

## **The Use of Experiments and Modeling to Evaluate Incineration of Chemical Warfare Agent Simulants Bound on Building Materials**

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### **ABSTRACT**

In the event of a terrorist attack with chemical warfare agents (CWAs), large quantities of materials, both indoor and outdoor, may be treated by thermal incineration during the site remediation process. CWAs in general are not particularly thermally stable and decompose readily in a high temperature combustion environment. Potential difficulties exist, however, in thermally processing waste building materials from a post-CWA event site remediation due to the refractory nature of many materials found inside and outside buildings, and the potential impacts that waste packaging at the site may have on the behavior of these materials and residual agent destruction in combustion systems. This paper reports on a study to examine the thermal decomposition of surrogate CWAs (in this case, Malathion) in a laboratory reactor, analysis of the results using reactor design theory, and subsequent scale-up of the results to a computer-simulation of a full-scale commercial hazardous waste incinerator processing ceiling tile contaminated with residual Malathion. The heating rates that the reactor was subjected to were based on previously determined heating rates of wet ceiling tile in a pilot-scale rotary kiln incinerator simulator, and are intended to simulate the thermal processing of building materials containing trace amounts of CWAs.

### **INTRODUCTION**

After a building or outdoor area has gone through decontamination activities following a terrorist attack with chemical warfare agents (CWAs), biological warfare agents (BWAs), or toxic industrial chemicals (TICs), there will be a significant amount of residual material and waste to be treated and/or disposed. Although it is possible that the materials to be disposed of will already have 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 either generated during cleanup activities or removed from the contaminated site. Thermal incineration is likely to be an important technology considered for treatment/disposal of these wastes. Thermal incineration facilities typically operate with gas temperatures above 800 °C, although due to the refractory nature of some building materials such as ceiling tile, significant time may elapse between the introduction of the material into the incinerator and the time where the core of the material bundles reaches temperatures approaching the gas temperatures. Previous work suggests that for some materials, times greater than 30 minutes at gas phase

temperatures in excess of 800 °C are needed before the core temperature of the material bundle exceeds 300 °C [1].

The U.S. Army operates several facilities for the purposes of chemical demilitarization activities. These facilities offer state-of-the-art technology for high temperature thermal destruction of CWAs [2]. Although it is technically possible that these military facilities may be made available in the event of a domestic CWA event, their operation is governed by very stringent regulatory controls and international treaties [3] on what materials they are allowed to process, and, at any rate, the materials handling systems of these military combustors are optimized for processing munitions, with relatively small charges containing pure CWA, not building materials, where the relative quantity of waste may be very large and the concentration of the bound CWAs may be very small. The more likely scenario for CWA-event-generated waste treatment and disposal is via hazardous waste incineration in a RCRA-permitted incinerator followed by disposal in a RCRA Subtitle-C landfill.

Although CWAs are not particularly thermally stable [4], and are readily destroyed 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 residual agent to escape the incinerator due to bypassing the flame zones, cold spots, and incomplete penetration of heat through the combustion bed. In particular, the refractory nature of many of the building materials used in construction (e.g., ceiling tiles) may inhibit penetration of heat into the bed within the nominal solid-phase residence times in a typical incineration system. The fact that a given incineration system is operating at high temperatures may not be sufficient to ensure complete destruction of chemical/biological (CB) agents. Previous experimental and modeling work suggests that complete destruction of building material-bound CWAs can be achieved once the core temperature of building materials exceeds 300 °C [5].

In the early 1990's, EPA performed testing of commercial medical waste incinerators [6] 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. 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 CB contaminated indoor and outdoor materials [7], initially including carpet, ceiling tile, and wallboard as model materials. Tests have been performed at bench- and pilot-scale [1, 8, 9], and a computer model has been developed to predict the behavior of building materials contaminated with CB agents in the EPA's research combustor and three commercial incinerator designs [10]. Work to date has focused on BWA destruction. A new phase of the research is being initiated to examine issues related to thermal destruction of indoor/outdoor building materials contaminated with residual CWAs in thermal incinerators. Initial modeling studies have been performed in an effort to scope out potential experimental conditions [5]. These modeling studies involve using a combination of a computational fluid dynamics and chemical kinetics approach to modeling the EPA's pilot-scale Rotary Kiln Incinerator and three commercial-sized incineration facilities, using a methodology developed as part of a Department of Defense Small Business Innovative Research project to assess CWA thermal destruction in the army's chemical demilitarization facilities [11, 12, 13]. This paper describes the initial experimental results.

## EXPERIMENTAL

The experiments consisted of a series of tests using a chemical warfare agent (CWA) simulant (the first simulant to be tested was Malathion [CAS 121-75-5], see Figure 1) under a thermal environment experienced by building materials (wet ceiling tile) loaded into the EPA's Pilot-Scale Rotary Kiln Incinerator Simulator (RKIS) [1], using a gas chromatograph oven (HP 5890 Series II), which not only provided a constant temperature during testing, but also multiple ramps. CB Simulant Carrier Chambers (see Figure 2) made of 304 stainless steel pipe and equipped with a thermocouple, containing carefully measured amounts of a CWA simulant, were placed into the oven for a range of equilibration times at the base temperature of 100 °C, and at different ramp-up rates to 400 °C. Samples were collected and submitted to the EPA's National Risk Management Research Laboratory's Air Pollution Prevention and Control Division (APPCD) Organics Support Laboratory for analysis. The CB Simulant Carrier Chambers were sealed (i.e., no gas flow through the chambers was allowed).

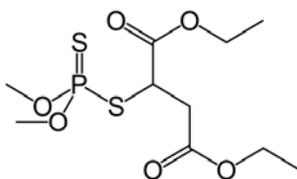


Figure 1. Malathion

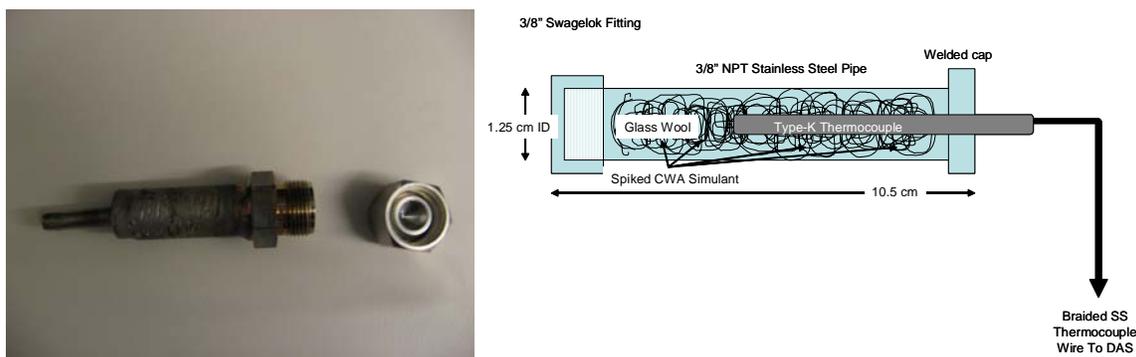


Figure 2. CB Simulant Carrier Chamber

A CWA simulant was carefully dispensed into the stainless steel pipe through a Swagelok fitting using a syringe (20  $\mu\text{L}$  of a 300  $\text{ng}/\mu\text{L}$  stock solution of Malathion in hexane, yielding an initial mass of 6,000  $\text{ng}$  per chamber). The chamber was then placed into the oven, ramped up to the final temperature at a set rate (5 or 10  $^{\circ}\text{C}/\text{min}$ ), then maintained at that temperature for a set amount of time. The temperatures were automatically logged by a data acquisition system during testing. A conceptual diagram of the temperature program is shown in Figure 3.

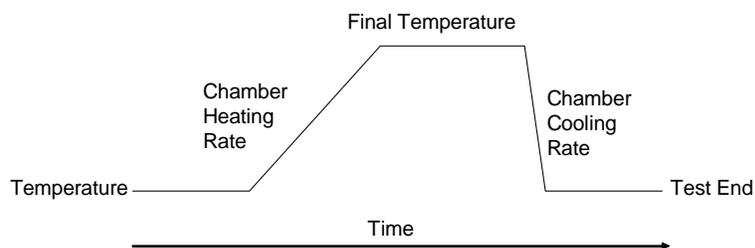


Figure 3. Conceptual Temperature Program for CB Simulant Carrier Chamber

At the completion of each test, the heated CB Simulant Carrier Chamber was removed from the oven and quickly quenched in a methanol-dry ice solution. The temperature of the methanol-dry ice mixed solution is approximately  $-70\text{ }^{\circ}\text{C}$ , enabling the pipe temperature to rapidly fall to  $20\text{ }^{\circ}\text{C}$  or below within 2 minutes, quenching any decomposition reactions occurring in the chamber so that the measured removal time equaled the total residence time of the chamber in the oven.

After quenching, the glass wool was collected from the chamber in a glass vial with a hexane solution. The chamber was rinsed three times with the hexane solution, which was placed into a glass vial using a glass funnel. Ten mL of total hexane was used and a 0.5 mL sample was sent to the APPCD Organics Support Laboratory for analysis by gas chromatography / mass spectrometry (GC/MS) using EPA Method 8270 [14] to quantify the remaining CWA simulant and decomposition by products using deuterated Malathion as the internal standard.

An inventory of CB Simulant Carrier Chambers was fabricated for use in these experiments. The chambers were reused after rinsing and heating in an oven at  $450\text{ }^{\circ}\text{C}$  for 6 hours. Fresh glass wool was used for each run.

## RESULTS AND DISCUSSION

The results are shown in Table 1. The temperature inside the pipes was continually measured and the exposure time started counting ( $t=0$ ) at the point where the difference between the oven temperature and the temperature inside the pipe enclosure reached 90% of the gas temperature. On some runs, there was a significant amount of variability for seemingly identical experimental conditions. It is possible that these are due to leaks that were not detected but still existed. For future experimental series, additional replicate runs will be performed to minimize the impact of such deviations. A potential approach that could be used in the future to justifiably eliminate these outlier runs would be to perform 5 replicate runs and use the median result rather than the mean result to develop the Arrhenius plots. This approach was used by the investigators in the past when analyzing data from the EPA Rotary Kiln Incinerator Simulator, where uncontrollable aspects of the experimental methods (e.g., the orientation of containers manually fed into the incinerator once they settle in the bed) resulted in occasionally significant outliers among repeat experiments that served to confound data analysis [15].

Table 1. Experimental Results

Max Oven Temperature (°C)	Exposure Time (min)	Malathion Concentration (µg/L)
125	15	5104
125	15	5405
125	15	5451
125	20	5329
125	20	5898
125	20	1980
125	30	4661
125	30	5132
125	30	5393
150	12	4431
150	12	3397
150	12	4639
150	15	3700
150	15	3845
150	15	4396
150	20	3516
150	20	3518
150	20	4069
150	30	1679
150	30	714
150	30	3777
175	15	2978
175	15	1886
175	15	2293
175	20	1220
175	20	2724
175	20	1623
175	30	765
175	30	1057
175	30	912

The pipe enclosure can be treated as a batch, constant volume reactor [16]. The initial concentration of Agent A (in this case, Malathion) is  $C_{A0}$ , and the concentration at any given time is  $C_A$ . A material balance over the reactor for Agent A gives:

$$\text{Input} - \text{Output} = \text{Accumulation} + \text{Disappearance} \quad (1)$$

For a batch reactor, input = 0 and output = 0, therefore

$$0 = \frac{dN_A}{dt} - r_A V \quad (2)$$

Where  $N_A$  is the number of moles of Agent A at any given time (moles),  $t$  is the time (min),  $r_A$  is the rate of reaction of Agent A (moles/min), and  $V$  is the volume of the reactor (L).

Rearranging,

$$-\frac{dN_A}{dt} = -r_A V \quad (3)$$

If  $V$  is constant,

$$-\frac{dC_A}{dt} = -r_A \quad (4)$$

Where  $C_A$  is the concentration of A (moles/L). Integrating this expression yields:

$$t = - \int_{C_{A0}}^{C_A} \frac{dC_A}{(-r_A)} \quad (5)$$

If the assumption that Agent A undergoes a first order one-step irreversible decomposition reaction is made from a global kinetic standpoint, where  $-r_A = kC_A$ , ( $k$  in units of  $\text{min}^{-1}$ ) then:

$$kt = \ln\left(\frac{C_A}{C_{A0}}\right) \quad (6)$$

Therefore for zero order if we plot  $C_A$  vs. time for each temperature that was tested, a linear fit of the curve yields  $-k$  as the slope of the line ( $k$  varies with temperature) and for first order if we plot  $\ln\left(\frac{C_{A0}}{C_A}\right)$  vs.  $t$ , a linear fit of the curve yields  $k$  as the slope of the line, as shown in Figure 4.

Note that for Figure 4 the  $t=0$  time represents the time at which the reactor was operating isothermally.

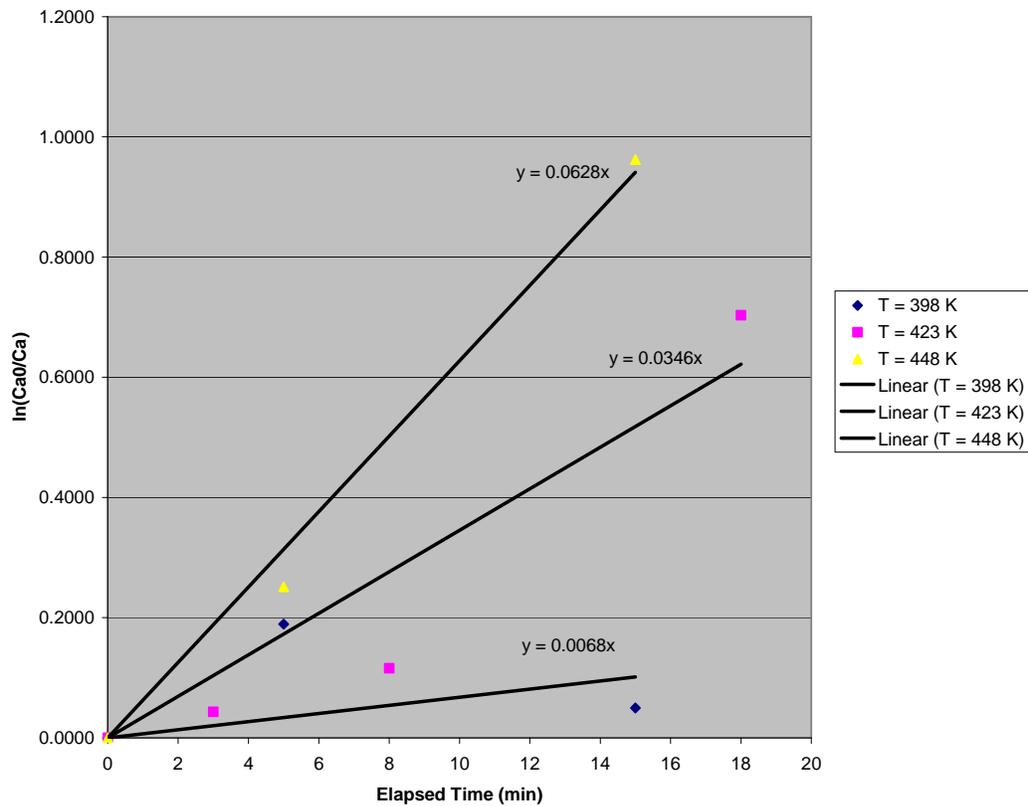


Figure 4. Plot of  $C_A$  vs.  $t$  for Malathion Tests; First Order Kinetics

If we assume that  $k$  is of the Arrhenius form, then

$$k = k_0 e^{-E_a/RT} \quad (7)$$

with  $k_0$  being the Arrhenius pre-exponential term, and  $E_a$  being the activation energy of the reaction. Thus,

$$\ln(k) = \frac{-E_a}{R} \frac{1}{T} + \ln(k_0) \quad (8)$$

Therefore, if  $\ln(k)$  is plotted vs.  $1/T$ , a straight line should result, with the slope of the line being  $-E_a/R$  and the Y-intercept of the line being  $\ln(k_0)$ . Figure 5 shows the plot of these lines for first order kinetics.

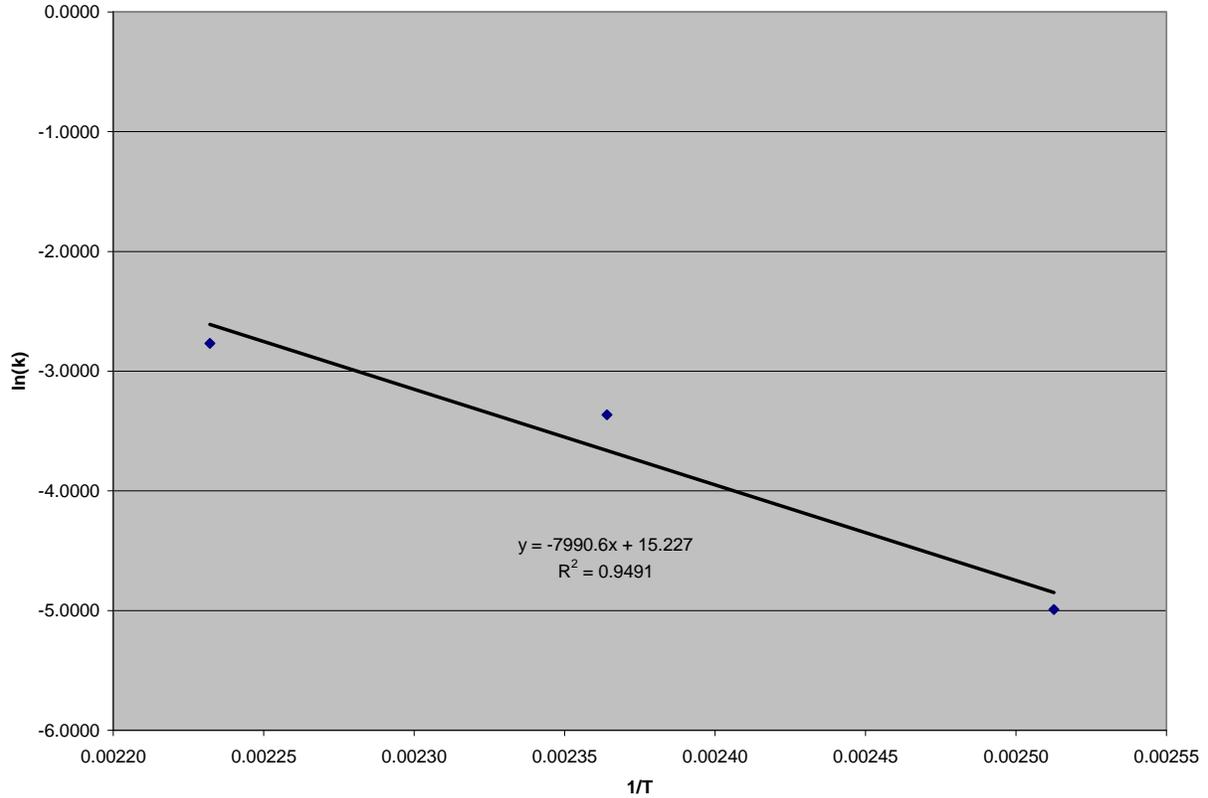


Figure 5. Arrhenius Plot of  $\ln(k)$  vs.  $1/T$ , First Order Kinetics

These fitted  $k$  values can then be used to predict the residual amount of Agent A present in a constant volume reactor as a function of time and temperature. Using Equation 6 evaluated at each time step and incrementally calculating the amount of Agent destroyed, Figure 6 can be produced (for first order kinetics).

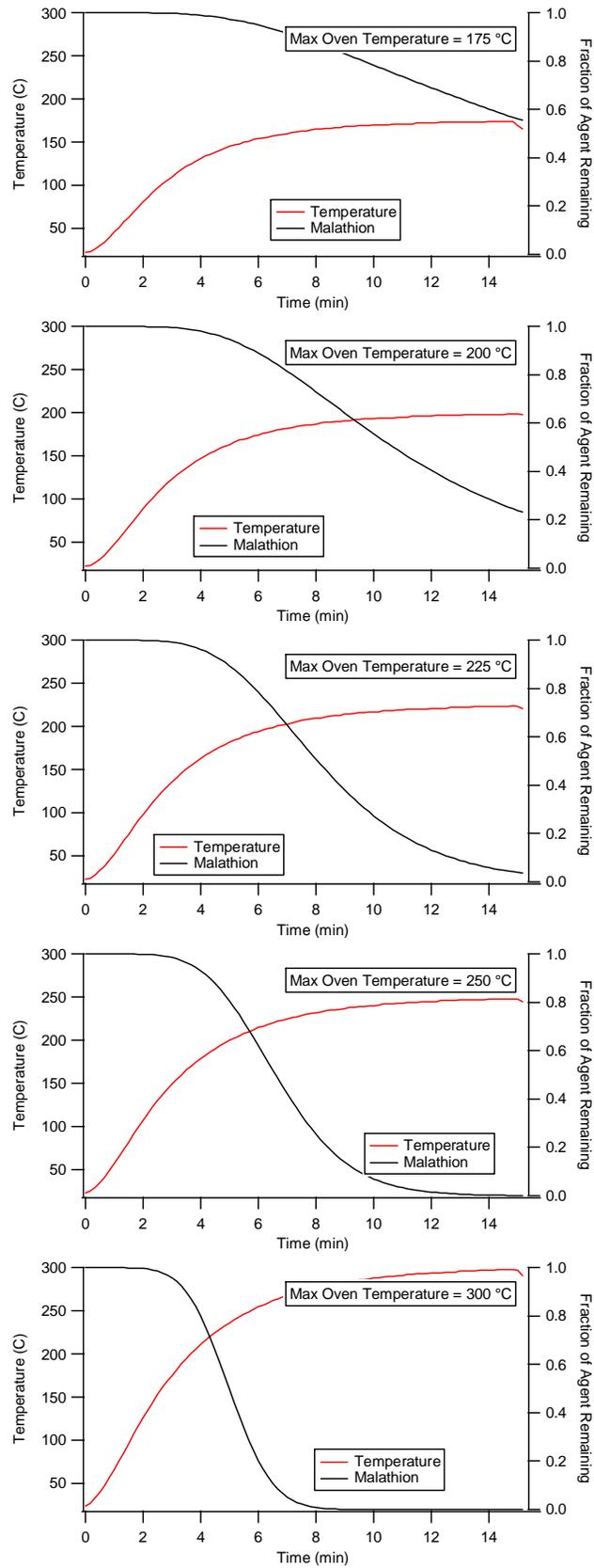


Figure 6. Predicted Malathion Destruction, First Order Kinetics

## CONCLUSIONS

A series of experiments have been performed to evaluate the thermal destruction of Malathion bound on building materials. The experiments were performed in a small reactor inside GC oven using heating rates previously determined in experiments measuring wet ceiling tile bundle center temperatures while being processed in a pilot-scale rotary kiln incinerator. Malathion was chosen for its properties as a simulant for chemical warfare agents. The overall goal of this experimental program is to investigate issues regarding thermal destruction of chemical warfare agents bound on common building materials that may be generated as waste in a response after a terrorist attack with chemical warfare agents.

The experiments were performed in small constant-volume reactor vessels at the bench-scale, using heating rates typical of those found inside bundles of building materials in a pilot-scale hazardous waste incineration system and fit to a first-order Arrhenius expression. For the most part, the results from run to run had a good degree of reproducibility; however, there were occasional significant deviations from run to run. It is believed that these outliers may be due to leakage from the reactor vessels. Future experiments will attempt to eliminate these apparent outlier runs by performing additional replicate experiments and utilizing the median value rather than the mean value.

The results from these experiments will be used to guide a future series of experiments done in the pilot-scale hazardous waste incineration system simulated by the bench-scale experiments to scale-up these experiments to predict behavior of building-material-bound Malathion in practical-scale incineration systems.

## DISCLAIMER

The U.S. Environmental Protection Agency through its Office of Research and Development managed the research described here. It has been subjected to the Agency's review and has been approved for publication. Note that approval does not signify that the contents necessarily reflect the views of the Agency.

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