DEVELOPMENT OF A LOW-TEMPERATURE CATALYTIC OXIDATION SYSTEM FOR DESTRUCTION OF CHEMICAL WARFARE AGENTS

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ABSTRACT

This project is to develop a low-temperature microwave catalytic oxidation system that will effectively decontaminate air containing aerosolized or gaseous chemical agents (CWAs). To protect personnel in shelters, catalytic oxidation systems should (1) destroy CWAs in air at low temperatures to avoid NOx formation, (2) remove sulfur dioxide produced from the oxidation of CWAs containing sulfur atoms, (3) operate for an indefinite period of time, and (4) destroy biological agents at low temperatures. This system will be used to supply clean breathing air to a bunker or other facility in a war zone that has been contaminated with chemical weapons. This work will be performed in two phases. Phase I of the experimental effort is to obtain the data needed to design and fabricate a prototype CWA catalytic oxidation system. During Phase II work the prototype microwave air decontamination system will be constructed and tested both at CHA Corporation and at a selected location to demonstrate the effectiveness of the microwave air decontamination system. Experimental results obtained to date indicate that microwave catalytic oxidation will be capable of destroying more than 99.5% of CWAs in air.

1. INTRODUCTION

During attacks by chemical and biological weapons, personnel in temporary and permanent shelter(s) are dependent on a constant supply of clean air. Without any effective means to destroy these chemical and biological warfare agents (CWAs), ventilation systems can be easily contaminated, making personnel within extremely vulnerable to incidental or malicious events. Current methods such as high-temperature catalytic oxidation require a significant amount of energy to heat the air to temperatures greater than 260–400°C to oxidize CWAs in air effectively. In addition, catalytic oxidation requires hours of startup time to reach steady-state operation and completely oxidize CWAs in air, and the catalysts are degraded by phosphorus and often by sulfur oxides and other by-products. Microwave energy is a form of electromagnetic energy that penetrates deeply into many materials, transforming energy directly into heat by exciting absorbing molecules into rapid oscillatory motion. With such unique attributes, microwaves offer several practical advantages, including reduced thermal gradients, selective heating, rapid energy decomposition, and acceleration of certain chemical reactions.

The Air Force Research Laboratory awarded a Small Business Innovation Research Phase I grant to CHA Corporation to develop a microwave low-temperature catalytic oxidation system that will effectively decontaminate air containing aerosolized or gaseous CWAs. The microwave catalytic oxidation system will operate at temperatures that do not generate any significant toxic by-products and can operate continuously for longer than 100 hours in a heavily contaminated environment. Also, this microwave catalytic oxidation system will be able to destroy more than 90% of the gaseous and aerosolized CWAs in air and it is equipped with microwave-regenerable filters to capture any harmful oxidation byproducts, such as sulfur dioxide and nitrogen oxides.

In this scenario, the main problems that need to be addressed focus on effectively destroying and removing the CWAs in air, up to 99.9% destruction and removal efficiency, creating a low-temperature operating system, and removal of the sulfur dioxide produced during the destruction of organic sulfur, a common component found in CWAs. Also, the interaction of phosphorus oxides such as P_2O_5, the oxidation byproduct of phosphorus CWAs, with the catalyst substrate should be minimized to avoid catalyst poisoning. The system must

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be able to operate at low temperature to avoid creation of NOx, a harmful chemical, and reduce energy consumption due to heating and then cooling the incoming air to buildings or shelters.

Simulated chemical agents will be used for the laboratory experiments. Yang et al (1992) listed several of these chemical agent simulants. For example, the monofunctional derivatives of mustard gas, RSCH2CH2Cl (R = methyl, ethyl, or phenyl) and RSCH2CH2X (X = tosylate, mesylate).

+A series of organophosphorus esters were used to simulate the G agents. These include dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), diisopropyl phosphorofluoridate (DFP), and *p*-nitrophenyl diphenylphosphate (PNPDPP). For the initial experiments we will use the diethyl sulfide (DES) to simulate HD gas and DMMP to simulate VX gas.

A comprehensive test plan was prepared to systematically investigate the effects of various parameters on the destruction efficiencies of selected chemical species in air. This report presents the results of the initial experimental investigation.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 Microwave Reactor Systems

Two microwave reactor systems have been designed and fabricated for performing the CWA simulant destruction tests. The first, a lab-scale reactor, will be used to conduct the catalyst selection tests and parametric studies. The small scale of the reactor allows for adequate testing of the catalyst properties while using only a small quantity of said catalyst. It consists of an aluminum waveguide that houses an 11/16-inch quartz tube. The waveguide is attached to a variable power Cober microwave generator. The microwave generator is capable of producing 0–3 kW microwave power, but will be run at powers less than one kW for the small-scale testing. Using the lab-scale system, the inlet concentration, outlet concentration, and outlet temperature will be measured. Figure 1 shows a photograph of the lab-scale microwave reactor system.

The second microwave reactor system (Figure 2) will be used for conducting a series of selected experiments. This bench-scale system consists of a 2.36-inch diameter quartz tube, 24 inches in length, located inside the ¼-inch diameter copper helix, which serves as a non-resonant cavity. This microwave reactor is capable of handling 12 times higher inlet air flow rate than the lab-scale reactor. The reactor is powered by two 1-kW magnetrons for a fixed system power of 2 kW. Using the bench-scale system, the inlet concentration, outlet concentration, outlet temperature, and column pressure drop will be measured. This will allow a substantial

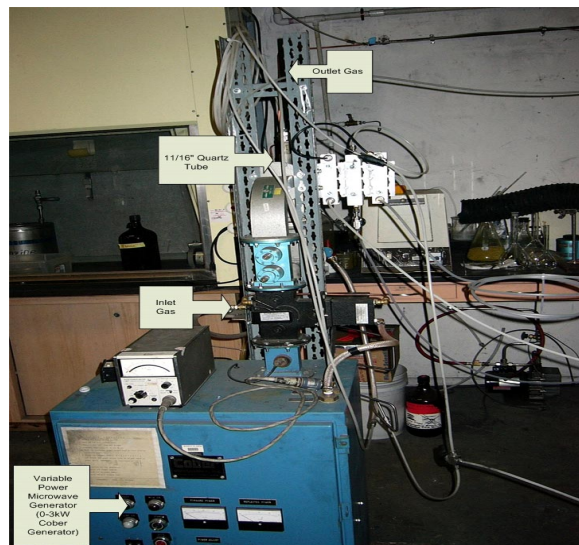amount of data to be collected for the main body of testing.

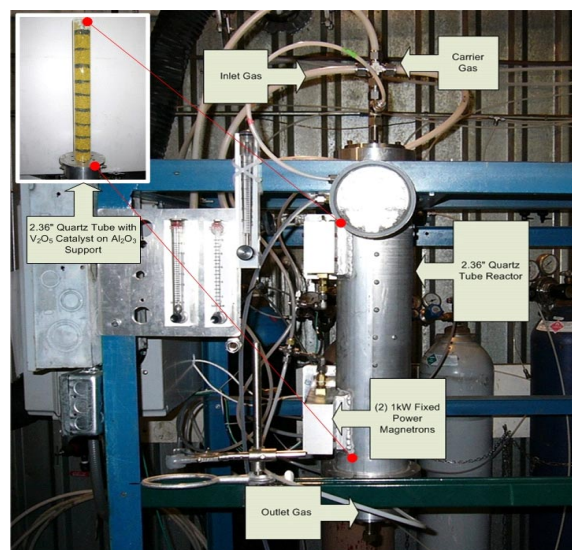**Figure 1: Lab-Scale Microwave Reactor System**

Figure 2: Bench-Scale Microwave Reactor System

2.2 Experimental Procedure

All of the parametric study tests are run using the same procedure to ensure that the results are fit for comparison. First, a feed concentration is determined. Once this number is steady, the lines are flushed of chemical. Once the lines are flushed, the reactor is warmed up for five minutes with no flow. The reactor is warmed at the same microwave power as the test is to be run at. Once the warm up period is completed, flow to the reactor is started. The initial flow to the reactor will contain the same chemical concentration as was measured earlier. Flow is started after the reactor is warmed up to reduce the amount of chemical in the

system before the reactor is started. This greatly reduces the response time of the system. After flow to the reactor is started outlet temperature and concentration measurements are taken at regular intervals as follows (in minutes):1, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, and 80. All experiments will be run for 80 minutes and measurements will be taken at the same intervals. After the experiment is concluded, air flow and microwave power are kept to the reactor while chemical flow is ceased. After 10 minutes, a new zero point for the analyzer is taken. This is done to ensure reliable results as the microwave Cat-Ox system also destroys some of the hydrocarbons in the incoming air stream. Once the final zero is recorded, the data are arranged and reported. The catalyst bed will be changed out after every test to ensure that the data aren't significantly affected by changes in catalyst activity. Originally the catalyst was changed every four tests, but there was evidence of activity changes in the catalyst between tests. During the test, the outlet simulant concentration is monitored by a VIG Industries F.I.D. Model-10 Total Hydrocarbon Analyzer. This instrument is accurate within 0.1 ppm (part per million). Additionally, during the test, inlet flow, inlet chemical concentration and outlet temperature are recorded.

3. RESULTS AND DISCUSSION

3.1 Evaluate and Select Oxidation Catalysts

The catalyst should absorb microwave energy to perform the microwave-induced chemical reactions. Most catalyst substrates, such as Al_2O_3, do not absorb microwave energy. Since silicon carbide (SiC) is an excellent microwave absorber, commercially available catalysts were mixed with SiC to carry out microwave-induced chemical reactions. Three different substrates were used to prepare the V_2O_5 catalysts for a series of tests to evaluate their performance of the oxidation reactions. The first catalyst was a V_2O_5 catalyst on silicon carbide. The second was a V_2O_5 catalyst on 50%SiC/50%Al_2O_3 support. The third was a V_2O_5 catalyst on Al_2O_3 support. An air stream containing either 300 ppm DMMP or 600 ppm DES was used to evaluate these three substrates for the V_2O_5 catalyst. Air flow rates of 35 bed volume per minute and 300-W microwave power were used for these experiments. Figure 3 and 4 present the results obtained from this series of tests.

The tests using the SiC-based vanadium catalyst showed very good removal and destruction efficiency (DRE = 97.5%). However, the V_2O_5 catalyst was stripped from the particle surfaces, which led to significant loss in activity over time.

A better DRE (99%) was obtained from tests using the 50%SiC/50%Al_2O_3-based vanadium catalyst, probably due to higher surface area. The V_2O_5 did not appear to be stripped from the alumina support.

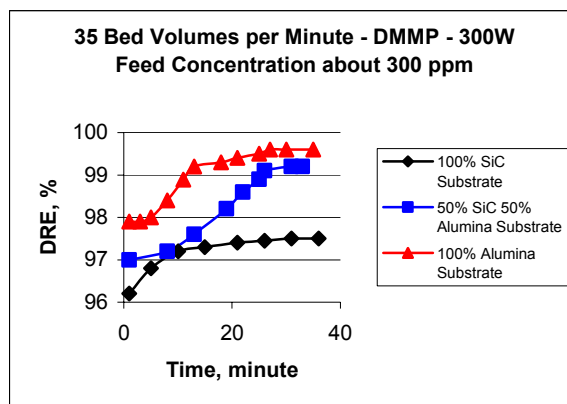However, the catalyst particles at the top portion of the bed turned black.

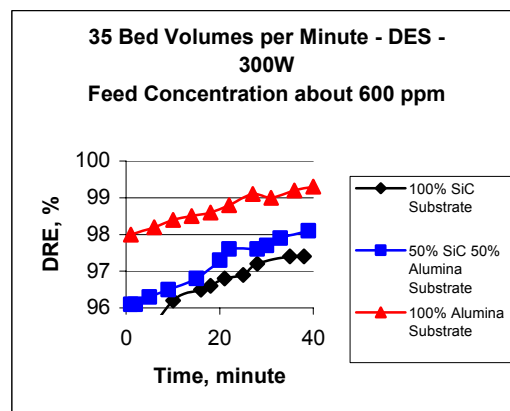**Figure 3 Percent Destruction of DMMP for Three Different V_2O_5 Catalysts**

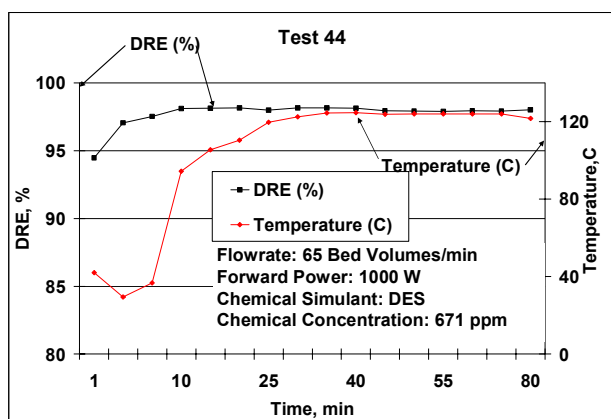**Figure 4 Percent Destruction of DES for Three Different V_2O_5 Catalysts**

The best DRE (>99.5%) was obtained from tests using the alumina-based vanadium catalyst. It appears that higher catalyst surface area yields greater DRE. Alumina alone does not absorb microwave energy. However, alumina impregnated with the V_2O_5 absorbs enough microwave energy to induce the oxidation reaction. It is not an excellent absorber of microwave energy but does well enough when low microwave power is used. Mixing a small amount of SiC with catalyst will be sufficient to initiate microwave-induced catalytic oxidation. Consequently, it was decided to perform parametric studies using the alumina-based V_2O_5 catalyst until better catalysts are found

3.2 Microwave Catalytic Oxidation of DES

A first series of experiments for the parametric studies were conducted using the V_2O_5 catalyst and DES as the CWA simulant. As soon as the DES tests are completed, the second series of experiments using DMMP as the CWA simulant will begin. These series of tests are a part of a comprehensive test matrix in our test
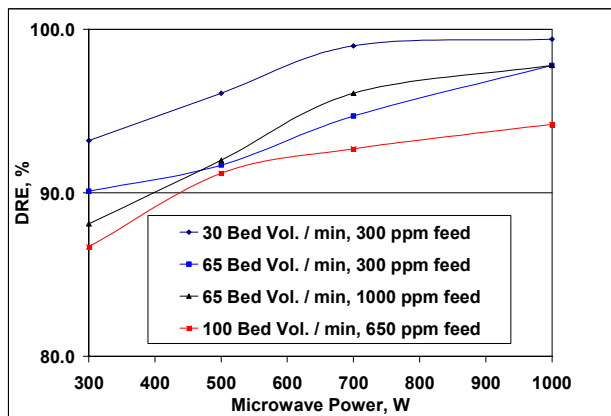
plan to determine the effects of operating conditions of the system on DREs, as well as the proper catalyst for use in the system. This test matrix is designed to systematically alter the values of flow rate, microwave power, chemical concentration, and chemical simulant. This should give a complete view of the parameters' effects on the microwave catalysis performance.

Figure 5 shows the DRE and the outlet air temperature as a function of time for a typical test. As shown in this figure, the DES outlet concentration reached the steady-state concentration within ten minutes after the experiment started. During most of experiments using DES, the outlet concentration reached steady state within 5–10 minutes. It took approximately 30 minutes for the outlet gas temperature to reach a steady-state value. All of the tests were performed using DES as the CWA simulant, and using a 10% by mass V_2O_5 catalyst impregnated on alumina beads.
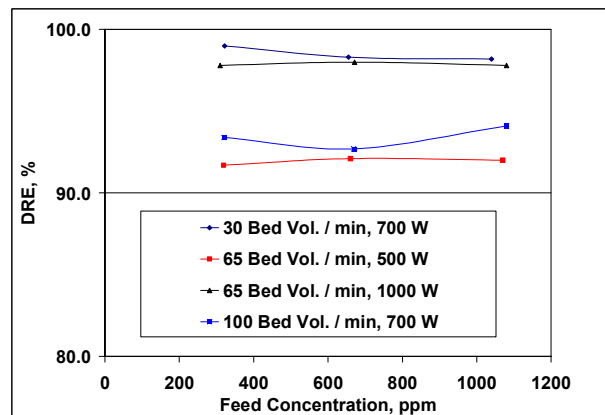

Figure 5 Typical Parametric Test Output

Figure 6 presents the DRE as a function of microwave power. The DRE increases as increasing microwave power applied to the reactor. This figure clearly illustrates that microwave power is one of the major controlling parameters for microwave catalytic oxidation of chemical warfare agents in air streams.
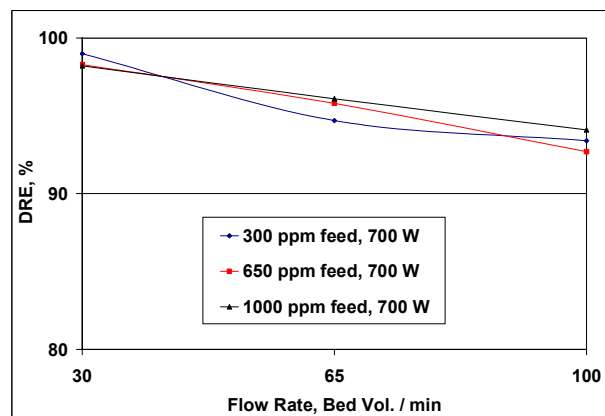

Figure 6 DRE as a Function of Microwave Power

The next variable is feed concentration. Figure 7 illustrates the effect of feed concentration on DRE. As shown by the representative set of data in this figure, feed concentration seems to have very little effect on the overall DRE of the system.

Figure 7 DRE vs. Feed Chemical Concentration

The relationship between DRE and inlet flow rate is shown in Figure 8. The air flow rate is expressed in units of bed volumes per minute, which was obtained dividing the bed volume (ft^3) by the inlet air flow rate (ft^3/min). As shown in the figure, there is a strong correlation between inlet air flow rate and DRE. As expected, the DRE decreases as the inlet air flow rate increases.
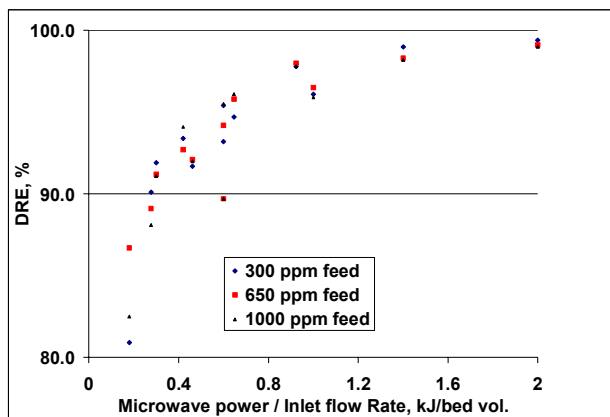

Figure 8 DRE as a Function of Inlet Flow Rate

Figures 6–8 clearly indicate that microwave power and inlet air flow rate are both major controlling parameters for microwave catalytic oxidation of chemical warfare agents. Finally, a combined correlation using the inlet flow rate and microwave power was created. Since the DRE increases with increasing microwave parameter and decreases as the inlet air flow rate increases, this parameter should be the quotient between microwave power and inlet flow rate giving rise to a parameter with the units kJ/bed vol. It should be noted that microwave power and inlet flow rate are given in term of kJ/s and the bed volume per minute,

respectively. Consequently, the unit of this combined parameter is kJ/bed volume. The bed volume in this parameter is in ft^3. The DRE is plotted as a function of this parameter in Figure 9.

Figure 9 shows a good correlation between the selected parameter (power/flow rate) and DRE. This is expected considering that microwave power and inlet flow rate were shown to be the major controlling parameters. This correlation will be used in the design of the microwave prototype system.

Figure 9 DRE as a Function of Microwave Power / Inlet Flow Rate

3.3 Future Experimental Work

The next series of experiments will be parametric studies using the V_2O_5 catalyst and DMMP to determine the effects of the operating parameters on DREs. Once the parametric studies are complete, we will conduct a longevity test using DES and DMMP. This will be used to determine if the V_2O_5 catalyst can withstand the reactor conditions for an extended period of time.

There is a concern that the V_2O_5 catalyst could be susceptible to phosphorus poisoning by plating of P_2O_5 or its polymers. From the longevity tests, used alumina-based V_2O_5 catalyst samples will be prepared for testing to determine if the surface is being chemically altered. In addition to used catalyst samples, fresh catalyst samples and fresh catalyst coated with P_2O_5 samples will be sent to the University of Florida for analysis. Several analyses will be carried out to characterize the potential interaction between P_2O_5 and the catalyst using facilities at the Major Analytical Instrumentation Center at UF. The analyses include Scanning Electron Microscopy (SEM; JEOL JSM 6400), Energy Dispersive Spectroscopy (EDS; Oxford OPAL system), X-Ray Diffraction (XRD; Philips APD 3720) and X-ray Photoelectron Spectroscopy (XPS; Perkin–Elmer PHI 5100 ESCA System). SEM provides a surface morphology comparison that helps visualize deposited material. EDS mapping gives information regarding surface distribution of elements. If P exists on the

surface, the distribution can be mapped. XPS provides information about surface elements and their binding nature. XRD identifies crystalline species.

If the catalyst surface is not being chemically altered, optimization tests with the bench-scale reactor can be started using the alumina-based V_2O_5 catalyst. If there are chemical changes to the catalyst surface, namely P_2O_5 plating, calculations need to be made to determine the catalyst life in a heavy aerosol CWA environment. This will determine if the catalyst, at the previously set operating conditions, is still a viable candidate. If the catalyst life is acceptable, testing can proceed. If the catalyst life is not acceptable, the operating conditions will be altered and testing of the alternate operating conditions will be used to determine if the catalyst life can be extended to an acceptable value. Should it not be possible to obtain enough useful life out of the selected catalyst, a new catalyst will be selected and tested by the aforementioned method.

4. CONCLUSIONS

The initial experimental results positively demonstrate that microwave catalytic oxidation is a strong candidate for the destruction of CWAs in air at low temperatures. The microwave power and inlet air flow rate are major parameters controlling the destruction and removal efficiency. The DRE is closely correlated to the combined parameter, microwave power/inlet flow rate (kJ/bed volume). For the V_2O_5 catalyst, DREs greater than 90% were obtained with the ratio of microwave power to inlet flow rate greater than about 0.3 kJ/bed volume (ft^3).

ACKNOWLEDGMENT

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Yang, Y.C., Baker, J.A. and Ward, J.R., 1992, "Decomposition of Chemical Warfare Agents," *Chem. Rev.*, **92**, 1729–1743