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ABSTRACT

Reported is the result of an experimental investigation of fire-induced response of a 96 kg/m^3 closed cell rigid polyurethane foam. The specimen is 0.37 m in diameter, and 152 mm thick, placed in a cylindrical test vessel. The fire condition is simulated by heating the bottom of the test vessel to 1283 K using a radiant heat source. Real-time x-ray shows that the degradation process involves the progression of a charring front into the virgin material. The charred region has a regular and graded structure consisting of a packed bubble outer layer and successive layers of thin shells. The layer-to-layer permeability appears to be poor. There are indications that gas vents laterally. The shell-like structure might be the result of lateral venting. Although the foam degradation process is quite complicated, the in-depth temperature responses in the uncharred foam appear to be consistent with steady state ablation. The measured temperature responses are well represented by the exponential distribution for steady state ablation. An estimate of the thermal diffusivity of the foam is obtained from the ablation model. The experiment is part of a more comprehensive program to develop material response models of foams and encapsulants.

KEY WORDS: Foam, Polyurethane, Degradation

1. INTRODUCTION

Foam is widely used for thermal protection of key engineering components and systems in fire environments. However, current material response models of foam and encapsulants have not been validated by experiment, and have not been integrated in a suite of detailed sub-models for analysis codes. A tool to predict *a-priori* the fire-induced response of organic potting materials would greatly enhance the development of reliable, safe, and cost-effective thermal protection systems. To meet this need, Sandia National Laboratories has initiated a Model Validation Project (MVP). The project will develop the capability to perform model-based design of engineering components, and systems with potted materials. The objective of this project is to perform well-characterized experiments to validate and further the development of models which predict the fire-induced response of potted materials such as foams and epoxies.

The end result of this project will be a validated transient, physically-based, engineering model to predict decomposition and burning processes, as well as the associated heat and mass transfer through the organic materials.

To achieve the stated objectives, the MVP has three main components:

- Model Development
  A thermal-mechanical-chemical code is being developed to model the thermal and mechanical response of potted material. The code is an adaptation of an existing code on reactive materials (Hobbs, et al., 1994) to charing reactive materials such as polyurethane foam. Laboratory characterization of thermal, and mechanical properties as well as the chemical kinetics of the thermal decomposition of foam will also be performed.
- Model Experiments
  Model development is supported by model experiments designed to investigate specific aspects of the degradation process. Typically, model experiments have simple geometries and well controlled thermal and mechanical boundary conditions so the results can be used directly in model development. The first series of model experiments will examine the one dimensional response of a confined foam sphere uniformly heated on the surface.
- Phenomenology Experiments - FoamChar Experiments
  These experiments are designed to reveal the major features and general trend of the foam degradation process as it exists in credible system designs. Parameters of interest include the pyrolysis zone growth rate and material recession rate in foam as a function of probable controlling parameters such as size, orientation, heat flux, heating rate, available oxygen, local pressure, and age.

The present paper summarizes the results of the first phenomenology experiment, FoamChar-1. Preliminary observations of the foam degradation process as well as a simple ablation interpretation of the degradation process are presented.

2. DESIGN OF FOAMCHAR EXPERIMENT

The test apparatus consists of a 0.37-meter-diameter stainless steel cylindrical test vessel partially filled with a layer of foam, Figure 1. During the experiment, the bottom surface of the vessel is heated with a three-panel radiant heat array and the bottom of the vessel in turn heats the front surface of the foam. The back of the foam layer is fixed by an aluminum back plate secured to the vessel wall. The heating array as well as the test vessel are installed in a frame that allows the front of the foam layer to be oriented upward, downward or vertical. Orientation is considered to be an important variable because some of the decomposition product might be in a liquid state, drainage of the product might influence the growth of pyrolysis zone.

The decomposition product from the experiment is collected through a flexible 50-mm stainless steel exhaust tube on the side of the test vessel, adjacent to the heated bottom of the test vessel, Figure 1. The decomposition products first bubble through approximately 0.46 m of cold water in a scrubbing tank where high molecular weight decomposition products are condensed. The non-condensable gases are vented to the atmosphere. A hot-wire velocity sensor near the vent is used to monitor the flow rate of the gaseous product. Gas samples are collected at intervals during the experiment, using 100 ml evacuated stainless sample bottles. To avoid line plugging due to condensation of high molecular weight decomposition products (Fernandez-Pello, 1995), the exhaust tube is heated with tape heaters to a nominal temperature of 644 K (700°F). An adjustable pressure relief valve can be attached to the vent to pressurize the test vessel up to 0.2 MPa. A pressure/vacuum relief valve located upstream of the scrubber is used to: (1) to prevent water being siphoned back into the test vessel if heating were interrupted during the experiment, and (2) to protect the test vessel if the scrubber line were clogged in the scrubber tank. The test vessel is further protected by a bursting diaphragm attached to the back plate next to the back of the foam layer. For FoamChar-1, the decomposition gas vents directly to the ambient pressure.

Mass loss as a result of the decomposition of the foam is monitored using a weighting platform. The 50-mm flexible exhaust tube allows independent movement of the test vessel for weight measurement.

3. EXPERIMENTAL MEASUREMENTS

In the FoamChar-1 experiment, a 152-mm-thick, 0.37-meter-diameter layer of foam was heated with the front surface facing downward. The foam sample is a rigid closed cell intumescent foam having a density of 96 kg/m^3 (6 lb/ft^3). The foam is a General Plastics product, FR3706 lot 06-05-3095; the blowing agent is Freon 11. The estimated solid volume percent is 7.5-8% (Henry, 1995). The test vessel, without the sample, was pre-heated to 870 K to provide a consistent oxide layer for infrared radiation absorption.

In FoamChar-1, due to the downward-facing configuration, mass loss as a result of the decomposition of the foam is monitored using a counter-weight and lever system. The weighting platform is placed under the counterweight. As the foam degrades and looses weight, there is a corresponding increase of the apparent weight of the counterweight. The gaseous decomposition product is vented directly to ambient without back pressure control.

The foam is instrumented with 11, type K, 0.76 mm, sheathed thermocouples with ungrounded junctions. The thermocouples are installed in pre-drilled radial holes from the side; the tips of the thermocouples coincide with the central axis of the foam layer, Figure 2. The thermocouple leads exit through a hole on the edge of the back plate, as a bundle. The distances between the thermocouples are nominally spaced at 12.7 mm intervals. The test vessel bottom (next to the front of the foam layer) was programmed to be heated to 1283 K (1850°F); a 1.6 mm sheathed thermocouple on the bottom surface is used to monitor and control its temperature. In addition, there are three thermocouples on the side of the test vessel at elevations 19 mm, 47 mm, and 130 mm above the front of the foam layer. All the thermocouples are secured by nickel straps welded to the test vessel.

The progression of the degradation of the foam is monitored by x-ray. In addition to documenting initial and final conditions on film, x-ray images of the entire experiment are recorded on video tape. While the image quality of the video tape is not quite as good as film records, video records offer the possibility of post-test image processing.

4. RESULTS

Observations of Foam Degradation The heating phase of the experiment lasted for 1320 seconds. It took approximately 200 seconds for the vessel bottom to reach the testing temperature of 1283 K. Post-test inspection indicated that all but a thin lens section of the foam was charred; the thickest uncharred section was approximately 30 mm, as shown in the cross-section of the post-test foam layer in Figure 3a. The char region has the structure similar to a finely layered pastry. The thickness of the char region is not entirely uniform. It has the appearance of several puffs anchored at the edge and center of the layer. The thickness of the layered char decreases more or less smoothly toward the edge and the center. The general shape of the shell is not unlike the merged surface of buns (or pastries) of comparable but different sizes baked together in a circular baking pan. The thickest part of the char region was approximately 95 mm. The combined thickness of the foam and char is less than the original 152 mm.

The cross-section of the char region has a regular and graded structure, Figure 3b. The front surface, the surface closest to the heating surface, is a thin, shiny and smooth shell, very much like an egg shell except thinner and remarkably lacking of porosity. Next to the outer shell is a highly structured layer, 4-5 mm thick, consisting of a center sublayer of frozen bubbles packed in a two-dimensional honeycomb like pattern. The center layer is sandwiched between much thinner layers, each with structure similar to the center sublayer, but of a much finer scale. Closer inspection of the center sublayer shows thin fibrous wisps interspersed in the cavities of the frozen bubbles. The fibrous wisp structure is thought to be a typical result of pyrolysis.

This packed bubble layer is thought to represent the end product of the degradation of an intumescent foam. As an intumescent foam degrades, a liquid layer is formed and in time the layer re-foams. The packed bubble pattern is the result of re-foaming. Next to the packed bubble layer, is a series of shell like layers. Moving inward, from the front toward the back of the layer, the individual shells first appear to be well separated and dry; then, the separation of layers becomes less distinct and the layers seem to have stuck together by once liquid degradation products. The shell-like layers do not appear to provide very effective interlayer permeability in the direction normal to the degradation front. It appears that the gaseous reaction product may have vented in a direction parallel to the degradation front. One can speculate that the packed bubble layer that first formed may have been rigid and impermeable enough to channel the subsequent gaseous product in a lateral direction. The lateral movement of the gases results in linked/coalesced bubbles of large lateral extent, and the layer-like shell structure. One indicator for lateral venting is the existence of colonies of vent holes on the outer rim of the char layer.

Adjacent to the shells is a 2-3 mm thick reacting layer of dark brown degraded foam with pores larger than virgin foam. There is a gap of varying thickness of the order of 1-3 mm between the shell region and the reacting layer. The reacting layer has the look of having been liquid laden, but not saturated. The reacting layer and the uncharred foam is separated by a large gap as wide as 15 mm. The uncharred foam has an altered region of 2-3 mm, with a continuous change of color from that of the reacting layer to that of the virgin foam. Looking into the gap, the surface of the uncharred region facing the reacting layer appears to be covered with frozen tar-like substance. Glistering slivers connecting the reacting layer and the uncharred region suggest that a liquid layer existed between the two layers. It is unclear whether the large inter-layer gap is formed during heating or upon cooling. An intermediate scenario of a liquid gap formed during heating, and enlarged upon cooling is perhaps more likely.

The x-ray video of the foam layer clearly shows the growth of a low density char region into the foam layer. Two video frames are reproduced in Figure 4. As heating progresses, the back edge (top edge on the video frame) of the foam begins to appear on the video screen, indicating a decrease of the overall thickness of the foam layer. However, the restraint of the thermocouple bundle prevented the layer from moving uniformly downward. The movement was more or less pivoted at the point where the thermocouple bundle exits the back plate.

Post-test inspection found degraded material in the slanted back surface of the foam layer; this suggests the possibility of material oozing onto the backside of the layer as the layer pivoted downward.

Post-test inspection indicated that the 100 mm section of straight 50-mm-diameter tube connecting the test vessel and the flexible exhaust tube was about 30% filled with charred solid. The rest of the reaction product lines, including tubes beyond the outlet of the condenser, were covered with a thin layer of tar/grease-like material. There was a heavy deposit on the hot-wire velocity sensor rendering the velocity data unusable. The largest amount of reaction product was trapped in the water scrubber. Analysis of reaction products including the gas samples are in progress.

Weight measurements were not successful during the experiment. It appears that there were extraneous forces interfering with the measurement. One possible source could be differential thermal expansions of experimental components.

Thermal Response Measurements Temperature history of the vessel bottom and the in-depth temperature response of the foam are plotted in Figure 5. The in-depth thermocouples are nominally equally spaced. The actual locations (in mm from the front surface) of the thermocouples as determined from the pre-test x-ray record, are shown in the table below:

TC Locations	12.7	28.4	34.5	47.2	61.7	77.7	88.9	101.6	114.3	127.0	139.7

Heating started at t = 120 seconds and ended at t = 1440 seconds. As shown in Figure 5, the driving temperature of 1283 K was reached within 200 seconds of initial heating. The initial temperature of the test vessel bottom was 298 K; the interior foam temperature ranged from 293 K at 12.7 mm, to 285 K at 88.9 mm, to 290 K at 139.7 mm.

Inspection of in-depth temperature responses of the foam interior indicates that the responses for depths between 34.5 mm and 101.6 mm, for temperatures up to 700 K, are essentially similar in shape but displaced in time similar to an ablation process. Ablation refers to the progression of a melting, evaporation or sublimation front with an associated chemical decomposition or liquification (Freeman, 1964). If the phase change zone and reaction zones are very narrow then these zones can be identified with a specific temperature. Under steady state assumptions, the ablation front moves with a constant velocity into the ablative material and the temperature distribution in the solid assumes a time-invariant shape with respect to the moving front (Landau, 1950, and Freeman, 1964).

5. AN ONE-DIMENSIONAL ABLATION MODEL EXAMINATION OF THE THERMAL RESPONSE MEASUREMENTS

Although the overall experiment is multi-dimensional as shown by the x-ray images, Figure 4, a one-dimensionl analysis is possible in the center of the material which is largely removed from wall effects. Post-test examination does show that the radial degradation of the foam layer to be much smaller than the axial degradation. Furthermore, side wall heating is not very significant because except for the first 70 mm (from the front of the foam surface) the side wall temperature never exceeded 700 K.

For an ablation interpretation to be applicable, it is necessary that pyrolysis/liquification take place in a narrow temperature range, and consequently in a narrow zone. The in-depth temperature responses in Figure 5 show a rather abrupt change of the rate of temperature increase near 700-728 K (800-850° F). This probably corresponds to the temperature range where significant pyrolysis or tar evaporation occurs. Significant mass loss has been observed in a Thermogravimetric Analysis (TGA) of a similar foam (Blackwell and Moya, 1995). For the purpose of the present discussion, the term pyrolysis temperature will denote this temperature range. The temperature range 700-728 K is somewhat higher than the observed temperature in a typical TGA. The somewhat higher pyrolysis temperature in this analysis results from a higher rate of temperature rise. The pyrolysis temperature used in the analysis is not based on the onset temperature, rather the temperature of maximum mass loss rate. The rate of about 250 K/min in the present experiment is about one order of magnitude higher than the typical 30 K/min rate under which TGA data are obtained. The range of pyrolysis temperature typically spans 100 K. With an estimated temperature gradient in the 50-100 K/mm, typical pyrolysis zone would be 1-2 mm, certainly small compare to the scale of the layer. With this somewhat qualitative justification, we will examine the temperature response in the foam in terms of a reaction front.

To determine the progression of the ablation front, we plotted the time of arrival of the 589 K (600° F) isotherm at thermocouple locations 34.5, 47.2, 61.7, 77.7, 88.9, and 101.6 mm, Figure 6. The plot is linear; implying, that the ablation process is steady. The front velocity, v, is calculated to be 0.073 mm/s. The temperature distribution with respect to the ablation front should be invariant. Under the assumption of constant thermal physical properties, the temperature distribution is a simple exponential function (Landau, 1950):

$$\frac{T-T_o}{T_m-T_o}=\exp\left\{-\frac{v}{\alpha}\left[x-v(\tau-\tau_i)\right]\right\} \qquad (1)$$

where T is temperature, T_o is the initial temperature, T_m is the effective pyrolysis temperature for maximum weight loss, v is the steady state front velocity, α is thermal diffusivity of the foam, x is the location of interest, τ is time, and τ_i is a fictitious starting time. For the present purpose, τ_i can be regarded as the virtual starting time needed to calculate the location of the ablation front using the steady state front velocity. It is not entirely clear why the present experiment corresponds so closely to the classical ablation process with a constant heat flux boundary conditions. But such discussion will be deferred until we have more experimental data available for examination.

The temperature responses at depths between 47.2 mm to 114.3 mm are plotted in terms of the variables in equation (1), in Figure 7. The ablation temperature is assumed to be 728 K (850° F) in the plots. The data is well represented by a straight line on the semi-log plot, indicating an exponential dimensionless temperature distribution. The slope of the line is v/α. From the slope, the thermal diffusivity of the foam is calculated to be 2.9×10^{-7} m^2/s (2.9×10^{-1} mm^2/s). Tewarson and Pion (1977) reported a value of $\alpha = 6\times10^{-7}$ m^2/s for a foam with a density of 47 kg/m^3. The present foam has a nominal density of 96 kg/m^3 (6 lb/ft^3); the ratio of the two α values is essentially inversely proportional to the density ratio. The value of α is independent of the assumed value of the pyrolysis temperature.

6. SUMMARY

A 152-mm-thick, 0.37-meter-diameter layer of foam was heated from the bottom using a radiant heat source maintained at 1283 K. The foam sample is a rigid closed cell intumescent foam having a density of 96 kg/m^3 (6 lb/ft^3). The blowing agent is Freon 11. Key preliminary findings of the experiment are:

1. As observed from video x-ray imaging and post-test inspection, under the present experimental conditions, the thermal degradation process involves the progression of a charring front into the virgin material.
2. The charred region has a regular and graded structure, consisting of a packed bubble outer layer, and shell like interior layers. Interlayer permeability does not appear to be significant. There is indication that lateral venting of gaseous products may have occurred.
3. Between the charred region and the virgin foam is a 2-3 mm thick reacting layer of degraded foam. The reacting layer appear to have been liquid laden, but not saturated.
4. The in-depth thermal responses of the foam layer is consistent with steady state ablation where a sharply defined reaction front progresses into the virgin material.
5. Use of the temperature response data in a steady state ablation model yields an estimated thermal diffusivity of the foam of 2.9×10^{-7} m^2/s.

7. ACKNOWLEDGMENT

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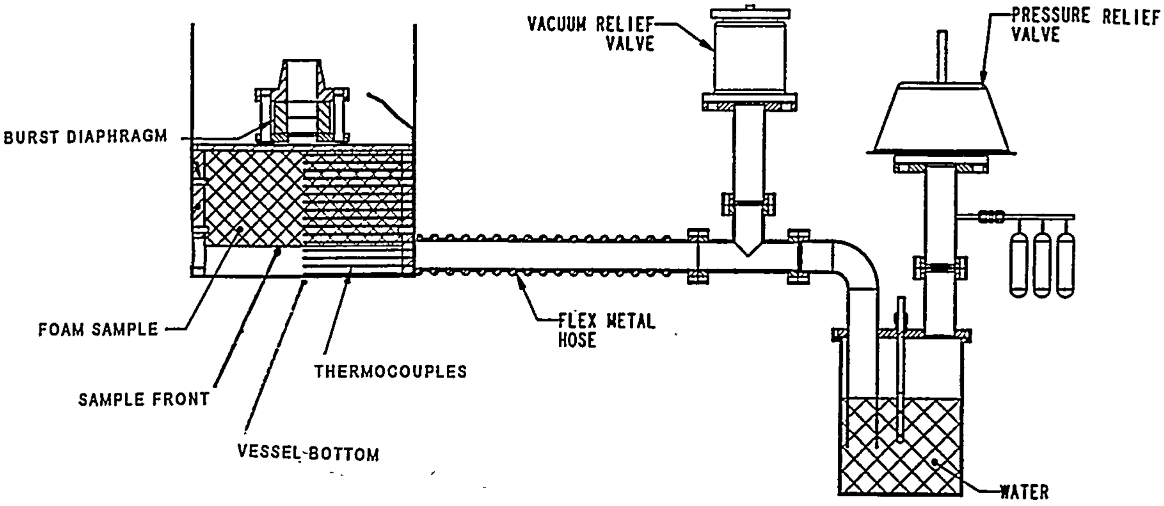

Figure 1. Schematic of the design of the FoamChar experiment

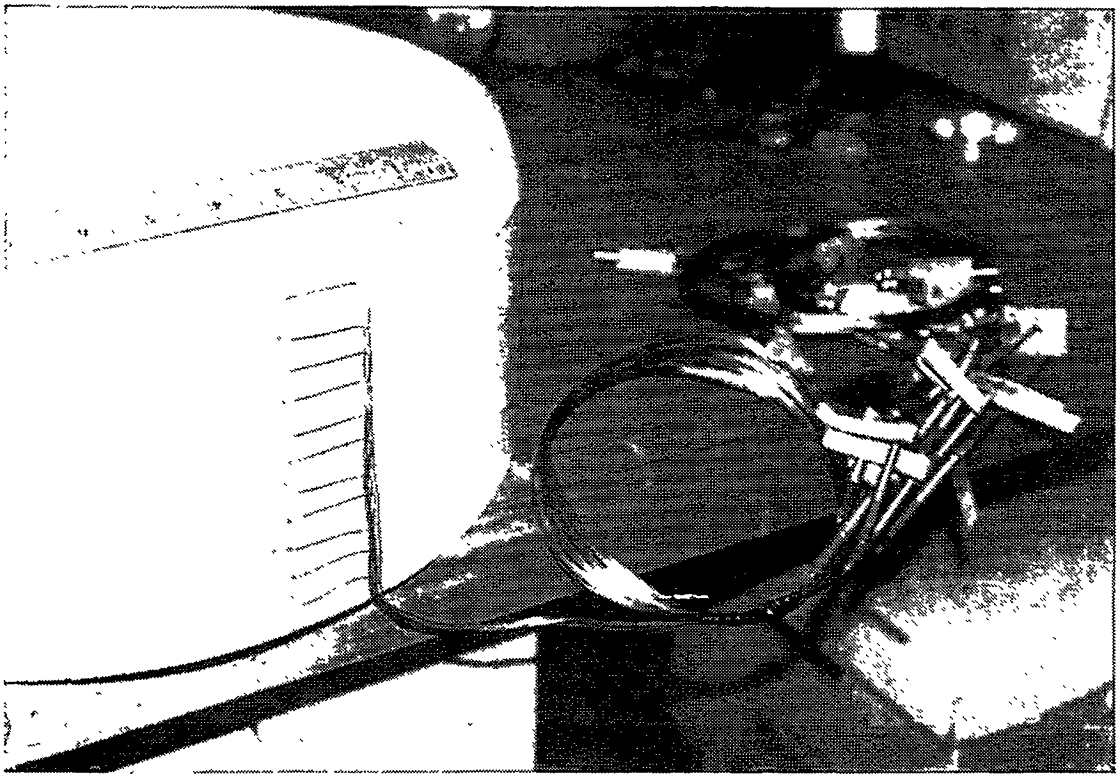

Figure 2. Foam specimen instrumented with thermocouples

Figure 3a General cross-section view of the degraded foam layer

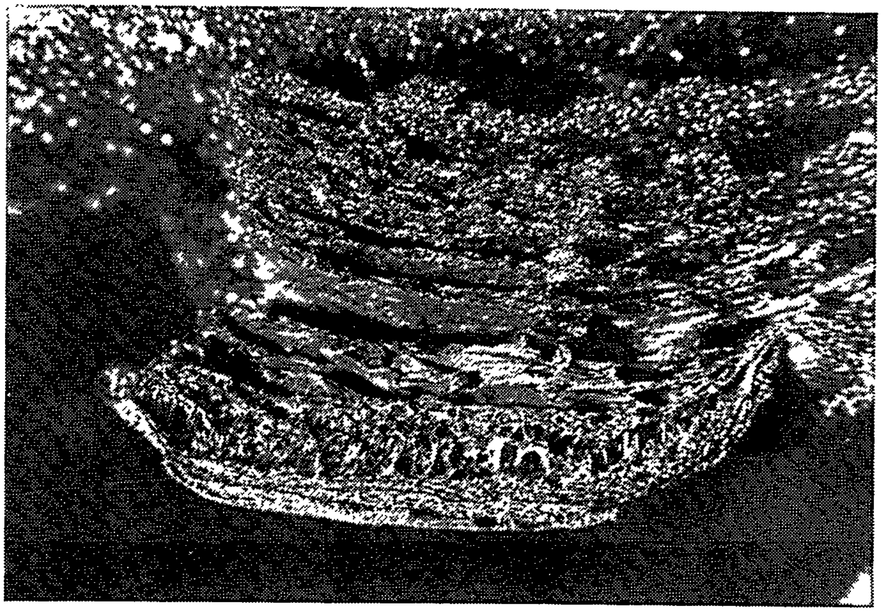

Figure 3b Close-up cross-section view of the degraded foam layer

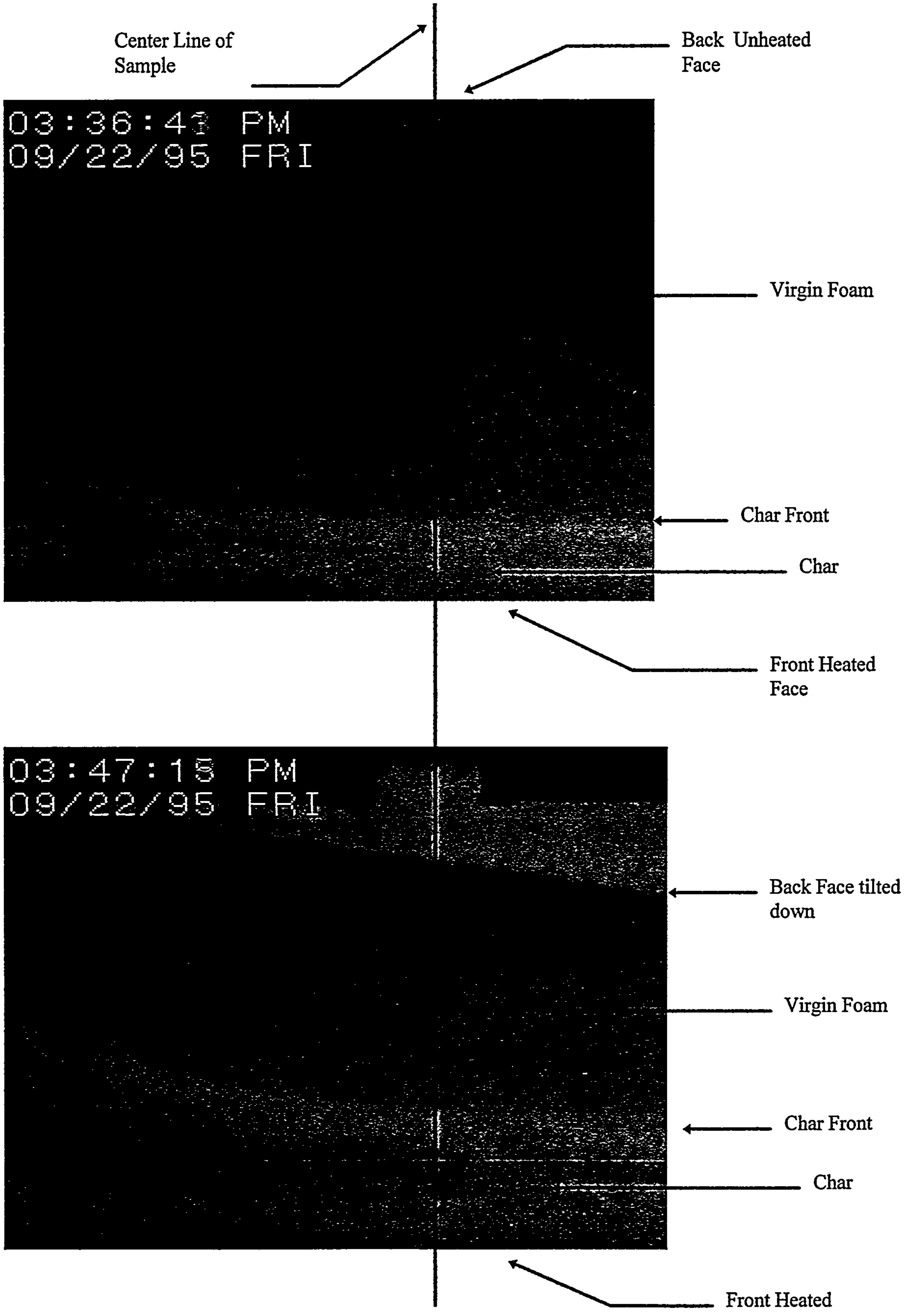

Figure 4. Video frames showing the progression of the charring front.

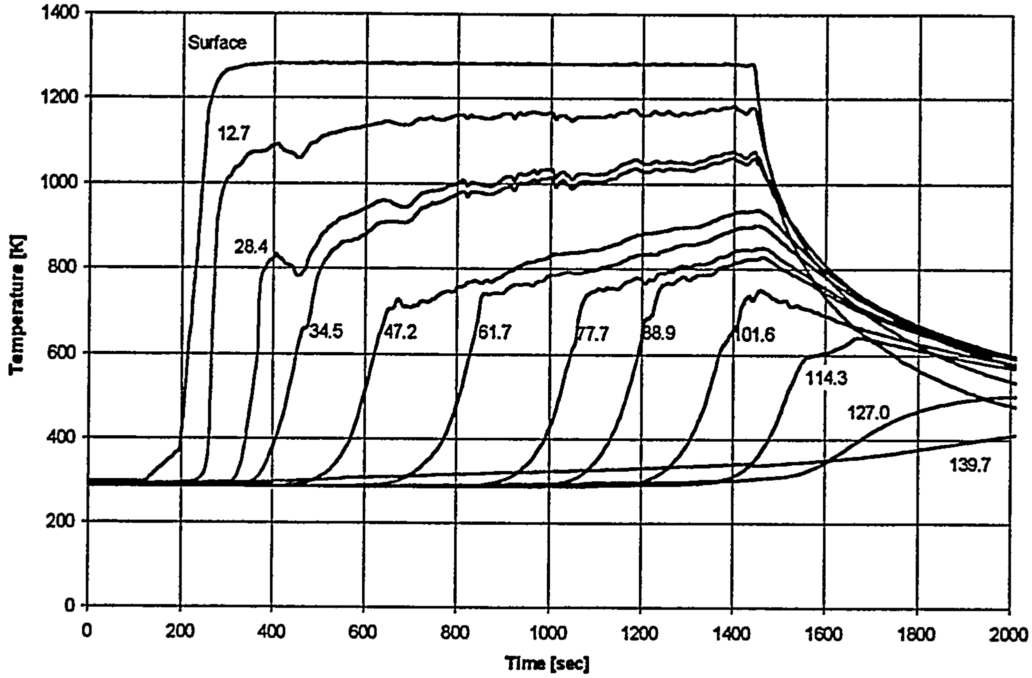

Figure 5. Temperature of the vessel bottom and in-depth temperature of the foam layer.

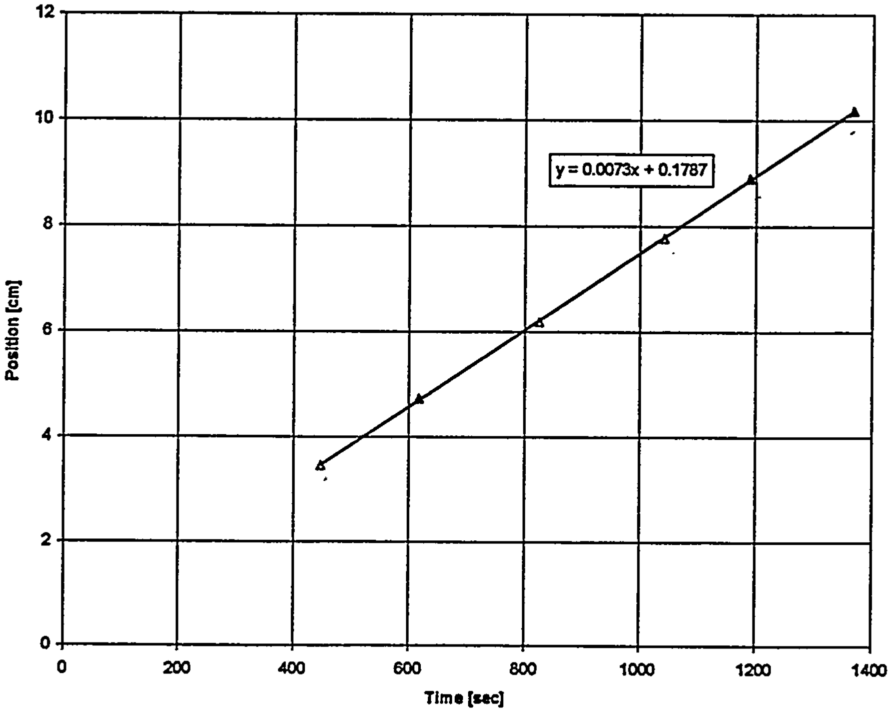

Figure 6. Progression of the ablation front as indicated by the time of arrival of the 589 K (600° F) isotherm at various thermocouple locations.

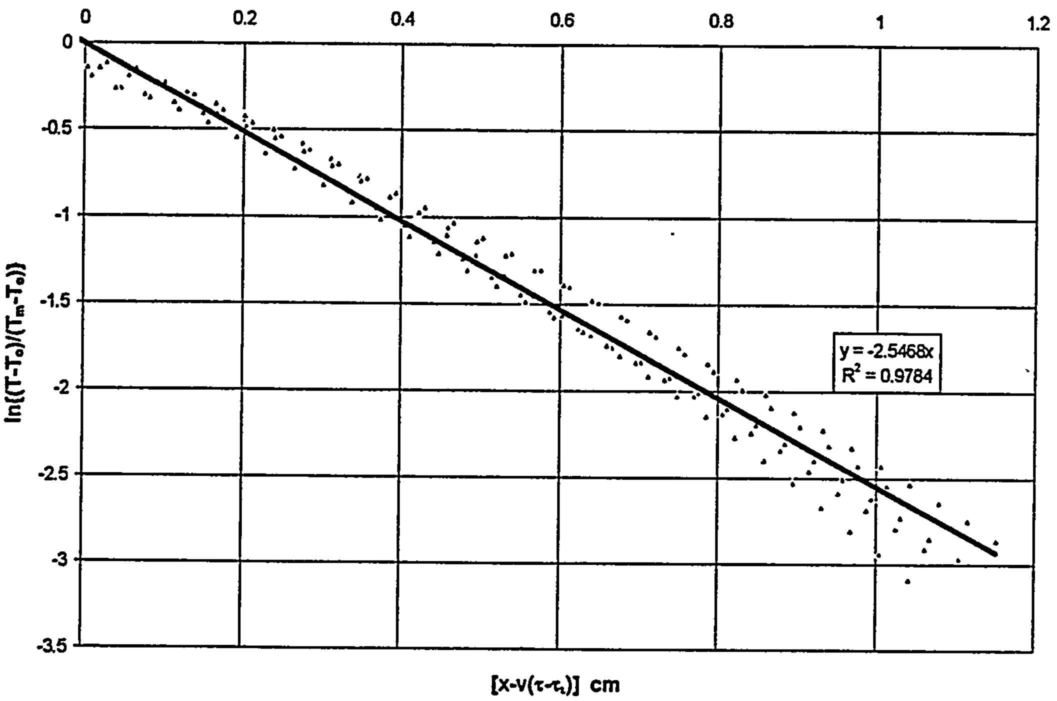

Figure 7. Temperature distribution in $\ln\left(\frac{T-T_o}{T_m-T_o}\right)$ vs $\left[x-v\cdot(\tau-\tau_i)\right]$ coordinate.