Disposal of Residues from Building Decontamination Activities

Paper # 05-A-581-AWMA

Prepared by Shannon D. Serre, Chun-Wai Lee, and Paul Lemieux

U.S. Environmental Protection Agency, Office of Research and Development, 109 TW
Alexander Drive, E305-01, Research Triangle Park, NC 27711

ABSTRACT

After a building has gone through decontamination activities from a chemical attack there will be a significant amount of building decontamination residue that will need to undergo disposal. This project consists of a fundamental study to investigate the desorption of simulated chemical warfare agents chloroethyl ethyl sulfide (CEES) and dimethyl methyl phosphonate (DMMP) from building materials. The physical and chemical surface properties of the building materials have been obtained, as well as the adsorption and desorption characteristics so that modeling can be performed to assess various combinations of building materials and contaminants in different incinerator or thermal treatment system designs and operations. The results from these studies can be used to evaluate incineration technologies for appropriateness for disposal of contaminated building cleanup waste materials. In addition, the results from these studies will be used to develop computer simulations to predict the behavior of contaminated residue as it is processed through incinerators.

INTRODUCTION

In 1990 the United States began disposing of chemical warfare agents using an incinerator in the Pacific Ocean. While data exists on the thermal destruction of these agents, little data exists in the literature on the thermal desorption of chemical agents from building materials. For this reason this project was undertaken to understand the adsorption properties and desorption of chemical agent simulants onto building materials.

After a building has gone through decontamination activities from a terrorist chemical attack, there will be a significant amount of residual material and waste that may be heavily contaminated. This material could include porous material such as contaminated carpet, fabric, ceiling tiles, and furniture, personal protective equipment used during cleanup activities, as well as contaminated air filters from the building's heating ventilation and air conditioning (HVAC) system. It is likely that much of this material will be disposed of in high temperature thermal incineration facilities, including medical/pathological waste incinerators, municipal waste combustors, or hazardous waste combustors. It is also a possibility that some sort of portable incineration technology might be brought into the field to dispose of these materials on-site in order to minimize exposure. Selection of appropriate disposal facilities requires fundamental knowledge of the behavior of the matrix-bound contaminants in various thermal environments. Very little is known about the behavior of the likely contaminants bound in these various matrices within incineration facilities, and complete destruction of the contaminants without releasing air emissions of contaminants and contaminated combustion residues from the disposal of these materials is very important.

The primary objective of this project was to measure the adsorption and desorption characteristics of chemical agent simulants on materials that are found in a typical office such as ceiling tiles, wallboard, particle board and carpet. Adsorption was measured as a function of temperature and concentration of the surrogates. Once adsorption was complete the substrate was heated to desorb the adsorbed species. Additional tests were performed where the substrate was spiked with liquid simulant and placed in an oven to observe the desorption of the simulant. The results from this work will be combined with a destruction model similar to that developed by Dennison et al.[1] to examine the destruction of the desorbed simulants in a thermal environment. The results from these studies will be used to evaluate incineration technologies for appropriateness for disposal of contaminated building cleanup waste materials.

EXPERIMENTAL APPROACH

All of the work presented in this paper used simulants in place of actual chemical agents. Simulants are substances with similar physical properties of chemical agents used in place of the actual chemical agents in training and research involving protective equipment. The ideal simulant would mimic all the chemical and physical properties of the actual agent (i.e., vapor pressure, density, reactivity). Several simulants have been identified whose characteristics partially resemble the physical properties for class G nerve agents and mustard agents. Dimethyl methylphosphonate (DMMP) has been used as a GB simulant in testing trials of military personnel protection such as gas masks and filters.[2] DMMP is part of the organophosphorous esters group and has a volatility similar to that of many non-persistent G agents.[3] Chloroethyl ethyl sulfide (CEES) is a monochloro dialkyl organosulfur compound used as a simulant for mustard gas (HD). [4-6] This compound is used because it has similar vesicant properties, but is much weaker than HD. CEES has been used as a simulant for mustard in studies involving decontamination, detection, and clothing protection.[2] Physical properties for DMMP and CEES are shown in Table 1.

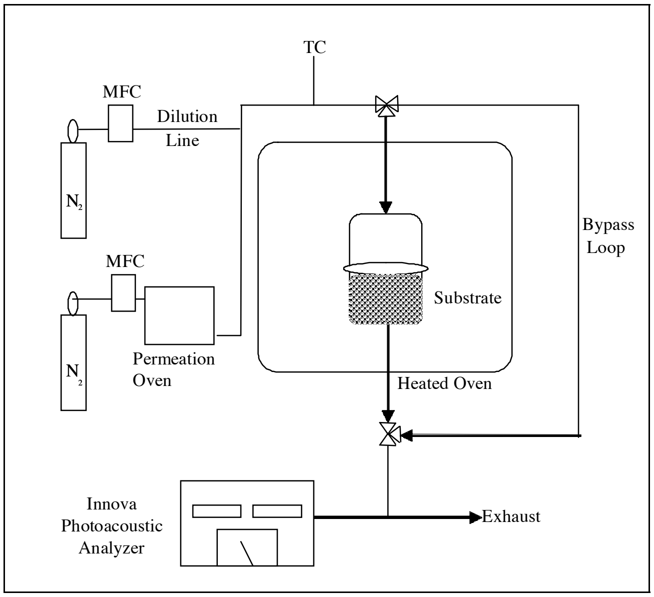
Table 1 Physical Properties for DMMP and CEES [1,4]

	DMMP	CEES
Molecular Weight	124.08	124.6
Boiling Point (°C)	181	156
Density (g/cm^3)	1.15	1.07
Vapor Pressure kPa (25 °C)	0.08	0.019

The experimental setup used in this research is shown in Figure 1. The chemical agent surrogate (DMMP or CEES) is placed in a diffusion vial and the vial is then placed inside of a VICI Metronics Model 190 permeation oven and allowed to equilibrate. The oven is used to raise the temperature and thus the vapor pressure of the chemical agent simulant. Dry nitrogen gas (N_2) is passed through the oven to transport the simulant through the system at a flow rate of 0.94 slpm. A glass reactor with a stainless steel frit is used to hold the building material samples (substrate). The reactor is housed inside of a convection oven to heat the material to the desired temperature. The concentration of the chemical agent simulant is measured using an Innova Model 1314 photoacoustic analyzer. All gas transfer lines were heat traced to prevent condensation of the simulants inside the transfer lines. Calibration checks of the Innova instrument were performed by connecting a calibration gas cylinder to the transfer line and allowing the gas to pass through the bypass loop to the analyzer. There was not any significant loss of DMMP or CEES at the concentrations examined in this work. All tests were performed under dry conditions. Adsorption tests were conducted at concentrations ranging from 5 to 21 ppm.

All gas flows in the system are controlled using Sierra Instruments Series 100 mass flow controllers. Initially the gas flow is directed through the bypass loop. The system is purged with N_2 (2 slpm), labeled as dilution line in Figure 1, to obtain a zero reading for the analyzer. Once a zero reading has been obtained the simulant is added to the gas stream by turning a three-way valve, to establish a baseline concentration. The total flow rate at this point is 2.94 slpm. Once the desired baseline has been established the gas is directed through the reactor containing the building material. The simulant that is not adsorbed by the building material is measured in the outlet gas stream. The difference between the simulant in the outlet gas stream and the baseline gas stream is attributed to adsorption of the simulant onto the building material. The building material is considered saturated when the outlet concentration is equal to the baseline concentration.

Figure 1. System used to study adsorption and desorption of chemical agent simulants.



Experiments were also performed to examine the desorption of the simulant from a saturated building material. The flow through the permeation oven is diverted to the exhaust so that only pure dry N_2 was allowed to pass through the reactor system to sweep any of the simulant that had desorbed from the surface of the substrate. The amount desorbed is characterized by the photoacoustic analyzer. The amount of simulant desorbed from the substrate is characterized as a function of temperature. Temperatures of 50, 100, 150, and 200 °C were used in the desorption tests. All tests were performed under dry conditions.

The Innova Model 1314 selectively detects down to ~15 ppb for the nerve agents and 0.15 ppm for mustard gas simulants.[7] Samples are pulled from the gas stream, using an internal sample pump, into the sample chamber. Light from an infra-red light source is reflected off a mirror, passed through a mechanical chopper, which pulsates it, and then through one of the optical filters in the filter carousel. The light transmitted through the optical filter is selectively absorbed by the gas being monitored, causing the temperature of the gas to increase. Because the light is pulsating, the gas temperature increases and decreases, causing and equivalent increase and decrease in the pressure of the gas (an acoustic signal) in the closed cell. Two microphones mounted in the cell wall measure this acoustic signal, which is directly proportional to the concentration of the monitored gas present in the cell. The analyzer is selective for the compound of interest by using an optical filter (Filter # UA0975 for DMMP and UA0978 for CEES) to generate a wavelength that will excite only the compound of interest. When the compound is excited it expands. Samples are taken at 1-minute intervals. The chamber was flushed with ambient air before a new sample is obtained. The monitor automatically compensates for any water or temperature changes in the gas stream. The monitor is calibrated at the factory prior to delivery. A calibration check is performed on a monthly basis with DMMP and CEES calibration gases procured from Scott Gas.

Three types of building materials were used as substrates: wallboard, ceiling tile, and 3 types of carpet which included nylon 6, nylon 6-6, and polypropylene. The carpet samples were prepared by cutting into coupons approximately 2” square. The wallboard and ceiling tile were cut into coupons approximately 1” wide by 2” long and ¼” thickness. The characteristics of these materials are included as Table 2.

Table 2. Physical Characteristics of Substrates

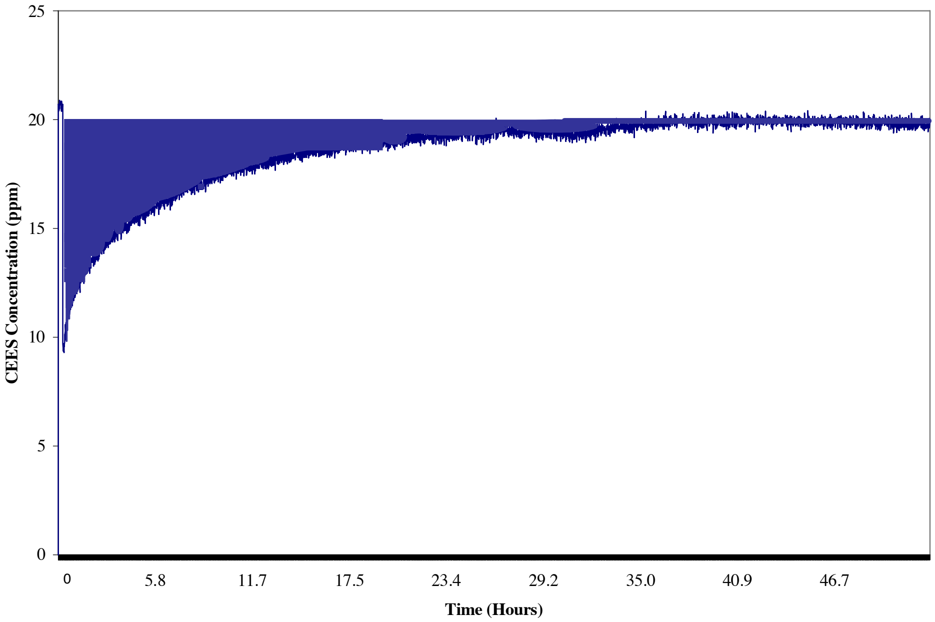
	Nylon 6	Nylon 6-6	Polypropylene	Ceiling Tile	Wallboard
Surface Area (m^2/g)	20	15	32	27	8
Moisture (%)	0.9	0.6	0.2	1.8	16.4
Volatile Matter (%)	61.9	65.6	69.1	14	16.6
Ash (%)	25.4	24	21.2	83	68.9
Fixed Carbon (%)	11.8	9.9	9.5	1.2	ND

ND= non detect

RESULTS AND DISCUSSION

In a typical adsorption experiment the substrate was exposed to the simulant in the reaction chamber. A typical run is shown in Figure 2 for CEES adsorption onto ceiling tile at a temperature of 25 °C and a baseline concentration of 20 ppm. At time zero the outlet concentration dropped to 10 ppm and continued to approach the baseline until the ceiling tile was saturated at 35 hours. The area under the breakthrough curve was then integrated, shaded in black, resulting in an uptake of 109 mg of CEES by the ceiling tile. For a sample weight of 12.1 grams the loading is 9 mg/g ceiling tile.

Figure 2. Adsorption Plot for CEES on Ceiling Tile at 25 °C and 20 ppm.



The desorption plot for the run shown in Figure 2 is shown in Figure 3. The saturated substrate was left in the reactor and pure N_2 was passed through the reactor as the temperature was ramped up from 50 °C to 150 °C. The temperature took less than 1 minute to jump between 50 to 100 °C and to jump from 100 to 150 °C. All of the CEES had been desorbed once the temperature had reached 150 °C.

Additional tests were performed where the substrate was spiked with a known amount of liquid simulant. These tests were designed to simulate disposal of a solid surface that had been in contact with a liquid agent. The substrate was then placed in the oven to assess how rapid the desorption would occur as a function of temperature. Figure 4 shows the desorption curves for 5.75 mg DMMP spiked onto three different substrates at a starting temperature of 50 °C. These breakthrough curves were integrated to perform a mass balance on DMMP. At 50 °C desorption occurred quicker for polypropylene carpet followed by ceiling tile and then wallboard. This could be a result of heat transfer to the material. Desorption was complete for the polypropylene carpet at a temperature of 50 °C, whereas the ceiling tile and wallboard required a temperature of 100 °C to completely desorb the DMMP. At a temperature of 50 °C the time required to completely desorb DMMP from the carpet approaches 90 minutes. This time exceeds the residence time of most continuous feed incinerator systems.

Figure 3. Desorption plot for CEES from ceiling tile at 50-150 °C.

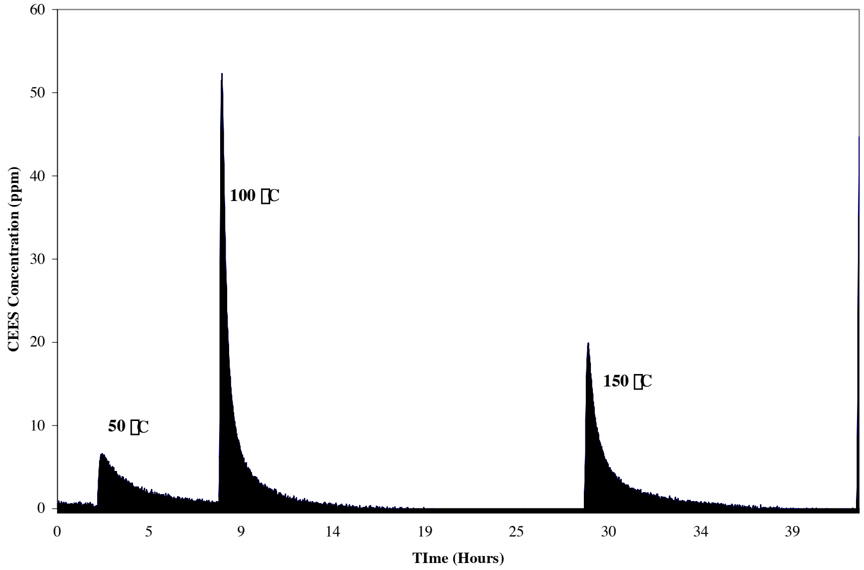
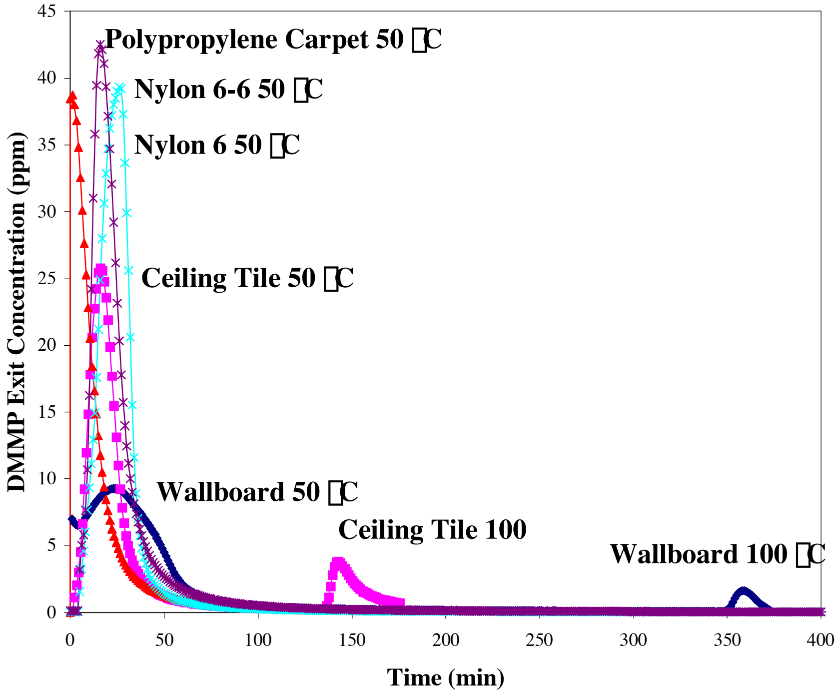


Figure 4. Desorption curves for DMMP spiking on polypropylene carpet, ceiling tile, and wallboard.

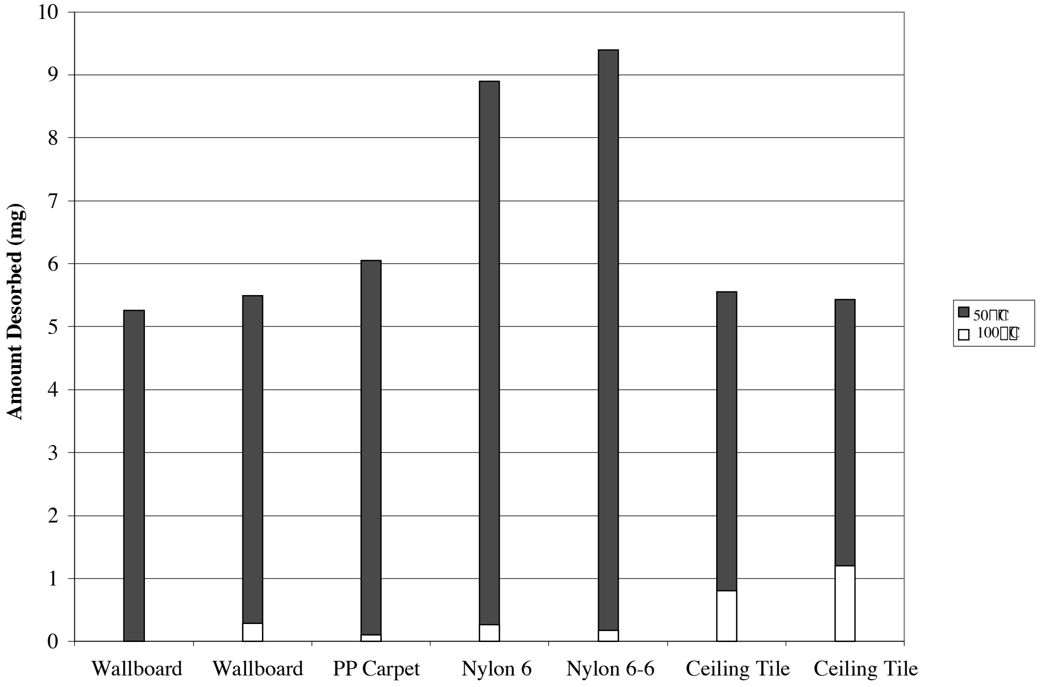


The curves in Figure 4 were integrated and the results are shown in Table 3 and graphically in Figure 5 for polypropylene carpet, nylon 6, nylon 6-6, ceiling tile, and wallboard. Repeat tests for the ceiling tile and wallboard are also shown. Figure 5 shows the amount of DMMP desorbed from the substrate at 50 °C (dark shaded bar) and 100 °C (white bar). As you can see most of the DMMP is desorbed from the surface at 50 °C. The ceiling tile is the only sample that retained a significant amount (~20%) after reaching 50 °C. The balance of the DMMP was desorbed after reaching 100 °C. Recoveries were 100 ± 20%, with the exception of the nylon 6 and nylon 6-6 carpets. The recoveries for these two samples exceeded 160%. There may be binders in the carpet that are off gassing and interfering with the gas-phase measurements. Tests are under way to characterize the binders.

Table 3. Desorption Results for DMMP

	Spiked Amount	Desorption at 50 °C	Desorption at 100 °C	Total Desorption	Recovery
Polypropylene Carpet	5.75 mg	6.05 mg	0.1	6.15 mg	107 %
Ceiling Tile	5.75 mg	5.55 mg	0.81 mg	6.36 mg	112 %
Wallboard	5.75 mg	5.49 mg	0.28 mg	5.77 mg	99 %
Nylon 6	5.75 mg	8.9 mg	0.26 mg	9.16 mg	159 %
Nylon 6-6	5.75 mg	9.39 mg	0.17 mg	9.56 mg	166 %

Figure 5. Desorption of DMMP from polypropylene carpet, nylon 6, nylon 6-6, ceiling tile, and wallboard at 50 and 100 °C.



SUMMARY

Fundamental tests were conducted to investigate the desorption of simulated chemical warfare agents (CEES and DMMP) from building materials. Known amounts of CEES and DMMP were spiked onto the surface of several building materials to determine the temperature required for desorption. Ceiling tile and wall board had desorption times much longer than that incurred for the carpets even though the surface area was lower for the ceiling tile and wall board. It was determined that CEES and DMMP were completely desorbed once the temperature of the material reached 150 °C. The compounds in this study are weakly bound to the building materials also known as physical adsorption (physisorption). The results from these studies can be used to evaluate incineration technologies for appropriateness for disposal of contaminated building cleanup waste materials. Future work will provide insight into the adsorption onto and subsequent desorption of these compounds from the building materials. The results from these studies will be used to develop computer simulations to predict the behavior of contaminated residue as it is processed through incinerators.

REFERENCES

1. Denison, M.K., Montgomery, C.J., Sarofim, A.F., Bockelie, M.J., Magee, R., Gouldin, F., McGill, G., "Detailed Computational Modeling of Military Incinerators," 20th International Conference On Incineration and Thermal Treatment Technologies, Philadelphia, PA, (May 2001).

2. Mahle, John; Mancinho, Derek; Buettner, Leonard; and Wayne Gulian, *Chemical filtration performance of a pressure and temperature swing absorber (PTSA) system Phase I: chloroethane, cyanogen chloride, ammonia, and 2-Chloroethyl ethyl sulfide pulse testing,* Edgewood Chemical and Biological Center, Aberdeen Proving Ground, Document ECBC-TR-306, July 2003.

3. Bennett, Steven R.; Bane, John M.; Benford, Pamela J.; and Robert L. Pyatt, *Environmental hazards of chemical agent simulants*, Aberdeen Proving Grounds, Document CRDC-TR-84055, August 1984.

4. Little, Arthur D.; Development of candidate chemical simulant list: *The evaluation of candidate chemical simulants which may be used in chemically hazardous operations*, Air Force Aerospace Medical Research Laboratory, Document AFAMRL-TR-82-87, December 1982.

5. Cataldo, Dominic, et al., *Acute environmental toxicology and persistence of a chemical agent simulant 2-Chloroethyl ethyl sulfide (CEES),* Dugway Proving Grounds, Document DPG-FR-C120A, CRDEC-CR-007, November 1988.

6. Chinn, Kenneth, *The effect of time and temperature on evaporation and transfer of thickened GD and thickened GD simulants,* Dugway Proving Grounds, Document DPG-FR-C120A, January 1979.

7. California Analytical Instruments, *Many applications for the model 1312 photoacoustic multigas monitor*, http://www.gasanalyzers.com/applications_for_1312.html, accessed January 2005.

KEY WORDS

Decontamination, disposal, building materials, chemical agents