1 of 1

Electrochemical Oxidation of Chemical Weapons

J. E. Surma

May 1994

**Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Richland, Washington 99352**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Summary

Catalyzed electrochemical oxidation (CEO), a low-temperature electrochemical oxidation technique, is being examined for its potential use in destroying chemical warfare agents. The CEO process oxidizes organic compounds to form carbon dioxide and water. A bench-scale CEO system was used in three separate tests sponsored by the U.S. Department of Energy's (DOE) Office of Intelligence and National Security through the Advanced Concepts Program. The tests examined the effectiveness of CEO in destroying sarin (GB), a chemical nerve agent. The tests used 0.5 mL, 0.95 mL, and 1.0 mL of GB, corresponding to 544 mg, 816 mg, and 1,090 mg, respectively, of GB. Analysis of the off gas showed that, under continuous processing of the GB agent, destruction efficiencies of better than six 9s (99.9999% destroyed) could be achieved.

Contents

Summary	iii
1.0 Introduction	1.1
2.0 Technology Description	2.1
2.1 Chemical Warfare Agent Destruction with the CEO Technology	2.2
2.2 Safety of the CEO Process	2.3
3.0 Experimental Approach	3.1
3.1 Equipment	3.1
3.2 Test Procedure	3.1
4.0 Results and Conclusions	4.1
4.1 Summary of Test Results	4.1
4.2 Conclusions	4.2

Figures

2.1 Electrochemical Oxidation Cell	2.1
2.2 Flowsheet for GB Destruction	2.3
3.1 Photograph of Bench-Scale CEO System	3.2
3.2 Schematic of Bench-Scale CEO System	3.3

Tables

4.1 Total GB Measured in Off-Gas Stream	4.1
4.2 Total GB Measured in Electrolyte from Anode Compartment After Test	4.1

1.0 Introduction

As mandated by international and U.S. law, the stockpile of chemical warfare agents in the United States must be destroyed by the year 2004. Incineration has been considered the baseline technology for destroying chemical warfare agents; however, growing interest in alternatives to incineration has led the U.S. Army to examine other potential disposal technologies.

Catalyzed electrochemical oxidation (CEO), a low-temperature electrochemical oxidation technique, has been used to destroy hazardous organic compounds and may have applicability in destroying chemical warfare agents. This technique can be used as an alternative to traditional incineration to oxidize organic compounds completely to carbon dioxide and water. The technique, developed at the Pacific Northwest Laboratory,^(a) was originally used to dissolve highly refractory oxides but has since been applied to treat hazardous organic compounds.

This report summarizes results from bench-scale tests using the CEO technique to destroy sarin (GB), a nerve agent. The tests described here were sponsored by the U.S. Department of Energy's (DOE) Office of Intelligence and National Security through the Advanced Concepts Program. The experimental work involving the actual nerve agent was performed at Battelle Memorial Institute's Hazardous Materials Research Facility in West Jefferson, Ohio. Section 2 of the report describes the CEO process and its applicability to chemical warfare agent destruction. Section 3 describes the experimental approach, and Section 4 provides the results and conclusions.

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

2.0 Technology Description

Catalyzed electrochemical oxidation is centered around the use of a regenerative oxidant in an electrochemical cell to oxidize organic compounds. The cell has two compartments, an anode and a cathode compartment, separated by a membrane separator (Figure 2.1). The organic to be destroyed is oxidized in the anode compartment using a regenerative catalyst such as the Ag(I)-Ag(II) couple. The anolyte, typically used for the silver couple, is 1 M to 4 M nitric acid; however, other acids may be used. The Ag(I) is oxidized to Ag(II) at the anode surface and then moves into the bulk anolyte solution, where it can react with the organic species present. The reduced silver (I) then returns to the anode surface and reoxidizes. The cycle is continuously repeated, maintaining a supply of oxidant in the anolyte. At the counter electrode (i.e., the cathode), a variety of electrochemical reactions are possible. Typically, the electrolysis of either nitric acid or water is carried out in the cathode compartment, producing NO_x or H_2 , respectively. Presented below are the possible electrochemical reactions that take place at either the anode or the cathode in this electrochemical process.

Figure 2.1. Electrochemical Oxidation Cell

Reactions at the Anode

Reactions at the Cathode

2.1 Chemical Warfare Agent Destruction with the CEO Technology

The destruction of hazardous organics, such as chemical warfare agents, requires a complete electrochemical oxidation process with ancillary equipment. The process uses an electrochemical cell, an ultrasonic generator, a pump, and a gas/liquid separator. Additionally, a simple off-gas treatment system ensures that all gaseous effluents are acceptable for discharge to the environment. All of these components are commercially available.

Presented below is the example of the electrochemical oxidation of GB, the agent used in the bench-scale test described here:

The balanced chemical equation shows that 26 faradays of charge are required for every mole of GB oxidized to CO_2 and the corresponding inorganic acids. This charge corresponds to an estimated power consumption of 10,000 kWh/ton of agent. It should be noted that many organics can be processed in this electrochemical system at nearly 100% coulombic efficiency (i.e., the amount of power actually used versus the theoretical amount of power required to completely oxidize the organic to CO_2 and H_2O , and possibly inorganic acids). The power consumption is relatively high; however, the system is very simple and, therefore, has a correspondingly low capital cost compared to incinerators. Figure 2.2 presents a conceptual flowsheet/material balance showing the relative quantities of products produced from the electrochemical destruction of GB. The process could be easily sized to fit the desired application. Because of its relatively simple design, it is also amenable for adaption to modular and transportable systems. The process does not pose a high risk to users or the environment as typical operating conditions involve temperatures ranging from 30°C to 80°C and ambient pressures. Oxidation of chemical warfare agents to carbon dioxide, water, and inorganic acids occurs just as it does with the traditional incineration process, but at low temperature and low pressure.

Power Consumption - 10000 kWh/ton
- @ \$0.03/kWh - \$300/ton

Figure 2.2. Flowsheet for GB Destruction

2.2 Safety of the CEO Process

The CEO technology represents an inherently safe process because of the relatively low-risk conditions under which total oxidation of chemical warfare agents takes place. Unlike incineration, during a process upset the power to the electrochemical oxidation process can be interrupted and all reactions will cease. Electrochemical oxidation is a very simple process and does not require a complex off-gas treatment system, as do high-temperature processes such as incineration. Therefore, the electrochemical oxidation process could replace incineration as a simple, safe alternative for destroying chemical warfare agents.

3.0 Experimental Approach

3.1 Equipment

A specially designed bench-scale system was used in this test (Figure 3.1). As shown in the figure, the equipment includes a three-compartment electrochemical cell and associated ancillary equipment to support the cell operation. Two of the cell compartments are used as the anode compartments and the third is used as the cathode compartment, as shown in Figure 3.2.

Pumps in each of the three loops include a pump for the primary anode, a pump for the secondary anode, and a pump for the cathode to recirculate the electrolyte solutions.

3.2 Test Procedure

Three separate agent destruction runs using the bench-scale electrochemical system were completed. The runs used 0.5 mL, 0.95 mL, and 1.0 mL of GB, corresponding to 544 mg, 816 mg, and 1,090 mg, respectively, of GB. Analyses of both the off gas from the process and the spent anolyte solution were completed for each of the three tests. A Minicam gas chromatograph (GC) was used to measure the concentration of GB in the gas stream drawn out of the scrubber. The GC was calibrated to quantitatively detect GB at a concentration of 0.0003 milligram per cubic meter (mg/m^3). The agent is introduced to the system through the primary anode compartment. The gases generated in the primary anode compartment pass through a secondary anode compartment that is arranged as a gas scrub column. The catholyte (HNO_3) recirculates in a separate loop where electrolysis of HNO_3 takes place, producing NO_x .

The anolyte solution was analyzed for residual GB following each test by first extracting any remaining GB with methylene chloride using three separate 50-mL methylene chloride contacts with the aqueous phase. The methylene chloride was concentrated, and the resultant solution was analyzed by GC with a flame photometric detector (GC/FPP) and by gas chromatography mass spectrometry (GC/MS).

Figure 3.1. Photograph of Bench-Scale CEO System

Figure 3.2. Schematic of Bench-Scale CEO System

4.0 Results and Conclusions

The results of this bench-scale test indicate that the CEO technology can successfully destroy the chemical warfare agent GB.

4.1 Summary of Test Results

Three tests were completed in the bench-scale CEO system using 0.5 mL, 0.75 mL, and 1.0 mL of GB. Tables 4.1 and 4.2 present results from the analysis of both the off gas from the CEO process and the residual anolyte solution. The off gas was analyzed using a Minicam GC to analyze for GB in the effluent of the CEO system. The total GB detected in the off gas was far below the acceptable emissions limits. This data was used to calculate the destruction efficiency of the process. As indicated in Table 4.1, the effectiveness of the process for destroying GB approaches seven 9s, i.e., 99.99999% destroyed.

The acid in the anolyte was analyzed to determine the residual concentration of GB in solution. Table 4.2 summarizes this analysis. Although GB was detected in the acid, the majority of the agent was electrochemically destroyed. It has been determined that many organic oxidations using the CEO technology follow second order reaction kinetics with respect to the organic concentration. Therefore,

Table 4.1. Total GB Measured in Off-Gas Stream

<u>Trial No.</u>	<u>Total (mg)</u>	<u>Feed (%)</u>	<u>GB Destroyed (%)</u>
1	1.59×10^{-5}	2.92×10^{-6}	99.999997
2	1.35×10^{-5}	1.65×10^{-6}	99.999998
3	7.85×10^{-7}	7.20×10^{-8}	99.9999999

Table 4.2. Total GB Measured in Electrolyte from Anode Compartment After Test

<u>Trial No.</u>	<u>Total (mg)</u>	<u>GB Destroyed (%)</u>
1	1.71×10^{-3}	99.9997
2	2.32×10^{-2}	99.9972
3	BDL ^(a)	> 99.9999

(a) Below detection limits.

near the end of a batch oxidation, such as at the end of the three tests completed for this work, the rate of oxidation drops off dramatically. In a continuous operation, the concentration of agent in the anolyte would be maintained to provide a maximum rate of reaction. As indicated from the gas analysis, even with high concentrations of agent in the anolyte, off-gas emissions are negligible. This is the case even for this nonoptimized bench-scale system.

4.2 Conclusions

The results of these bench-scale tests indicate that the CEO technology is a promising low-temperature alternative to incinerating GB. It was shown through analysis of the off gas that under continuous processing of the GB agent in the CEO system, destruction efficiencies of better than six 9s (99.9999% destroyed) could be achieved. This work clearly indicates that further investigation and optimization of the CEO technology would provide a useful alternative to incineration for destroying chemical warfare agents.

Distribution

No. of
Copies

OFFSITE

- 12 DOE/Office of Scientific and
Technical information

Mr. Dan Beatty
DOE/NN-20
1000 Independence Avenue, SW
Washington, D.C. 20585

ONSITE

DOE Richland Operations Office

R. B. Goranson, K8-50

- 64 Pacific Northwest Laboratory

C. R. Allen, P7-43
K. A. Blanchard, P7-18
G. H. Bryan, P7-25
T. R. Fox, K6-48
L. K. Holton, P7-43
J. E. Surma, P7-43 (50)
H. A. Udem, K6-48 (2)
N. A. Wogman, K6-48
Publishing Coordination
Technical Report Files (5)

DATE

FILMED

12/16/94

END