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EVALUATION OF KINETIC PARAMETERS APPROPRIATE FOR MODELING URETHANE FOAM INSULATION PERFORMANCE*

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Computer codes which model the pyrolysis of thermal insulators for in-depth temperature response are particularly sensitive to the kinetic parameters used in the code. The parameter values, which are evaluated from thermogravimetric analysis (TG), are, in turn, sensitive to the heating and gas flow rates in the TG sample environment as well as the composition of the gas. In this study, the effects of these experimental variables on computer code predictions and their correlations with experimental data are demonstrated. The insulators are urethane foams and were subjected to simulated and actual instantaneous fire test conditions. The Charring Material Ablation computer code was used to model insulator performance.

Systems sensitive to heat that must be exposed to high temperatures require special consideration in the choice of their insulation, since margins of weight and size in the insulation are often critical to the overall system performance. It is desirable, therefore, to minimize insulation requirements. Computer codes have been developed to estimate the thermal requirements and to reduce the amount of confirmatory testing required to assure acceptable performance. Unfortunately, in some cases poor agreement with large scale test data was obtained when the kinetic parameters derived from conventional laboratory data were used in the calculations [1–3]. To obtain satisfactory correlations between computations and observed test data, effective parameters derived from test data had to be substituted for parameters from laboratory data.

This study addressed the importance of test conditions for data acquisition from thermogravimetric analysis (TG). These data were used to evaluate kinetic parameters which, in turn, were used to model the degradation of a urethane foam exposed to an instantaneous fire with a high heating rate. Thermal property data

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were also necessary for the model. Another study [3] addresses the thermal property data acquisition problem for evaluating heat capacities, thermal conductivities and diffusivities appropriate for organic insulators subject to high heating rate conditions.

The decomposition of a polymeric material such as a urethane foam is a complex process [4, 5]. It involves a series of competitive and consecutive reactions as well as physical transitions that are time and temperature dependent. The final product is a char whose conductivity is higher than that of the original foam because it is largely carbonaceous. Factors which reduce the decomposition and preserve the virgin foam can play a significant role in the time-temperature history of an insulated surface. Two factors are heating rate and foam environment. Higher heating rates provide less decomposition at a given temperature because decomposition is time as well as temperature dependent. Oxygen and flow rates will also determine the rate of decomposition. Kinetic parameters suitable for a given thermal exposure, therefore, become important for predicting insulator performance.

This study was motivated by the insulation requirements for a nuclear waste shipping container that could be subject to an instantaneous fire environment with high heating rates. Because the foam was enclosed within steel sheets, no accessible air and static flow conditions existed. To optimize the model, TG data were generated under several instrumental conditions. Kinetic parameters evaluated from the TG data were used in the Charring Material Ablation (CMA) computer code [6] which provides temperature versus time predictions for a thermal insulator exposed to a heat source. The objective of this report is to provide an empirical method for evaluating effective kinetic parameters from TG data, and to show the importance and sensitivity of experimental conditions for TG data acquisition for the resultant modelling of polymer degradation.

The two foams involved in this study were obtained from General Plastics Mfg. Their properties are given in Table 1.

Table 1 Urethane foam properties 25 °C

Foam	Density kg/m^3	Specific heat $J/kg \cdot K$	Thermal conductivity $W/m \cdot K$
FR 6704	64	1050	0.028
FR 9606	96	1047	0.067

Experimental

Thermogravimetric analyses

TG analyses were conducted with the DuPont 951 Thermal Analyzer which has a temperature-rise rate capability of 0.1–100 deg/min. Although temperature-rise rate calibrations were not performed before this series of analyses, when calibrations were performed, the rates were within 10% of the settings. The thermocouple was 0.5–0.8 mm above the sample. The foam samples were cut as very thin slices to maximize the surface area for heating and to minimize temperature gradients. No attempt was made to measure the temperatures or temperature-rise rates within the samples since the chars from the foams could interfere with the electrical response. These values would probably differ from the measured values. Accurate values, however, were not critical for this study since one of the objectives was to show semi-quantitatively the importance of heating rate in the evaluation of kinetic parameters.

Radiant heat simulation test

A radiant heat facility was used to simulate insulation performance. Figure 1 is a drawing of the container sample and the quartz lamp array heat source. The foam

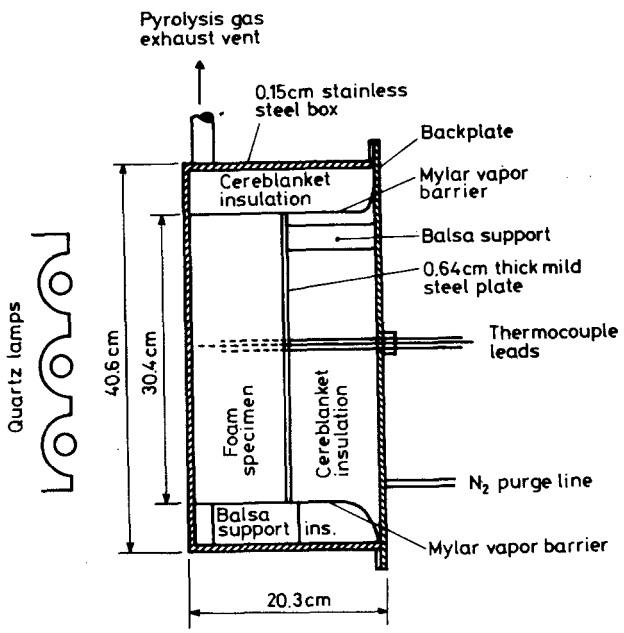

Fig. 1 Radiant heat test simulator design

specimens were placed in the container with their front faces against one side of the box. The other sides were insulated with 16 kg/m^3 ceriblanket fiber insulation. The front surface was painted with Pyromark flat black paint. A vent hole allowed gases to escape. A nitrogen purge was used to eliminate air before heating and to prevent air from entering during pyrolysis. This test was conducted with a block of urethane foam FR 6704, 30.5 by 30.5 by 10.2 cm in size. Six thermocouples, type *K*, were inserted in the foam. Their positions were established by X-ray. The temperature was maintained at 1060° for 2260 s. The quartz lamp array provided 20.6 W/cm^2. Test equipment and design are described and data acquisition and posttest analyses were performed by Suchland et al. [7].

Pool fire test

A fire environment was also used to evaluate the insulation capability of the foams. A 22.9 cm cube of urethane foam FR 9606 was supported over a pool of JP-4 jet fuel in the facility shown in Fig. 2. The wind-shielded test facility was

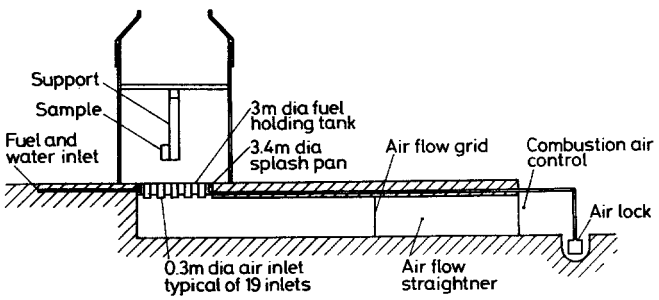

Fig. 2 Pool-fire test facility

fabricated from steel plate with high temperature insulation batting on the interior surface. The chimney top which prevented back flow closed at à 45 degree angle to a 2.4 m diameter opening. During a typical fire test, water is placed in the holding pool and fuel floated on the surface. The air inlet system, which operates on natural draft, consists of an air plenum located directly below the pool with an access duct leading to a louvered opening. The air entered the chimney through 19 pipes, 0.3 m in diameter, and passed through the pool. An electronic controller regulated air flow through the louvers to maintain the temperature at 800°. The test was conducted for 3600 s. The test facility and procedure are described in greater detail by Hudson [8].

Charring Material Ablation Program

The Charring Material Ablation Program [6] is used to model dimension, weight and energy changes of insulators under high temperature conditions. It is a one dimensional code that can calculate the in-depth thermal response of a charring and/or ablating material. Decomposition reactions are based on a three component model. Material properties such as thermal conductivity, specific heat and emissivity are input as functions of temperature for the virgin foam and char. The program also requires the density, heat of formation of the resin, the decomposition gas enthalpy and kinetic parameters for the Arrhenius equation. The output provides temperatures, mass ablation rates and blowing parameters for char and pyrolysis gas, total recession and recession rates of the surface, the char line and the pyrolysis line.

The degradation rate relationship used in the CMA code requires values for the kinetic parameters A, E and n. These are evaluated from Eq. (1) using TG data.

$$-\frac{dw_i}{dt} = A_i \exp(-E_i/RT) w_i^n \tag{1}$$

where

w_i residual weight fraction
A_i pre-exponential factor in the Arrhenius relationship, s^{-1}
E_i activation energy, J/mol
R universal gas constant, J/mol-K
T temperature, K
n reaction order
t time, s
Subscript i = component, i = 1–3

Although the degradation of organic materials can involve a series of consecutive and competitive reactions, CMA limits the modeling of the degradation process to three independent decomposition steps. Generally, three steps have been sufficient to model the organic decompositions encountered in our studies. Although the arbitrary partition of a molecularly uniform material into three components appears anomalous, it will be seen that very good agreement is obtained between experimental TG data and computed values. The agreement is due largely to the fact that the evaluation is a curve fitting process involving three coefficients (parameters) in Eq. (1) and another equation in which the sum of the three component fractions is equal to one. The opportunity to vary a large number of unknowns provides the potential for good agreement.

Results and discussion

Evaluation of the kinetic parameters

The kinetic parameters were evaluated with the least squares Kinetic Parameter Evaluation Program (KPE) [9]. The program provides values for the three sets of parameters A, E and n and the component fraction Γ. Since the fraction sum is one, it is necessary to solve for only two fraction values. Thus, eleven unknown exist. Experimental data, $w_e(t)$, are compared with computed values of $w(t)$. Values for A, E/R, n and Γ are determined which will minimize the following sum.

$$\sum_{k=1}^{m} [w(t_k) - w_e(t_k)]^2 \qquad (2)$$

where m = number of experimental values.

The three ordinary differential equations are solved numerically. To initiate the computation, estimates of the eleven parameters are required. Unique solutions are not obtained and different sets of estimates can provide different values for A, E/R, n and Γ. Computation stops when the approximated data attain a certain specified accuracy. Since the solutions are not unique, the values cannot be associated with specific reactions in the thermal degradation of the foam.

Figure 3 shows typical examples of the good correlations realized between KPE computations and experimental TG data. Foam FR 9606 was selected to demonstrate the capability of the KPE code to reproduce typical as well as complex TG curves. The parameter values and component fractions are given in Table 2.

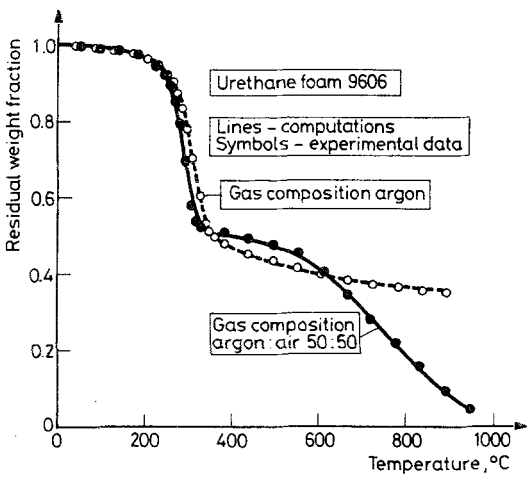

Fig. 3 Representative plots showing the agreement between TG experimental data and computations from the KPE program; flow rate – 100 ml/min; temperature rise rate – 100 deg/min

Table 2 Kinetic parameter and component fraction values obtained from the KPE program for urethane foam FR 9606

Gas composition: argon–air 50:50

	Component		
	1	2	3
A	1.367×10^{11}	1.703	18.41
E	1.849×10^{5}	7.282×10^{4}	4.159×10^{2}
n	1.000	1.112	0.6352
Γ	0.4573	0.5115	0.0312

Gas composition: argon

	1	2	3
A	5.955×10^{8}	0.1520	0.4216
E	1.626×10^{4}	3.457×10^{3}	2.806×10^{3}
n	0.3352	1.1713	1.280
Γ	0.3978	0.3768	0.2255

They were obtained with a gas flow rate of ~100 ml/min of argon or a 50:50 mixture of argon–air. The temperature rise rate was 100 deg/min.

Effects of heating and flow rates on the kinetic parameters

The importance of temperature rise rates, gas flow rates and composition during TG data acquisition became evident when CMA computed results from the various sets of TG data were compared with experimental test results. A radiant heat simulation test was conducted with a block of urethane foam FR 6704. The test is described in the experimental section. The conventional TG conditions of a 5–10 deg/min temperature rise rate and 50–150 ml/min purge gas flow rate did not lead to good correlations between CMA computations and observed temperature data. Since the foam was between metal walls, access to air and significant gas circulation in the decomposing foam were absent.

Substituting an argon environment and a zero flow rate provided improved correlations. Additional improvement was realized with TG data generated at a 100 deg/min temperature rise rate, the maximum rate available with the DuPont 951 Thermal Analyzer. The following figures demonstrate the effects of these conditions on the TG response

Figure 4 shows the effects of argon flow rates on the TG response at a 10 deg/min temperature rise rate. The increasing flow rate increases the degradation rate and

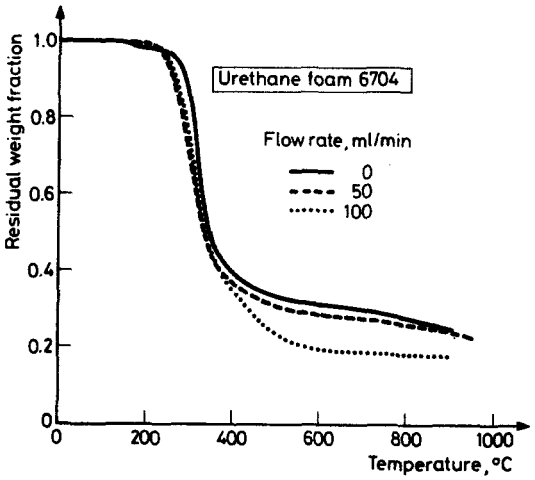

Fig. 4 Effect of argon gas flow rates on the TG curve; temperature rise rate 10 deg/min

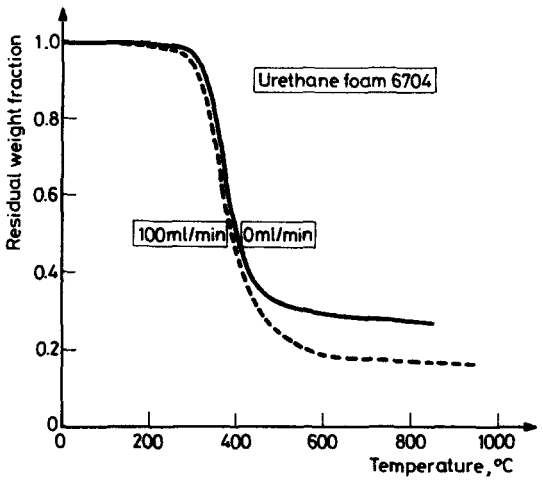

Fig. 5 Effect of argon gas flow rates on the TG curve; temperature rise rate 100 deg/min

reduces the residual char at temperatures above 600°. Char can also act as a thermal insulator, although it is much less effective than virgin foam. Its reduction in density with the resultant increase in free volume will increase the thermal conductivity due to convection and radiation and will provide higher computed internal temperatures. Figure 5 shows an even greater effect at the increased temperature rise rate of 100 deg/min.

Since insulation performance was being evaluated, the maximum temperatures developing on the insulated metal surface from a given heating rate were of primary

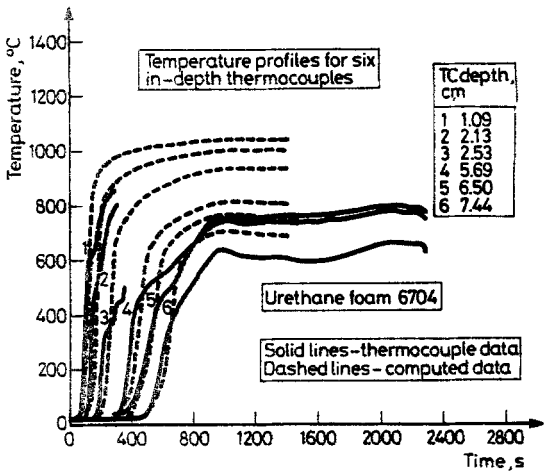

Fig. 6 Comparative observed and computed temperatures; computed temperatures obtained from TG data at 10 deg/min and 100 ml/min

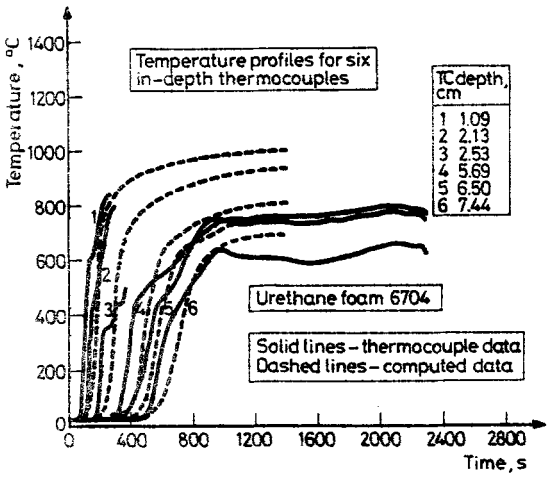

Fig. 7 Comparative observed and computed temperatures; computed temperatures obtained from TG data at 10 deg/min and 0 ml/min

importance. Figures 6 and 7 show the effects of the gas flow rate during the TG measurements on the correlation between computed and observed temperature response. Flow rates of 100 and 0 ml/min of argon were used in Figs 6 and 7, respectively, in conjunction with a 10 deg/min temperature rise rate. The 50 ml/min flow rate provided intermediate curves. It is evident that the zero flow rate provides the better correlation between computed and experimental results in the range where the temperatures begin to level off. The broken and incomplete experimental

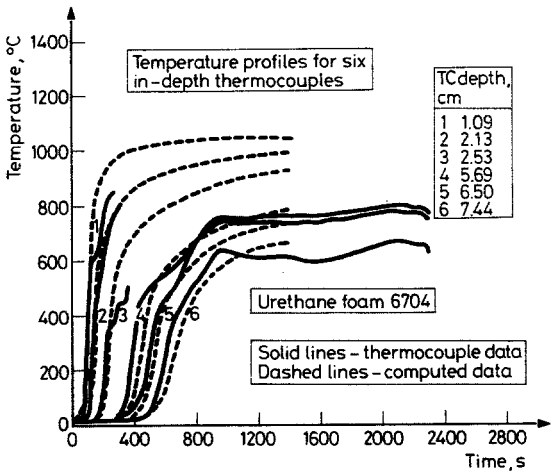

Fig. 8 Comparative observed and computed temperatures; computed temperatures obtained from TG data at 100 deg/min and 0 ml/min

curves from thermocouples 1, 2 and 3 are due to mechanical failures of the thermocouples in the higher temperature range.

The best correlations were realized when TG data were obtained with a temperature rise rate of 100 deg/min and a flow rate of 0 ml/min. Figure 8 shows the comparative data and underscrores the improvement in the correlations between computations and observations that is possible by matching TG data acquisition conditions with application conditions.

The capability of the foam to protect the contents of the transport container in a fire was also determined in a realistic fire environment. A cube of Urethane Foam FR 9606 was supported over a pool of jet fuel in a cylinder with a chimney. The fuel was ignited and the flame enveloped the foam. The test facility and procedure are described in the experimental section. The results from this test illustrate the importance in TG data acquisition not only of flow rate but also the environmental gas composition on the kinetic parameters and their resultant effects on the computed data. The TG data were generated under two gas composition conditions. In one, the foam specimen was heated in a 50–50 argon–air mixture at a combined flow rate of 110 ml/min, and in the second condition pure argon was used at 100 ml/min. The temperature rise rate for both was 100 deg/min.

The TG plots are shown in Fig. 3. The residual char in the argon air environment is appreciably less than that for the anaerobic environment at 800°. Since the flow rates were very similar, the difference is probably due to the added oxidative decomposition.

The fire test was conducted in an environment with a surplus of air for

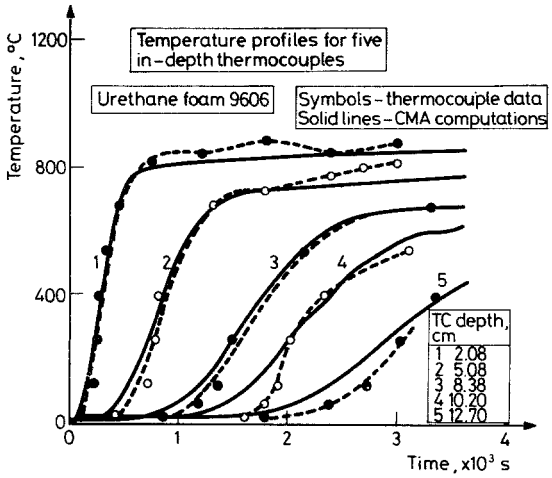

Fig. 9 Comparative observed and computed temperatures; computed temperatures obtained from TG data generated at 100 deg/min and flow rates of 55 ml/min each for air and argon

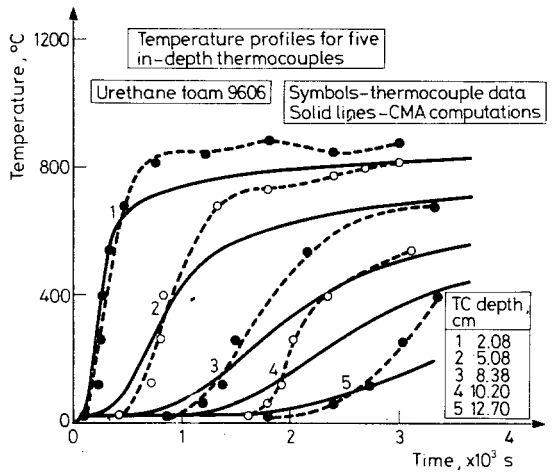

Fig. 10 Comparative observed and computed temperatures; computed temperatures obtained from TG data generated at 100 deg/min and a flow rate of 100 ml/min of argon

combustion. The foam was, therefore, enveloped in a heated gas with residual oxygen, a condition approximating the 50–50 argon–air mixture. Figures 9 and 10 show the correlations of the fire test data with CMA predictions. It is evident that the TG data from the 50–50 gas mixture, Fig. 9 provided the better correlation. This result was expected since this mixture approximated the depleted oxygen environment in the fire test. The computation involving TG data generated in the

absence of oxygen, on the other hand (Fig. 10), predicted appreciably lower temperatures at extended times. This result was due to the absence of the temperature increment from the exothermic oxidative reaction.

Conclusions

Improvement in the capability of the Charring Material Ablation code to predict performance of thermal insulators can be obtained when Arrhenius kinetic parameters are evaluated from TG data under the heating rate and environmental conditions appropriate for the insulator application. The availability of appropriate values at the laboratory level can reduce the need to define effective values from simulated test data, and thus can lead to appreciable savings in time, effort and cost.

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Zusammenfassung — Computercode zur Modellierung der Pyrolyse von Wärmeisolatoren sind den im Code verwendeten kinetischen Parametern gegenüber besonders empfindlich. Die aus der thermogravimetrischen Analyse (TG) abgeleiteten Parameterwerte sind dagegen empfindlich gegenüber den Aufheiz- und Gasstromgeschwindigkeiten in der Umgebung der TG-Proben sowie gegenüber der Gaszusammensetzung. In vorliegender Arbeit wird der Einfluß dieser experimentellen Variablen auf die Computercodevoraussagen und deren Übereinstimmung mit den Versuchsdaten dargestellt. Die

Isolatoren waren Urethanschäume und wurden simulierten und wirklichen Momentfeuertestbedingungen unterzogen.

Резюме — Компьютерные коды, используемые при моделировании пиролиза термических изоляторов для глубины температурного отклика, особенно чувствительны к кинетическим параметрам, используемым в таком коде. Величины параметров, определяемые на основе термогравиметрического анализа, в свою очередь, чувствительны к скорости нагрева и скорости потока газа, а также к составу газа. Показано влияние таких экспериментальных переменных на компьютерные кодовые прогнозы и их корреляции с экспериментальными данными. Изоляционные пеноуретаны были подвергнуты моделированию и определению действительной температуры воспламенения. Для проведения моделирования этого изолирующего материала был использован компьютерный код типа Удаление Обугленного Материала.