U.S. Army
Chemical Materials Agency (Provisional)
Program Manager for Elimination of Chemical Weapons

FY03 Technology Evaluation for Chemical Demilitarization

Wet Air Oxidation Technology Assessment

Contract: DAAD13-01-D-0007
Task: T-03-S-002

Final

Science Applications International Corporation

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NOTICE

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

EXECUTIVE SUMMARY

The Program Manager for Chemical Demilitarization (PMCD) continues to actively seek, monitor, and evaluate potentially useful, alternative, non-incineration technologies for application to chemical demilitarization. This report evaluates the wet air oxidation (WAO) process for these applications.

WAO is a moderate temperature and high-pressure technology. WAO is an aqueous phase process in which soluble and suspended organic constituents are oxidized by dissolved oxygen. Direct application of this technology to chemical agents was considered in the evaluation of Alternate Technologies by the National Research Council (NRC) in 1993 and was determined to be unsafe because of the combination of high operating pressure and the highly toxic nature of agents. As the toxicity of agents is significantly reduced by neutralization, WAO is considered to be suitable for neutralents or hydrolysates. The WAO process was also evaluated under the Office of Product Manager for Non-Stockpile Chemical Materiel by a separate NRC Committee in 2001 and was considered to be a strong candidate for treatment of neutralents/hydrolysates.

The overall objective of this task is to assess the WAO process in supporting the PMCD mission for disposal of unitary and binary chemical agents. The principal means of doing so is to review the published literature on WAO along with the findings from earlier assessments under the PMCD office. The scope of the review and the assessment includes:

- Consideration of this technology for the treatment of neutralents from the Non-Stockpile Chemical Materiel Product (NSCMP).

- The Zimpro WAO Process Evaluation and related bench-scale and pilot testing performed with simulants of various neutralents and binary products.

- A summary of comments made by the NRC.

- An update of the WAO technology and a discussion of the potential applications of the WAO process for various wastes from the demilitarization program.

- An economic analysis for a specific WAO application onsite treatment of neutralents from the Pine Bluff Non-Stockpile Facility (PBNSF).

The major conclusions related to the testing performed are:

- The tests completed so far have provided preliminary information on the corrosion and plugging issues for the NSCMP wastes. Additional tests in progress at Zimpro are expected to afford more specific design information of operating temperature, pressure, and residence time. Material compatibility for auxiliary system components needs careful evaluation, since gasket failures for pressure control valves were observed during bench-scale testing at Zimpro.

- Sodium carbonate is formed at a pH of 10 or more by reaction of sodium hydroxide with carbon dioxide. As sodium carbonate has reverse solubility at temperatures above 30°C, its formation needs to be minimized to avoid plugging and scaling problems. Operation of the WAO system at a pH of 7 to 8 needs to be further investigated. Use of potassium hydroxide instead of sodium hydroxide may alleviate the problem associated with reverse solubility.

- Plugging problems in the WAO process can be overcome by incorporating a short cycle of water rinse. This cycle time was 5 minutes every hour during the testing of the neutralent simulant of mustard agent, H. The rinse cycle will affect the process availability and will extend the duration of the campaign for a selected processing rate. The recent pilot testing

(Phase IIIa) at Zimpro had used a modified configuration from the previous tests for preheating of feed material. Instead of preheating a mixture of organic and dilution liquid (caustic), only the dilution liquid was preheated. The system with this modified configuration was operated for 100 hours continuously without any rinsing. The modified configuration may eliminate the rinsing requirement indicated by the earlier tests (Phase IIa). (A review of Phase IIIa report is not included here and will be a part of the future revision.)

- The screening tests for materials of construction indicated Inconel 600 to be the most appropriate material for H neutralent simulant. Use of this material for other neutralents will require additional tests in actual or simulated environments.

The conclusions related to design issues are as follows:

- As O-ethyl-2-diisopropylaminoethyl methylphosphonite (QL) contains nitrogen, there is a possibility of ammonia formation during WAO processing of QL neutralent. This ammonia will dissolve and may require stripping prior to additional biotreatment of the liquid effluent from the WAO process.

- If the liquid effluent from the WAO process is discharged into a publicly-owned treatment works (POTW) or federally-owned treatment works (FOTW), the regulatory limitations for phosphate, sulfate, and heavy metals will need to be considered. It may be necessary to remove these components by precipitation prior to biotreatment in a POTW or FOTW.

- The reactor design for NSCMP application will require careful review. During bench-scale tests for methylphosphonyldifluoride (DF), a residence time of 360 minutes was required. The normal residence time in WAO is 1 to 2 hours. The reactor size would have to be considerably larger for a

6-hour residence time and would contain a large inventory of material (3,600 gallons) at high pressure in order to realize anticipated throughput rates.

- The WAO process generates lower molecular weight compounds (refractory compounds) such as acetic acid, which will require additional treatment or a catalyst will need to be used in the WAO process for destruction of the refractory compounds.

- Objectionable pollutants such as nitrogen oxides, sulfur oxides, dioxins, furans, and particulates are not formed during the low temperatures of operation for WAO, so no equipment would be necessary to minimize these pollutants.

The cost- and schedule-related findings are summarized as follows:

- The capital cost, including installation and facility for a 10-gallon per minute WAO system, is estimated to be approximately $9.75 million and operating cost is on the order of $900,000 per year. The total disposal cost of neutralents by an onsite WAO process at the Pine Bluff Arsenal for NSCMP is estimated to be about $12.3 million.

- The vendor, Zimpro, has roughly estimated a maximum of 18 months for design, construction, and delivery of a full-scale WAO unit.

- The estimated cost for offsite disposal of WAO liquid effluent of 32,000,000 pounds is $1.6 million for the NSCMP. This cost is based on the dilution necessary (5 to 15 times) for the neutralents prior to treatment by WAO.

The recommendations from this evaluation are summarized as follows:

- Pilot testing of the WAO process for DF and QL neutralents is currently in progress at Zimpro. It is recommended that the test results from the DF and QL neutralent testing be reviewed (when available) and captured in a supplement to this report.

- WAO continues to be a technology option for non-stockpile neutralents and should continue to be monitored.

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SECTION 1
INTRODUCTION

The Program Manager for Chemical Demilitarization continues to actively seek, monitor, and evaluate potentially useful alternative technologies for application to chemical demilitarization. The wet air oxidation (WAO) technology is one of the alternative technologies that can be considered for treatment of the wastes from the demilitarization operations.

WAO is a moderate temperature (150° to 320°C) and high-pressure (150 to 3,200 pounds per square inch absolute [psia]) technology. Direct application of this technology to chemical agents was considered in the evaluation of Alternate Technologies (NRC, 1993) by the National Research Council (NRC) and was determined to be unsafe because of the combination of high operating pressure and the highly toxic nature of agents. As the toxicity of agents is significantly reduced by the neutralization, WAO is considered to be suitable for neutralents or hydrolysates. This process was also evaluated (NRC Committee on Review and Evaluation, 2001) under the Office of Product Manager for Non-Stockpile Chemical Materiel for treatment of neutralents from the Rapid Response System (RRS) and the Munitions Management Device (MMD) by a separate NRC Committee and was considered to be a strong candidate for these applications. This process can also be applied to the neutralents generated from the binary chemical agents (methylphosphonyldifluoride [DF] and O-ethyl-2-diisopropylaminoethyl methylphosphonite [QL]) and the non-stockpile chemical agent neutralents.

1.1 Purpose

The overall objective of this task is to assess the WAO process in supporting the PMCD mission for disposal of unitary and binary chemical agents. The specific objectives are:

- Summarize prior technical evaluations conducted on WAO

- Summarize NRC comments

- Review current literature on WAO and provide an update of the WAO technology

- Assess the applicability and potential for use of WAO to treat the wastes from chemical demilitarization processes

- Perform technical and economic analysis for a specific WAO application.

Phase IIIa testing was in progress at Zimpro, a supplier of WAO systems located in Wisconsin, under the non-stockpile program when the initial draft of this report was prepared in November 2002. The test results were reported in March 2003. A review of the test results should be considered as part of an update to this report at a later date.

1.2 WAO Technology Background

WAO is an aqueous phase process in which soluble and suspended organic constituents are oxidized by dissolved oxygen. The reaction takes place in the liquid phase where the water plays an important role. Water not only provides a medium for the dissolved oxygen to react with the organics (oxidation reaction), but can also react in part with the organics (hydrolysis). The oxidation is theorized to be a free radical reaction and can be catalyzed using homogeneous or heterogeneous catalysts.

The WAO process oxidizes and hydrolyzes organic contaminants in water at temperatures of 150° to 320°C and pressures of 150 to 3,200 psia. These conditions are below the critical temperature of 374°C and critical pressure of 3,204 psia for water. The residence time for WAO reactions is normally in the range of 1 to 2 hours. Dissolved oxygen in water participates in the oxidation reaction for this process. Either compressed air or high-pressure oxygen (or a combination of both) is used as a source of the oxygen. Use of oxygen instead of air reduces the operating pressure and/or residence time requirements and also reduces the gas volume that may need further treatment. Use of oxygen, however, may create a safety problem. As the total volume of gas decreases, the volatile organic compound (VOC) concentration in the gas stream increases and may reach the lower explosive limit.

The WAO process converts organic compounds containing carbon, hydrogen, and oxygen into carbon dioxide (CO_2), water, and short-chain biodegradable compounds such as acetic acid and formaldehyde. Thus, WAO can have high destruction efficiency for breaking down higher molecular weight organic compounds, but the efficiency for destruction of total organic carbon (TOC) is not as high, because the organic carbon in the form of shorter chain compounds still exists. Should these short chain refractory compounds be undesirable, then higher temperatures or catalytic operations can be employed. The presence of elements such as sulfur, chlorine, fluorine, phosphorus, and nitrogen in organic compounds also react in the WAO process and form respective ions such as sulfate, chloride, fluoride, phosphate, and nitrate or ammonium. All these elements are present in the chemical agents. Most of these ions create highly acidic conditions, if not neutralized by caustic or other basic solutions. Corrosion is a major problem, if neutralization is not conducted. At the same time, salts are formed during neutralization, which may create plugging problems if their solubility limits are exceeded.

The WAO process is exothermic in nature. The temperature of the reaction mixture increases as the reaction proceeds, if there is no cooling provided. The release of heat that can be tolerated in a WAO system limits the concentration of oxidizable material that is fed to a WAO system. Dilution of feed containing excessive oxidizable material is necessary to control the temperature.

During the oxidation reaction in the WAO process, no dioxins or furans are formed and negligible amounts of nitrogen oxides (NO_x) and sulfur oxides (SO_x) may be formed. VOCs such as aldehydes, ketones, and alcohols may be in the off-gas from a WAO system depending upon the composition of feed material. A thermal or catalytic oxidizer would be necessary to destroy these unwanted VOCs to meet environmental regulations.

The WAO process has been in existence for more than 90 years. The first patent for oxidation of sulfite liquor from pulp production by compressed air at 180°C was granted to a Swedish inventor in 1911 (Strehlenert, 1911). Extensive testing and development work took place in the United States 50 to 60 years ago, resulting in refinement of the process and expansion into processing of sewage sludge and industrial wastewaters. The first commercial WAO process was the Zimpro process invented by F. J. Zimmerman in 1950. The WAO process is commercially mature. Currently, the process is offered commercially by several organizations, including:

- US Filter/Zimpro Products
- Nigata Engineering (a Japanese licensee of the Zimpro Process)
- Nippon Shokubai (a Japanese firm with a heterogeneous catalytic process)
- Toyo Engineering (a Japanese firm)
- Bertrams (a Swiss firm with a catalytic process)
- Kenox Technology Corporation (a Canadian firm).

Battelle has developed an assisted hydrothermal oxidation process in its Pacific Northwest Laboratories, but it has not reached the commercial stage.

Zimpro is currently the largest supplier of WAO systems with in excess of 300 units installed worldwide. More than 130 units are for sewage sludge oxidation; about 90 are for treatment of waste streams from petrochemical, chemical, and pharmaceutical industries; and 25 catalytic units are for oxidation of spent caustic from ethylene plants (Luck, 1999). The Environmental Protection Agency (EPA) has specified WAO as a best-demonstrated available technology for the treatment of hazardous wastewater containing a variety of wastes classified under the P and U categories in 40 Code of Federal Regulations 261.

The simplest reactor design for the WAO process is usually a co-current vertical bubble column (as shown in figure 1-1) with a height-to-diameter ratio in the range of 5 to 20. Design of the bubble column reactors for WAO using computer modeling has been discussed in the paper by Debellefontaine, et al. Additional equipment required for the WAO process includes a compressor for air or oxygen, a liquid pump, a heat exchanger, and a phase separator. The off-gas from the WAO process may require treatment by a thermal or catalytic oxidation unit. Liquid effluent from a WAO process may require ammonia stripping and further oxidation such as a biotreatment.

1.3 Report Organization

A summary of the prior technical evaluations of the WAO technology under the PMCD program is described in section 2. A compilation of the NRC's comments for the WAO process is also included in section 2. An update of the WAO technology by means of a current literature review is discussed in section 3. A discussion of the potential applications of the WAO process for various wastes from the demilitarization program is provided in section 4. A technical and economic analysis for a specific application of WAO process for the Non-Stockpile Chemical Materiel Product (NSCMP) is provided in section 5. The conclusions and recommendations from this evaluation are presented in section 6.

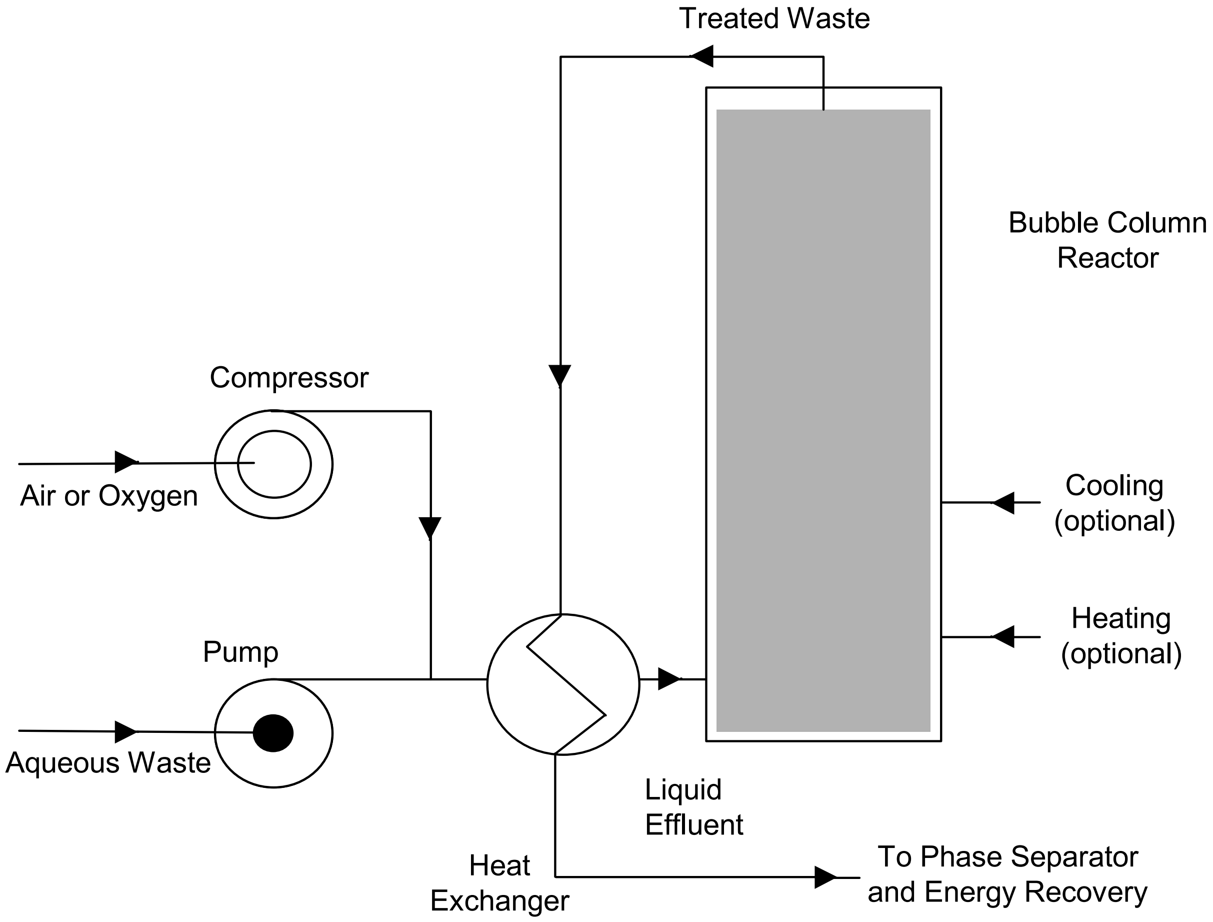

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Figure 1-1. WAO Bubble Column Reactor

SECTION 2
SUMMARY OF PRIOR EVALUATIONS

2.1 Zimpro WAO Process

Stone and Webster, Inc., evaluated the Zimpro WAO process in April 2001 (Stone and Webster, April 2001) for the oxidization of neutralents from the NSCMP. The assessment was based on the technical information provided by the vendor. Zimpro has compiled data from previous bench and pilot-scale testing in their laboratory. The bench-scale results included the materials such as pesticide, glyphosate (with organic phosphono bond structure similar to sarin [GB] and O ethyl S-(2-diisopropylaminoethyl)methylphosphonothioate [VX] agents), and dimethyl methylphosphonate (DMMP), which is a surrogate compound for GB and QL (a binary agent). The bench-scale test results for these two materials are summarized in tables 2-1 and 2-2.

Zimpro has also compiled data on pilot- and commercial-scale testing of compounds similar to chemical agents and NSCMP neutralents. These include the pesticide, malathion (a phosphonodithioate compound with a phosphorus-sulfur bond similar to that found in the structure of VX), and spent caustic wastes from refinery operations. The spent caustic wastes contain several organic sulfides with structures similar to the mustard blister agent, H. The test results for the spent caustic and malathion are summarized in tables 2-3 and 2-4.

The estimated equipment cost from Zimpro (Stone and Webster, Inc., April 2001) for a 10-gallon per minute (gpm) unit was $4.3 million in 2001. This cost included a regenerative thermal oxidizer for VOC treatment. It is to be noted that the cost does not include installation and facility costs. The delivery schedule was 12 to 18 months.

Table 2-1. Destruction of Glyphosate by WAO[a]

	Feed	200°C	240°C	280°C
Residence Time (minutes)		60	60	60
COD (mg/L)	27,500	14,400	9,300	6,900
COD Destruction (%)		47.6	66.2	74.9
pH	4.89	5.85	5.49	4.49
TKN (mg/L)	2,320	2,440	2,190	1,320
Ammonia (mg/L)	1,157	1871	1,739	1,463
Nitrate (mg/L)	<0.5	1	9	87
Total Phosphorus (mg/L)	2,890	2,463	2,264	2,353
Ortho-P (mg/L)	14	2,277	2,120	2,226
Glyphosate (mg/L)	14,600	73	66	33
Glyphosate Destruction (%)		99.5	99.5	99.8
Total Carbon in Off-gas (mg/L)		1,900	4,100	5,700

Notes:

[a] Copa and Momont, 1995.

COD = chemical oxygen demand
mg/L = milligrams per liter
TKN = Total Kjeldahl Nitrogen

Table 2-2. Destruction of DMMP by WAO

	Feed	200°C	240°C	260°C	280°C
Residence Time (minutes)		60	60	60	60
COD (mg/L)	14,600	13,600	13,706	13,596	13,596
COD Destruction (%)		6.8	6.1	6.9	6.9
pH	3.6	1.9	1.8	1.8	1.8
DMMP (mg/L)	19,900	<500	<500	<500	<500
DMMP Destruction (%)		>97.5	>97.5	>97.5	>97.5

Notes:

COD = chemical oxygen demand
DMMP = dimethyl methylphosphonate
mg/L = milligrams per liter

Table 2-3. WAO Processing of Refinery Spent Caustic

	Feed	260°C	280°C
Residence Time (minutes)		60	60
COD (mg/L)	81,300	24,200	18,000
COD Destruction (%)		70.2	77.9
Total Sulfur (mg/L)	7,900	9,260	8,972
Sulfide Sulfur (mg/L)	5,024	<4	<4
Sulfate Sulfur (mg/L)	<54	6,350	6,727
Mercaptans as Methyl (mg/L)	8,680	<10	<10

Note:

mg/L = milligrams per liter

Table 2-4. Demonstrated WAO Destruction Efficiency for Pesticides

Compound	Temp (°C)	Res. Time (minutes)	% Destruction (Compound)	% COD Removal
Dinoseb	281	182	99.5	95.3
Methoxychlor	281	182	99.8+	95.3
Carbaryl	281	182	98	95.3
Malathion	281	182	99.9	95.3
Organophosphorus	300	60	94+	-
Phthalimide	225	60	99	-
Organo-nitrogen/phosphorus	260	60	99.6	-
Organo-nitrogen/sulfur	260	60	99.4	-

Notes:

COD = chemical oxygen demand
Res. = Residual

The major conclusions from this evaluation include:

- The Zimpro WAO process is commercially mature and has potential for partial treatment of chemical warfare materiel (CWM) and related neutralents. The liquid effluents remain relatively high in organic contents and will require further treatment prior to discharge.

- Previous commercial and pilot-scale processing of materials with bond structures similar to those in CWM indicate that WAO is capable of achieving destruction efficiencies of more than 99 percent for the specific compounds, but actual TOC reductions will be less.

- Zimpro had recommended operation of WAO at 260° to 300°C, 700 to 1,200 psia, and with a 60-minute residence time from their previous experience with materials similar to NSCMP application (prior to conducting any tests with non-stockpile feeds).

- WAO, being exothermic, requires a limit on organic concentration in the feed. Corrosion also plays a role in dilution of feed, as the concentration of corrosive ions such as chloride (Cl) and fluoride (F) need to be maintained below certain limits established by material of construction (MOC) studies. Thus, dilution of feed is often necessary. The recommended dilution factors for the CWM neutralents and binary agents are listed in table 2-5.

- The WAO process will generate more liquid effluent than the raw neutralent because of the dilution requirement. Thus, disposal cost of liquid effluent may be significantly impacted.

- If the WAO processing rate is not capable of keeping up with the neutralent generation rate because of the high dilution factor, then storage of neutralent will be necessary.

Table 2-5. NSCMP Neutralent Feeds[a]

Chemical Agent	Major Component	Chemical Formula	wt% in Neutralent	WAO Dilution Factor	wt% in WAO Feed	ppm Cl in WAO Feed	ppm F in WAO Feed
H Neutralent in MEA	MEA	C_2H_7NO	78		5.2		
	Water	H_2O	9.5		94.0		
	MEA HCl	C_2H_8ONCl	7.25		0.5	1,747	
	HETM	$C_6H_{13}NOS$	5.25		0.3		
	TOTAL		**100**	**14**[b]	**100**	**1,747**	
GB Neutralent in MEA	MEA	C_2H_7NO	38		4.8		
	Water	H_2O	50		93.7		
	MEA IMP	$C_4H_{10}O_3P$	5		0.6		
	MEA HF	C_2H_8ONF	4		0.5		1,173
	GB MEA	$C_6H_{15}NO_3P$	3		0.4		
	TOTAL		**100**	**7**[b]	**100**		**1,173**
H & L Neutralent in MEA	MEA	C_2H_7NO	78		5.2		
	Water	H_2O	9.5		94		
	MEA HCl (H)	C_2H_8ONCl	7.25		0.5	1,747	
	HETM	$C_6H_{13}NOS$	1.94		0.1		
	As Product		3.31		0.2		
	TOTAL		**100**	**14**[b]	**100**	**1,747**	
H in Red Neutralent	DCDMH	$C_5H_6Cl_2N_2O_2$	4.3		0.1	516	
	Chloroform	$CHCl_3$	31.1		1.0	9,248	
	t-Butyl Alcohol	$C_4H_{10}O$	60.5		2.0		
	Water	H_2O	2.8		96.8		
	H	$C_4H_8Cl_2S$	1.3		0.1	190	
	TOTAL		**100**	**29**[c]	**100**	**9,954**	

Table 2-5. NSCMP Neutralent Feeds[a] (Continued)

Chemical Agent	Major Component	Chemical Formula	wt% in Neutralent	WAO Dilution Factor	wt% in WAO Feed	ppm Cl in WAO Feed	ppm F in WAO Feed
DF	DF	CH_3F_2OP	100		1.0		3,900
	Water	$\mathbf{H_2O}$	**0**		**99**		
	TOTAL		100	99[d]	100		
QL	QL	$C_{11}H_{26}NO_2P$	100		5.55		
	Water	H_2O	0		94.45		
	TOTAL		**100**	**17**[b]	**100**		

Notes:

[a] Stone and Webster, Inc., April 2001.
[b] Dilution based on organic content.
[c] Dilution based on Cl content.
[d] Dilution based on F content. Dilution may be reduced, if DF hydrolyzes.

Cl = chloride
DCDMH = 1,3-dichloro 5,5’-dimethylhydantoin
DF = methylphosphonyldifluoride
F = fluoride
GB = nerve agent sarin
H = mustard agent
HCl = hydrogen chloride
HETM = N-(2-hydroxyethyl thiomorpholine)
HF = hydrogen fluoride
IMP = iso-methyl phosphonate
L = lewisite
MEA = monoethanolamine
ppm = parts per million
QL = O-ethyl-2-diisopropylaminoethyl methylphosphonite
t = tertiary
wt% = weight percent
WAO = wet air oxidation

- When treating monoethanolamine (MEA)-based neutralents, the WAO effluent may require ammonia stripping prior to biotreatment.

- The gaseous effluent from the WAO process may contain volatile organics, which may need additional treatment.

2.2 Bench-Scale Testing of the Zimpro WAO Process to Treat NSCMP Neutralents and Binary Product Feeds

Stone and Webster reported in February 2002 (Stone and Webster, Inc., February 2002a) on the evaluation of bench-scale testing of the Zimpro's WAO process. The primary objectives of the testing were to assess the WAO process' applicability to processing of NSCMP neutralents and binary agents. Two MEA-based agent (H and GB) neutralent simulants and two binary agent (DF and QL) simulants (with high dilution factors to account for the dilution during neutralization) were tested. The process was evaluated based on the following objectives:

- Demonstrate WAO effectiveness in treating the selected liquid feeds in a bench-scale apparatus.

- Identify and demonstrate a post-treatment method for the WAO process effluent.

- Verify appropriate materials of construction for the anticipated pilot-scale testing.

- Develop a full-scale processing concept for this application.

The conclusions from this testing were as follows:

- The operating temperature for all performance tests was 320°C, but residence time varied from 60 minutes for H neutralent simulant to

360 minutes for DF neutralent simulant. The DF inventory in conjunction with such a long residence time would need to be evaluated to properly size the WAO unit for processing DF.

- The demonstrated destruction efficiency for specific compounds was 99.99 percent for DMMP and 99.96 percent for dimethyl sulfoxide (DMSO), as shown in table 2-6.

- The demonstrated destruction efficiencies for TOCs were 97.74 percent for H neutralent simulant, 99.57 percent for GB neutralent simulant, 99.76 percent for QL simulant, and 99.56 percent for DF simulant. (See table 2-6.)

- TOC concentration in the liquid effluent varied from 10.9 parts per million (ppm) for QL simulant to 153 ppm for H-neutralent simulant indicating that post-treatment would be necessary.

- Post-treatment using ultraviolet light (UV)/ozone oxidation could not be evaluated because of low contaminant levels in WAO liquid effluent.

- MOC testing indicated Inconel 600 to be the most appropriate material for H-neutralent simulant, but additional tests are necessary for other types of feed.

- The gaseous effluent from the WAO process contained trace amounts of several volatile organic compounds suggesting that off-gas treatment would be necessary.

- Zimpro estimated the equipment cost for a 10-gpm unit based on the observed test results. This estimate was $4.5 million in 2002. Additional cost for installation and facility was not considered. There would be additional cost associated with the further treatment of the liquid effluent.

Table 2-6. Destruction Efficiencies from Bench-Scale Performance Tests

Simulant	Temp (°C)	Hold Time (minutes)	Residual TOC	Residual MPA/MSA (ppm)	Residual DMMP/DMSO (ppm)	TOC Reduction (%)	Comp/Bond Reduction (%)	Comment
H/MEA	320	60	153	< 0.05	0.19	97.74	> 99.997	Based on MSA
							99.968	Based on DMSO
GB/MEA	320	180	25.1	< 50	< 0.18	99.57	>97.098	Based on MPA
							>99.992	Based on DMMP
QL	320	180	10.9	< 50	< 0.18	99.76	> 97.955	Based on MPA
							> 99.994	Based on DMMP
DF	320	360	14.1	8.2	< 0.18	99.56	99.84	Based on MPA
							> 99.997	Based on DMMP

Notes:

Comp = Compound
DF = methylphosphonyldifluoride
DMMP = dimethyl methylphosphonate
DMSO = dimethyl sulfoxide
GB = sarin
H = mustard agent
MEA = monoethanolamine
MPA = methylphosphonic acid
MSA = methane sulfonic acid
ppm = parts per million
QL = O-ethyl-2-diisopropylaminoethyl methylphosphonite
TOC = total organic carbon

Stone and Webster, Inc., made the following recommendations:

- The WAO full-sized processing concept should be compared to the other candidate processes (such as chemical oxidation and UV oxidation) in low to moderate temperature and pressure ranges. If justified by this analysis, further testing of the WAO process should proceed.
- The additional testing should include pilot testing with all the simulants.
- An MOC testing program should be initiated to identify appropriate materials of construction and provide a quantitative indication of the reliability of the materials for pilot and full-scale operation. The testing should include all prospective feed materiel and should have appropriate long exposure durations.
- A series of tests should be initiated through the Edgewood Chemical Biological Center (ECBC) to evaluate biotreatment of the WAO liquid effluent.

The following are the review comments on the testing and observations:

- The capital equipment cost of $4.3 million in 2001 (Stone and Webster, Inc., April 2001) is basically the same as $4.5 million in 2002 (Stone and Webster, Inc., February 2002a): It is not clear whether Zimpro has considered the effect of a longer residence time (6 hours for DF) rather than the previously assumed value of 1 hour on their cost estimate.
- The MOC screening tests were conducted at pH 10 and 12 for H neutralent simulant. It is not evident why pH 8 was not selected. It is necessary to maintain pH above 7 to minimize corrosion, but excessively high pH causes too much carbonate formation by scrubbing CO_2 generated by the oxidation reaction. The excessive carbonate precipitates

and causes plugging problems. Including testing at pH 8 in future tests is suggested.

- The MOC screening test matrix included H neutralent simulant and QL simulant. It is not clear why DF simulant was not included. DF has two corrosive elements, F and P, compared to QL, which just contains P. DF simulant would have been a better choice compared to QL simulant.

- The MOC testing used a dilution factor of 20 for H neutralent simulant, but performance testing was conducted at a dilution factor of 50. There is no explanation for this difference in the report. It is suggested that future tests should maintain the same dilution factor for both types of tests.

- There was no recommendation for the test conditions for the pilot scale testing in this report. The pilot scale for H neutralent simulant did not use the bench-scale performance test conditions. The initial dilution factor for the pilot-scale test was 20 and was increased to 30 to minimize plugging problems. The bench scale testing was done with a dilution factor of 50 for H neutralent simulant.

2.3 Pilot-Scale Limited Engineering Design Study Testing of the Zimpro WAO Process to Treat NSCMP H-Neutralent Simulant

Stone and Webster reported on the evaluation of pilot-scale testing of the Zimpro WAO process in February 2002 (Stone and Webster, Inc., February 2002b). The primary objective of the testing was to assess the performance of the continuous flow WAO process, as applied to processing a feed-simulating H neutralent. The process was evaluated based on the following objectives:

- Demonstrate effectiveness of the WAO process in treating the selected liquid feed at the maximum continuous flow (MCF) rate of the existing pilot unit.

- Demonstrate steady state, 8-hour continuous, safe operation of the WAO pilot system in a configuration similar to that of a full-scale system.

The conclusions from the test observations were summarized as follows:

- The Zimpro WAO process operated continuously for an 8-hour performance test at the pilot unit's maximum flow rate of 7 gallons per hour (gph), which corresponded to 0.23 gph of H neutralent simulant with 30:1 dilution.

- Operating at a temperature of 300°C with a 60-minute residence time, the WAO process demonstrated a TOC destruction efficiency of 97.57 percent for H neutralent simulant, producing a liquid effluent with a TOC of less than 300 ppm. The carbon-sulfur bond destruction efficiency was 99.9999 percent.

- The WAO reactor experienced blockage during work-up testing, which was eliminated by instituting a 5-minute water rinse every hour. This operating philosophy should be acceptable and successful in a full-scale design.

- Post-treatment of the WAO residual using UV/ozone oxidation could not be adequately evaluated. The liquid effluent from the WAO contained such low levels of contaminants that the performance of the post-treatment could not be quantified.

- The liquid effluent from the process contained various concentrations of metals attributed to corrosion of the reactor vessel. Materials of construction and corrosion management need to be addressed through additional studies in subsequent phases.

- The liquid effluent from the WAO test contained trace amounts of several VOCs, but none were at a level that would pose a problem with final disposal of the liquid effluent.

- Based on the test results, Zimpro developed a preliminary full-sized processing concept. The fixed unit would process up to 10 gpm of dilute NSCMP materiel (H and GB neutralents and DF and QL binary products). Zimpro estimated an order-of-magnitude capital cost for the WAO-only system as $4.5 million. Additional equipment (UV/ozone oxidation and fluoride/phosphorus precipitation) may be necessary to further treat the WAO effluent before disposal, increasing the total system cost.

The evaluator made the following recommendations based on the test observations:

- The WAO full-sized processing concept should be compared to the other candidate processes (such as chemical oxidation and UV oxidation) in low to moderate temperature and pressure ranges. If justified by this analysis, further testing of the WAO process should proceed.

- The additional testing should include all of the remaining simulants to identify the potential for plugging of the reactor system and evaluate alternatives to control or eliminate this phenomenon.

- An MOC testing program should be initiated to identify appropriate materials of construction and provide a quantitative indication of the reliability of the materials for pilot- and full-scale operation. The testing should include all prospective feed materiel and should have appropriately long exposure duration. The program should include an evaluation of achieving corrosion management through chemistry control. It should also include a rigorous material testing protocol with pre-inspection of the test coupons.

- A series of tests should be initiated through ECBC to evaluate biotreatment of the WAO liquid effluent.

The following are the review comments on the testing and observations:

- It is not clear whether Zimpro's cost estimate is based on the longer residence time of 6 hours for DF during bench-scale tests or the shorter residence time of 1 hour used during the pilot tests for H neutralent simulant.

- The cost estimate from Zimpro is based on a 10-gpm processing rate. The actual processing rate in the unit will be less than 10 gpm, because of the water rinsing cycle every hour to eliminate plugging problems. Thus the effective rate will depend upon the rinsing cycle time for the full-scale unit. It will be 9.1 gpm based on a 5-minute rinsing cycle, which would extend the total campaign time. Moreover, the liquid effluent generated from WAO would increase by 9 percent in comparison to a process not requiring any rinsing cycle. This change will also impact the total disposal cost.

- The dilution factor for H neutralent simulant during the bench-scale performance tests was 50, but it was changed to 20 to 30 for pilot tests. There is no explanation for this change. There were plugging problems encountered at the reduced dilution factor. It would be cheaper to run a bench-scale test rather than a pilot-scale test, if there is a need to change the established successful operating conditions from bench-scale tests.

- The operating conditions were changed from 320° to 300°C to overcome the salt precipitation problem, as the carbonate salts have inverse solubility above 50°C. The change in solubility is very small for the temperature change of 20°C (from 320° to 300°C). The liquid pH has a more drastic effect on the amount of carbonates formed. Future testing to investigate pH control near 8 is suggested.

- A failure of a pressure control valve gasket was reported twice during these tests. It is suggested that compatibility of all the materials in contact with the process fluid should be carefully examined to avoid such failures of system components.

2.4 Systems and Technologies for the Treatment of Non-Stockpile CWM

This is a report (NRC, 2002) prepared in 2002 by the NRC Committee on Review and Evaluation of the Army Non-Stockpile Chemical Materiel Disposal Program. It evaluates mobile destruction systems and semi-permanent facilities being used or considered by the Army's Non-Stockpile Product Manager for the treatment of non-stockpile CWM and makes recommendations on the systems and facilities that could be employed by the Army. The report describes the non-stockpile chemical weapons inventory, which contains unitary and binary munitions.

The committee assessed the specific options available to Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) to safely destroy these items and matches the treatment options with the materiel or munitions to be treated. The options included facilities, mobile systems, and individual treatment technologies. The facility options identified in the report are:

- Stockpile chemical disposal facilities

- Two non-stockpile facilities including the Munitions Assessment and Processing System in Aberdeen and the Pine Bluff Non-Stockpile Facility (PBNSF)

- Research and development facilities including the Chemical Transfer Facility at Aberdeen Proving Ground and the Chemical Agent Munitions Disposal System in Tooele, Utah

- Commercial treatment, storage, and disposal facilities.

The mobile system options include:

- RRS

- Explosive Destruction System

- Donovan Blast Chamber.

The treatment technologies being evaluated for NSCMP are:

- Plasma arc

- Gas-phase chemical reduction

- Continuous supercritical water oxidation (SCWO)

- Batch SCWO

- Persulfate oxidation

- Electrochemical oxidation

- UV oxidation

- WAO.

The committee considered 10 categories of non-stockpile CWM that the Army currently faces or is likely to face in the near future and found that the Army has tools available or under development for seven of these categories. These seven categories are the first seven in the following list of ten categories:

- Chemical agent identification set (CAIS) package for in-transit gas shipment
- Individual CAIS vials and bottles
- Small quantities of small munitions
- Chemical agent in bulk containers
- Binary CWM components
- Unstable explosive munitions that cannot be moved
- Secondary liquid waste streams
- Large quantities of non-stockpile CWM items currently in storage
- Large non-stockpile CWM items
- Large quantities of not-yet-recovered small munitions.

The committee's recommendations for all the categories in this report include the following recommendation for the binary CWM component.

The binary precursors (DF and QL) stored at Pine Bluff Arsenal (PBA) should be destroyed directly in the Pine Bluff Chemical Agent Disposal Facility (PBCDF) incinerator or by plasma arc treatment. Additional testing of plasma arc technology should be done to ensure that the proposed plasma arc systems are capable of meeting EPA requirements and state requirements. If these facilities cannot handle the fluorine rich DF destruction products, the committee recommends that the neutralization followed by oxidative post-treatment of neutralent be developed. The committee believes that the easiest post-treatment would be shipment to a commercial incinerator capable of dealing with a high level of fluorine.

The committee's recommendations for the secondary liquid waste streams such as neutralents and aqueous rinsates were as follows:

- The PMNSCM should continue its research and development program on chemical oxidation and WAO.
- There should be no further funding for the development of biological treatment, electrochemical oxidation, gas-phase chemical reduction, solvated electron technology, and continuous SCWO for the treatment of neutralents and rinsates.
- PMNSCM should monitor progress in technologies being developed by the Assembled Chemical Weapons Assessment (ACWA) program, but should evaluate ACWA technologies for the treatment of non-stockpile neutralents and rinsates only if no additional investment is required.

Regarding the previously-mentioned recommendations from the NRC Committee, there is still a potential for WAO in the treatment of the binary neutralents and the secondary liquid waste streams. There was one issue identified by the committee for the WAO process permit. The committee felt that there would be no problems in obtaining the necessary regulatory approvals for the WAO process, but the Resource Conservation and Recovery Act prohibits dilution as a means of achieving treatment standards. The Army may need to demonstrate that the dilution is inherent to this process to achieve the appropriate conditions under which the technology normally operates.

2.5 NRC Comments

The NRC Committee on Alternative Chemical Demilitarization Technologies had reported its findings on the WAO process in 1993 (NRC, 1993). These findings are summarized as follows:

- The high-pressure WAO process can detoxify and demilitarize agent; however, some organic compounds remain. The waste gas stream contains organic chemical compounds and may require further treatment. The gas-handling problem is reduced if pure oxygen is used, but would require additional development work. The waste gas stream from this process could be further reduced by the capture of CO_2 with lime.

- Objectionable pollutants such as NO_x, dioxins, and particulates do not form at the relatively low temperatures used. Some nitrogen may show up as nitrous oxide or ammonia.

- Achieving a high destruction efficiency will require the reactor to operate much like a plug flow, which is difficult to achieve in a reactor with a long residence time and a very slow flow rate. For the very high destruction efficiency required for chemical warfare agents (does not include hydrolysate and neutralents from chemical agents), it appears that several reactors in series would be preferred.

- Corrosion is a concern with WAO conditions, particularly for materials containing chlorine, fluorine, sulfur, and phosphorus, which all form acids in solution on agent oxidation. Caustic may be needed to neutralize such acids and corrosion. Addition of caustic beyond that required by stoichiometry for corrosion control would react with CO_2 to form carbonate and bicarbonate salts, adding greatly to the solid salts that must be handled.

- The fluoride ion is particularly corrosive. A current limitation for WAO processing is 200 ppm of fluoride for normal materials of construction such as 304L and 316L stainless steels used for piping, valves, and tanks. Because fluorine is 14 percent of GB in weight, this corrosion limitation implies a GB feed concentration of only 1,500 ppm.

- Insoluble deposits appear to aggravate corrosion and scaling problems in heat exchangers, reactors, piping, valves, and tanks. (Zimpro has stated that most of their commercial systems do not use heat exchangers—in most cases it is cheaper to heat the feed electrically than to maintain and operate a heat exchanger [conversation between Bill Adams, PMCD and D. Lehmann, Zimpro, October 2002].)

- WAO is highly exothermic. Larger throughputs with a higher concentration of organics would result in larger heat releases and the possibility of larger temperature excursions. The organic concentration in feed should be limited to below 5 percent.

- The use of oxygen rather than air would reduce gas volume, but some fixed volume is desirable for stable operation. Lower gas volume limits the amount of water that can evaporate into the gas stream at the operating temperature and pressure, and makes temperature control more difficult.

- The large water dilution could be a significant advantage in treating energetic materials (propellants and explosives). Explosion or detonation should not occur if there is adequate mixing, although this would require demonstration.

- WAO operates at high pressures. There might be some concern about operating with agent under high pressure. It might be preferable to use WAO to oxidize products from pretreatment of agent, such as the products of hydrolysis.

The NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Project had reviewed all the information compiled by the NRC Committee on Alternative Chemical Demilitarization Technologies in 1994 (NRC, 1994) and recommended the use of WAO in combination with neutralization as one of the four options identified by them for agent processing.

There was an additional study by the NRC Review and Evaluation Committee on the Non-Stockpile Chemical Materiel Disposal Program in 2001 (NRC Committee, 2001). This committee had selected eight technologies for further evaluation for neutralent treatment. WAO was among these eight technologies. Their findings for WAO are summarized as follows:

- WAO is a promising treatment for both RRS and MMD neutralents. The process is used commercially and has an established track record with compounds similar to those found in neutralents.

- Depending upon reaction conditions, further biotreatment of the liquid effluent may be necessary. Toxic heavy metals in the neutralents would have to be precipitated and filtered out prior to biotreatment.

- WAO is most effective on dilute aqueous solutions. RRS and MMD neutralents might have to be diluted with water to reduce their chemical oxygen demand (COD). A dilution factor of 4 to 14 may be necessary.

- The effect of high salt concentration on rates of destruction remains to be tested.

As per the committee’s evaluation, WAO is a strong candidate for the treatment of both RRS and the MMD, Version 2, neutralents because the process requires only the addition of water and air or oxygen and no dioxins are formed.

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SECTION 3
TECHNOLOGY UPDATE

The WAO process can be catalytic or non-catalytic. Low conversion of TOCs and challenging operating conditions of the non-catalytic WAO process had provided a strong driving force for development work on the catalytic WAO process. A number of academic studies for heterogeneous catalytic WAO processes were reported in the late nineties using supported precious metal catalysts. Several commercial catalytic processes were developed as a result of these studies.

There was a recent academic study on WAO of solid wastes made of polymers. This study has potential application for treatment of demilitarization protective ensemble (DPE) suits in slurry form. Some enhancements in the mass transfer rate by use of static mixing were also reported in the current literature.

The WAO process forms carboxylic acids such as acetic acid. It may also form inorganic acids from S, Cl, F, and P in waste streams, if the pH is below 7. Thus corrosion can be severe unless pH is raised above 7. If the pH is too high, then CO_2 generated during the oxidation reaction is converted to carbonate salts that may cause precipitation, plugging, and scaling problems. Use of calcium carbonate for pH control to minimize corrosion was also recently reported in the literature.

The following paragraphs describe the above-mentioned developments in WAO technology.

3.1 Heterogeneous Catalytic WAO Processes

Three Japanese processes are commercially available for heterogeneous catalytic WAO systems. These include the NS-LC process, the Osaka gas process, and the Kurita process (Luck, 1999). A process flow diagram for a heterogeneous catalytic WAO process is shown in figure 3-1.

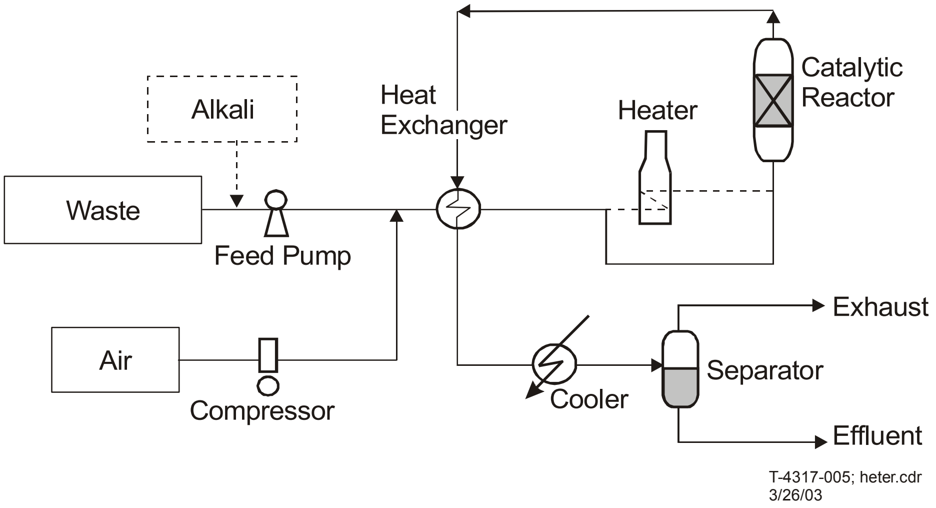

Figure 3-1. Heterogeneous Catalytic WAO Process

The NS-LC is a Nippon Shokubai catalytic process using platinum-palladium titanium oxide-zirconium oxide honeycomb catalyst. The operating conditions are 220°C temperature, 600 psia pressure, and 30 minutes residence time. A destruction efficiency of more than 99 percent is reported for compounds such as phenol, formaldehyde, acetic acid, and glucose.

The Osaka gas process is based on a mixture of precious and base metals on titania or titania-zirconia carriers (honeycomb or spheres). The operating conditions are 250°C temperature, 1,000 psia pressure, and 24 minutes residence time for wastewater from coke ovens. Phenol and cyanide together with ammonia are destroyed to below detection limits. The vendor claims a catalyst lifetime longer than 8 years.

The Kurita process uses supported platinum catalyst. It is tailored to abate ammonia (a very difficult compound for non-catalytic WAO processes). It uses nitrite instead of oxygen and the operating temperature is 170°C.

3.2 Homogeneous Catalytic WAO Processes

An alternative to insoluble precious metal catalysts is the use of homogeneous transition metal catalysts, which need to be separated and recycled back to the reactor or discarded. Three processes were developed in the last decade using this concept. They are the Ciba-Geigy process, the LOPROX process, and the WPO process (Luck, 1999).

The Ciba-Geigy process uses copper salt as a catalyst. It is operated at 300°C and claims to achieve destruction efficiencies of 95 to 99 percent for chemical and pharmaceutical wastes, as well as acetic acid, a refractory compound for non-catalytic WAO processes.

Bayer AG developed the LOPROX (low pressure oxidation) process. The oxidation reaction in this process is carried out in acidic conditions using iron (Fe^{+2}) ions and quinone-generating substances as catalyst. These catalysts are provided by the sludge. The operating conditions, temperatures below 200°C and pressures of 75 to 300 psia, are relatively mild. The residence time is about 2 hours.

The WPO process was derived from the classical Fenton's reagent. It uses hydrogen peroxide catalyzed by Fe^{+2} as the oxidant at a pH of 3. The operating conditions are very mild with a 90 to 130°C temperature and a pressure of 15 to 75 psia. High oxidation efficiencies (up to 98 percent) are achieved at these conditions.

3.3 Advanced WAO Process

The advanced WAO process (Kenox Technology Corp.) is a patented (1997) process from Kenox Technology Corporation in Ontario, Canada. They have achieved two breakthroughs. One is enhanced mass transfer through static mixing and the other is an accelerated induction period. The Kenox process uses the combined effects of controlled temperature, pressure, and static mixing, along with optional fixed catalysts and ultrasonic energy, in a dynamic recirculation reactor. The process is capable of treating a variety of dissolved and suspended oxidizable contaminants in wastewaters, sludges, and slurries. Chemicals amenable to treatment by this process include acrylonitrile, phenols, dichloroethane, vinyl chloride, carbon tetrachloride, cyanides, pesticide plant wastewater, trinitrotoluene (TNT) red water, and toluene. It can also be used to regenerate spent powder-activated charcoal and to desulfurize pyrites. Typically, the Kenox process operating conditions range between a 200 to 250°C temperature and a 450 to 1,200 psia pressure. COD reduction was from 80 to 99 percent depending on the specific waste and operating conditions. The destruction efficiency for specific compounds varied from 90 percent to more than 99 percent.

The process has the distinct advantage of treating a broad range and concentration of pollutants and has lower capital and operating costs than competing technologies or incineration. Its operation is continuously monitored and controlled by computer, thereby reducing operating and labor costs. The company offers skid-mounted, transportable treatment plants or custom-built treatment plants. They have several commercial plants in operation and have patents in countries located on five continents.

The Kenox system has potential for demilitarization process applications in the areas of treatment of agent neutralents and hydrolysates in solution form, as well as propellant, activated carbon, and DPE suits in slurried form.

3.4 WAO of Solid Wastes Made of Polymer

The use of polymer slurry as a feed has a potential application in the destruction of materials such as contaminated DPE suits. Use of calcium carbonate as a pH control media could significantly reduce carbonate salt formation due to lower pH, and, thereby, minimize corrosion, plugging, and scaling problems.

The experimental work on WAO of synthetic and natural polymers was carried out at a university in France (Krisner, Ambrosio, and Massiani, March 2000) using a batch process. The polymers were finely ground and suspended in deionized water for WAO processing. The polymer materials used for the tests included polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene, cotton, paper, and sawdust. The operating conditions were 280°C temperature, pressure of 300 psia, and a 3-hour residence time. The overall destruction efficiency expressed in terms of TOC was in the range of 69 to 85 percent. The lower destruction efficiency was due to the formation of more refractory compounds such as acetic and benzoic acids and acetone.

After destruction of polymers by batch WAO, a second step is needed to achieve further breakdown of the refractory compounds formed. The investigators suggest using a continuous flow reactor in catalytic mode or a higher temperature to increase destruction efficiency. Use of a one-step process could be considered if a procedure for the introduction of solids into the continuous flow reactor was developed. The investigators also observed that adding calcium carbonate as a neutralizing agent had proved to be efficient in avoiding formation of gaseous chlorine and hydrogen chloride and in preventing corrosion.

3.5 Engineering Design Study Testing for WAO Treatment of NSCMP Neutralent Feeds – Phase IIIa

The work plan for Phase IIIa testing was prepared by US Filter/Zimpro Products for Stone and Webster in July 2002 (US Filter/Zimpro Products, 2 July 2002). This testing is an extension of the previous activities to evaluate the WAO process in a continuous flow configuration with additional candidate feedstocks. The primary objective of this testing is to demonstrate applicability of WAO treatment for the destruction of GB neutralent and DF and QL hydrolysates, and to provide basic operating data to demonstrate the process efficacy and reliable operation of the WAO system. The proposed testing is to validate the overall operation over the sustained period of the processing campaigns in order to verify the process and corrosion assumptions, and to indicate reliability and operability of the full-scale application.

The test plan includes bench WAO optimization tests and continuous flow pilot WAO demonstration tests. Bench-scale MOCs screening tests will be performed to determine appropriate MOCs in the pilot plant for this test work. Additional MOC tests will be performed in the continuous pilot unit.

3.5.1 Objectives. The test plan is designed to meet the following objectives:

- Determine the optimum operating conditions for GB neutralent and Binary hydrolysate treatment by conducting bench-scale autoclave tests at various temperature, pH, and residence time settings.

- Demonstrate the process' efficacy in treating the selected liquid feeds in a continuous flow unit at the MCF rate for the test unit.

- Demonstrate steady state, continuous, safe operation of the WAO system in a configuration similar to that of a full-scale unit.

- Evaluate performance of materials of construction for commercial application of the WAO process for the feedstock.

- Develop engineering data to support development of a full-scale processing concept for this application.

3.5.2 Assessment Criteria. The assessment criteria to evaluate the success of these tests will be as follows:

- The system must achieve 99.9 percent destruction of Schedule 2 compounds as defined by the Chemical Weapons Convention.

- Demonstrate operation of the continuous flow unit in a manner similar to the full-scale concept in a safe mode at MCF for a minimum of 24 hours for each feed material.

- Generate sufficient test data to develop a preliminary concept of a full-scale process.

- Provide recommendations for an appropriate material of construction for the full-scale unit.

3.5.3 Planned Testing. The testing will be conducted in the Zimpro facility located in Wisconsin under the guidance of Stone and Webster, Inc. Zimpro plans to dilute the neutralents for these tests. The GB neutralent will be diluted by a factor of 13 to control the oxygen demand, and the DF neutralent will be diluted by a factor of 2.3 minimum to lower the F concentration below 5,000 milligrams per liter (mg/L). The plan includes 10 bench-scale test runs for optimization and 2 to 4 pilot tests for confirmation with each feedstock. The bench-scale tests will vary the operating parameters in the following ranges to optimize the pilot tests:

- Temperature: 280° to 320°C

- Residence Time: 60 to 180 minutes

- pH: 5 to 11.

The preliminary MOC testing will be conducted in the existing autoclaves at Zimpro. The duration of these tests will be 500 hours. A total of eight tests will be conducted using simulants for the feeds. The test conditions will vary for each test run with two temperatures and two pH levels for each feed. The anticipated materials for the test are Ni-200, In-600, C22, In-690, and Ti-12.

The MOC tests in the pilot unit will be of shorter duration (compared to the time for the autoclave tests) with a minimum 24-hour length for each feedstock. The candidate materials for the pilot MOC study include In-690 (solution annealed), In-690 (mill annealed), and Ni-201 (solution annealed).

3.5.4 Current Status. The bench-scale and pilot-scale tests for the GB neutralent were completed late in 2002 and the results were released in March 2003. The performance tests for DF neutralent were performed in the second week of December 2002. In addition, the test plan was expanded to include QL neutralent. The QL study was also completed in the second week of December 2002, and the results were reported in March 2003. The reported results are not analyzed for inclusion in this document.

SECTION 4
POTENTIAL CHEMICAL DEMILITARIZATION APPLICATIONS OF WAO TECHNOLOGY

The Chemical Demilitarization Program generates a variety of wastes that can be generally categorized into three groups:

a. Primary wastes (stockpile and non-stockpile)

b. Secondary wastes

c. Closure wastes.

The WAO process could potentially be used for some of the wastes (such as neutralents or hydrolysates in solution form and spent carbon, explosives, and DPE suits in slurry form) in each group for the stockpile sites, but all stockpile sites except the Blue Grass Chemical Demilitarization Facility (BGCDF) have already selected technologies for processing their wastes. The BGCDF is also very likely to choose one of the technologies already used by the other stockpile sites. Thus, there is no apparent potential for WAO application at the stockpile sites.

NSCMP primary wastes are those generated by destruction of non-stockpile chemical materiel and include:

- MEA-based and sodium hydroxide–based agent neutralents

- 1,3-dichloro 5,5'-dimethylhydantoin–based agent neutralents from the RRS processing of CAIS material

- Binary precursors DF and QL, and their neutralents.

Extensive testing has been conducted for treating these materials by the WAO process to address the technical problems and to collect design information. Some of the problems have been resolved, and more testing is currently in progress to develop the waste-specific design information for DF and QL neutralents. Thus, the WAO process has considerable potential for the treatment of non-stockpile neutralents. If WAO is to be applied to the treatment of spent carbon or DPE suits from NSCMP sites, then additional testing with these materials will be necessary.

The NSCMP is intending to solicit for a contractor to build an offsite non-incineration facility to process neutralents including those from the binary destruction facility (BDF) and PBNSF. This solicitation provides an opportunity for WAO to be selected as the non-incineration process.

The U.S. Army Construction Engineering Research Laboratories completed WAO batch studies on TNT red water (Joint Services Pollution Opportunity Handbook). Based on the successful results from this study, the WAO process also has a potential to treat any waste containing explosives for the NSCMP.

SECTION 5
TECHNICAL AND ECONOMIC EVALUATION OF WAO PROCESS FOR NSCMP

This section presents a technical and economic analysis of the WAO application for processing the neutralents from agents and binary products for the NSCMP PBA.

5.1 Technology Overview

The technology provider for the WAO process is US Filter/Zimpro Products. They have recommended a non-catalytic WAO process for the NSCMP neutralents, and have conducted bench-scale testing using simulants for neutralents from H and GB agents and simulants for DF and QL binary products. They have also performed pilot testing for H-neutralent simulant, and currently are in the process of conducting pilot testing for DF and QL hydrolysates. Their testing so far has indicated that the WAO process is capable of destroying the toxic compounds in the neutralents and hydrolysates to a concentration below 25 ppm, but the operating conditions have not been optimized. The corrosion testing in their autoclave apparatus had identified Inconel 600 as an appropriate material of construction for H-neutralent, but suitability of this material for other neutralents has not been confirmed. The pilot reactor for Phase IIIa (not evaluated for this report) testing is Inconel 690, based upon additional (Phase IIIa) MOC tests.

5.2 Process Description

The WAO process operates in an aqueous medium at moderate temperatures and high pressures. Pressure is maintained at the steam saturation point to ensure that the water remains liquid. The liquid in the reactor absorbs heat generated from the exothermic oxidation reaction. This heat raises the temperature of the incoming fluid to the saturation temperature for the controlled pressure. If there is any extra heat, then water vaporizes into steam. Heat in the effluent liquid is recovered by preheating the feed.

A simple process flow diagram for the WAO process is shown in figure 5-1. Liquid feed and compressed air are fed to the reactor concurrently. Prior to entering the reactor, the reactants pass through a heat exchanger where heat is absorbed from the liquid effluent by the feed. A control valve regulates the pressure in the reactor. The liquid effluent enters a vapor/liquid separator after passing through the heat exchanger. The vapor effluent from the separator may require further treatment in a thermal oxidizer to remove any VOCs that exceed regulatory limits. The liquid effluent may require ammonia stripping and further oxidation by biotreatment, since WAO does not oxidize the waste completely. Precipitation and separation of heavy metals, if present, may be necessary prior to biotreatment in a publicly-owned treatment works (POTW). A block diagram for an integrated WAO system is shown in figure 5-2. (In order to prevent plugging, the preheating approach described in this section has been modified recently by Zimpro. In this modified approach, the system heats the water/caustic solution, and the waste is fed at ambient temperature through a separate, unheated port into the reactor. This prevents the mineralization of the waste from starting in the small

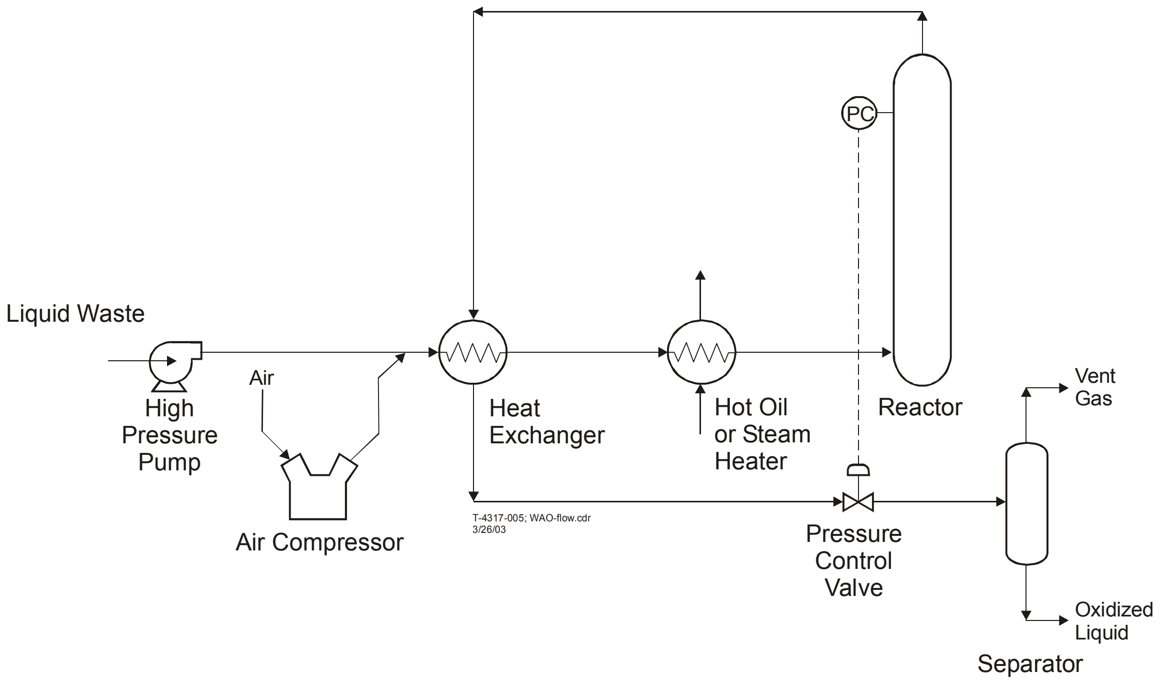

Figure 5-1. WAO Flow Diagram

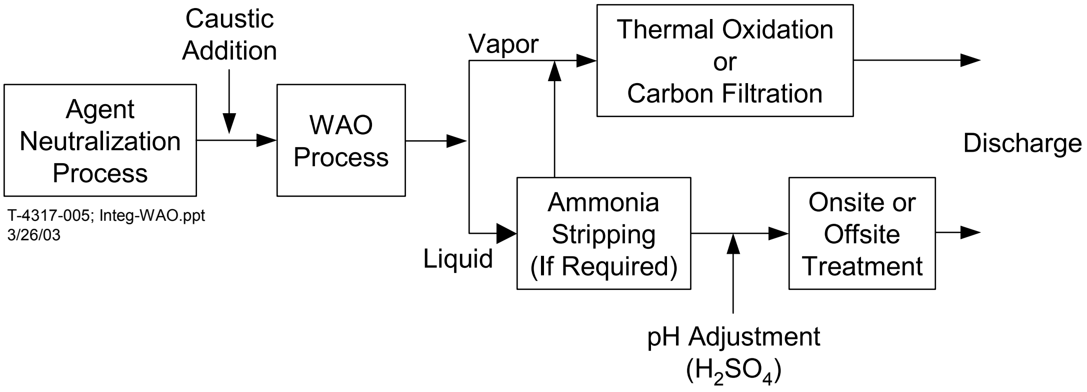

Figure 5-2. Integrated WAO Process

diameter feed lines downstream of the preheater, which is where the plugging occurred in the HD pilot test.)

5.3 Equipment Description

The major equipment components included in the WAO system for the NSCMP application are:

- Bubble column reactor
- High-pressure air compressor (1,500 psia)
- Two high-pressure pumps (primary and standby)
- Feed/effluent heat exchanger
- Process cooler
- Trim heat exchanger

- Liquid/vapor separator
- Instrumentation and valves
- Process piping
- Thermal oxidizer.

The design parameters used in this analysis are as follows:

- The WAO system shall be designed to process diluted material at a nominal rate of 10 gpm. The reactor shall be designed for 400°C temperature and a pressure of 3,500 psia (operating conditions will be lower and will depend upon the type of material processed), and shall provide a maximum residence time of 360 minutes. The material of construction for the reactor and associated equipment shall be the alloy Inconel 600. (This selection may change based on the additional tests for other neutralents). Stainless steel (SS 316) shall be used for the lower temperature components such as feed tanks.
- The thermal oxidizer shall be designed for 2,000°F (or 1,100°C), but be operated at 1,600°F (or 870°C) with a 1-second residence time. The thermal oxidizer shall be refractory lined with a carbon steel shell.
- Each pump shall be capable of pumping feed at 15 gpm with a 1,500 psia discharge pressure. The compressor shall have a capacity of 150 standard cubic feet per minute or 11 pounds per minute air at 1,500 psia. All the heat exchangers shall be a shell and tube type.
- The reactor shall be equipped with a pressure control device. All the heat exchangers shall have temperature controllers.

A preliminary equipment layout for the WAO system is presented in figure 5-3. The facility area is estimated to require approximately 3,000 square feet.

5.4 Technical Analysis of WAO

The WAO process technical analysis is primarily focused on three areas: process efficacy, process safety, and permit issues. Efficacy addresses the major issues associated with the WAO process. These include processing rate; operating conditions; capabilities for destruction and volume or weight reductions; need for process development; commercialization state; and process robustness and reliability. Process safety addresses worker, public, and environmental safety. Permit issues are basically related to the ease of acquiring a regulatory permit for the process.

The WAO process is very mature with many commercial plants in operation. It has an established safety record and is considered to be the best-demonstrated available technology by the EPA for wastewaters.

Some of the disadvantages of the WAO process include:

- It may require additional treatment for destruction of low molecular weight refractory compounds such as acetic acid, formed during WAO process.
- It may require an ammonia stripper for the liquid effluent prior to an additional treatment in the biotreatment process.
- It may need additional development work to address the corrosion issue.
- A thermal oxidizer or carbon filter may be required to treat gaseous effluent from the WAO process.
- The dilution requirement increases the volume of liquid effluent from the WAO process.

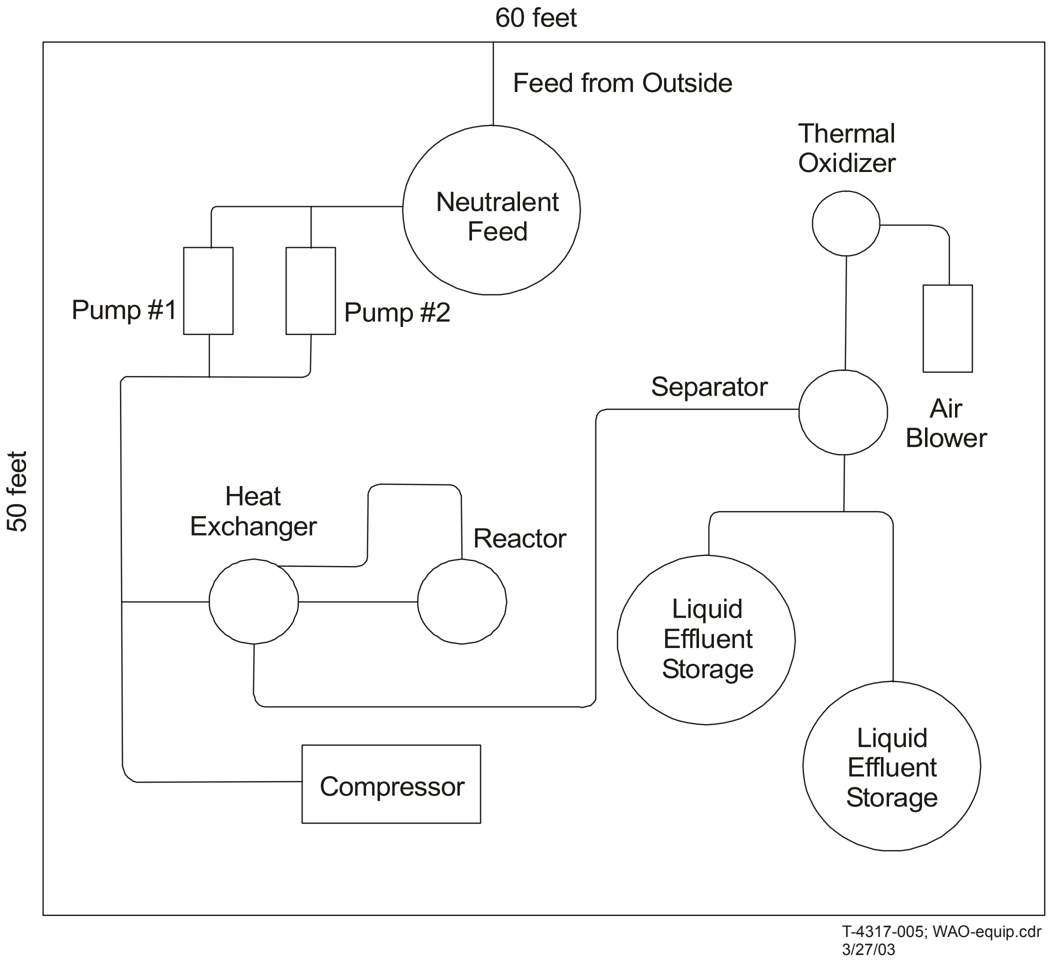

Figure 5-3. WAO Equipment Layout

A technical analysis of the WAO process for the NSCMP application (based on the available information at the time of preparing the draft report, November 2002) is summarized in table 5-1.

5.5 Economic Analysis of WAO for NSCMP

The following analysis includes a preliminary economic evaluation of the WAO process for the NSCMP application at the PBA. This evaluation is based upon rough-order-of-magnitude (ROM) estimates of capital and operating costs for the WAO system.

5.5.1 Schedule. The amount of neutralents to be generated is calculated from the quantities of agents and binary products in the inventory at the PBA and the required dilution factors, as described in table 2-5. The results are summarized in table 5-2. The total quantity of WAO liquid effluent is about 32,000,000 pounds. The processing duration is 1.04 years for all neutralents and binary products based on a 10 gpm processing rate (see table 5-2). Currently, the plans include two separate NSCMP facilities for neutralization at the PBA, one for the agents and the other for the binary products. The WAO processing duration for the BDF will be about 0.9 years and for the PBNSF it will be 0.14 years. These times are based on 24-hour, 7-day operation and would extend about 40 percent, if the operation would be 5 days per week. Even with the 5-day operation, the total processing duration for the BDF would be 15 months and for the PBNSF it would be less than 3 months. These durations are within the allocated time frame of 2 years for the BDF and 1 year for the PBNSF at the PBA. A single onsite WAO system for both facilities would be advisable to minimize cost without any impact on the schedule.

5.5.2 Cost Estimate. The cost analysis presented here is based on a processing rate of 10 gpm. The specific equipment included in the cost is provided in section 5.3. Not included are an ammonia stripper, and phosphate and heavy metal precipitators. The capital equipment ROM estimate was provided to Stone and Webster by the vendor, US Filter/Zimpro Products, and was $4.5 million, as shown in table 5-3. This estimate

Table 5-1. Technical Analysis of WAO for NSCMP

Criteria	WAO
Process Efficacy	
Processing Rate	10 gallons per minute
Auxiliary Systems Required	Additional oxidation and ammonia stripper for liquid effluent, and thermal oxidizer for gaseous effluent
Need for Development	Some pilot testing required for design data; plugging problem resolved by incorporating a rinse cycle for 5 minutes every hour; corrosion studies with simulants have identified Inconel 600 as a choice for the material of construction for H-neutralent
Commercial Availability	Many commercial plants in operation
Destruction/Removal Efficiency (DRE)	High for specific compounds, but may be low for TOC
Materials of Construction	Some testing may be required
Auxiliary Requirements	Compressed air or oxygen and electric power
Availability/Reliability	Assumed to be about 0.7; the impact of rinse cycle on availability needs to be considered if necessary
Operating Conditions	Temperature about 300°C; pressure about 3,200 psia
Controls	Established
Robustness	Process has a long commercial history of treating other organics similar to H, GB, DF, and QL hydrolysates or neutralents
Waste Weight Reduction	Very small weight reduction, but large dilution required for neutralent
Waste Volume Reduction	No volume reduction; increase in volume of neutralent due to dilution requirement (organic concentration below 6 percent)
Process Safety	
Worker Safety	High-pressure operation; leakage through pump may spray liquid on operating personnel in the area; protective clothing would be necessary
Public Safety	Large inventory in a reactor during abnormal conditions; secondary containment around pumps and reactor would be necessary.
Environment Safety	Further treatment of gaseous and liquid effluents necessary
Permit Issue	EPA has designated WAO as the best available technology for wastewater treatment

Notes:

DF = methylphosphonyldifluoride
EPA = Environmental Protection Agency
GB = sarin
H = mustard agent
psia = pounds per square inch absolute
QL = O-ethyl-2-diisopropylaminoethyl methylphosphonite
TOC = total organic carbon
WAO = wet air oxidation

Table 5-2. WAO Liquid Effluent Generation and Processing Times

Liquid Effluent	NSCMP
H (pounds)	40,000
GB (pounds)	3,000
DF (pounds)	254,000
QL (pounds)	98,000
MEA-based H-neutralent (pounds)[a]	320,000 (S&W, February 2002a)
MEA-based GB-Neutralent (pounds)[b]	25,000 (S&W, February 2002a)
WAO Liquid Effluent from H neutralent (pounds)	4,800,000
WAO Liquid Effluent from GB Neutralent (pounds)	200,000
WAO Liquid Effluent from DF (pounds)[c]	25,400,000
WAO Liquid Effluent from QL (pounds)[d]	1,800,000
Total Liquid Effluents (pounds)	32,000,000
WAO Processing Time (hours)[e]	6,400
WAO Processing Duration (hours)[f]	9,150
WAO Processing Duration (years)	1.04

Assumptions:

[a] MEA-based H-neutralent is 8 times the weight of agent, and WAO liquid effluent is 15 times the weight of neutralent.
[b] MEA-based GB-neutralent is 8.5 times the weight of agent, and WAO liquid effluent is 8 times the weight of neutralent.
[c] DF is diluted by a factor of 100 (weight basis) prior to WAO treatment.
[d] QL is diluted by a factor of 18 (weight basis) prior to WAO treatment.
[e] WAO processing rate is assumed to be 5,000 pounds per hour (or 10 gallons per minute).
[f] WAO availability is assumed to be 0.7 to calculate processing duration.

DF = methylphosphonyldifluoride
GB = sarin
H = mustard agent
MEA = monoethanolamine
NSCMP = Non-Stockpile Chemical Materiel Product
QL = O-ethyl-2-diisopropylaminoethyl methylphosphonite
S&W = Stone and Webster, Inc.
WAO = wet air oxidation

Table 5-3. Cost Analysis of WAO Process for NSCMP Application

Parameter	Onsite WAO
Diluted Neutralent Amount for WAO Processing (pounds)	32,000,000 (table 5-2)
Process Rate (pounds/hour)	5,000
Processing Time (hours)	6,400 (table 5-2)
Availability Factor	0.7
Processing Duration (years)	1.04 (table 5-2)
Man Power Required	8
Annual Labor Cost ($/year)[a]	600,000
Annual Utility Cost ($/year)	300,000
Annual Operating Cost ($/year)	900,000
Effluent Liquid Disposal Cost ($)[b]	1,600,000
Capital Equipment Cost ($)	4,500,000 (S&W, February 2002b)
Equipment Installation Cost ($)[c]	2,250,000
Facility Cost ($)[d]	3,000,000
Total Capital Cost for Installation ($)	9,750,000
Total Operating Cost ($)	950,000
Total Cost for Disposal ($)	12,300,000

Notes:

[a] Manpower cost is assumed to be $75,000 per year.
[b] The cost of WAO effluent liquid is assumed to be $0.05 per pound.
[c] The installation cost is assumed to be 50 percent of equipment cost.
[d] The facility size is 3,000 square feet and facility cost is assumed to be $1,000 per square foot.

S&W = Stone and Webster, Inc.
WAO = wet air oxidation

assumes the reactor residence time of 360 minutes (Stone and Webster, Inc., 2002b) and the material of construction to be alloy Inconel 600. The equipment cost includes engineering and design but does not include the cost of installation. Adding 50 percent of the equipment cost for installation raises the estimate to $6.75 million. The facility square footage is estimated to be about 3,000 square feet as shown in figure 5-3. Using an average cost of $1,000 per square foot for the facility, the facility cost is projected to be $3 million. Thus, the total cost of the WAO facility, including installed equipment, is $9.75 million (see table 5-3).

The previously-mentioned ROM is in fair agreement with another independent cost estimate reported by U.S. Army Construction Engineering Research Laboratories. Their estimate was $12 million for total installation of a WAO system with a capacity of 16,000 gallons per day, which is equivalent to 11.1 gpm. The residence time for the reactor is 60 minutes, and the waste to be processed is TNT red water. The capacity of the unit is about 10 percent higher, and the total cost is about 22 percent higher. Both estimates are based on the same year dollars (year 2001). The operating and maintenance cost reported by them was $974,000 per year. This is comparable to the estimated annual operating cost of $900,000, as shown in table 5-3. This operating cost includes annual labor costs of $600,000 for eight people at $75,000 per person and $300,000 per year for utilities. The liquid effluent generated from the WAO process will need additional treatment. A cost of $0.05 per pound is assumed for its disposal, which amounts to $1.6 million (see table 5-3) for 32,000,000 pounds of liquid effluent. The annual operating cost is multiplied by the processing duration in years, and the liquid effluent disposal cost is added to arrive at the total operating cost. The addition of capital and operating costs provided the estimate for the total cost to dispose of the waste. It is estimated to be about $12.3 million for a WAO process for treating the combined neutralent waste from the BDF and PBNSF.

Stone and Webster, Inc. (Stone and Webster, February 2002b) estimated the capital cost for treating the liquid effluent from the WAO process onsite, using the post-oxidation treatment stages and fluoride/phosphate precipitation stage, to be $1.8 million. The installation and facility costs would need to be added to this estimate and there would be additional utility costs associated with this equipment, resulting in an overall cost considerably higher than the offsite disposal cost estimate of $1.6 million in table 5-3. Therefore, sending the liquid effluent from the WAO process for offsite treatment is preferred.

SECTION 6
CONCLUSIONS AND RECOMMENDATIONS

The major conclusions and findings from this evaluation of the WAO process are categorized in different groups and are summarized in the following paragraphs.

6.1 General

- The WAO process is mature and commercially available. More than 300 WAO plants are safely operating worldwide. The process has been in use in municipal, commercial, and industrial facilities for more than 50 years; thus, the WAO process has a proven safety record.

- The WAO process normally operates in a temperature range of 150° to 300°C, a pressure range of 150 to 3,150 psia, and a residence time of 1 to 2 hours. It is capable of destroying the higher molecular weight toxic constituents in neutralent liquids with more than 99 percent destruction efficiency.

- The WAO process generates lower molecular weight compounds (refractory compounds) such as acetic acid, which will require additional treatment or the use of a catalyst in the WAO process for destruction of the refractory compounds.

- Objectionable pollutants such as NO_X, SO_X, dioxins, furans, and particulates are not formed during the low temperatures of operation for WAO.

- Large water dilution could be a significant advantage in treating energetic materials (propellants and explosives). Explosion or detonation should not occur if there is adequate mixing, although this would require demonstration.

6.2 Test Findings

- The tests completed so far have provided preliminary information to address the corrosion and plugging issues for the NSCMP wastes. Additional tests in progress at Zimpro will provide more specific design information for operating temperature, pressure, and residence time. Material compatibility for auxiliary system components needs careful evaluation, since gasket failures for pressure control valve were observed during bench-scale testing at Zimpro.

- Plugging problems in the WAO process can be overcome by incorporating a short cycle of water rinse. This cycle time was observed to be 5 minutes every hour during H-neutralent simulant testing. The rinse cycle will affect the process availability and will extend the duration of the campaign for a selected processing rate.

- Sodium carbonate is formed at a pH of 10 or higher by the reaction of caustic with CO_2. As sodium carbonate has reverse solubility at temperatures above 50°C, its formation needs to be minimized to avoid plugging and scaling problems. Operating the WAO system at a pH of 7 to 8 needs to be further investigated.

- The screening tests for materials of construction indicated Inconel 600 to be the most appropriate material for H-neutralent simulant. Use of this material for other neutralents will require additional tests in actual or simulated environments for the neutralents.

6.3 Auxiliary Equipment Needs

- Because QL contains nitrogen, there is a possibility of ammonia formation during WAO processing of QL neutralent. The ammonia will dissolve in the liquid medium and may require stripping prior to biotreatment of the liquid effluent from the WAO process.

- A thermal or catalytic oxidizer may be necessary for treatment of gaseous effluent from the WAO process.

- If the liquid effluent from the WAO process is discharged into a POTW or FOTW, the regulatory limitations for phosphate, sulfate, and heavy metals need to be considered. It may be necessary to remove these components by precipitation prior to biotreatment in a POTW or FOTW.

6.4 Design

The reactor design for NSCMP application will require careful review. During bench-scale tests for DF, a residence time of 360 minutes was observed. The normal residence time in WAO is 1 to 2 hours. The reactor size would be considerably larger for a 6-hour residence time and would contain a large inventory of material (3,600 gallons) at high pressure.

6.5 Other Applications

The WAO process has potential for treatment of spent activated carbon and contaminated DPE suits, if they are converted into slurry form. If WAO is selected for treatment of neutralent or hydrolysate at a site, then its application for these wastes should be explored. Additional testing would be required.

6.6 Cost and Schedule

- The capital cost including installation and facility for a 10 gpm WAO system is estimated to be approximately $9.75 million and the operating cost is on the order of $900,000 per year. The total disposal cost of neutralents by an onsite WAO process at PBA for NSCMP is estimated to be about $12.3 million.

- The vendor, Zimpro, has roughly estimated a maximum of 18 months for design, construction, and delivery of a full-scale WAO unit.

- The estimated cost for offsite disposal of the WAO liquid effluent of 32,000,000 pounds is $1.6 million for the NSCMP. This cost is based on the dilution necessary (5 to 15 times) for the neutralents prior to treatment by WAO.

The application of the WAO process for the NSCMP is a possibility because of the extensive testing already done with the WAO process for neutralents for the NSCMP and some problems have already been resolved.

The recommendations from this evaluation are summarized as follows:

a. Pilot testing of the WAO process for DF and QL neutralents is currently in progress at Zimpro. It is recommended that the test results from the DF and QL neutralent testing be reviewed (when available) and captured in a supplement to this report.

b. WAO continues to be a technology option for non-stockpile neutralents and monitoring should continue.

APPENDIX A

ACRONYMS/ABBREVIATIONS

APPENDIX A

ACRONYMS/ABBREVIATIONS

ACWA	Assembled Chemical Weapons Assessment
BDF	binary destruction facility
BGCDF	Blue Grass Chemical Agent Disposal Facility
CAIS	chemical agent identification set(s)
Cl	chloride
CO	carbon monoxide
CO_2	carbon dioxide
COD	chemical oxygen demand
CWM	chemical warfare materiel
DF	methylphosphonyldifluoride
DMMP	dimethyl methylphosphonate
DMSO	dimethyl sulfoxide
DPE	demilitarization protective ensemble
ECBC	Edgewood Chemical Biological Center
EPA	Environmental Protection Agency
F	fluoride
Fe^{+2}	iron
FOTW	federally-owned treatment works
GB	sarin (isopropyl methyl phosphonofluoridate)
gph	gallons per hour
gpm	gallons per minute

H	mustard agent (distilled), [bis(2 chloroethyl) sulfide]
H_2	hydrogen
HF	hydrogen fluoride
L	lewisite
MCF	maximum continuous flow
MEA	monoethanolamine
mg/L	milligrams per liter
MMD	Munitions Management Device
MOC	material of construction
N_2	nitrogen
NO_x	nitrogen oxides
NRC	National Research Council
NSCMP	Non-Stockpile Chemical Materiel Product
PBA	Pine Bluff Arsenal
PBNSF	Pine Bluff Non-Stockpile Facility
PMCD	Program Manager for Chemical Demilitarization
PMNSCM	Product Manager for Non-Stockpile Chemical Materiel
POTW	publicly-owned treatment works
ppm	parts per million
psia	pounds per square inch absolute
QL	O-ethyl-2-diisopropylaminoethyl methylphosphonite
ROM	rough order of magnitude
RRS	Rapid Response System
SCWO	supercritical water oxidation
SO_x	sulfur oxides

t	tertiary
TNT	trinitrotoluene
TOC	total organic carbon
UV	ultraviolet light
VOC	volatile organic compound
VX	nerve agent, O ethyl S-(2-diisopropylaminoethyl)methylphosphonothioate
WAO	wet air oxidation

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APPENDIX B
REFERENCES

APPENDIX B
REFERENCES

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