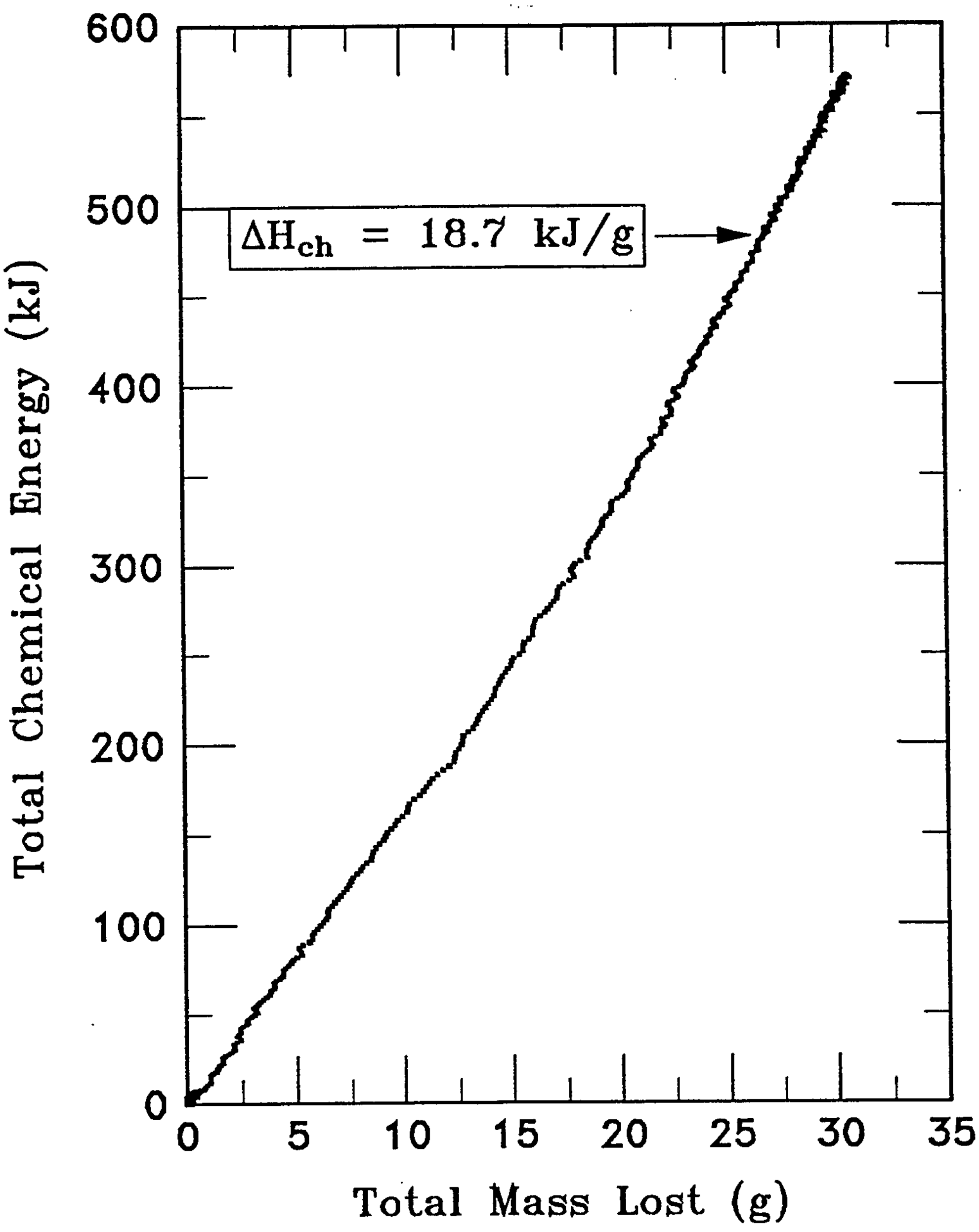

Figure D-2. Total Chemical Energy Generated in the Combustion of Graphite/Cyanate (#10) Composite System Versus the Total Mass Lost for an External Heat Flux Exposure of 50 kW/m^2.

Table D-1
Chemical Heat of Combustion for the Composite Systems for the Combat Vehicle Hull Structures

Sample No.	Composite System	Glass/Resin (Weight %)	External Heat Flux (kW/m^2)	Chemical Heat of Combustion (kJ/g)
#1[a]	S2 Glass/Polyester	70/30	-	17.9
#2[a]	S2 Glass/Polyester	70/30	-	16.0
#3[a]	S2 Glass/Polyester	70/30	-	9.3
#4[a]	Kevlar/Phenolic	84/16	-	14.8
#5[a]	S2 Glass/Phenolic	80/20	-	11.9
#6[b]	S2 Glass/Epoxy	65/35	-	11.9
#7[b]	S2 Glass/Epoxy	65/35	-	10.0
#8[b]	S2 Glass/Epoxy	65/35	-	10.2
#9[c]	S2 Glass/Epoxy	76/24	30 40 50 60 Average	18.8 18.7 18.5 18.5 18.6
#10[c]	Graphite/Cyanate	73/27	30 40 50 60 Average	19.1 18.9 18.7 18.9 18.9
#11[c]	S2 Glass/PPS	84/16	40 50 60 Average	16.8 17.3 17.0 17.0
#12[c]	Glass/Epoxy/Phenolic	82/18	60	11.5
#13[c]	AS4 Graphite/Epoxy	71/29	30 60 Average	17.3 18.2 17.8

[a]: Ref.7;
[b]: Ref. 9;
[c]: This study.

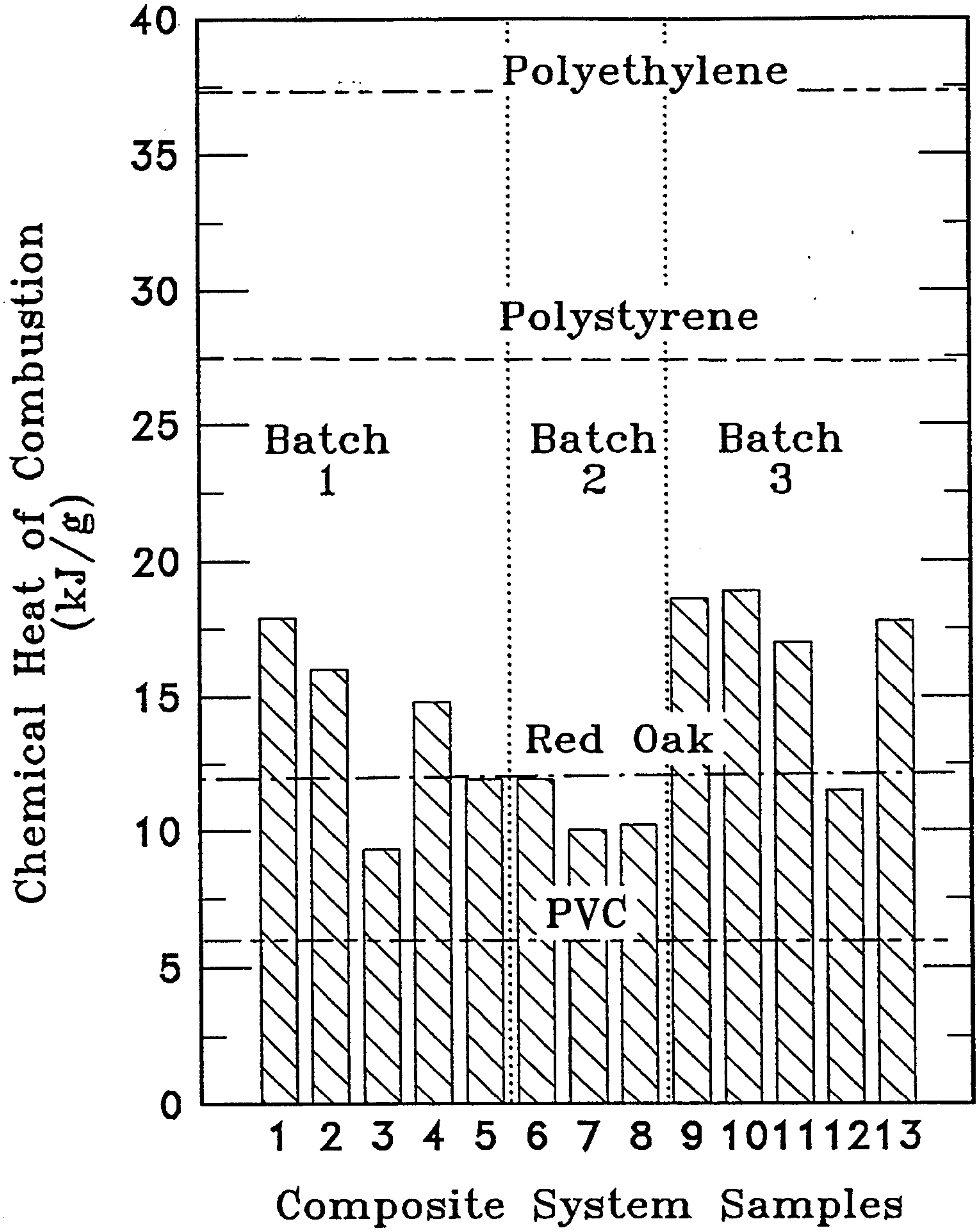

Figure D-3. Chemical Heat of Combustion of the Composite Systems for the Combat Vehicle Hull Structures. Batch 1: Ref. 7; Batch 2: Ref 2; Batch 3: This Study.

The chemical heats of combustion of the composite systems are lower than the heats of combustion of thermoplastics (polyethylene and polystyrene), but are higher than the halogenated polymer (PVC) and wood (red oak), consistent with the nature of the resins present in the composite systems.

The lower the chemical heat of combustion, the lower the heat release rate and the higher the degree of fire hardening.

D.1.5 Heat Release Parameter (HRP)

The *Heat Release Parameter (HRP)* is defined as the amount of energy generated per unit of energy absorbed, expressed as the ratio of the chemical heat of combustion to heat gasification[13,18]. HRP is related to the heat release rate by the following relationship (Eqs. D-1 and D-9):

$$\dot{Q}''_{ch} = \left[\frac{\Delta H_{ch}}{\Delta H_g}\right](\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) \qquad \text{(D-11)}$$

where $\Delta H_{ch}/\Delta H_g$ is the *Heat Release Parameter (HRP)*, ΔH_{ch} is the chemical heat of combustion (kJ/g), and ΔH_g is the heat of gasification (kJ/g). The HRP values are characteristic fire properties of materials, dependent on fire ventilation but independent of fire size. For the same fire size, external heat flux, and/or flame heat flux, materials with lower values of HRP have lower heat release rates. *The HRP values decrease with increase in the degree of fire hardening.*

The HRP values for the composite systems can be determined by measuring the heat release rates at various external heat flux values, plotting the data which should show a linear relationship and determining the slope, such as shown in Figure D-4. The HRP values obtained in this fashion are listed in Table D-2. The HRP values calculated from the data reported by the US. Navy[11] are listed in Tables C-2 and C-3 and data measured in Europe in Table C-4.

The lower the HRP value, the lower the heat release rate, fire intensity and thermal damage. Also the lower the heat flux from the flame to the surface of the composite, the smaller the time-temperature-thickness profile and the better the composite structural performance.

Composite systems with HRP ≤ 4.0 have low intensity fires, which could be used as one of the criteria for the selection of the composite systems for the combat vehicle hull structures.

Table D-2
Heat Release Parameter for the Composite Systems
for the Combat Vehicle Hull Structures

Sample No.	Composite System	Glass/Resin (Weight %)	Heat Release Parameter
#1[a]	S2 Glass/Polyester	70/30	5.4
#2[a]	S2 Glass/Polyester	70/30	3.8
#3[a]	S2 Glass/Polyester	70/30	5.1
#4[a]	Kevlar/Phenolic	84/16	4.0
#5[a]	S2 Glass/Phenolic	80/20	1.2
#6[b]	S2 Glass/Epoxy	65/35	6.3
#7[b]	S2 Glass/Epoxy	65/35	4.7
#8[b]	S2 Glass/Epoxy	65/35	5.6
#9[c]	S2 Glass/Epoxy	76/24	4.0
#10[c]	Graphite/Cyanate	73/27	2.0
#11[c]	S2 Glass/PPS	84/16	3.0
#12[c]	Glass/Epoxy/Phenolic	82/18	3.7
#13[c]	AS4 Graphite/Epoxy	71/29	4.0

D.2 GENERATION OF FIRE PRODUCTS AND CONSUMPTION OF OXYGEN

Fire products (smoke, toxic, corrosive and odorous compounds) are the main contributors to non-thermal hazard and thus the assessments of their chemical natures and generation rates, relative to the air flow rate, are of importance for the protection of life and property[2].

In fires, products are generated as a result of gasification and decomposition of the material and burning of the species in the gas phase with air in the form of a diffusion flame. In general, generation of the fire products and consumption of oxygen in diffusion flames occur in two zones[20]:

1) Reduction Zone: In this zone, the material melts, decomposes, gasifies and/or generates species which react to form smoke, CO, hydrocarbons and other intermediate products. Very little oxygen is consumed in this region. The extent of conversion of the material to smoke, CO, hydrocarbons and other products depends on the chemical nature of the material.

2) Oxidation Zone: In this zone, the reduction zone products (smoke, CO, hydrocarbons, and other intermediates) react with varying degrees of efficiency with the oxygen from air and generate chemical heat and varying amounts of products of complete combustion, such as CO_2 and H_2O. The lower the reaction efficiency, the higher the amounts of reduction zone products emitted from a fire. The reaction efficiency of the reduction zone products with oxygen depends on the concentrations of the products relative to the oxygen concentration, temperature, and mixing of the products and air. For example, in laminar diffusion flames, smoke is emitted when the temperature of the oxidation zone falls below about 1300 K.

The hot ceiling layer in enclosed spaces may be considered in terms of oxidation and reduction zone products. For fires in enclosed spaces with plenty of ventilation, the concentrations of the reduction zone products are higher in the central region of the ceiling layer, whereas the concentrations of the oxidation zone products are higher closer to the opening to the enclosed spaces. As the air supply rate or oxygen concentration, available to the fire, reduces due to restrictions in the ventilation, the ceiling layer expands and starts occupying greater volumes of the enclosed spaces with increase in the concentrations of the reduction zone products. Under these conditions, large amounts of the reduction zone products are released within the enclosed spaces, increasing the nonthermal hazard.

D.2.1 Mass Generation Rates of Fire Products

The mass generation rates of fire products and mass consumption rate of oxygen are determined by measuring the volume fractions of the products and oxygen and the total volumetric or mass flow rate of the fire products-air mixture:

$$\dot{G}_j'' = \frac{f_j \dot{V} \rho_j}{A} = f_j \dot{W} \left[\frac{\rho_j}{\rho_g A} \right] \tag{D-12}$$

$$\dot{C}_o'' = \frac{f_o \dot{V} \rho_o}{A} = f_o \dot{W} \left[\frac{\rho_o}{\rho_g A} \right] \tag{D-13}$$

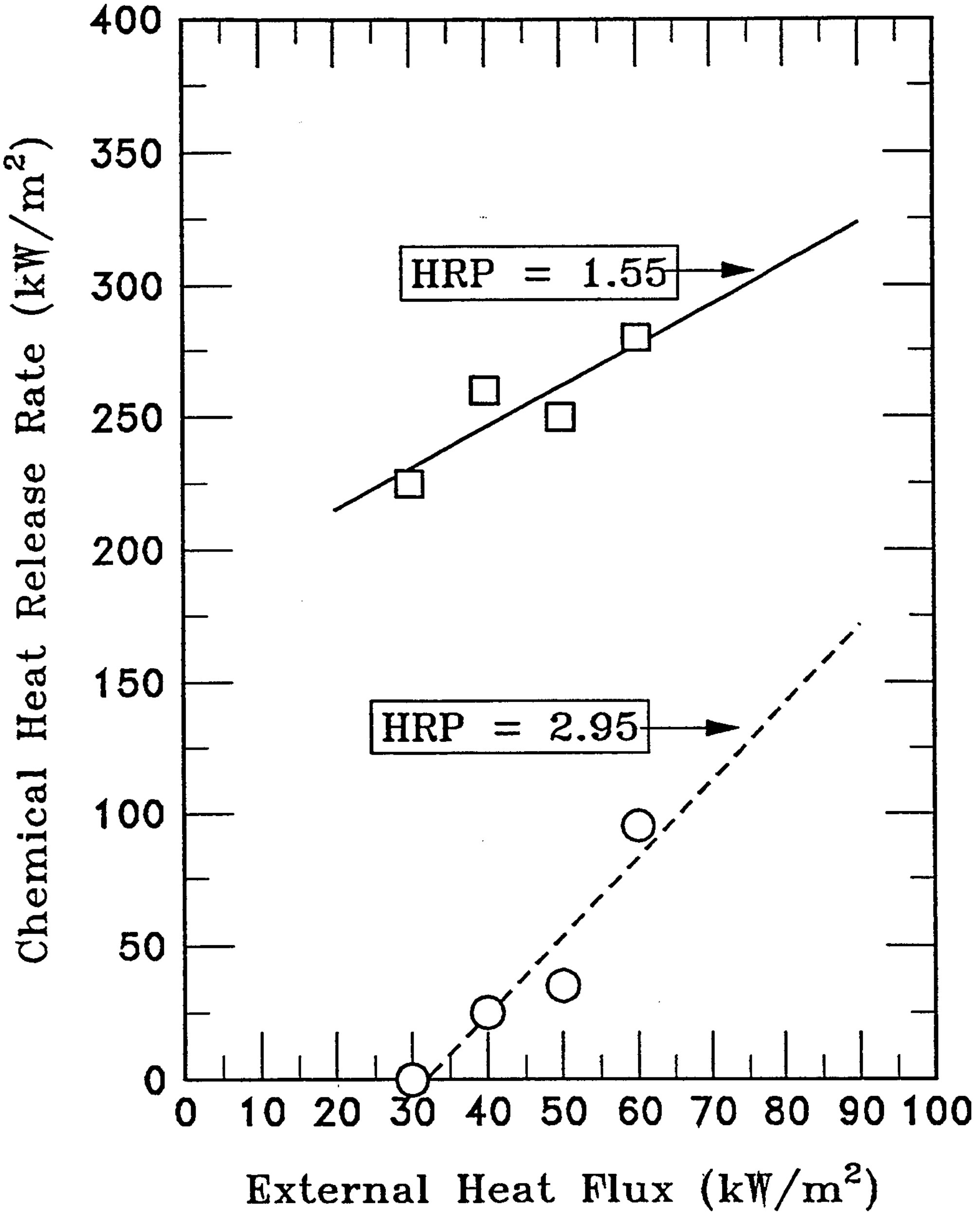

Figure D-4. Chemical Heat Release Rate Versus External Heat Flux. : Graphite/Cyanate (#10); O: Glass/PPS (#11) Composite Systems.

where f_j is the volume fraction of product j, f_o is the volume fraction of oxygen, $\dot{V}$ the total volumetric flow rate of the fire product-air mixture (m^3/s), $\dot{W}$ is the total mass flow rate of the fire product-air mixture (g/s), ρ_j is the density of product j at the temperature of the fire product-air mixture (g/m^3), ρ_g is the density of the hot fire product-air mixture (g/m^3), ρ_o is the density of oxygen at the temperature of the fire product-air mixture (g/m^3), and A is the total area of the material burning (m^2).

The volume fraction measurements are made in the sampling duct of the FMRC Flammability Apparatus (Figs. A-1 and A-2), where fire products and air are well mixed. The measurement locations in the sampling duct are shown in the figures. The volume fractions of the gaseous products are measured by gas analyzers.

Figure D-5 shows an example of the generation rate of CO determined from the above relationships for the composite systems examined in this study at an external heat flux of 60 kW/m^2. The volume fraction of smoke is measured by the FMRC turbidimeter. The turbidimeter measures the optical density defined as:

$$D = \frac{\ln\left(\frac{I_o}{I}\right)}{l} \tag{D-14}$$

where D is the optical density (1/m), I/I_o is the fraction of light transmitted through smoke, and ℓ is the optical path length (m). The volume fraction of smoke is obtained from the following relationship[17]:

$$f_s = \frac{D\lambda \times 10^{-6}}{\Omega} \tag{D-15}$$

where f_s is the volume fraction of smoke, λ is the wave length of the light source (μm), and Ω is the coefficient of particulate extinction taken as 7.05[2]. In the FMRC Flammability Apparatus, optical density is measured at wavelengths of 0.4579 μm (blue), 0.6328 μm (red), and 1.06 μm (IR) μm.

From Eqs. D-12 and D-15:

$$\dot{G}_s'' = \frac{f_s \dot{V} \rho_s x\ 10^{-6}}{A} = \left(\frac{D\lambda}{7}\right)\left[\frac{\rho_s \dot{V}\ x\ 10^{-6}}{A}\right] = \left(\frac{D\lambda}{7}\right)\left(\frac{\rho_s}{\rho_a}\right)\left[\frac{\dot{W}\ x\ 10^{-6}}{A}\right] \qquad \text{(D-16)}$$

In the FMRC Flammability Apparatus, the fire products in the sampling duct are diluted about 20 times and thus using the density of air, $\rho_a = 1.2 \text{ x } 10^3$ g/m^3 and the density of smoke, $\rho_s = 1.1 \text{ x } 10^6$ g/m^3:

$$\dot{G}_s'' = \left(\frac{1.1\ x\ 10^6 x\ 10^{-6}}{7}\right)\left(\frac{\dot{V}}{A}\right) D\lambda = \left(\frac{1.1\ x\ 10^6 x\ 10^{-6}}{7\ x\ 1.2\ x\ 10^3}\right)\left(\frac{\dot{W}}{A}\right) D\lambda \qquad \text{(D-17)}$$

1) <u>For Blue Wavelength of Light (λ = 0.4579 μm)</u>

$$\dot{G}_s'' = 0.0720\left(\frac{D_{blue}\dot{V}}{A}\right) = 0.0600\ x 10^{-3}\left(\frac{D_{blue}\dot{W}}{A}\right) \qquad \text{(D-18)}$$

2) <u>For Red Wavelength of Light (λ = 0.6328 μm)</u>

$$\dot{G}_s'' = 0.0994\left(\frac{D_{red}\dot{V}}{A}\right) = 0.0829\ x\ 10^{-3}\left(\frac{D_{red}\dot{W}}{A}\right) \qquad \text{(D-19)}$$

3) <u>For Infra Red Wavelength of Light (λ = 1.06 μm)</u>

$$\dot{G}_s'' = 0.1666\left(\frac{D_{ir}\dot{V}}{A}\right) = 0.1388\ x\ 10^{-3}\left(\frac{D_{ir}\dot{W}}{A}\right) \qquad \text{(D-20)}$$

where D_{blue}, D_{red} , and D_{IR} are the optical densities measured at wavelengths of 0.4579, 0.6328, and 1.06 μm respectively. These optical densities and total mass flow rate of the fire products-air mixture, $\dot{W}$, are measured continuously in the Flammability Apparatus. The generation rates of smoke obtained from the optical densities are averaged.

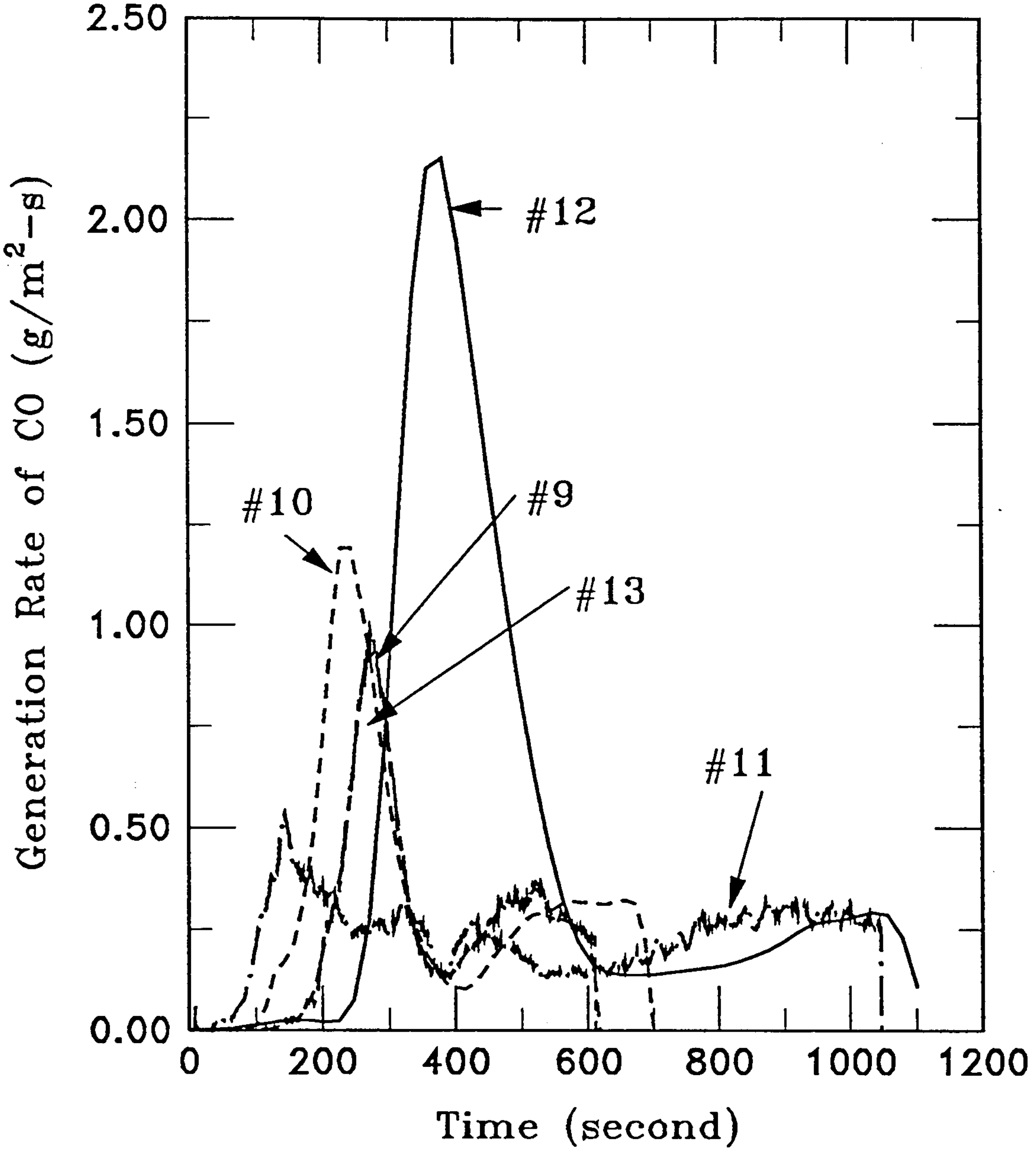

Figure D-5. Generation Rate of CO from the Combustion of Composite Systems of 0.008 m^2 Surface Areas Exposed to 60 kW/m of External Heat Flux.

Figure D-6 shows an example of the generation rate of smoke determined from the above relationships for the composite systems examined in this study at an external heat flux of 60 kW/m^2.

D.2.2 Yield of a Fire Product

The generation rate of a fire product is directly proportional to the mass loss rate, the proportionality constant being defined as the yield of the product[6-16]:

$$\dot{G}_j'' = y_j \dot{m}'' \tag{D-21}$$

where $\dot{G}_j''$ is the mass generation rate of product j (g/m2-s) and y_j is the yield of the product (g/g). The total mass of the product generated is obtained by the summation of the generation rate :

$$W_j = A \sum_{n=t_0}^{n=t_f} \dot{G}_j''(t_n)\Delta t_n \tag{D-22}$$

where W_j is the total mass of product j generated (g/g). The yield of a product is defined as the ratio of the generation rate of the product to the mass loss rate of the material or the average yield of a product is the ratio of the total mass of the product generated (Eq. D-22) and total mass of the material lost (Eq. D-8):

$$\overline{y_j} = \frac{W_j}{W_f} \tag{D-23}$$

Figure D-7 shows a plot of the total mass of CO and smoke versus the total mass of graphite/cyanate (#10) composite system lost during combustion at 30 kW/m^2 of external heat flux. The slopes of the lines are the average yields of CO and smoke.

The average yields of CO and smoke obtained from this procedure are listed in Table D-3 and plotted in Figs. D-8 and D-9 for the composite systems examined in this and previous two studies[7,9]. The yields of CO and smoke for ordinary combustibles are included in the figures by dashed lines. The data in the figures show that the yields of CO and smoke for most of the composite systems are higher than or comparable to the yields for the halogenated and aromatic-

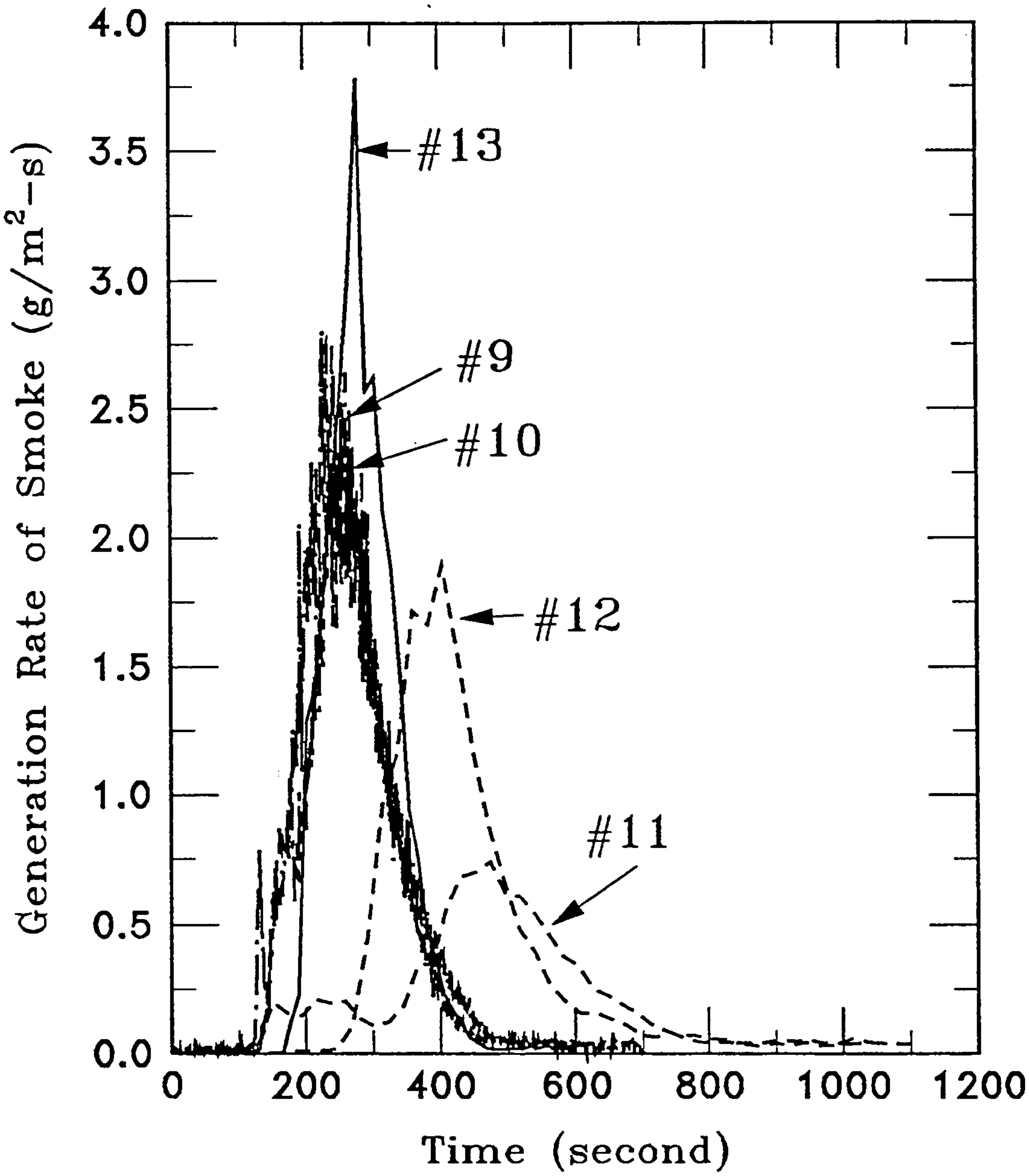

Figure D-6. Generation Rate of Smoke for the Composite Systems Burning at an External Heat Flux Exposure of 60 kW/m^2 with a Surface Area of 0.008 m^2.

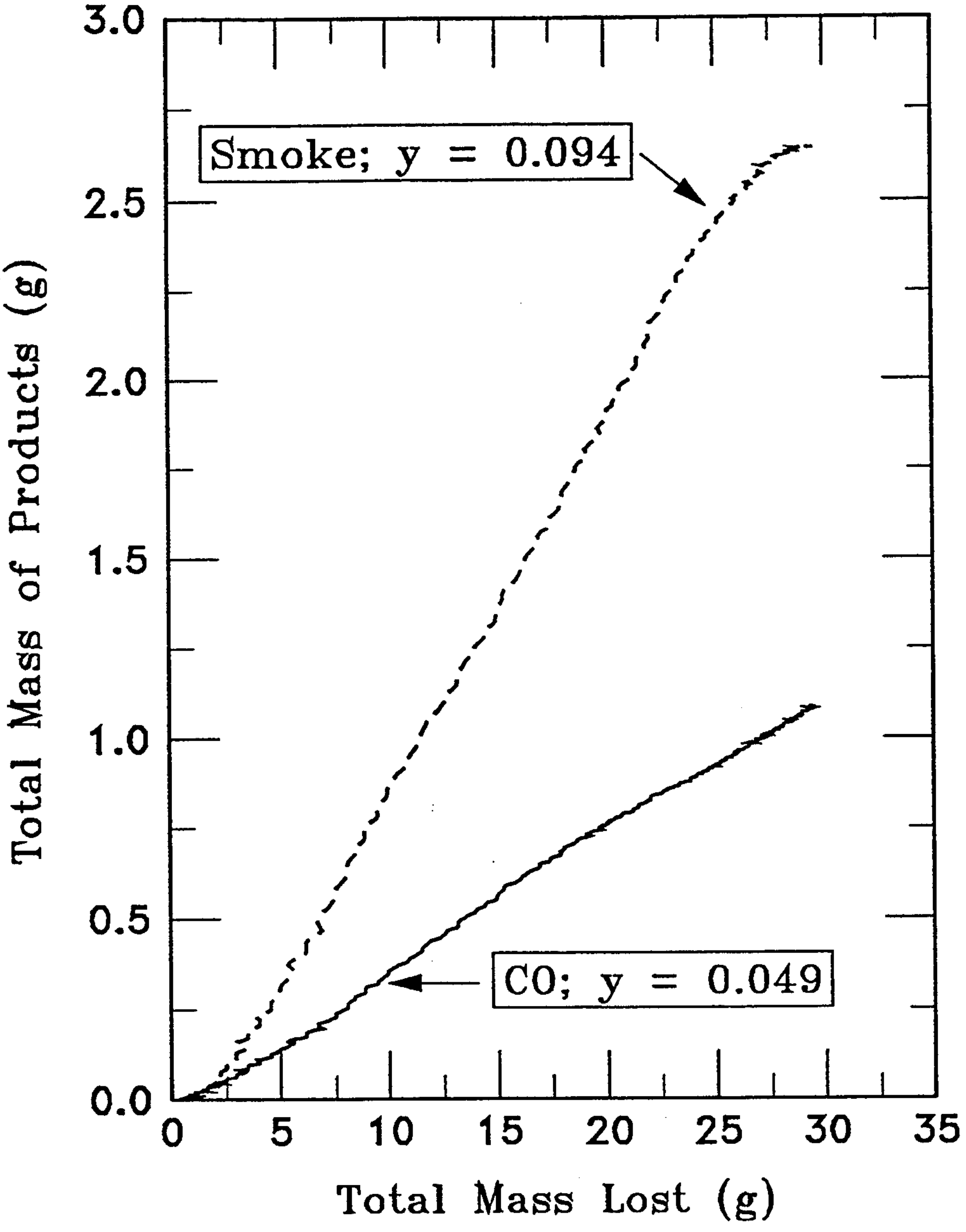

Figure D-7. Total Mass of CO and Smoke Generated Versus the Total Mass Lost During the Combustion of Graphite/Cyanate (#10) Composite System Exposed to an External heat Flux of 30 kW/m^2.

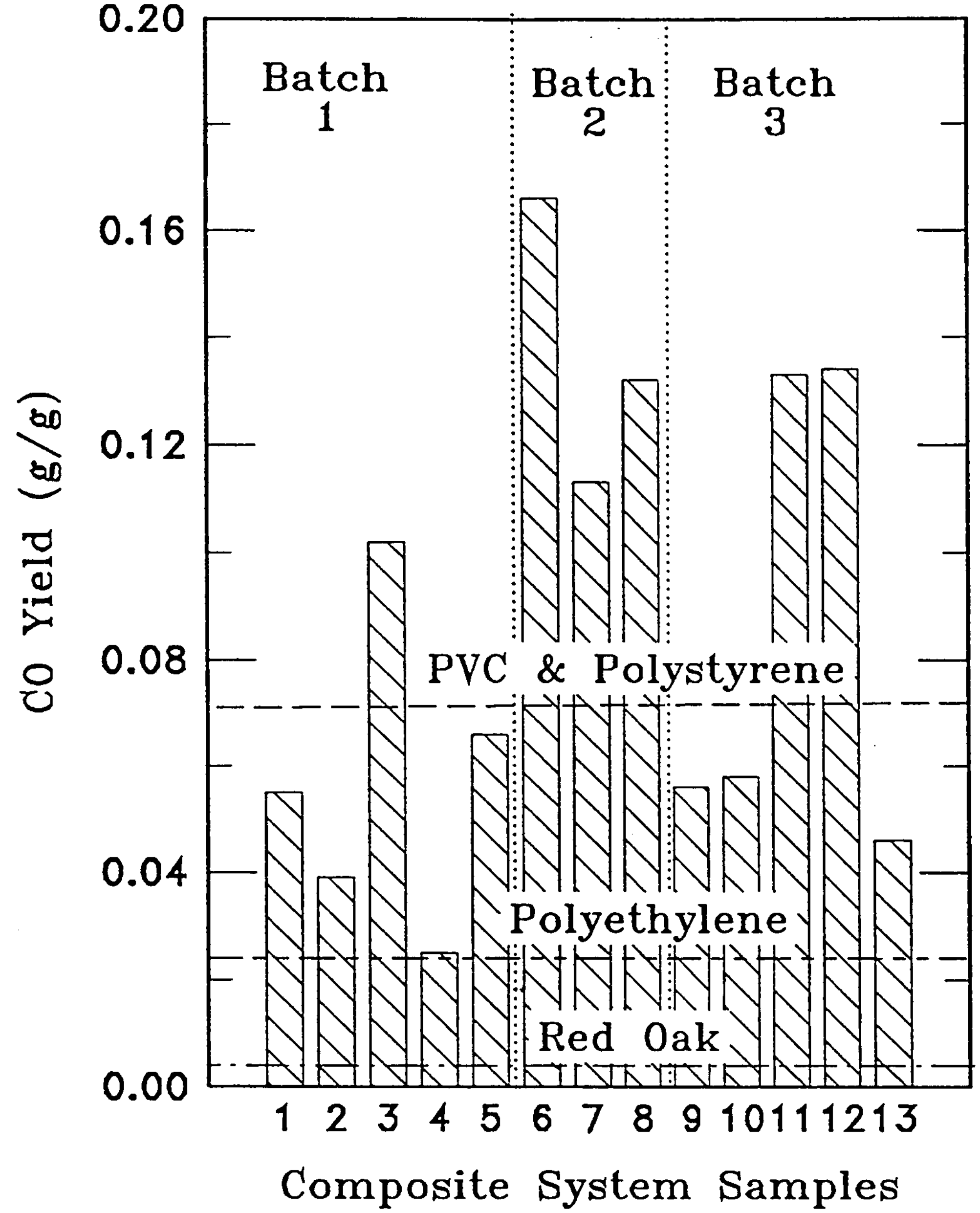

Figure D-8. Yield of CO in the Combustion of Composite Systems for the Combat Vehicle Hull Structures. Batch 1: Ref. 7; Batch 2: Ref. 9; Batch 3: This Study.

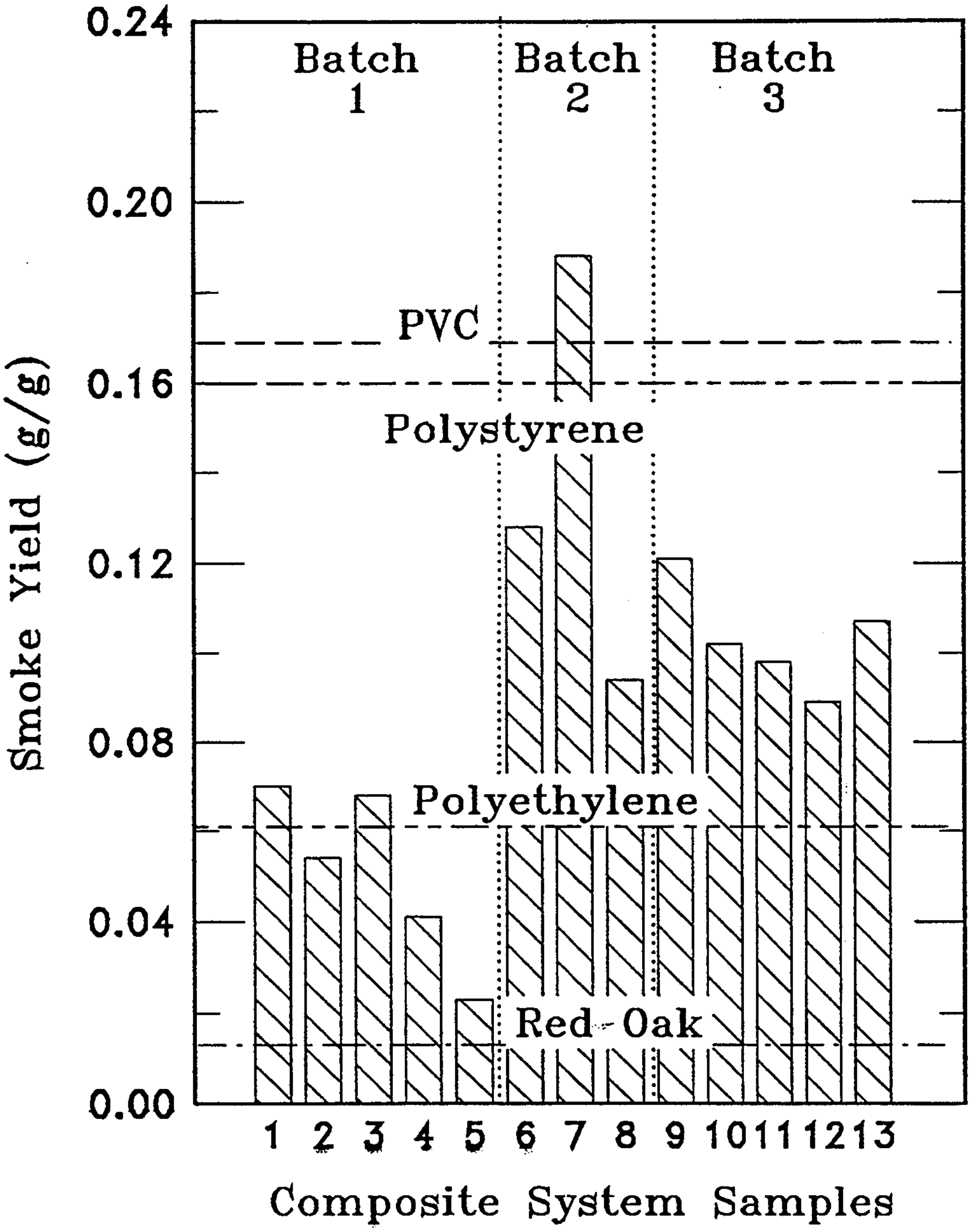

Figure D-9. Yield of Smoke in the Combustion of Composite Systems for the Combat Vehicle Hull Structures. Batch 1: Ref. 7; Batch 2: Ref. 9; Batch 3: This Study.

Table D-3
Yields of CO and Smoke from the Combustion of Composite Systems
Examined in This and Previous Two Studies

Sample No.	Composite System	Fiber/Resin (Weight %)	External Heat Flux (kW/m^2)	Yield (g/g)	
				CO	Smoke
#1	S2 Glass/Polyester	70/30	-	0.055	0.070
#2	S2 Glass/Polyester	70/30	-	0.039	0.054
#3	S2 Glass/Polyester	70/30	-	0.102	0.068
#4	Kevlar/Phenolic	84/16	-	0.025	0.041
#5	S2 Glass/Phenolic	80/20	-	0.066	0.023
#6	S2 Glass/Epoxy	65/35	-	0.166	0.128
#7	S2 Glass/Epoxy	65/35	-	0.113	0.188
#8	S2 Glass/Epoxy	65/35	-	0.132	0.094
#9	S2 Glass/Epoxy	76/24	30 40 50 60 Average	0.052 0.055 0.061 0.056 0.056	0.116 0.121 0.127 0.120 0.121
#10	Graphite/Cyanate	73/27	30 40 50 60 Average	0.049 0.053 0.064 0.065 0.058	0.094 0.101 0.107 0.104 0.102
#11	S2 Glass/PPS	84/16	40 50 60 Average	0.143 0.130 0.127 0.133	0.093 0.098 0.102 0.098
#12	S2 Glass/Epoxy/Phenolic	82/18	60	0.134	0.089
#13	As4 Graphite/Epoxy	71/29	30 60 Average	0.047 0.045 0.046	0.102 0.111 0.107

type of materials, consistent with the nature of the resins present in the composite systems examined in this study.

D.2.3 Product Generation Parameter (PGP)

The *Product Generation Parameter (PGP)* is defined as the amount of a product generated per unit amount of energy absorbed, expressed as the ratio of the yield of the product to the heat of gasification. PGP is related to the generation rate of the product by the following relationship (Eqs. D-1 and D-21):

$$\dot{G}_j'' = \left[\frac{y_j}{\Delta H_g}\right](\dot{q}_e'' + \dot{q}_f'' - \dot{q}_{rr}'') \tag{D-24}$$

where $y_j/\Delta H_g$ is the *Product Generation Parameter (PGP)*, y_j is the yield of the product (g/g), ΔH_g is the heat of gasification (kJ/g), $\dot{q}_e''$ is the external heat flux per unit surface area of the sample (kW/m^2), $\dot{q}_f''$ is the flame heat flux per unit surface area of the sample (kW/m^2), $\dot{q}_{rr}''$ is the surface re-radiation loss per unit surface area of the sample (kW/m^2). PGP represents the amount of a product generated per unit amount of energy released in a fire and is one of the characteristic fire properties of materials. It depends on fire ventilation but is independent of fire size. For the same fire size, external heat flux, and/or flame heat flux, materials with lower values of PGP, have lower product generation rates. *The PGP values decrease with increase in the degree of fire hardening.*

The PGP values can be determined by measuring the generation rates of the products at various external heat flux values by plotting the data. One typically obtains a straight line whose slope yields the PGP value as shown in Fig. D-10 for CO for graphite/cyanate (#10) and glass/PPS (#11) composite systems. Table D-4 lists the PGP values for CO and smoke for the composite systems examined in this study and the previous two studies[7,9] for the combat vehicle hull structures.

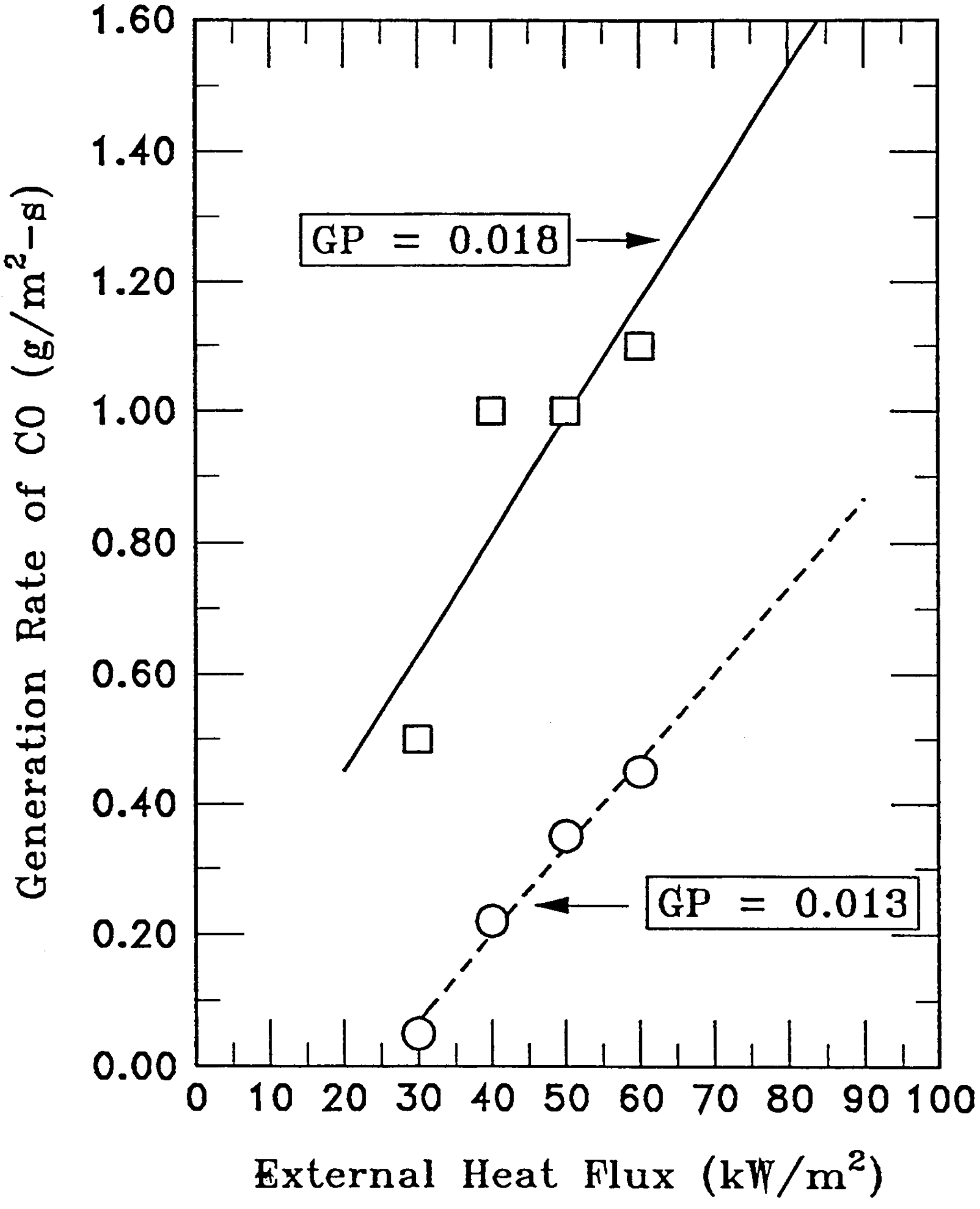

Figure D-10. Generation Rate of CO Versus External Heat Flux. : Graphite/Cyanate (#10); O: Glass/PPS (#11) Composite Systems.

Table D-4
Product Generation Parameter for CO and Smoke for the
Composite Systems for the Combat Vehicle Hull Structures

Sample No.	Composite System CO	Fiber/Resin (weight %)	Product Generation Parameter	
			CO	Smoke
#1[a]	S2 Glass/Polyester	70/30	0.017	0.021
#2[a]	S2 Glass/Polyester	70/30	0.009	0.013
#3[a]	S2 Glass/Polyester	70/30	0.056	0.037
#4[a]	Kevlar/Phenolic	84/16	0.002	0.003
#5[a]	S2 Glass/Phenolic	80/20	0.007	0.002
#6[b]	S2 Glass/Epoxy	65/35	0.088	0.068
#7[b]	S2 Glass/Epoxy	65/35	0.053	0.088
#8[b]	S2 Glass/Epoxy	65/35	0.072	0.052
#9[c]	S2 Glass/Epoxy	76/24	0.012	0.026
#10[c]	Graphite/Cyanate	73/27	0.006	0.011
#11[c]	S2 Glass/PPS	84/16	0.023	0.017
#12[c]	Glass/Epoxy/Phenolic	82/18	0.043	0.029
#13[c]	AS4 Graphite/Epoxy	71/29	0.010	0.024

The data in Table D-4 show that polyester and epoxy based composite systems in general have higher PGP values for CO and smoke.

D.2.4 Smoke Damage Parameter (SDP)

Both fire products and heat are released in fires; the *Product Generation Parameter (PGP)* and *Heat Release Parameter (HRP)* are related as follows (from Eqs. D-11 and D-24):

$$\frac{PGP}{HRP} = \frac{\dot{G}_j''}{\dot{Q}_{ch}''} = \frac{y_j}{\Delta H_{ch}} \qquad \text{(D-25)}$$

The ratio of PGP and HRP for smoke is defined as the *Smoke Damage Parameter (SDP)*.

Table D-5
Smoke Damage Parameter for Composite Systems for the Combat Vehicle Hull Structures and Ordinary Combustibles

Combustible	Smoke Damage Parameter (mg/kJ)	Group Classification
Polyvinylchloride	30.2	5
S2 Glass/Epoxy (#7)	18.8	5
Polyethylene/48% Chlorine	18.6	5
XLPE/ neoprene cables	17.0	5
Fire Retardant Polypropylene	15.6	5
Polyethylene/36% Chlorine	13.1	4
S2 Glass/Epoxy (#6)	10.8	4
Flexible polyurethane foams	10.7	4
Silicone/PVC cables	9.4	3
S2 Glass/Epoxy (#6)	9.2	3
PP/Hypalon cables	8.3	3
S2 Glass/Epoxy/Phenolic (#12)	7.7	3
Polystyrene foams	7.6	3
S2 Glass /Polyester (#3)	7.3	3
Rubber Tires	7.0	3
Rigid polyurethane foams	7. 0	3
PE/XLPE cables	6.9	3
S2 Glass/Epoxy (#9)	6.5	3
Polystyrene	6.1	3
Silicone	6.1	3
As4 Graphite/Epoxy (#13)	6.0	3
Glass/PPS (#11)	5.8	3
Graphite/Cyanate (#10)	5.4	2
Epoxy	5.3	2
Polyethylene/25% Chlorine	5.1	2
PE/PVC cables	4.5	2

Combustible	Smoke Damage Parameter (mg/kJ)	Group Classification
Polyester	4.4	2
S2 Glass /Polyester (#1)	3.9	2
S2 Glass /Polyester (#2)	3.4	2
Kevlar/Phenolic (#4)	2.8	2
Nylon	2.8	2
Fluoropolymer	2.4	2
Polyethylene foams	2.2	2
PTFE cables	2.2	2
S2 Glass/Phenolic (#5)	1.9	2
Polyethylene	1.6	2
Non-Fire Retardant Polypropylene	1.5	2
Red Oak	1.2	1
Plexiglas	0.9	1

The *Smoke Damage Parameter (SDP)* values for the composite systems for the combat vehicle hull structure and ordinary combustibles are listed in Table D-5. The composite systems and the ordinary combustibles have been tentatively classified into five groups. The *SDP* values used for classification are: Group 1, SDP $\leq$ 1.4 mg/kJ; Group 2, 1.5 $\leq$ SDP $\leq$ 5.4 mg/kJ; Group 3, 5.5 $\leq$ SDP $\leq$ 10.4 mg/kJ; Group 4, 10.5 $\leq$ SDP $\leq$ 14.4 mg/kJ; Group 5, SDP > 14.5 mg/kJ. The smoke damage expected in fires involving the Group 1, Group 2, Group 3, Group 4 and Group 5 materials are low, medium, medium-high, high, and very high.

D.2.5 Corrosion Index (CI)

Corrosion by the fire products in the gas phase is determined by using a 2500 Å high sensitivity atmospheric corrosion probe (model P610-TF50-C11000, Rohrback Cosasco, designed for the Flammability Apparatus), shown in Fig. D-11. The probe is located in the sampling duct of the Flammability Apparatus as shown in Fig. A-1. The probe consists of two strips embedded in an epoxy-fiberglass plate. One strip is coated and acts as a reference and the other noncoated

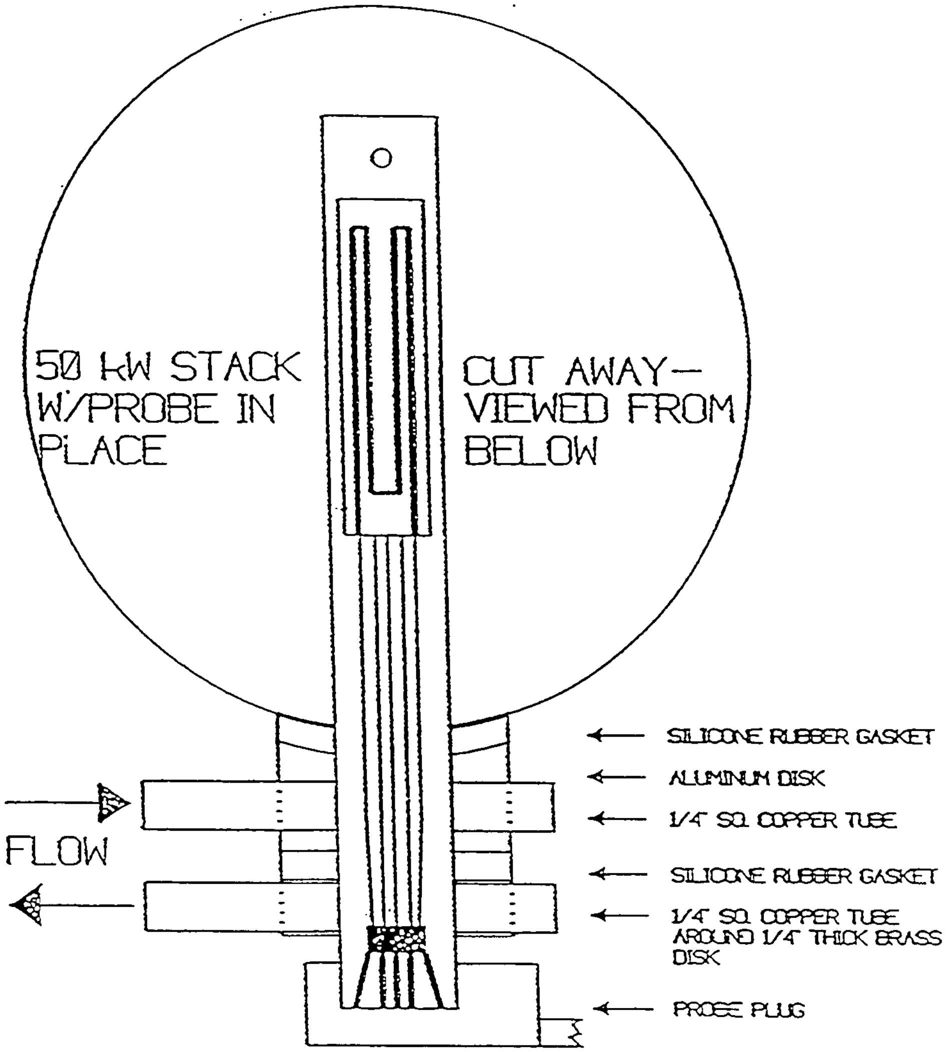

Figure D-11. 2500 Å Copper High Sensitivity Atmospheric Corrosion Probe in the Sampling Duct of the Flammability Apparatus.

strip acts as a sensor. As the sensor strip corrodes and looses its thickness, its resistance changes. The change in resistance, which represents the extent of corrosion of the metal, is measured by the difference in the resistance between the two strips by a Corrosometer (Model 4208, Rohrback Cosasco) and analyzed by Xess spreadsheet on the SUN workstation.

The gas phase corrosion is measured every minute for the first hour and then every hour for 16 to 24 hours. The corrosion rate, r_{corr}, is calculated from the following relationship:

$$r_{corr} = \frac{d_2 - d_1}{t_2 - t_1} \qquad \text{(D-26)}$$

where r_{corr} is in Å/min, d_1 is the metal thickness (Å) at time t_1 (s), d_2 is the metal thickness (Å) at time t_2 (s). Figure D-12 shows a typical example of corrosion of copper probe exposed to the combustion products of glass/ epoxy (#9) composite system. The gas phase corrosion rate, normalized by the average fire products concentration, is defined as the *Corrosion Index* (*CI*) (Å/min)/(g/m^3). The average fire products concentration in the gas phase is obtained from the ratio of the total mass of the sample lost to the total volumetric flow of the fire products-air mixture through the sampling duct during the period between the initial appearance and final disappearance of the vapors of the sample.

The peak values of the *Corrosion Index* (*CI)* for the composite systems are shown in Fig. D-13. The *CI* values for PVC are also included. The CI values are negligibly small compared to the value for PVC, with the exception of graphite/cyanate (#10) and graphite/PPS (#11).

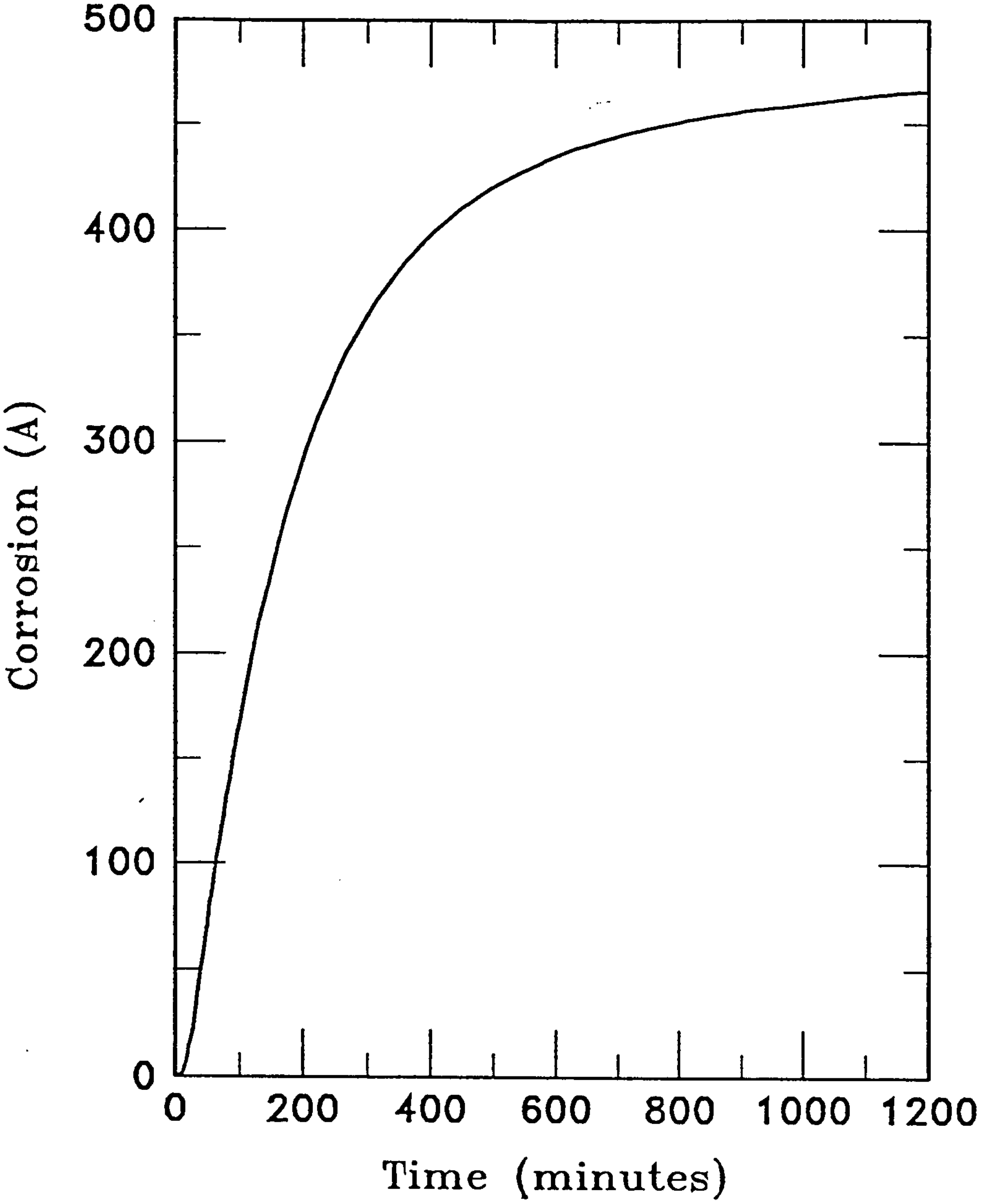

Figure D-12. Corrosion of Copper Probe Exposed to Flowing Combustion Products of Glass/Epoxy (#9) Composite System.

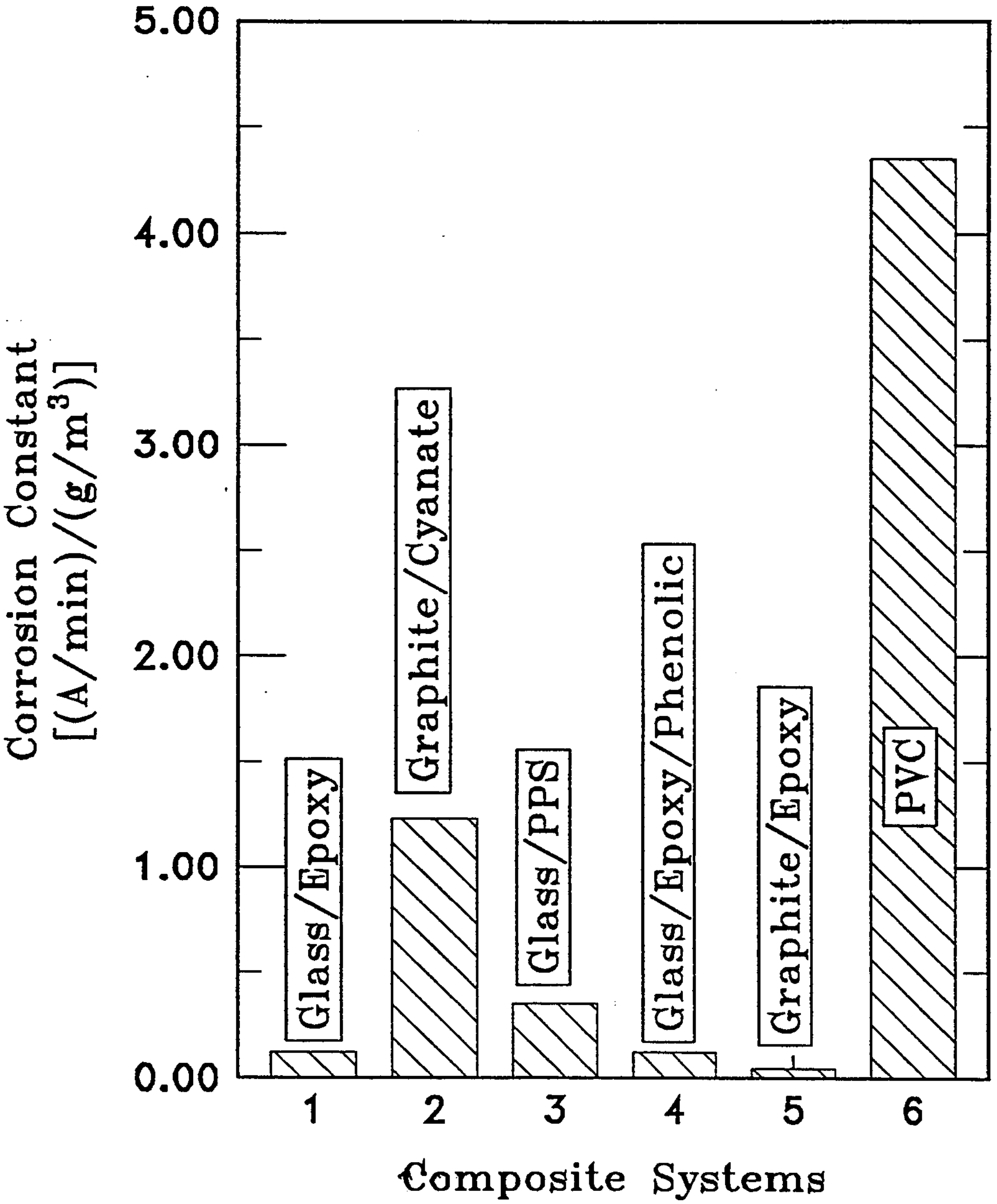

Figure D-13. Peak Values of the Corrosion Index for the Combustion Products of Composite Systems and PVC.

APPENDIX E

FIRE PROPAGATION

As a material is exposed to heat flux from internal and/or external heat sources, it vaporizes, in a process defined as *pyrolysis*, and forms a flammable mixture with air. The flammable mixture ignites as it comes in contact with a flame or hot spot and a flame anchors itself on the surface in the ignition zone. As the flammable mixture burns in the flame, it releases heat at a certain rate, defined as the *Chemical Heat Release Rate*. Part of the chemical heat release rate is transferred to the unburned fuel beyond the ignition zone.

If the heat flux transferred beyond the ignition zone satisfies the *Critical Heat Flux* (CHF), *Thermal Response Parameter* (TRP), and the gasification requirements of the material, the pyrolysis and flame fronts move beyond the ignition zone and the flame anchors itself over additional surface. Due to the increase in the burning surface area, the flame height, chemical heat release rate and heat flux transferred ahead of the pyrolysis front all increase. The pyrolysis and flame fronts move again and the process keeps repeating itself and burning area keeps increasing. Fire propagation on the surface continues as long as the heat flux transferred ahead of the pyrolysis front (from the flame or external heat sources) satisfies the CHF, TRP values and the gasification requirements of the material.

The resistance to fire propagation is determined by the fire propagation rate beyond the ignition zone. For thermally thick materials, the fire propagation rate is proportional to the ratio of the flame heat transferred ahead of the pyrolysis front and the TRP value. TRP is expressed as $\Delta T_{ig}(k\rho c_p)^{1/2}$ and the flame heat flux transferred ahead of the front is expressed as a function of the heat release rate by one of the several semi-empirical relationships for the fire propagation rate[12]:

$$\sqrt{u} \propto \{(\chi_{rad}/\chi_{ch})\ \dot{Q}'_{ch}\}^{1/3}/\Delta T_{ig}\sqrt{k\rho c_p} \qquad \text{(E-1)}$$

where u is the fire propagation rate; $\dot{Q}'_{ch}$ is the chemical heat release rate in the actual combustion during fire propagation (kW/m), and χ_{ch} and χ_{rad} are the combustion efficiency and radiative component of the combustion efficiency, respectively. Experimental data show that for flames with high radiation and lower combustion efficiencies, typical of large-scale fires, $\chi_{rad}/\chi_{ch} \simeq 0.40$, and Eq. E-1 becomes:

$$\sqrt{u} \propto (0.40\ \dot{Q}'_{ch})^{1/3}/TRP \qquad \text{(E-2)}$$

Equation E-2 suggests that the fire propagation rate is expected to be affected more strongly by the first power TRP term than by the one-third power heat release rate term, $\dot{Q}'_{ch}$. The right hand side of Eq. E-2 when multiplied by 1000 is defined as the *Fire Propagation Index (FPI)*[6-10,13,18-20]:

$$FPI = 1000\ x\ (0.40\ \dot{Q}'_{ch})^{1/3}/TRP \qquad \text{(E-3)}$$

From Eqs. E-2 and E-3:

$$FPI \propto 1000\ x\ \sqrt{u} \qquad \text{(E-4)}$$

Thus the FPI value is an indicator of the rate with which fire is expected to propagate beyond the ignition zone.

Small and large-scale flame spread experiments for variety of materials[13,18,20] show that flames do not propagate beyond the ignition zone for FPI < 7 (*defined as the non-propagating fire*). For FPI > 7, flame spread is self-sustained beyond the ignition zone (*defined as the propagating fire*).

The FPI profiles for the composite systems are shown in Fig. E-1. The FPI values for all the composite systems examined in this study are less than 7 and thus they are not expected to have self-sustained fire propagation beyond ignition. Table E-1 and Fig E-2 compare the FPI values for the composite systems examined in this study and the two previous studies[7,9].

The FPI values for the 13 composite systems examined by FMRC for the U.S. Army are indicated by numbers in Fig. C-3 in Appendix C. The results show that composite systems based on kevlar and glass fibers (≥70% by weight) need modifications of resins for fire hardening. Composite systems based on graphite fibers (≥ 60 % by weight) provide adequate fire hardening. Use of boron, beryllium, aluminum oxide (sapphire), boron carbide, silicon carbide and nitride would further enhance fire hardening.

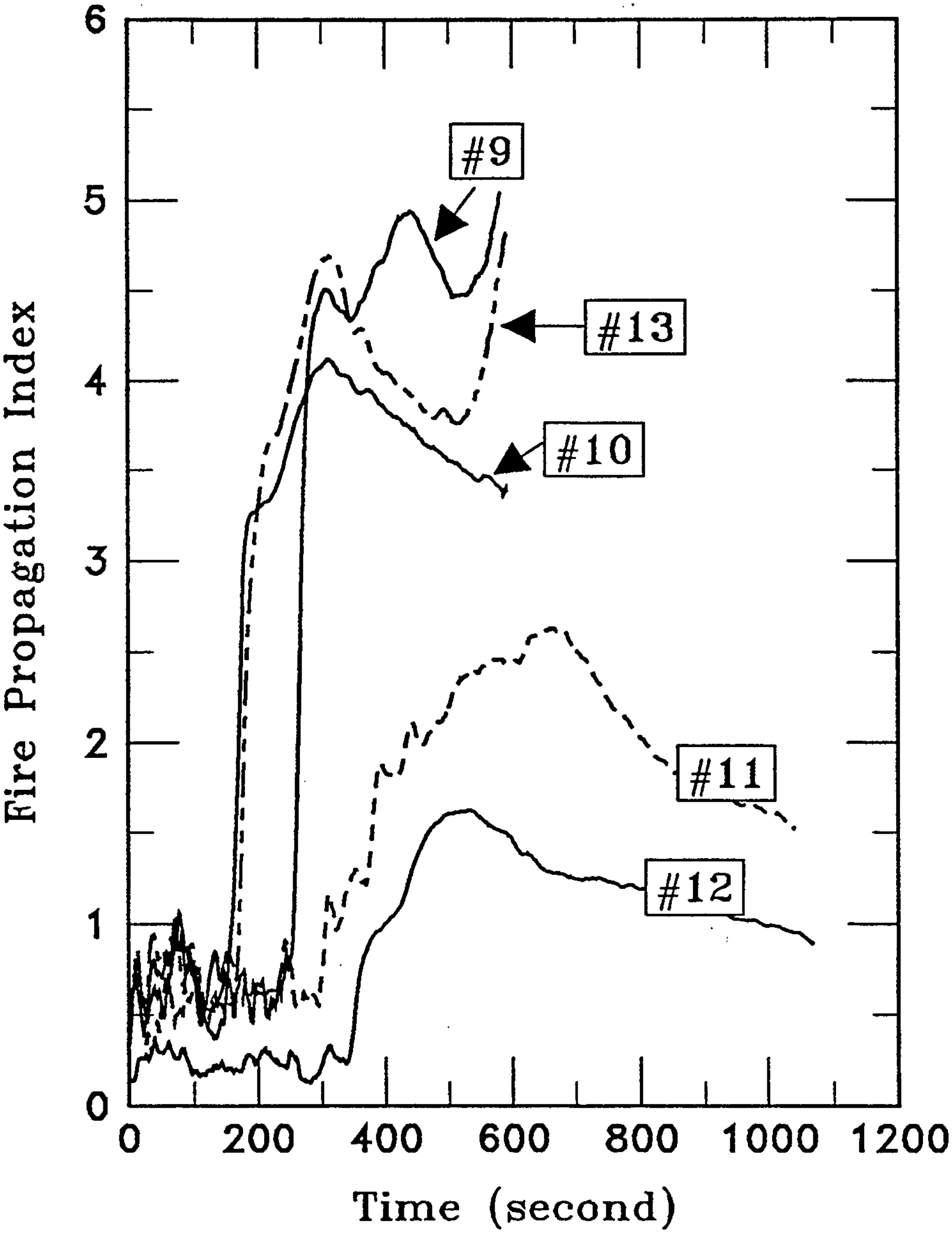

Figure E-1. Fire Propagation Index for the Composite Systems Examined in This Study.

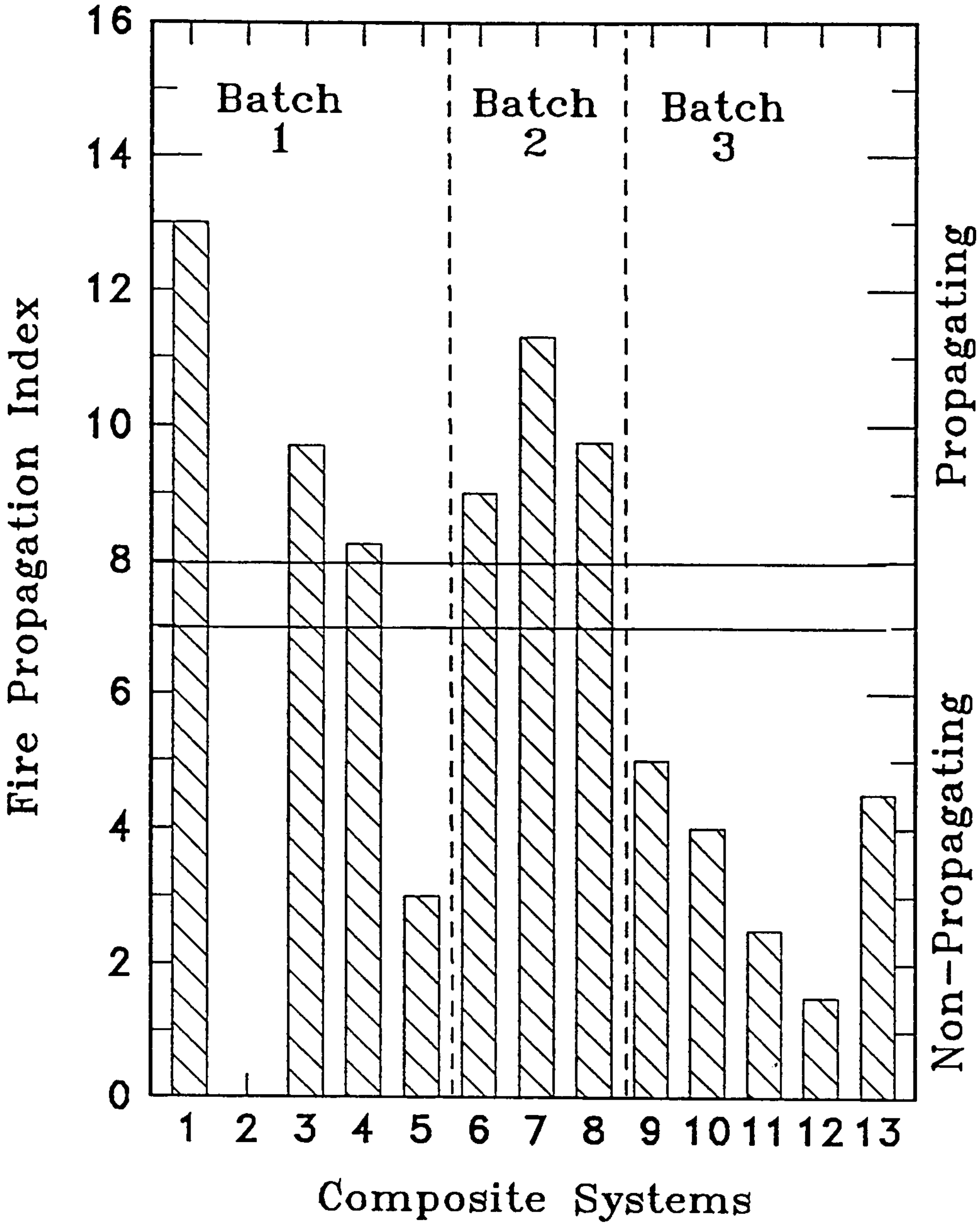

Figure E-2. Fire Propagation Index for the Composite Systems for Combat Vehicle Hull Structures. Batch 1: Ref. 7; Batch 2: Ref. 9; Batch 3: This Study.

Table E-1
Fire Propagation Indices of Composite Systems for the Combat Vehicle Hull Structures

Sample No.	Composite System	Glass/Resin (weight %)	Fire Propagation Index
#1	S2 Glass/Polyester	70/30	13
#2	S2 Glass/Polyester	70/30	-
#3	S2 Glass/Polyester	70/30	10
#4	Kevlar/Phenolic	84/16	8
#5	S2 Glass/Phenolic	80/20	3
#6	S2 Glass/Epoxy	65/35	9
#7	S2 Glass/Epoxy	65/35	11
#8	S2 Glass/Epoxy	65/35	10
#9	S2 Glass/Epoxy	76/24	5
#10	Graphite/Cyanate	73/27	4
#11	S2 Glass/PPS	84/16	3
#12	S2 Glass/Epoxy/Phenolic	82/18	2
#13	As4 Graphite/Epoxy	71/29	5

APPENDIX F

FLAME EXTINCTION

For the prevention of loss of life and property in fires, both active and passive fire protection techniques are used. Passive fire protection techniques deal with the prevention of fire by: 1) using materials with high resistance to ignition and fire propagation; 2) incorporating fire retardants with the materials; 3) coating and wrapping the surfaces; 4) separating materials by inert fire barriers, modifying configuration and arrangement of materials, etc. Active fire protection techniques deal with the application of flame extinction agents to fire. The most commonly used liquid and gaseous agents at the present time are water, CO_2, N_2, and Halon-1211 ($CBrClF_2$), 1301 ($CBrF_3$), and 2402 ($CBrF_2CBrF_2$). Because of the contribution of Halons to depletion of the stratospheric ozone layer, they will not be used in the future. There is thus an intense effort underway to develop alternative fire suppressants to replace ozone layer depleting Halons.

The Halon alternatives belong to one of the following classes:

1) Hydrobromofluorocarbons (HBFC);
2) Chlorofluorocarbons (CFC);
3) Hydrochlorofluorocarbons (HCFC);
4) Perfluorocarbons (FC);
5) Hydrofluorocarbons (HFC);
6) Inert gases and vapors.

The Environmental Protection Agency (EPA) has provided the following information for the use of the Halon alternates[23]:

Acceptable Total Flooding Agents Feasible in Normally Occupied Areas

1) HFC-23: CHF_3 (Du Pont FE13)
2) HFC-227ea: CF_3CHFCF_3 (Great Lakes FM 200)
3) FC-3-1-10: C_4F_{10} (3M PFC 410) {restricted use}
4) [HCFC Blend] A (NAF S III) (N.A.Fire Guardian)
5) [Inert Gas Blend] A (Inergen).

Other Acceptable Total Flooding Agents

1) HBFC-22B1: CHF_2Br (Great Lakes FM100)

2) HCFC-22: $CHClF_2$ (Du Pont FE 232)

3) HCFC-124: CF_3HClF

4) HFC-125: CF_3CHF_2 (Du Pont FE-25)

5) HFC-134a: CF_3CH_2F

6) Powdered Aerosol (Spectrex)

7) Solid Propellant Gas Generator (Rocket Research).

Streaming Agents:Commercial and Military Uses Only

1) [HCFC Blend]B (Halotron I)

2) HCFC-123: CF_3CHCl_2 (Du Pont FE-241)

3) FC-5-1-14: C_6F_{14} (3M PFC 614)-(restricted use)

4) HBFC-22B1: CHF_2Br (Great Lakes FM 100).

Total Flooding Agents (Pending)

1) Water Mist (Securiplex; Yates)

2) Powder Aerosols (Spectrex; Service)

3) Inert Gas Blends (Securiplex; Minimax)

4) SF_6 (Discharge test agent)

5) C_3F_8 (3M CEA-308; PFC-218)

6) Fluoroiodocarbons (CF_3I)

Streaming Agents (Pending)

1) HCFC-124: CF_3HClF

2) HFC-134a: CF_3CH_2F

3) HFC-227ea: CF_3CHFCF_3 (Great Lakes FM-200)

4) HCFC/HFC Blewnd (NAF P III)

5) HCFC Blend (NAF Blitz III)

6) Powdered Aerosol/HFC or /HCFC Blend (Powsus).

Flame extinction by liquid and gaseous agents is mainly due to physical processes (such as removal of heat from the flame and burning surface and creation of non-flammable mixture) and/or chemical processes (such as termination of chemical reactions). The effectiveness of water is mainly due to removal of heat from the burning surface as a result of vaporization. The effectiveness of Halons is mainly due to termination of chemical reactions. N_2 and CO_2 are effective mainly due to creation of non-flammable mixtures by reducing the oxygen concentration in the environment.

In the combustion experiments in the Flammability Apparatus with reduced ventilation[16], flame instability and extinction are found for equivalence ratio greater than or equal to 4, where combustion efficiency is less than about 0.40. Equivalence ratio is the fuel-to-air mass ratio normalized by the stoichiometric fuel-to-air mass ratio. Combustion efficiency is defined as the ratio of chemical heat release rate to heat release rate for complete combustion[14].

In the flame extinction experiments in the Flammability Apparatus with Halon 1301 with polymethylmethacrylate (PMMA) as a fuel, combustion efficiency decreases with increase in the agent concentration, and at about 5.5%, where combustion efficiency is about 0.42, flames become unstable and are extinguished at about 6%, where combustion efficiency is below about 0.40[21]. The decrease in the combustion efficiency is accompanied by a significant increase in the yields of CO and hydrocarbon, suggesting extensive chemical changes in the combustion of PMMA by Halon 1301, as expected.

In the flame extinction experiments with water with heptane as a fuel, flame extinction is found to occur when the combustion efficiency becomes less than 0.40[21]. *The critical flame extinction thus appears to be one at which the combustion efficiency becomes less 0.40.*

The most common test to screen the Halon alternates is the "Cup Burner" test, where concentrations of alternates required for extinction of a small laminar diffusion flame are determined. Table D-4 lists the "Cup Burner" for the agents taken from Ref. 24.

F.1 Flame Extinction by Halon 1301 for Composite Systems Exposed to 60 kW/m² of External Heat Flux

Application of Halon 1301 to the flame shifts the combustion towards incomplete combustion as discussed in the previous section. Visually one observes an increase in smoke production and decrease in flame height, which is indicative of a shift towards incomplete combustion as expected. For composite systems, application of Halon 1301 results in the decrease in the chemical heat release rate as shown in Fig. F-1 and increase in the products of incomplete combustion, such as CO and smoke as shown in Figs. F-2 and F-3.

Figure F-4 shows the concentrations of Halon 1301 required for the flame extinction of the composite systems exposed to 60 kW/m^2 of external heat flux. The concentrations vary between 3.0 and 4.5% by volume.

F.2 Flame Extinction by Halon Alternates for Composite Systems Exposed to 60 kW/m^2 of External Heat Flux

The "Cup Burner" test data listed in Table F-1 show that alternates acceptable as total flooding agents in occupied areas are: 1) FE 232 (HCFC-22, Du Pont) with a requirement of 4 times the concentration of Halon 1301; 2) FM200 (HFC-227 ea, Great Lakes) with a requirement of 2.1 times the concentration of Halon 1301; and 3) PFC614 (FC-5-1-14, 3M) with a requirement of 1.90 times the concentration of Halon 1301.

If we assume that the relative concentration from the "Cup Burner" are applicable to the flame extinction tests performed by FMRC in this and two previous studies for the U.S. Army, then we can predict the following concentrations of the Halon alternates required for flame extinction: 1) FE232 (HCFC-22, Du Pont): 12 to 18%; 2) FM 200 (HFC-227a, Great Lakes): 6 to 10%, and 3) PFC 614 (FC-5-1-14, 3M): 6 to 9%.

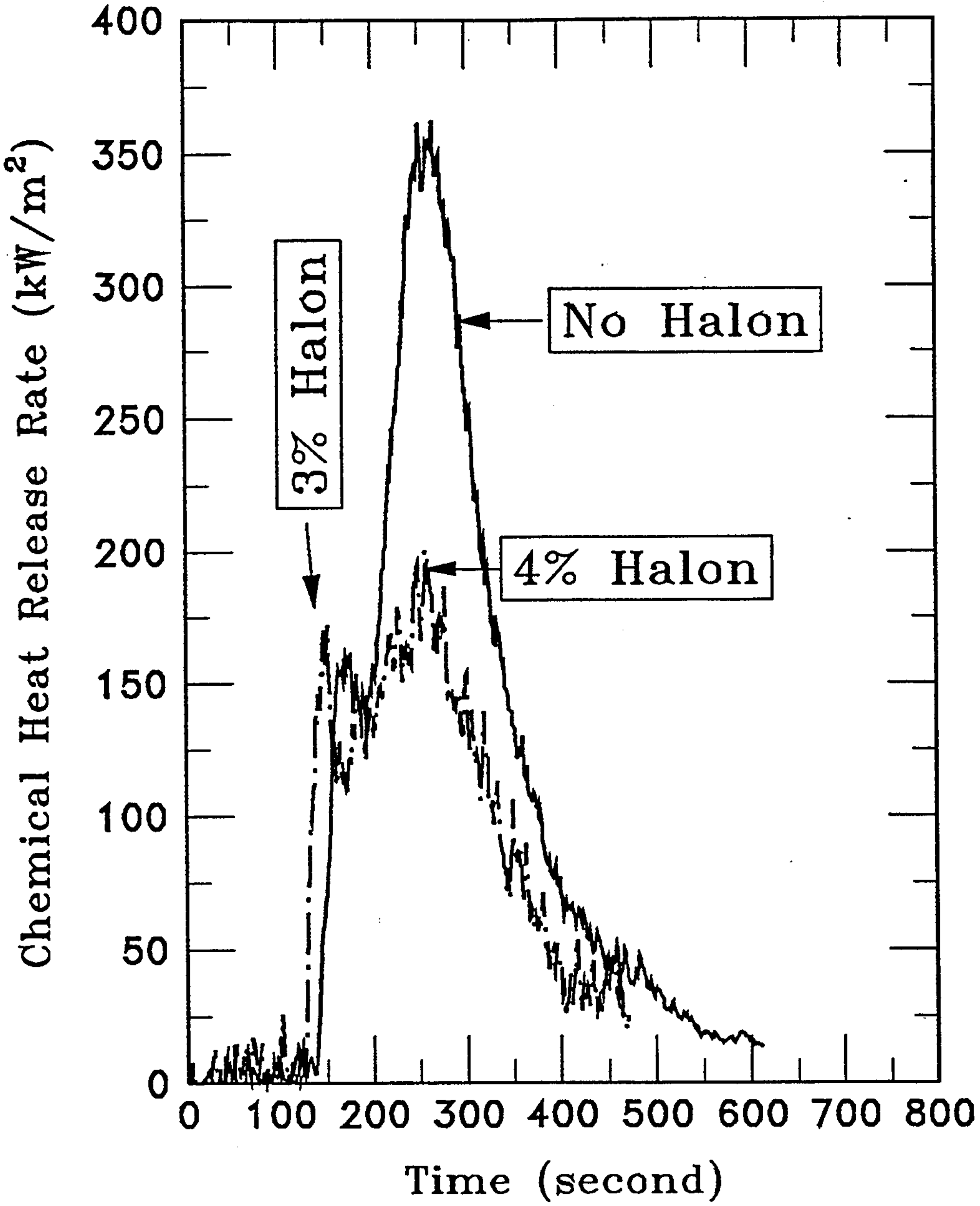

Figure F-1. Chemical Heat Release Rate in the Combustion of Glass/Epoxy Composite (#9) Exposed to 50 kW/m^2 of External Heat Flux in the Absence and Presence of Halon 1301.

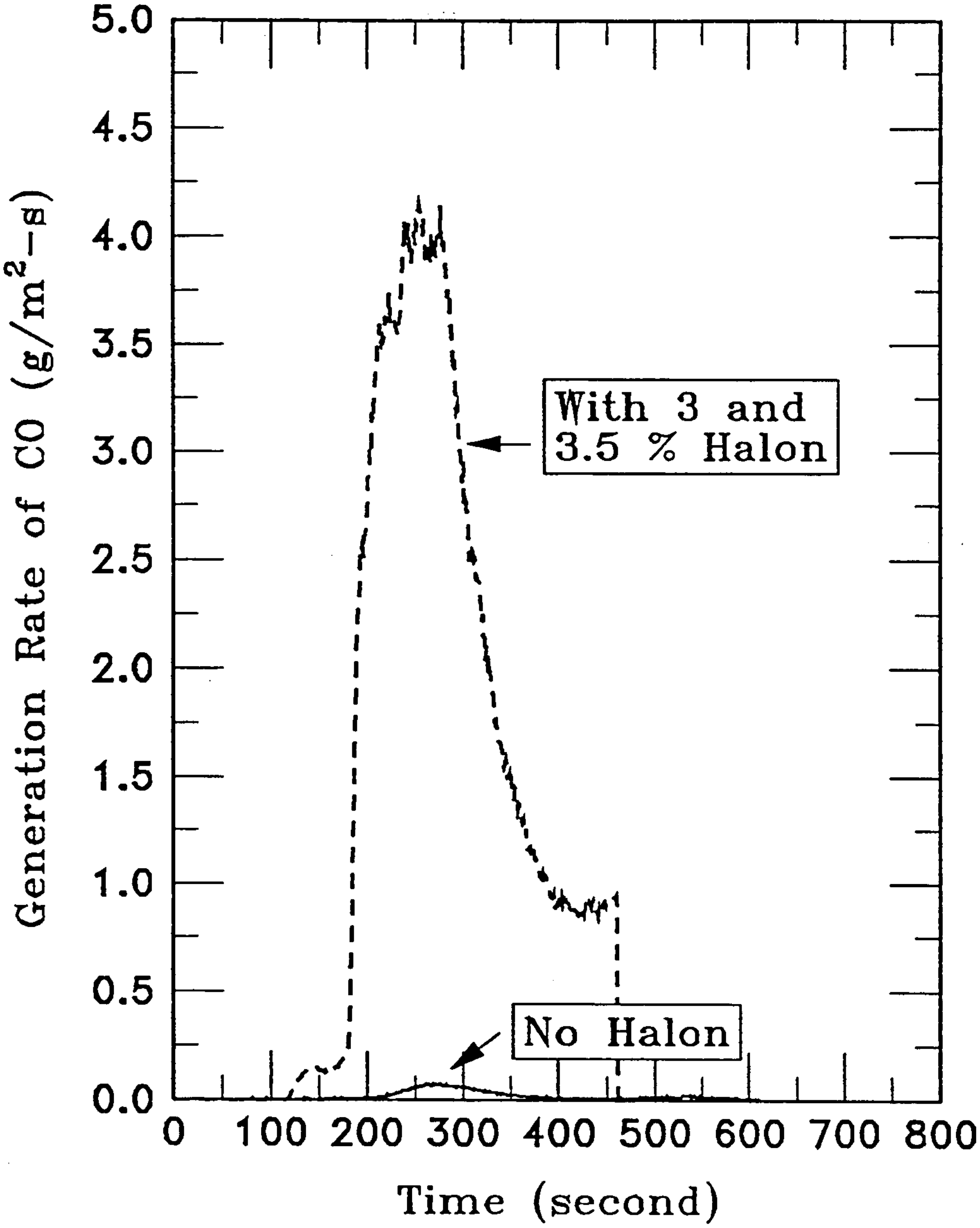

Figure F-2. CO Generation Rate in the Combustion of Glass/Epoxy Composite (#9) Exposed to 50 kW/m^2 of External Heat Flux in the Absence and Presence of Halon 1301.

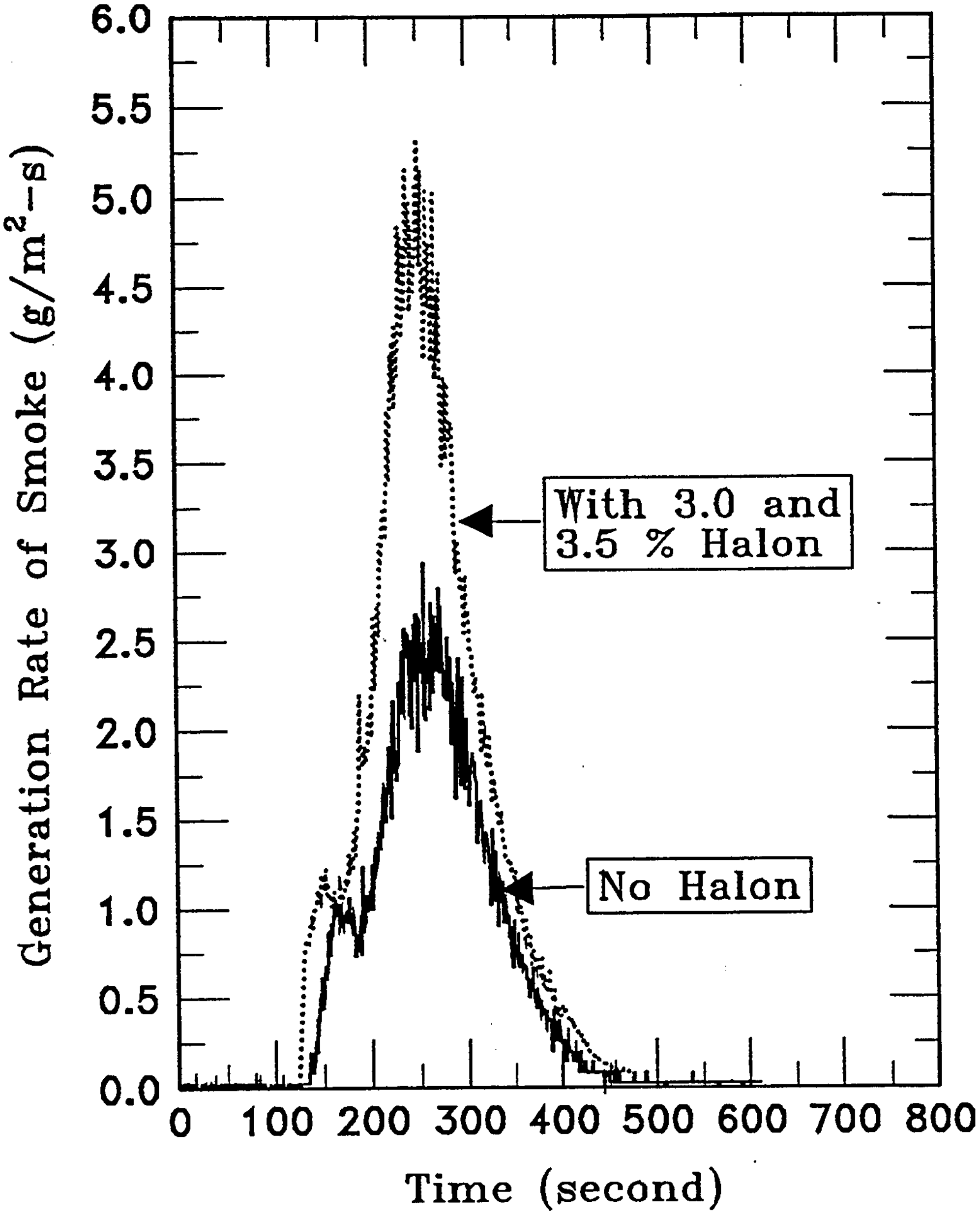

Figure F-3. Smoke Generation Rate in the Combustion of Glass/Epoxy Composite (#9) Exposed to 50 kW/m^2 of External Heat Flux in the Absence and Presence of Halon 1301.

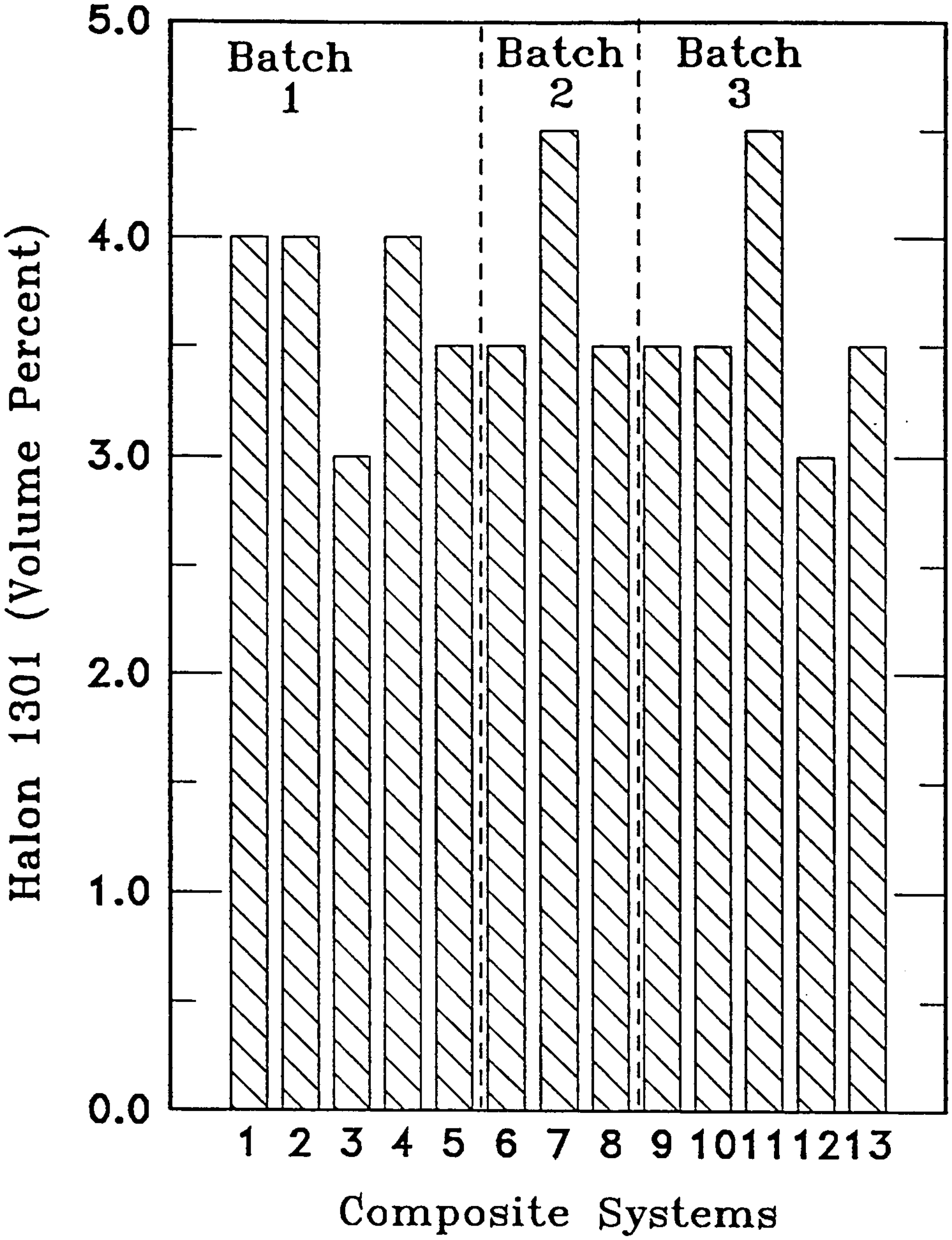

Figure F-4. Concentration of Halon 1301 for Flame Extinction for Composite Systems for Combat Vehicle Hull Structures. Batch 1: Ref. 7; Batch 2: Ref. 9; Batch 3: This Study.

Table F-1
Concentrations of Halon 1301 and Alternates Required for Flame Extinction in the "Cup Burner" Test[a]

Agent Name	Formula	Concentration (Volume %)	Relative Concentration
Halon 1301	CF_3Br	2.9	1.0
Trifluoromethyl Iodide 1311	CF_3I	3.0	1.03
FC-14	CF_4	13.8	4.76
HCFC-22 (Du Pont FE 232)	$CHClF_2$	11.6	4.00 [b]
HBFC-22B1 (Great Lakes FM100)	$CHBrF_2$	4.4	1.52
HFC-23 (Du Pont FE13)	CHF_3	12.4	4.28
HFC-32	CH_2F_2	8.8	3.03
FC-116	CF_3CF_3	7.8	2.69
HCFC-124	$CHClFCF_3$	8.2	2.83
HBFC-124B1	CF_3CHFBr_3	2.8	0.97
HFC-125 (Du Pont FE 25)	CF_3CHF_2	9.40	3.24
HFC-134	CHF_2CHF_2	11.2	3.86
HFC-134a	CF_3CH_2F	10.5	3.62
HFC-142b	$CClF_2CH_3$	11.0 (calc)	3.79
HFC-152a	CHF_2CH_3	27.0 (calc)	9.31
HFC-218	$CF_3CF_2CF_3$	6.1	2.10
HFC-227ea (Great Lakes FM 200)	CF_3CHFCF_3	6.1	2.10[b]
C318	C_4F_8	7.3	2.52
FC-5-1-14 (3M PFC 614)	C_4F_{10}	5.5	1.90[b]

[a] from Ref. 24;

[b] acceptable total flooding agents in normally occupied areas

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