Paper for presentation at 2005 Scientific Conference on Chemical and Biological Defense Research, Timonium, MD, November 14-16, 2005.

THERMAL DESTRUCTION OF CB CONTAMINANTS BOUND ON BUILDING MATERIALS: EXPERIMENTS AND MODELING

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ABSTRACT

An experimental and theoretical program has been initiated by the U.S. EPA to investigate issues of chemical/biological agent destruction in incineration systems when the agent in question is bound on common porous building interior materials. This program includes 3-dimensional computational fluid dynamics modeling with matrix-bound agent destruction kinetics, bench-scale experiments to determine agent destruction kinetics while bound on various matrices, and pilot-scale experiments to scale-up the bench-scale experiments to a more practical scale. Finally, model predictions are made to predict agent destruction and combustion conditions in two full-scale incineration systems that are typical of modern combustor design.

INTRODUCTION

After a building has gone through decontamination activities following a terrorist attack with chemical warfare (CW) agents, biological warfare (BW) agents, or toxic industrial chemicals (TICs), there will be a significant amount of residual material and waste to be disposed. This material is termed "building decontamination residue" (BDR). Although it is likely that the BDR to be disposed of will have already been decontaminated, the possibility exists for trace levels of the toxic contaminants to be present in absorbent and/or porous material such as carpet, fabric, ceiling tiles, office partitions, furniture, and personal protective equipment (PPE) and other materials used during cleanup activities. It is likely that much of this material will be disposed of in high-temperature thermal incineration facilities, such as medical/pathological waste incinerators, municipal waste combustors, and hazardous waste combustors.

Although pathogens such as *Bacillus anthracis* (anthrax) present in BDR are killed at typical incineration temperatures (> 800 °C), gas-phase residence times (> 2 s), and solid-phase residence times (> 30 min), it is possible for some of the pathogens to escape the incinerator due to bypassing the flame zones, cold spots, and incomplete penetration of heat through the bed. In the early 1990's, EPA performed testing of commercial hospital waste incinerators[1] by introducing large quantities of *Geobacillus stearothermophilus* (an anthrax surrogate) spores into the combustors and measuring the number leaving in the stack emissions and in the incinerator bottom ash, in terms of Log reduction in spore concentration. It was found that, in certain cases, only a 3-Log reduction in spore destruction was found, in spite of acceptably high operating temperatures and sufficiently long residence times.

As a result of the 2001 anthrax attacks, the EPA instituted an experimental and theoretical research program to investigate issues related to the thermal destruction of contaminated BDR[2] initially including carpeting, ceiling tile, and wallboard. Tests are being performed at bench- and pilot-scale, and a computer model is being developed to predict BDR-bound agent behavior in two commercial incinerator designs. Contaminants that are being tested will include BW simulants (Geobacillus stearothermophilus) and CW simulants (dimethyl methylphosphonate). These tests would examine time/temperature requirements for agent destruction, issues related to facility compliance with relevant permits (e.g., emissions of nitrogen oxides), predicting potential operational difficulties in full-scale systems, and understanding which facilities may or may not be appropriate to handle certain types of BDR.

Thermal processing of the BDR material in commercial incinerators is evaluated using an incinerator-modeling tool provided by Reaction Engineering International (REI). The models provided to the EPA are derived from models developed through funding from a DoD-Army Small Business Innovative Research (SBIR) project in which REI created a simulator to predict the performance and destruction of chemical agent in the US Army baseline Chemical Weapons Incineration facilities[3]. In that work the simulator included a range of models, from time-dependent process models to detailed Computational Fluid Dynamic (CFD) models. Using computational chemistry methods, detailed chemical kinetic mechanisms were developed that describe the incineration of mustard blister agent and the nerve agents GB and VX. The kinetic mechanisms describe the complete decomposition of the agent, including products of incomplete destruction and final product speciation. Although reliable data are not available for agent destruction, the kinetic mechanisms have been benchmarked against high quality experimental data for similar substances (where available) and peer reviewed by an Advisory Panel of experts[4]. Agent destruction in the furnaces is computed using finite-rate chemistry CFD models of the incinerator units. The incinerator simulator was benchmarked to data from the Johnston Atoll Chemical Disposal Facility (now de-commissioned). The simulator has been used to address a variety of operational questions for the US Army and its system contractors[3,5]. The modeling techniques, combustion models and agent destruction models from the Army funded project were re-configured to the specific incinerator units of interest to the EPA, aspects of which have been benchmarked to data from the EPA rotary kiln incinerator simulator (RKIS) (see below)[6,7].

Although the methodology described in this paper will be use for both chemical and biological contaminants, the experiments completed so far have been limited to biologicals. Bench-scale experiments on CW agent simulants have been completed, but no pilot-scale experiments on CW agent simulants have been completed, and because of that no model runs have been performed to compare to the pilot-scale results.

APPROACH

The approach taken to develop the computer simulations for the current project will be as follows:

- Bench-scale experiments were performed to investigate matrix effects on BW agent simulant destruction at various temperatures
- Bench-scale experiments wee performed to investigate matrix effects on CW agent simulant adsorption/desorption at various temperatures
- Pilot-scale experiments were performed to investigate operational issues, permit compliance issues (e.g., air pollutant emissions), and to calibrate model scale-up efforts
- Computer simulations will be conducted. These simulations will be based on bench- and pilot-scale experimental data and CW agent combustion kinetic mechanisms already developed by REI to predict agent behavior in commercial incinerators, including a medical/pathological waste incinerator and a commercial hazardous waste-burning rotary kiln

The three combustion systems that are modeled include:

- The EPA RKIS, located in RTP, NC – See Figure 1
- A commercial dual-chambered modular medical pathological waste incinerator – See Figure 2

- A commercial hazardous waste-burning rotary kiln – See Figure 3

The first unit, the EPA RKIS facility, is a simulated pilot-scale rotary kiln incinerator located at the EPA research facilities in RTP, NC. It has a primary and secondary burner, each rated at 73 kW (250,000 Btu/hr). The RKIS can feed a variety of liquid and solid surrogate hazardous waste, and is described in detail elsewhere[8].

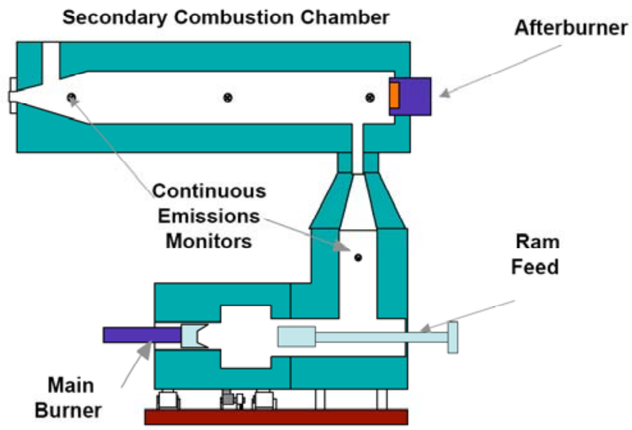

Figure 1. EPA Rotary Kiln Incinerator Simulator (RKIS).

The second combustion unit is a commercial dual-chamber starved-air modular medical/pathological waste incinerator that is currently being operated jointly by the EPA and National Institutes of Environmental Health Sciences (NIEHS) on their RTP, NC campus. This facility has a nominal firing rate of 1 MW (3.4 MMBtu/hr) and is capable of processing about 400 kg/hr (900 lb/hr) of wastes which mostly consist of animal bedding.

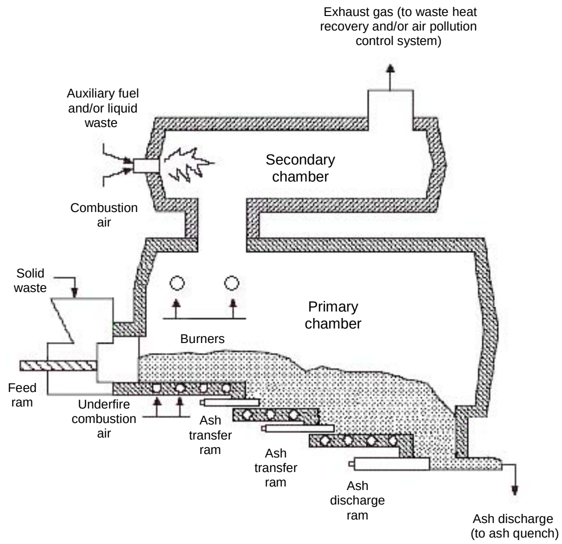

Figure 2. Medical/Pathological Waste Incinerator

The third combustion unit is a commercial hazardous waste-burning rotary kiln system currently in operation in East Liverpool, OH. This unit has a nominal firing rate of 35 MW (120 MMBtu/hr) and processes about 8100 kg/hr (9 tons/hr) of hazardous waste from various sources.

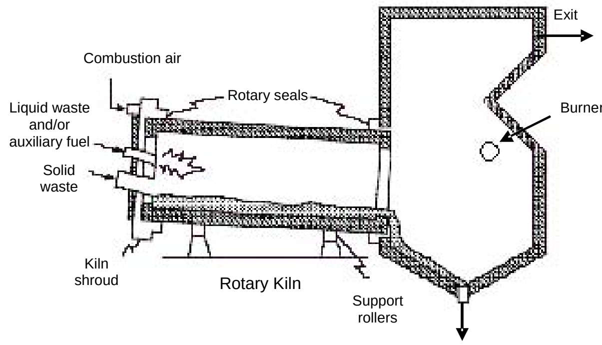

Figure 3. Commercial Hazardous Waste Burning Rotary Kiln.

The geometries, operating parameters, and sample emissions data for the three combustors were acquired from the operators of the facilities. Computational grids and model input parameters were generated by REI based on this information. Currently only the BW simulant experiments have progressed to the point of being able to compare experimental and model results. Bench-scale CW simulant adsorption/desorption experiments have been performed, but the modeling and pilot-scale experiments have not been completed yet.

EXPERIMENTAL RESULTS

Results have been obtained using bulk building materials consisting of carpet, ceiling tile, and wallboard. Ceiling tiles that had been in use for approximately 1 year in a laboratory were made available due to construction changes. These were Class A, standard-white, fire-retardant, textured-faced ceiling tiles composed of wood fiber (0 - 60%) and fibrous glass (0 - 13%). New drywall was used for these tests, which consisted of gypsum core wrapped with a paper lining. Carpet was nylon 6-6 carpeting acquired directly from Shaw, the manufacturer.

For the bench-scale tests, the building materials were cut into sample sizes measuring 7.62 x 3.81 cm, weighed, individually wrapped in aluminum foil and steam sterilized by autoclaving. The sterile samples were inoculated with either 1.0 ml of *Bacillus subtilis* spores for a final concentration of 10^8 spores/ml or 1.0 ml of *Geobacillus stearothermophilus* spores for a final concentration of 10^6 spores/ml. Once inoculated the building material pieces were placed on a sterile tray and allowed to dry overnight within a biological safety cabinet. Once dried, the samples were prepared by stacking two (7.62 x 3.81 cm) pieces with the inoculated sides facing each other and then tested in thermal destruction experiments. In the thermal destruction experiments, the BDR samples were heated in a quartz reactor operating at various temperatures, for various time intervals. The samples were recovered and analyzed for viable spores. These tests are described in more detail elsewhere[9]. Figure 4 shows a sample set of results illustrating the destruction of *Bacillus subtilis* inoculated onto ceiling tile.

It must be noted that the bench-scale tests on carpet had not been performed at the time this paper was written. Because of the behavior of carpeting at elevated temperatures (melting, pyrolysis), the carpet tests were put off to the end for the bench-scale experiments. However, for the very same reasons, the carpet was tested first in the pilot-scale experiments – the carpet combusted completely leaving little to no ash behind in the RKIS. For this reason, the bench-scale tests discuss only ceiling tiles, and the pilot-scale tests and the modeling only discuss carpeting.

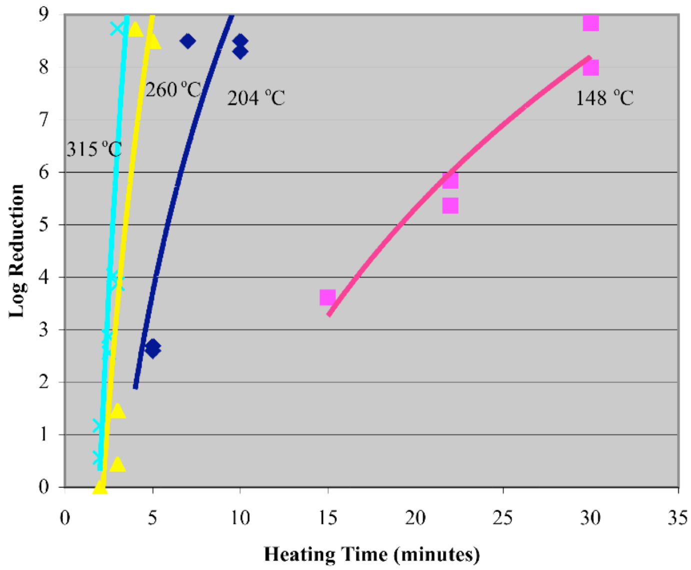

Figure 4. Sample Bench-Scale Results – Effect of Heating Temperature and Time on Reduction of *Bacillus subtilis* Spiked on Ceiling Tile

Once the destruction studies were completed, the destruction of the spores bound on the building materials (shown in Figure 4) were fitted to an Arrhenius-type expression analogous to a zero-order reaction:

$$spore_{living} \rightarrow spore_{dead} \quad (1)$$

The results from this curve fit are shown in Figure 5, both in terms of the Arrhenius fit and the more conventional Z value type approach.

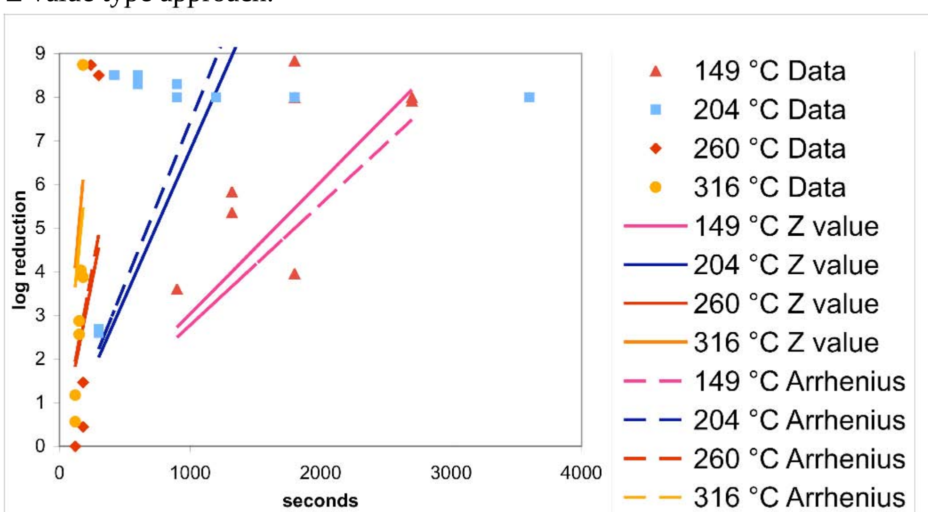

Figure 5. Log reduction versus time for *B. subtilis* on ceiling tile at various initial temperatures.

Tests were also performed on the pilot-scale RKIS facility, where biological indicator (BI) strips containing 10^6 spores of Geobacillus stearothermophilus were enclosed in a sealed 0.95 cm (3/8 in) OD steel tube with a thermocouple and embedded into a 454 g (1 lb) bundle of wetted carpeting. The carpet bundles were fed manually into the RKIS operating at 850 °C (1562 °F), removed from the RKIS at different times and quenched with water. The BI strips were recovered and viable spores were measured. Figure 6 illustrates the temperature profiles and results from the tests that are described in more detail elsewhere[10]. Note that the profile for Run 4 was slightly different than the other runs because more water was absorbed on the carpet, so the time for complete drying was longer. It was found that total spore kill was achieved between 4 and 5 minutes.

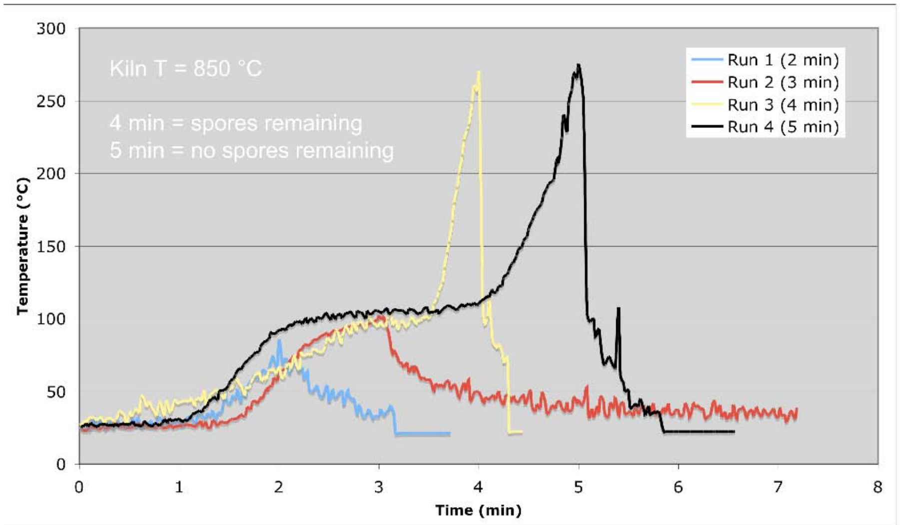

Figure 6. Internal Carpet Bundle Temperature vs. Time

MODEL RESULTS

The periodic loading of materials into the RKIS results in an inherently time-dependent operation that must be adequately captured. Modeling the operation with a true transient computational fluid dynamics (CFD) simulation would require excessive computing resources. To represent the time-dependent nature of the RKIS in a computationally efficient manner, it is modeled using a combination of a fast running, transient process model and a steady-state, reacting CFD model. The transient process model and the CFD model contain accurate representations of the geometry details contained within the RKIS (primary chamber, secondary chamber, connecting ductwork). The transient process model captures the transient effects of building matrix combustion, on the chamber temperature, overall gas composition and heat-up of the matrix pieces being processed. In addition, the transient model can mimic the use of burner turndown, water (quench) sprays and variable air injection to maintain setpoints (e.g., thermocouple temperature, exit O_2 concentration) used by the control system for the RKIS. The conditions predicted by the transient model are subsequently used to define the boundary conditions used by a steady-state, reacting 3D CFD model which computes the local mixing and CW/BW agent destruction for a prescribed instant in time. The CFD models include the detailed chemistry and physics required to analyze the RKIS. These models include the full coupling of turbulent fluid mechanics, all modes of heat transfer (including radiation) and equilibrium combustion chemistry for agent and fuel. After establishing the combustion flow field, a post-process calculation is used to evaluate CB agent destruction.

The model of the RKIS is described in detail elsewhere[6]. Figure 7 shows example model outputs compared to RKIS experimental results for the kiln exit temperature and the secondary combustion chamber (SCC) exit oxygen (O_2) concentration, using carpet bundles as the model input feed. The model does a reasonable job predicting the overall transient behavior while the RKIS is burning carpeting. These example plots show kiln exit temperature, however, many output parameters are available from the model results, including various temperatures, velocities, and species concentrations within the kiln.

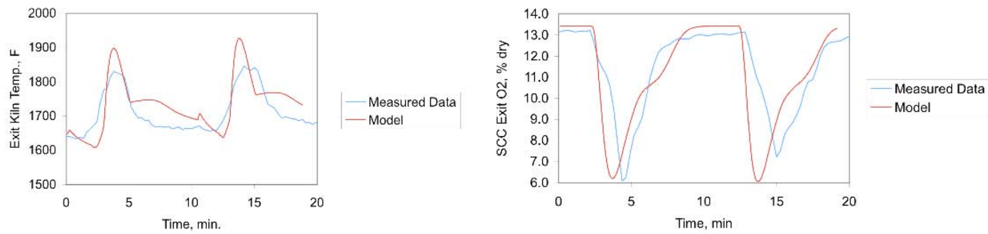

Figure 7. Model Predictions vs. RKIS Measured Parameters.

The model was then used to predict BW agent destruction from spores bound on a carpet bundle. Because the bench-scale experiment for the carpet samples was yet to be completed, the BW agent destruction kinetics bound on ceiling tile were used for these preliminary runs. Figure 8 shows the model predictions for spore destruction, using both the Arrhenius-type fit and the Z value type fit. This prediction is in terms of the total number of initial spores that were converted to “dead” as per Equation 1. Note that total spore destruction is predicted to occur between 4 and 5 minutes. This is entirely consistent with the experimental results from the RKIS.

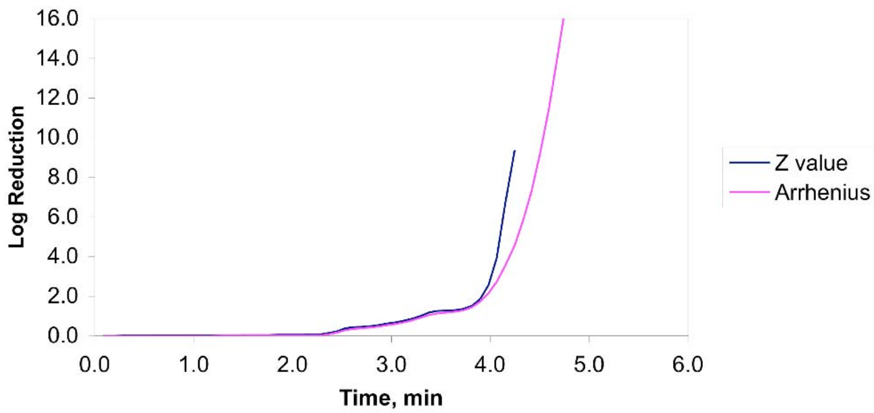

Figure 8. Predicted Log Reduction of Spores

Figures 9 to 11 show visualizations of the gas temperature field from sample runs on the RKIS model, the med/path incinerator model, and the hazardous waste burning rotary kiln models, respectively. Data available for interrogation from the CFD model includes gas temperature, velocity, agent concentration, combustion products (major and minor species), pressure as well as wall and equipment surface temperatures and incident heat fluxes. These diagrams show temperature distributions of the various combustors. Note the outlines of the burning carpet bundles in Figures 9 and 10.

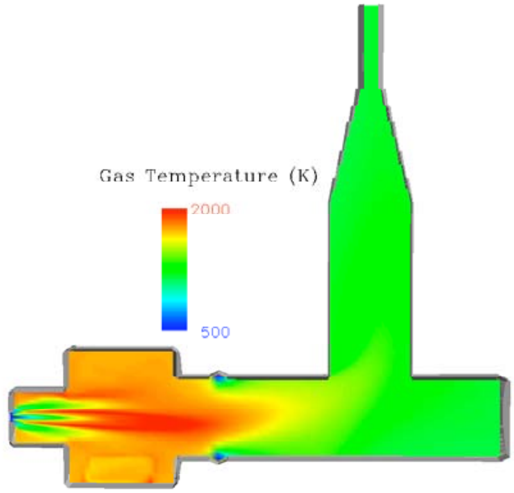

Figure 9. A Sample Predicted Gas Temperature Field In The EPA RKIS.

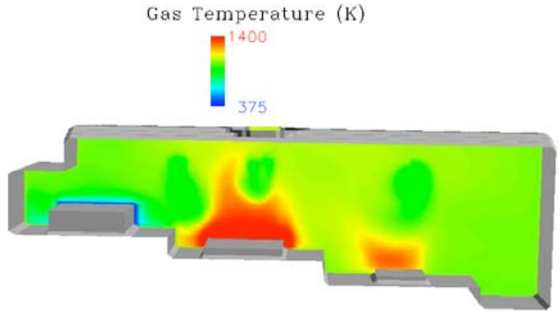

Figure 10. A Sample Predicted Gas Temperature Field In The Med/Path Incinerator Primary Chamber.

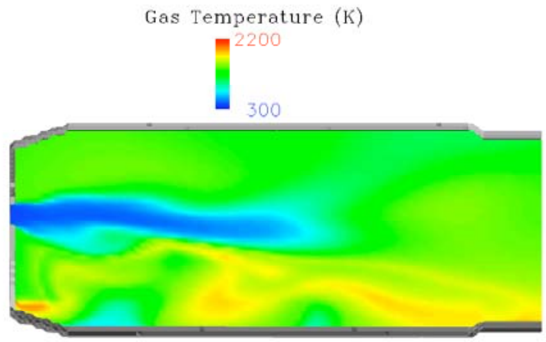

Figure 11. A Sample Predicted Gas Temperature Field In The Hazardous Waste Kiln Primary Chamber.

CONCLUSIONS

A combined experimental and theoretical program has been initiated to understand and predict the behavior of CB agents bound on building decontamination residue in thermal incineration systems. Bench-scale experiments were used to develop kinetics of BW agent destruction. Pilot-scale experiments were used to calibrate the models. Initial comparisons between model predictions and agent simulant destruction show reasonable agreement.

Future work will include:

- Pilot-scale CW agent simulant experiments and model comparisons
- Inclusion of outdoor materials to the matrices being studied
- Addition of stoker-fired incinerators to the modeling efforts

- Full-scale testing to compare model results to the full-scale incinerators upon which the models were based

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