
Using Supercritical Water Oxidation to Treat Hydrolysate from VX Neutralization

Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program
Board on Army Science and Technology
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Preface

The United States has maintained a stockpile of highly toxic chemical agents and munitions for more than half a century. In 1985, Public Law 99-145 mandated an “expedited” effort to dispose of M55 rockets containing unitary chemical warfare agents because of their potential for self-ignition. This program soon expanded into the Army Chemical Stockpile Disposal Program (CSDP), whose mission was to eliminate the entire stockpile of unitary chemical weapons. The CSDP developed the current baseline incineration system for that purpose. Since 1987, the National Research Council (NRC), through its Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee), has overseen the Army's disposal program and has endorsed the baseline incineration system as an adequate technology for destroying the stockpile. In 1992, after setting several intermediate goals and dates, Congress enacted Public Law 102-484, which directed the Army to dispose of the entire stockpile of unitary chemical warfare agents and munitions by December 31, 2004.

In response to growing public concerns about, and opposition to, incineration, the Army has been investigating alternatives. In 1993-1994, the Stockpile Committee reviewed an earlier NRC study of alternative technologies and recommended that the Army continue research on four alternative technology combinations for agent destruction, all based on neutralization (chemical hydrolysis). The committee was concerned, however, that neutralization alone might not be sufficient to meet destruction and disposal requirements and recommended that the Army consider four different post-neutralization treatment options: biodegradation; incineration; wet air oxidation followed by biological oxidation; and supercritical water oxidation. The Army decided that it could pursue only two options within its funding and time constraints: neutralization; and neutralization followed by biological treatment.

In 1995, at the request of the assistant secretary of the Army for research, development and acquisition, the NRC established the Panel on Review and Evaluation of Alternative Disposal Technologies (AltTech Panel) to reexamine the status of a limited number of maturing alternative chemical disposal technologies (including the two neutralization-based processes on which the Army was then conducting research) for possible implementation at the two bulk-storage sites at Aberdeen Proving Ground, Maryland, and the Newport Chemical Activity, Indiana.

The AltTech Panel's NRC report recommended that the Army pilot-test VX neutralization with sodium hydroxide solution at Newport. The report also recommended that, if on-site disposal of the VX hydrolysate (from the neutralization process) was preferable to shipping it off site for treatment, existing commercial processes other than biodegradation should be considered because research on existing biodegradation processes has shown that they do not achieve adequate destruction.

In 1997, after reviewing several secondary treatment options, the Army selected supercritical water oxidation (SCWO) as the most promising technology for treating the VX hydrolysate. SCWO technology has developed from bench-scale testing to a few pilot-scale demonstrations, as well as one current and several pending full-scale operations to treat hazardous wastes. The Army recognized that further development and testing would be necessary before a full-scale SCWO treatment system could be designed, installed, and operated and requested that the NRC evaluate whether SCWO would be an effective and appropriate method for treating VX hydrolysate for ultimate disposition. The NRC was not asked to conduct an in-depth analysis of the entire VX bulk agent destruction and disposal process for the Newport Chemical Agent Disposal Facility. When the facility design is being finalized (March 1999–April 2000), the NRC may be asked to assess all aspects of the facility design, including monitoring, containment, process control, and redundancy, as well as the quantitative risk assessment (QRA).

This report has been reviewed by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's

Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the authors and the NRC in making the published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The content of the review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their participation in the review of this report:

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While the individuals listed above have provided many constructive comments and suggestions, responsibility for the final content of this report rests solely with the authoring committee and the NRC.

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Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program

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Acronyms

COD	chemical oxygen demand
CSDP	Chemical Stockpile Disposal Program
CWC	Chemical Weapons Convention
DMMP	dimethyl methylphosphonate
DRE	destruction removal efficiency
EFFDRUM	effluent drum
EMPA	ethyl methylphosphonic acid
EPA	Environmental Protection Agency
HEPA	high-efficiency particulate air
$\mu\text{mhos/cm}$	micro siemens/centimeter (unit of conductance equal to the reciprocal of the ohm)
MPA	methylphosphonic acid
NECDF	Newport Chemical Agent Disposal Facility
NEPA	National Environmental Policy Act
NMR	nuclear magnetic resonance
NRC	National Research Council
PPE	personal protective equipment
QRA	quantitative risk assessment
RCRA	Resource Conservation and Recovery Act
SCWO	supercritical water oxidation
SIP	State Implementation Plan
TC	ton container
TCC	ton container cleanout
TDS	total dissolved solids
TOC	total organic carbon
TSDF	treatment, storage, and disposal facility
VOC	volatile organic compound
VX	a specific type of nerve agent

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Executive Summary

The U.S. Army has asked the National Research Council (NRC) to evaluate whether supercritical water oxidation (SCWO) is an effective and appropriate means of eliminating hazardous or toxic organic constituents in VX hydrolysate for ultimate disposition. The NRC was not asked to conduct an in-depth analysis of the entire integrated VX bulk agent destruction and disposal process for the Newport Chemical Agent Disposal Facility. As the facility design is being finalized (March 1999-April 2000), the NRC will probably be asked to assess all aspects of the facility design, including monitoring, containment, process control, and redundancy, as well as the quantitative risk assessment (QRA). This report outlines the elements of the proposed neutralization/SCWO technology, evaluates the results of ongoing SCWO tests, and makes recommendations concerning aspects of the technology that require further development. The scope of this evaluation did not include evaluations of other potential technologies or management options for the treatment of VX hydrolysate.

BACKGROUND

The United States undertook the destruction of its stockpile of chemical weapons long before the passage of the Chemical Weapons Convention (CWC), which came into force April 29, 1997. The U.S. Army, as the executive agent for the U.S. Department of Defense, presently uses a combination of incinerators to destroy chemical agents in bulk containers and assembled munitions (e.g., rockets and artillery projectiles) at two sites. The Army also plans to use incinerators at several other stockpile storage sites. However, public concerns associated with incineration have prompted the Army to consider alternative destruction technologies at two sites (Aberdeen, Maryland, and Newport, Indiana) where chemical agents are stored in bulk and are more accessible than those contained in weapons. The technology chosen for these two sites was chemical neutralization, which detoxifies chemical agents. This decision was reached with input from the NRC Panel on Alternative Chemical Disposal Technologies (AltTech Panel). For the stockpile site at Aberdeen, Maryland, chemical neutralization followed by microbial degradation was selected by the Army for the destruction of mustard, which is the only agent in the stockpile stored there. The overall process for treatment of the nerve agent VX at Newport, Indiana, (shown in [Figure ES-1](#)) consists of four primary operations in series:

- draining VX from ton containers and ton container cleanout operations (ton container cleanout)
- neutralization of the agent and ton-container cleanout fluids (neutralization)
-
- evaporation followed by condensation of water for recycling and filtration to recover crystallized salts for disposal (evaporation)

The overall process is planned to be operated 24 hours a day, seven days a week, with up to six ton containers of VX being processed each day (1,689 ton containers holding a total of 1,269 tons of VX are stored at the Newport site).

VX ($C_{11}H_{26}NO_2PS$) is one of the most toxic chemical agents. It has a low vapor pressure and evaporates slowly under normal atmospheric conditions. As little as 10 mg of the agent absorbed through the skin or lungs will kill or incapacitate a 70 kg individual by a massive disruption of central nervous system function. Thus, the cleaning of containers and the processing of streams that contain VX can only be done in carefully designed and ventilated enclosures.

In the first processing step, ton container cleanout, the ton containers will be drained, cut in half, and cleaned with steam and hot water sprays. The wash water will contain small amounts of VX and will be treated during the agent neutralization process.

In the second processing step, neutralization, VX will be hydrolyzed in a hot (90°C) solution of about

13 wt. percent NaOH (sodium hydroxide) in water in a six-hour batch process. Parallel systems of batch processing will be provided to facilitate continuous operation and allow for periodic maintenance. The main function of the neutralization process is to break the phosphorus-sulfur bond in the VX molecule, which greatly reduces the toxicity of the neutralization/hydrolysis products. The main reaction products are the sodium salt of ethyl methylphosphonic acid (EMPA) and a thiol (a hydrocarbon derivative that also contains nitrogen and sulfur atoms). A side reaction produces methylphosphonic acid (MPA), a relatively innocuous substance. Laboratory and pilot-scale neutralization tests indicate that the neutralization process has an overall destruction efficiency for VX of more than 99.9999 percent. Prior to release from the neutralization process step to subsequent treatment steps, both VX and EA-2192¹ must be nondetectable in the hydrolysate, with detection limits established at 20 ppb for VX and 5 ppm for EA-2192.

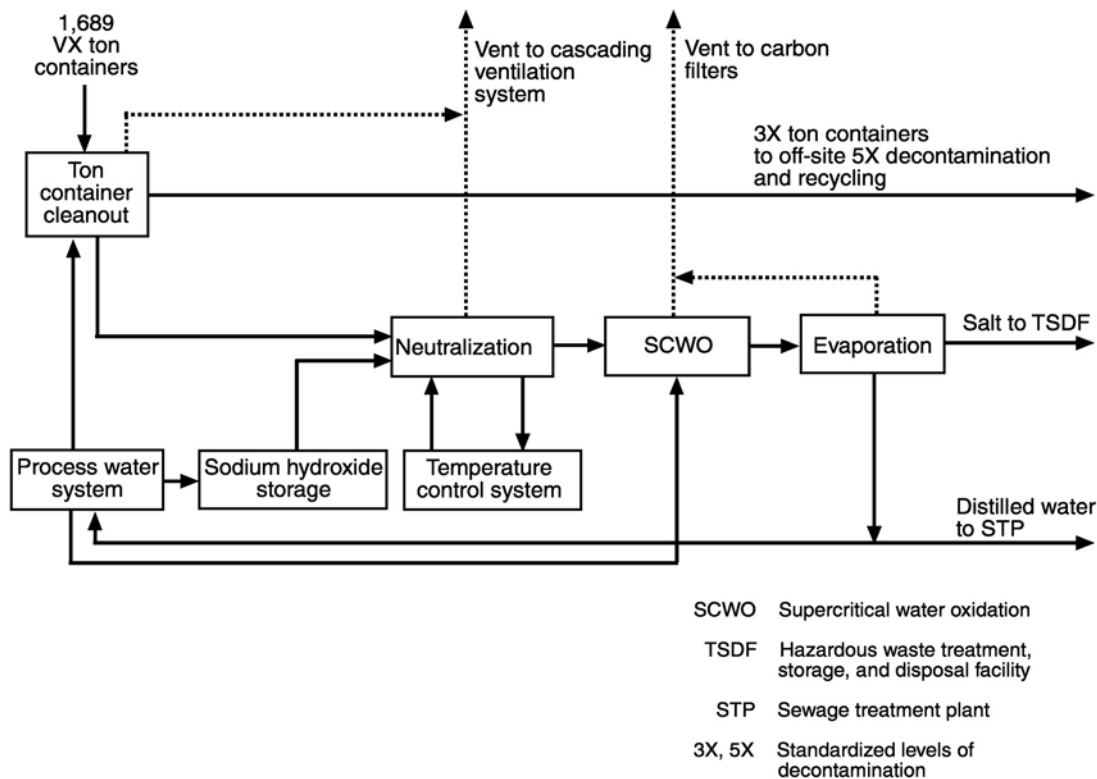


FIGURE ES-1 Overview of the disposal process for VX ton containers.

However, EMPA and MPA and some other trace compounds in the hydrolysate still contain carbon-phosphorus bonds and are considered “Schedule 2 precursors” in the CWC because they could potentially be reconverted to nerve agent. Therefore, the hydrolysate must be treated further to meet CWC requirements, as well as general requirements for safe and environmentally acceptable disposal.

After reviewing several options for secondary treatment, the Army has selected SCWO as the most promising technology for the third processing step, although further development and testing will have to be done before a full-scale treatment system can be built. The Army's schedule for implementing SCWO technology is ambitious but consistent with CWC treaty deadlines. The SCWO system is a hydrothermal process for the oxidation of the VX hydrolysate that yields a wastewater stream and salts.

In the fourth processing step, evaporation, the waste-water will be evaporated to provide distilled water, which can be recycled back to the process, and residual salts, which will be disposed of in a suitable hazardous waste facility. Excess distilled water from the evaporator will be discharged to a sewage treatment plant.

¹EA-2192, an intermediate product during the neutralization reaction, further reacts to form EMPA. EA-2192 is a nerve toxin.

The tank cleaning, neutralization, and evaporation processing steps are all based on well known technologies, although some adaptations will be needed. However, SCWO is a relatively new technology being used for some hazardous waste treatment applications. For the evaluation of SCWO technology for the treatment of VX hydrolysate, the Stockpile Committee reviewed documents on SCWO process fundamentals, previous applications, testing carried out specifically for application to VX hydrolysate, and the planned process design for the Newport facility; met with SCWO academic researchers, process developers from Sandia National Laboratory, and vendors; visited a pilot-scale SCWO testing facility; and discussed the process with the Army and its process design contractors.

SCWO technology involves operations above the critical temperature and pressure of pure water ($T_c = 374^\circ\text{C}$, $P_c = 221$ bar), where the properties of water are significantly altered. At supercritical conditions, organic compounds that are insoluble at ordinary temperatures usually become more soluble, whereas salts that are soluble at ordinary temperatures become much less soluble. Thus, organic materials in supercritical water can be rapidly oxidized using air or oxygen to produce fully oxidized species, with the salts precipitating out. In the last two decades, SCWO technology has evolved from the bench-scale treatment of certain organic hazardous wastes to limited, modest commercial operation. However, using this technology to treat VX hydrolysate raises several challenges. These include the reaction kinetics, full-scale reactor design, the management of the large volumes of salts generated, and corrosion problems associated with the fluid streams and salt deposits.

The reaction mechanisms for the destruction of organic compounds by SCWO generally involve free radical chain reactions with oxidative radicals (mostly $\bullet\text{OH}$ and $\bullet\text{OOH}$). Thermal bond cleavage and polar or ionic reactions, including hydrolysis, also occur under these severe conditions. With residence times of seconds to minutes at temperatures of 400 to 650°C, very high destruction efficiencies (> 99 percent to 99.9999 percent) have been reported for the destruction of a large number of organic compounds. Aqueous organic wastes with sufficient fuel value can be autogenic; i.e., they can sustain the necessary reaction temperatures for extensive oxidation without supplemental fuel.

In a SCWO process, the aqueous input stream is pressurized, heated, and mixed with oxidant (e.g., air or pure oxygen), then pumped through a flow reactor at the supercritical conditions designed to provide the required residence time. Heat produced by the oxidation can be recovered (or must be removed) based on the heat content of the waste stream. If the input stream has inadequate fuel value to heat the reactor, make-up fuel can be added. Downstream of the reactor, the pressure in the system is “let down” either before or after cooling. Solids produced from oxidation reactions can be recovered prior to or following pressure let-down. Cooling prior to pressure let-down often results in the redissolution of salts, which can be removed later via evaporation.

A number of pressure let-down schemes have been devised—predominantly valves or capillary tubes that restrict the release of fluids from the process equipment. The effluent is then passed through gas/liquid separators, and the gas stream and aqueous streams can be treated further, as required for responsible disposal. All gases produced during the SCWO treatment step are filtered prior to release using activated carbon to remove any residual volatile organic contaminants. With adequate salt removal, most of the water effluent can be recycled within the plant. The plant design will be expected to include a final evaporator where the water will be distilled to produce a dry salt. Any excess water requiring disposal should be very clean.

SCWO technology has matured from bench-scale testing to a few pilot-scale demonstrations, as well as one current and several pending full-scale operations. Although it has been tested on a laboratory scale for treatment of a wide variety of wastes ranging from hazardous waste to sewage sludge, pilot-scale testing for the treatment of more complex wastes (e.g., heterogeneous wastes, wastes containing high concentrations of heteroatoms that generate salts, and corrosive wastes) has been limited. Wastes characterized by high salt or salt producing content and corrosivity during treatment have presented major technological challenges.

The implementation of SCWO technology has evolved into three basic reactor configurations and two approaches to temperature and pressure reduction after reaction at supercritical conditions. The three basic reactor configurations are tubular, vertical cylindrical, and transpiring wall. All three configurations mix the reactants (waste, supplementary fuel [if required], and oxidant) at the entrance or in the uppermost zone of the reactor.

Only the vertical cylindrical configuration has been demonstrated at pilot-scale for the treatment of VX hydrolysate and similar wastes. Tubular reactors utilize relatively small-diameter high pressure tubing with long

lengths (about 3 cm dia. × 36 m) to achieve the required residence times for reaction. The relatively high flow velocities (e.g., 1 m/s) could be helpful for moving precipitated salts along. However, the long reactor lengths are usually oriented horizontally with several passes (i.e., U-bends) or spirals. The narrow inner diameter and the bends in these configurations make them less desirable for systems at pressures of approximately 400 bar and with high salt loadings because of the presence of a solid salt phase and the possibility of salt deposition and plugging. The vertical cylindrical reactor has a larger diameter and much shorter length (9 to 25 cm diameter × 2 to 5 m length) to achieve the residence time required for reaction. Transpiring wall reactors inject significant quantities of water through porous walls to limit salt deposition. Limited experience with transpiring wall reactors suggests that counterdiffusion of reaction constituents can still create corrosion and salt deposition problems. This type of reactor requires additional development testing before it can be scaled up for corrosive, high salt, full-scale applications.

Using SCWO to treat VX hydrolysate raises many challenges. The operating conditions (temperature, pressure, and residence time) for the destruction of the carbon-phosphorus bond in EMPA and MPA, combined with the transition from alkaline to acidic composition during oxidation of the hydrolysate components, creates severe requirements for the materials of construction to prevent corrosion. In addition, the large amount of inorganic salt-producing elements present in the original VX (P, S) and added during the neutralization process (Na as NaOH) require that a high solids content fluid be managed in and downstream of the SCWO reactor. Experience has shown that salts that are insoluble in the SCWO reactor fluid phase have a propensity to adhere to the reactor walls, which can cause reactor plugging, and to erode the components of pressure let-down systems.

These problems have been overcome for the treatment of other wastes. However, the composition of VX hydrolysate is significantly different from other wastes treated by SCWO technology because VX has a high solids-producing content, and the solution is severely alkaline. Pilot-scale testing of SCWO technology specifically for the treatment of VX hydrolysate has been limited to tests of a vertical cylindrical reactor (1) for intervals of a few hours using surrogates for the hydrolysate and (2) three tests with actual VX hydrolysate (two tests for less than two hours and one test for approximately eight hours). Therefore, a specific development program for using SCWO to treat VX hydrolysate will have to be conducted before SCWO can be applied at full scale. The treatment of hydrolysate represents a new type of application for SCWO and consequently is the focus of the findings and recommendations presented here.

FINDINGS

Finding 1. Limited pilot-scale testing has demonstrated the ability of SCWO to achieve high destruction efficiencies for the organic constituents of VX hydrolysate. Effluent from SCWO treatment of VX hydrolysate has been shown to have negligible acute toxicity in intravenous testing in mice, gavage testing in rats, and dermal testing in rabbits. The separation of salts in the effluents from SCWO through an evaporator system should produce relatively pure water suitable for discharge and solid salts suitable for disposal. Treatment requirements for VX hydrolysate are less stringent than they are for VX because the hydrolysate has low toxicity relative to the agent. However, criteria for process destruction efficiency and final disposal standards have not been established.

Finding 2. Using SCWO to treat VX hydrolysate is significantly different and more complex than previous applications. SCWO systems on a pilot scale have been used to treat several other types of wastes, but SCWO is in commercial operation at only one site. There has been only limited pilot-scale or operational-scale experience with wastes that are similar to VX hydrolysate in being highly corrosive and salt-laden. Operation with VX hydrolysate or appropriate surrogates at design conditions, equipment configuration, or approximate scale for full-scale operations has not been demonstrated. A vertical cylindrical reactor is the only reactor configuration that has been successfully demonstrated to date at pilot scale for the treatment of VX hydrolysate and similar waste streams. Additional development and pilot-scale testing of SCWO technology will be necessary to ensure sustained, reliable operation of a full-scale integrated treatment system. Sufficient time appears to be available in the Army's implementation schedule for the Army to carry out development and testing for using SCWO at the Newport site, provided they are carried out expeditiously.

Finding 3. Pilot-scale operation of SCWO in a vertical cylindrical reactor at the temperature and pressure necessary for the effective destruction of hydrolysate constituents has been limited to one eight-hour and two less than two-hour tests. During pilot-scale testing with hydrolysate, the following factors were identified that could create difficulties in sustaining system performance:

- Large quantities of insoluble salts were produced, which must be effectively managed within, and downstream of, the SCWO reactor.
- Unexpected fluctuations were observed in temperature, pressure, and salt expulsion from the SCWO reactor.
- High levels of corrosion and erosion of materials of construction were observed in the reactor liner and pressure let-down valves.
- The sustained performance and reliability of the pressure let-down system was not demonstrated.

Although at this point in development the Stockpile Committee cannot be certain, it believes that a SCWO system for the treatment of VX hydrolysate with sufficient sustained performance can be achieved with additional development and testing.

Finding 4. Limited bench-scale and pilot-scale tests have demonstrated operating regimes under which SCWO can effectively destroy carbon-phosphorus bonds and oxidize the organic constituents present in VX hydrolysate. The demonstrated conditions for high levels of destruction (> 99 percent) include temperatures between 640°C and 730°C and pressures between 234 and 261 bar. At temperatures and pressures below this regime, effluent from SCWO processing may contain significant concentrations of residual organic species that are difficult to destroy, including constituents with carbon-phosphorus bonds.

A basis for the reliable scale-up and operation of SCWO technology for the treatment of VX hydrolysate has not yet been demonstrated. Fundamental knowledge about the following processes within the SCWO reactor is still not available:

- the number and characteristics of the physical phases, including large quantities of entrained and adhered solids and potentially liquid, gas, and supercritical fluid phases
- fluid dynamics and mixing processes complicated by relatively high loadings of insoluble salts
- heterogeneous and homogeneous reaction mechanisms and kinetics
- salt nucleation, particle growth, agglomeration and adhesion mechanisms, and kinetics

Because the understanding of fundamental processes is limited and the process operational data and experience are sparse, empirical design and engineering judgment will be required for the selection of a prudent scale for development prior to full-scale demonstration. This is common engineering practice.

Finding 5. Alkaline VX hydrolysate and its destruction products under SCWO reaction conditions create an extremely corrosive and erosive environment that requires the careful selection of materials of construction. Although preliminary data indicate that certain noble metals, such as platinum and gold, may have acceptable properties, the data currently available are insufficient for the selection of materials of construction. The Army has initiated further testing of materials of construction.

Finding 6. Process monitoring and control strategies for the management of salts within the SCWO reactor and the destruction of the organic constituents of the hydrolysate have not been demonstrated.

RECOMMENDATIONS

Recommendation 1. A pilot-scale SCWO process facility with the critical characteristics of the full-scale design should be constructed and operated to further define operating characteristics and demonstrate sustained continuous operation of the process. Objectives for process development and demonstration should include:

- operation with either hydrolysate or a suitable surrogate to demonstrate reliable operation for periods similar to full-scale design operating cycles
- the development and validation of process monitoring and control strategies for salt management and the destruction of organic constituents
- the definition of stable operating regimes, including the temperature, pressure, and the use of the oxidant (liquid oxygen or compressed air) selected for full-scale operation

- the definition of a basis for process scale-up, operation, and maintenance of a full-scale system
- the development and demonstration of a reliable pressure let-down system

Because the understanding of the fundamental process mechanisms and operating characteristics is limited, the committee recommends that the pilot-scale system be within an order of magnitude of the total mass and heating throughput of a full-scale design unit. Based on testing and reactor scale-ups to date, a vertical cylindrical reactor configuration is recommended as the system that will probably require the least amount of additional development. Other reactor configurations may perform at required levels but would require significant additional development.

Recommendation 2. Testing of materials of construction should be carried out as necessary to finalize the selection of materials for critical components, including the SCWO reactor and the pressure let-down system. Additional pilot-scale testing indicated in Recommendation 1 should include fabrication with the materials of construction selected from testing smaller samples and evaluation of corrosion and erosion rates for critical components.

Recommendation 3. Flexibility and redundancy of critical components should be incorporated into the design of the full-scale system to allow for uncertainties about the basis for scale-up and operation. Trade-offs should be evaluated to establish an appropriate balance between two 100 percent capacity SCWO reactors or a greater number of smaller reactors. The analysis should consider performance uncertainties associated with process scale-up and complexity, as well as the reliability of operating several reactors in parallel.

Recommendation 4. The Army should make provisions for targeted research and development to resolve problems identified during pilot-scale testing and the full-scale implementation of SCWO technology.

Recommendation 5. Requirements for process destruction efficiencies and final disposal standards for all effluent streams from SCWO treatment should be clearly defined to ensure that the final design meets regulatory standards.

1

Introduction and Background

The United States began the destruction of its stockpile of chemical weapons long before the passage of the Chemical Weapons Convention (CWC), which came into force April 29, 1997. The U.S. Army, as the executive agent for the U.S. Department of Defense for stockpile destruction, is using a combination of incinerators at two sites (Johnston Island and Tooele, Utah) where the chemical agents are present in assembled munitions, such as rockets and artillery projectiles. The Army plans to use incinerators at some additional stockpile sites with assembled munitions, as well.

In response to public concerns associated with incineration, the Army is currently proceeding with development of alternative technologies for two sites (Aberdeen, Maryland, and Newport, Indiana) where chemical agents are stored in bulk and are more accessible than those contained in weapons and where the destruction of explosives and propellants is not required. The technology chosen was chemical neutralization, which detoxifies the chemical agent but does not completely destroy its potential precursors. This decision was reached with input from the National Research Council (NRC) Panel on Alternative Chemical Disposal Technologies (AltTech Panel) (NRC, 1996a). A number of technologies have been considered for the safe and environmentally sound disposal of the neutralization products, including biodegradation, incineration, wet air oxidation followed by biodegradation, and supercritical water oxidation (SCWO)(NRC, 1994a).

SELECTION OF NEUTRALIZATION FOLLOWED BY SUPERCRITICAL WATER OXIDATION FOR STOCKPILE DISPOSAL AT NEWPORT, INDIANA

The U.S. Army plans to destroy VX nerve agent stored in bulk at its Newport, Indiana, facility with a disposal technology based on chemical neutralization. This destruction process results in the production of a solution, called "hydrolysate,"¹ that retains some undesirable characteristics.

The hydrolysate produced by the neutralization reaction is greatly reduced in toxicity compared to the agent but requires further treatment to meet the requirements for safe and environmentally acceptable disposal. Further treatment is also required to destroy remaining constituents that contain carbon-phosphorus bonds to meet the requirements of the CWC. The Army has tested biological oxidation to destroy the organic compounds that remain in the solution. However, research to date, under the auspices of the Program Manager for Chemical Demilitarization, has shown that biodegradation does not effect adequate destruction. As an alternative, the Army has selected SCWO, an approach that was recommended by the NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee) in its 1994 report (NRC, 1994a).

VX STORAGE AT NEWPORT, INDIANA

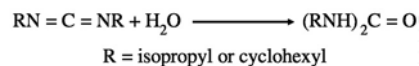
The Newport Chemical Activity was the U.S. production facility for VX nerve agent. The agent is no longer produced there or at any other U.S. site, but 1,689 ton containers holding a total of 1,269 tons of VX are stored on the site.

VX is one of the most toxic chemical agents. As little as 10 mg of VX absorbed through the skin or lungs will

¹ Chemical neutralization of other agents (e.g., blister agents such as mustard and nerve agents such as GB) also produces hydrolysates. However, the composition and potentially viable treatment alternatives for each hydrolysate varies based on the type of agent. For the purposes of this document, "hydrolysate" and the discussion of treatment process effectiveness refer only to hydrolysate produced by the neutralization of VX with aqueous sodium hydroxide.

kill or incapacitate a 70 kg individual by massive disruption of the central nervous system (U.S. Army, 1996a). Moreover, VX exhibits a characteristic persistence if released into the environment because it has a low vapor pressure and evaporates slowly under normal atmospheric conditions. It is slowly deactivated by moist air but can persist for a long time in an arid climate.

The VX agent stored at Newport is of reasonably pure chemical composition. The major impurities are derived from a dialkylcarbodiimide, which was added to the agent to prevent hydrolysis during transfer operations and storage. The carbodiimide additive reacts with water to form a dialkyl urea:

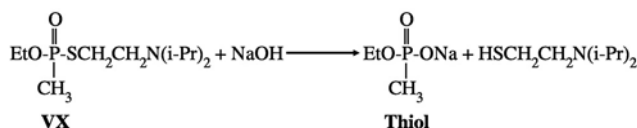


Based on a 1996 survey of the VX stored at Newport, the VX stored in a typical container is about 94 percent pure, with the remainder consisting of a large number of minor impurities. The largest percentage of impurities are diisopropylcarbodiimide (1.74 percent), diethyl dimethylpyrophosphonate (0.99 percent), and 2-(diisopropylamino)ethane thiol (0.89 percent) (U.S. Army, 1996b).

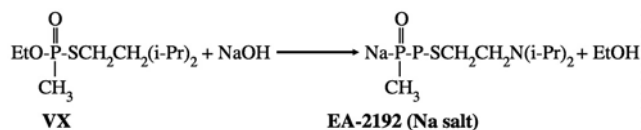
NEUTRALIZATION OF VX

The Army has evaluated several ways to neutralize (detoxify) VX by chemically destroying the phosphorus-sulfur bond associated with the neurotoxicity of the VX molecule. Chemical hydrolysis of this bond by neutral or alkaline aqueous solutions appears to be the most attractive approach based on the general simplicity of the process. The ease of process control was a significant factor in the selection of hydrolysis by aqueous caustic solution as the best candidate for further development. Other neutralization process options studied by the Army include using nonaqueous bases, such as methanolic KOH and monoethanolamine (U.S. Army, 1996c; NRC, 1993; Yang, 1995).

In the hydrolysis of VX, the primary reaction is cleavage of the phosphorus-sulfur bond to form the sodium salt of ethyl methylphosphonic acid (EMPA) and a thiol:



An undesirable side reaction is the cleavage of a phosphorus-oxygen bond in VX to form ethyl alcohol and a salt of EA-2192:



Because EA-2192 retains a phosphorus-sulfur bond, its toxicity is only slightly reduced from the toxicity of VX. Fortunately, extending the reaction time for the caustic hydrolysis of VX also causes hydrolysis of EA-2192 to the relatively innocuous methylphosphonic acid (MPA). With a reaction time of six hours at 90°C, the overall efficiency for destruction of VX exceeds 99.9999 percent, and the toxicity of the resulting aqueous solution is 40,000-fold less than the toxicity of VX (NRC, 1996a).

The alkaline hydrolysis of VX has been tested on a substantial bench scale in the Army's research and development facility at Edgewood, Maryland. Many of the tests were carried out in highly instrumented 12-liter reactors, but several tests were conducted on a larger scale in 114-liter reactors. The latter experiments, which typically destroyed 24 to 30 kg of VX per test, produced large quantities of hydrolysate for tests of predisposal treatment and provided operating experience that should be valuable in future tests of pilot plants. All of the bench-scale tests were done using munitions-grade nerve agent similar to the agent stored in ton containers at the Newport facility. Procedures for decontaminating emptied VX storage containers were also tested.

A key finding in the bench-scale tests was that vigorous mixing is required to ensure the complete destruction of VX, which has only limited solubility in the alkaline reaction mixture. The VX dissolves as the reaction progresses because the major hydrolysis products (EMPA, MPA, EA-2192, and thiol) are soluble in the strongly basic mixture. However, a significant complication for subsequent treatment prior to disposal is that several minor products are insoluble. These compounds form a small liquid layer (up to 10 weight percent) that floats atop the alkaline layer that contains the major reaction products. The water-insoluble products largely derive from the thiol and the carbodiimide stabilizer that were added to the agent. The composition of the VX hydrolysate that was used for SCWO treatability studies

is presented in [Table 1-1](#).² This composition is typical of the VX hydrolysate produced by neutralization using sodium hydroxide.

TABLE 1-1 Composition of Hydrolysate from Neutralization of VX

Component	Concentration (mg/l)
Ethylmethylphosphonic acid (EMPA)	152,673
Methylphosphonic acid (MPA)	13,348
Diisopropylaminoethanethiol (Thiol)	160,000
Bis (diisopropylaminoethyl) disulfide	13,000
Bis (diisopropylaminoethyl) sulfide	970
1,9-bis (diisopropylamino)-3,4,7-trithianonane	1,700
Total organic carbon (TOC)	140,000
Sulfate	96.9
Phosphate (as phosphorus)	2.19
Total sulfur (S)	38,400
Total phosphorus (P)	37,700
Arsenic (As)	0.125
Barium (Ba)	0.236
Calcium (Ca)	121
Chromium (Cr)	1.38
Copper (Cu)	1.53
Iron (Fe)	2.97
Lead (Pb)	0.50
Magnesium (Mg)	2.79
Mercury (Hg)	0.004
Selenium (Se)	2.0
Sodium (Na)	87,900
Titanium (Ti)	0.25
Zinc (Zn)	0.25

Source: Adapted from General Atomics, 1997a.

As [Table 1-1](#) shows, the primary P-containing products are EMPA and MPA. Prior to release from the neutralization process step to subsequent treatment steps, both VX and EA-2192³ must be nondetectable in the hydrolysate, with detection limits established at 20 ppb for VX and 5 ppm for EA-2192. Release to the treatment and disposal operations (the next step) will not be permitted unless concentrations of VX and other toxic constituents meet appropriate standards. The Army should evaluate and confirm that the standard for releasing hydrolysate from VX neutralization to subsequent treatment steps is adequate and verifiable. Although EMPA and MPA have low toxicity, destruction of these compounds is required for environmentally responsible disposal, as well as for meeting the requirements of the CWC, which designates these compounds as “Schedule 2 precursors” because they could potentially be reconverted to nerve agents if they could be recovered from the hydrolysate.

The thiol resulting from VX hydrolysis gives rise to several by-products through secondary reactions. These by-products include disulfides (RSSR') and an assortment of diisopropylaminoethyl compounds, listed in [Table 1-1](#). Minor products that derive from the stabilizer are not included in the analysis reported in the table. The thiol-derived products have foul odors, and, like MPA derivatives, they must be destroyed before disposal. The thiol itself is a Schedule 2 precursor and must be destroyed to comply with CWC treaty obligations.

The Army has decided to destroy the mixture of organic compounds listed in [Table 1-1](#) by oxidative processes that “mineralize” the materials, i.e., convert the elements in these compounds to oxidized forms, such as carbon dioxide, water, phosphate, and sulfate. Of the various oxidation technologies, SCWO was considered the most likely to adequately destroy the organic constituents in the hydrolysate.

Because there is little operating experience with SCWO on an industrial scale, however, the Stockpile Committee was asked to evaluate whether SCWO is an effective and appropriate means of preparing VX hydrolysate for ultimate disposition. The NRC was not asked to conduct an in-depth analysis of the entire integrated VX bulk agent destruction and disposal process for the Newport Chemical Agent Disposal Facility (NECDF). As the facility design is being finalized (March 1999-April 2000), the NRC will probably be asked to assess all aspects of facility design, including monitoring, containment, process control, and redundancy, as well as the quantitative risk assessment (QRA). This report outlines the elements of the proposed neutralization/SCWO technology,

²The numbers used in tables throughout this report are reproductions of the numbers reported in the original citation. Precision of the numbers should not be inferred by the number of significant figures reported.

³EA-2192 is an intermediate form during the neutralization reaction which further reacts to form MPA. EA-2192 is a nerve toxin. Analysis for VX and EA-2192 is carried out on a homogenized sample (including both aqueous and organic layers) of the hydrolysate.

evaluates the results of ongoing SCWO tests, and makes recommendations concerning aspects of the technology that require further development. The scope of this evaluation did not include evaluations of other potential technologies or management options for the treatment of VX hydrolysate.

For the evaluation of SCWO technology for treatment of VX hydrolysate, the Stockpile Committee reviewed documents on SCWO process fundamentals, previous applications, testing carried out specifically for the treatment of VX hydrolysate, and the planned process design for the Newport facility; met with SCWO academic researchers, process developers from Sandia National Laboratory, and vendors; visited a pilot-scale SCWO testing facility; and held discussions with the Army and its process design contractors.

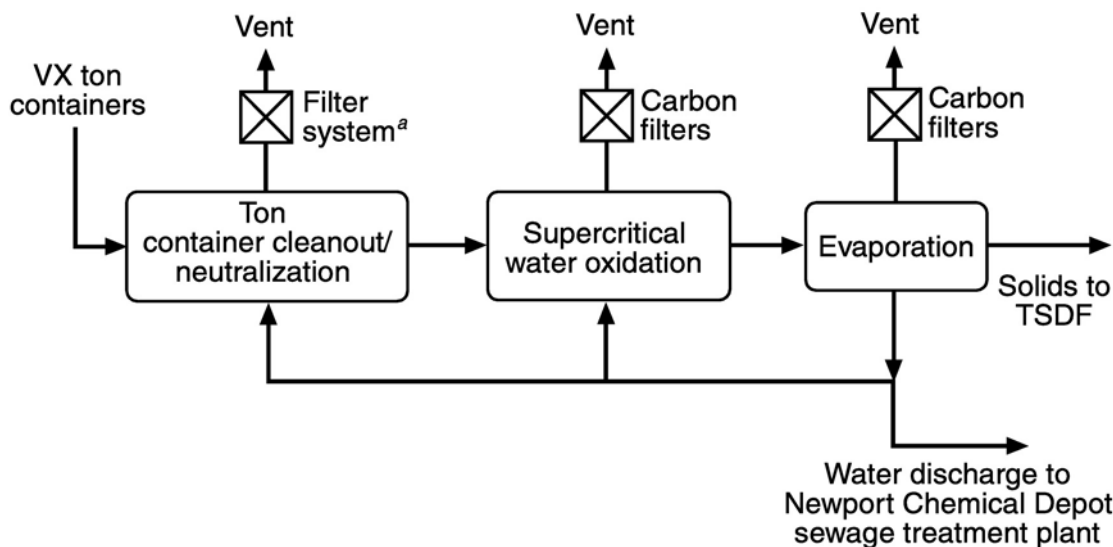
2

Process Description and Scientific Principles

PROCESS OVERVIEW

The general scheme for the neutralization of VX and treatment of the neutralization residues is shown in [Figure 2-1](#) (Stone and Webster, 1997a). The block diagram indicates a number of discrete operations in the overall process of VX destruction. Each block in the diagram represents more than one unit operation. For example, the left block (TCC/Neutralization) represents activities associated with removing VX from its storage cylinders, decontaminating the cylinders, and neutralizing the agent.

The ton containers (TCs) in which the agent is stored are transported to a ton container cleanout (TCC) facility where they are perforated with a mechanical punch and drained of liquid agent (U.S. Army, 1996b). This operation is very similar to the “punch and drain” operation at the chemical stockpile destruction facilities at Johnston Island and Tooele, Utah. However, in contrast to the thermal decontamination process used to decontaminate the drained containers at incineration sites, the Newport TCC process involves cutting the drained containers into two sections and using steam and hot water sprays to rinse and decontaminate the metal surfaces. The liquid collected from the decontamination process, which contains small amounts of VX as well as some agent hydrolysis products, will be collected and treated by the agent neutralization process. The Army intends to thermally treat and smelt the decontaminated metal parts at another Army facility.



^aCascading ventilating system including carbon filters

FIGURE 2-1 Block diagram of the overall neutralization and SCWO treatment process. Source: Adapted from Stone and Webster, 1997a.

The liquid VX drained from the TCs is treated with hot (90°C) 13.6 wt. percent aqueous NaOH solution in

a vigorously stirred reactor for three to four hours, during which time the VX is almost completely hydrolyzed (described in [Chapter 1](#)). The hot reaction mixture is then transferred to a second stirred reactor that contains rinse water from the TCC operation. This mixture is heated for an additional four to five hours to destroy the VX and EA-2192 to concentrations below their analytical detection limits (Stone and Webster, 1997a). Prior to release from the neutralization process step to subsequent treatment steps, both VX and EA-2192 must be nondetectable in the hydrolysate, with detection limits established at 20 ppb for VX and 5 ppm for EA-2192. After completion of the neutralization reaction, the hydrolysate is held in the reactor for several hours to allow time to certify by chemical analysis that it is suitable for release from the TCC/neutralization process area to the SCWO process unit (see [Figure 2-1](#)). The residual EA-2192, which could be present in higher concentration than VX, poses no vapor hazard because this highly acidic compound will be present only as its sodium salt in the alkaline hydrolysate. However, the liquid does have some toxic characteristics.

After analysis has verified that adequate destruction of VX and EA-2192 has been achieved, the VX hydrolysate is transferred to the SCWO unit, which is the focus of this report. The strongly alkaline hydrolysate is heated and pumped into a SCWO reactor along with an oxidizing agent (air or oxygen) and heated to 600 to 650°C under about 275 bar pressure. In the course of about 30 seconds, the organic components are largely (about 99.99 percent) oxidized to water and sodium carbonate, phosphate, and sulfate, as well as gaseous nitrogen-containing products (e.g., N₂ and NO_x). This mixture of materials is cooled by adding quench water and through heat exchange and then released from the SCWO reactor through a pressure reduction system. The resulting effluent is a mixture of gases (O₂, N₂, CO₂), a concentrated aqueous salt solution, and entrained solid salts (Stone and Webster, 1997b). Trace concentrations of partially oxidized organic constituents (e.g., MPA and acetic acid) may also be present. Complete analyses are shown in [Table 3-7](#) and [Table 3-8](#).

The aqueous products from the SCWO reactor, including entrained solids, are then fed to the evaporation unit, where the mixture is heated to distill excess water. At this point, the salts that have crystallized from solution are filtered and packaged for disposal in a secure landfill. A large portion of the water distilled from the SCWO effluent is recycled back to the TCC and SCWO units, which reduces the amount of fresh water needed for process operations. In the case of VX, the amount of water produced by oxidation is generally greater than the amount required to satisfy process needs; consequently, some water will be discharged to the Newport Chemical Depot sewage treatment facility or another acceptable water treatment facility.

Each major unit in the process will have a vent for the release of gaseous materials. Each vent will pass through a bed of activated carbon that will collect residual traces of organic vapors prior to releasing the gas into the atmosphere.

SCIENTIFIC PRINCIPLES

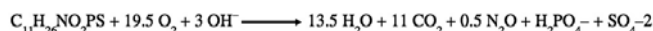
SCWO (supercritical water oxidation) is a hydrothermal process for the oxidative destruction of organic wastes using air or oxygen in the presence of high concentrations of water heated above the critical temperature and pressure of pure water ($T_c = 374^\circ\text{C}$, $P_c = 221$ bar). In the last two decades, SCWO technology has been the subject of several reviews (Modell, 1989; Shaw et al., 1991; Gopalan et al., 1995; Tester et al., 1993). The reaction mechanisms for the destruction of organic compounds generally involve free radical (mostly $\bullet\text{OH}$ and $\bullet\text{OOH}$) chain reactions with oxidative radicals. Thermal bond cleavage and polar or ionic reactions, including hydrolysis, also occur under the severe reaction conditions. Very high destruction efficiencies (> 99 percent to 99.9999 percent) have been reported for the destruction of a large number of organic compounds when they are treated for residence times of seconds to minutes at temperatures of 400 to 650°C. Aqueous organic wastes with sufficient heating value can be autogenic and can sustain the necessary reaction temperatures for extensive oxidation without the addition of supplemental fuel. Tests by General Atomics showed that the VX hydrolysate was autogenic under test conditions (General Atomics, 1997b). Although fuel was added during some tests, it appears to have been unnecessary for sustaining the reaction (Stone and Webster, 1997b).

In a SCWO process like the one in [Figure 2-1](#), the feed stream (aqueous waste to be treated) to the SCWO reactor is heated, pressurized, and mixed with oxidant (as air, pure oxygen, or hydrogen peroxide). It is then pumped through a flow reactor at supercritical conditions designed to provide the required residence time (seconds to one minute typically). Heat produced by the oxidation reactions can be recovered (or must be

removed) based on the heating value of the feed stream. If the feed stream has inadequate heating value to heat the reactor, supplemental fuel can be added. The Army will choose one of three oxidants. Liquid oxygen can be pumped, whereas air must be compressed; compressors are noisy and complicated (for the high pressure required here). There is little experience with the third choice, hydrogen peroxide.

Downstream of the reactor, the system is depressurized ("let down"), either before or after cooling. Solids produced from oxidation reactions can be recovered prior to or following pressure let-down. Cooling prior to pressure let-down often results in the redissolution of salts, which can be precipitated later via solvent evaporation. Alternatively, pressure let-down at high temperature can result in the direct removal of salts as a concentrated brine stream or solid. A number of pressure let-down schemes have been devised—mostly valves or capillary tubes that restrict the release of fluids from the process equipment. The effluent is then passed through gas/liquid separators, and the gas stream and aqueous streams can be treated further, as required, for responsible disposal. With sufficient salt removal, the water effluent can often be recycled within the system.

In general, organic carbon is oxidized to carbon dioxide or carbonate. Under the strong oxidizing conditions of this medium (assuming sufficient oxidant is available), most heteroatoms in organic material (e.g., Cl, P, and S) are converted to their oxidized mineral acids (HCl, H₃PO₄ and H₂SO₄, respectively) or the corresponding salts, depending on effluent pH and cation concentration. The fate of nitrogen in organics is unclear; it has been reported to yield mixtures of N₂ and nitrogen oxides, including N₂O, with the possible formation of nitrate as well (Killilea et al., 1992). Nitrate has been shown to be an effective oxidant in SCWO systems reactions to yield N₂ and N₂O (Proesmans et al., 1997; Dell'Orco et al., 1995). In the treatment of VX hydrolysate, the oxidation would produce large quantities of inorganic salts:



Very hot water, near or above its critical point, behaves much differently from water at standard conditions. The density of water at its critical point (T_c = 374°C, P_c = 221 bar) is about 0.3 g/cm³. As water is heated and pressurized, its dielectric constant decreases precipitously (from 88 at 0°C to less than 20 at 300°C and significantly less than 10 at much higher temperatures). For a pure substance at its critical point, the density of the vapor and the liquid is identical, and the two fluids become indistinguishable. At temperatures above the critical point, a single phase of the substance is formed, which is known as a "supercritical fluid." Supercritical water is highly compressible; its density depends on both temperature and pressure. Its solubility properties and most other physical properties (e.g., diffusivity, dielectric constant, viscosity) depend on its density.

A significant factor is that the solvent properties of very hot water differ greatly from those of normal water. Simple gases like oxygen or nitrogen are miscible at relatively high concentrations. Organic compounds often are soluble or miscible in supercritical water because of its low dielectric constant. At pressures much greater than at the critical point, and therefore at high density, salts can be soluble and can even dissociate. However, at the lower densities (0.1-0.2 g/cm³) common to most SCWO conditions (206 bar and > 600°C), most salts are practically insoluble.

KINETICS

The oxidation kinetics of some simple organic compounds under homogeneous SCWO conditions have been measured and modeled (Li et al., 1991; Li et al., 1993; Gopalan and Savage, 1995). Phenomenologically, a near zero order dependence on oxygen concentration is observed if sufficient oxygen is present. The oxidation of certain compounds, such as methane, show nonintegral dependence on oxygen. Most organic compounds can be destroyed to concentrations below detection limits within short reaction times at temperatures of 400 to 650°C. However, some small molecules, notably ammonia and acetate ion, are more recalcitrant and require higher temperatures or longer reaction times for complete oxidation. MPA (methylphosphonic acid) has been demonstrated to react only slowly in bench and pilot test studies of VX hydrolysate, suggesting slow cleavage of the carbon-phosphorus bond (Gloyna and Li, 1997).

The complete oxidation of even simple organic compounds requires a large number of elementary reactions. Although a number of reactions have been measured and modeled extensively in simple systems, most organic wastes have been described best by phenomenological kinetic models. For more complex systems, only empirical models specifying the residence times required to achieve certain destruction efficiencies at the

specified temperature and pressure have been developed. Moreover, the reaction mechanisms for complex wastes in SCWO systems are poorly understood, including the elementary steps, the interplay or relative contribution of homogeneous and heterogeneous reactions, and pyrolytic or hydrolytic chemical pathways.

PHASE BEHAVIOR

Understanding the phase behavior of the reaction medium within a SCWO reactor is essential for confident scale-up and smooth operation. A number of attempts have been made to model or predict phase behavior for ideal systems (Chiavlo et al., 1995; Bischoff and Rosenbauer, 1988; Bischoff and Pitzer, 1989; Marshall et al., 1981; Valyashko, 1976). They have generally assumed the miscibility of water, organics, and air and, on that basis, assumed homogeneous reactions near or above the critical point. However, this simple assumption is true only for dilute solutes in water. The phase behavior of concentrated systems (even systems with just a few percent solute like VX hydrolysate) can be very complex and is probably multiphase because the critical point of water depends strongly on the concentration of solutes (e.g., gases, organic compounds, and salts). Thus, the critical point of a concentrated stream could be significantly higher than the critical point of pure water (Armellini et al., 1994; Bischoff and Rosenbauer, 1988; Bischoff and Pitzer, 1989), suggesting that vapor phases or concentrated and dilute aqueous phases could persist considerably above the critical temperature. Salt precipitation would lead to additional phases. The presence of more than one phase or the presence of subcritical phases in the reactor can significantly alter reaction mechanisms, kinetics, and destruction efficiencies, as well as solids retention and corrosion rates.

3

Technology Status

PREVIOUS APPLICATIONS OF SUPERCRITICAL WATER OXIDATION TECHNOLOGY

Since SCWO was invented in the early 1980s, the technology has developed from bench-scale discovery to significant pilot-scale demonstrations and one current and several pending full-scale operations. Although using SCWO for treatment of a wide variety of wastes, ranging from hazardous waste to sewage sludge, has been tested on a laboratory scale, pilot-scale testing for the treatment of more complex wastes (e.g., heterogeneous wastes, wastes containing high concentrations of heteroatoms that generate salts, and corrosive wastes) has been limited. Wastes characterized by high salt or salt producing content and corrosivity during treatment have presented significant technological challenges.

Three basic reactor configurations and two approaches to temperature and pressure reduction after reaction at supercritical conditions have been developed. The three basic reactor configurations are tubular (Gloyna and Li, 1997), vertical cylindrical (General Atomics, 1995, 1997a, b), and transpiring wall (Haroldson et al., 1996). All reactor configurations mix the reactants (waste, supplemental fuel [if required], and oxidant) at the entrance or in the uppermost zone of the reactor. Tubular reactors utilize relatively small-diameter high pressure tubing with long lengths (about 3 cm diameter \times 36 m) to achieve the required residence times for reaction. The long reactor lengths typically are achieved through horizontal orientation with several passes (i.e., U-bends) or spirals. The narrow inner diameter and bends in these configurations make them less desirable for systems at pressures of approximately 275 bar and with high salt loadings because of the presence of a solid salt phase and the possibility of salt deposition and plugging.

Vertical cylindrical reactors consist of larger-diameter (about 9 to 25 cm diameter) vertical pipes with solid walls designed to meet the pressure and temperature requirements of the process. Larger diameters allow shorter reactors (about 2 to 5 m) to achieve the required residence times for reaction. Turbulence and downflow operation facilitate the transport of solids out of the reactor. Designing the nozzle for injecting fluids into the reactor and designing the entrance region are important for controlling solids adhesion in the reactor. (The design of the nozzle is considered proprietary technology.)

A transpiring wall reactor consists of a vertical cylindrical configuration with an inner wall containing embedded channels through which clean water flows into the reactor ([Figure 3-1](#)). The embedded channels are created by assembling multiple layers of perforated sheets into a single cylinder (referred to as a "platelet"). A larger diameter pipe (referred to as a "plenum") surrounds the platelet to distribute the water to the platelet channels. The purpose of the water flowing through the platelet is to provide a boundary layer of lower salt content and lower temperature along the inner surface of the reactor to reduce solids adhesion and corrosion. However, because reaction constituents can diffuse through the boundary layer, materials of construction must be carefully selected for a severe, although potentially somewhat less, corrosive environment. This reactor configuration also requires balancing the pressure and water distribution through the wall in three zones along the length of the reactor, which adds operational complexity to the overall system. The inner diameter and length of the transpiring wall reactor are similar to vertical cylindrical reactors.

Temperature and pressure reduction after reaction at supercritical conditions has been achieved through a sequence of additions of quench water at high pressure, followed by heat exchange at high pressure to further reduce temperature, and finally, pressure relief through pressure reduction valves or capillaries. Multiphase flow is present through most of the process because of entrained gases and residual solids at subcritical conditions. The quench water, which is used to reduce the temperature to below supercritical conditions and resolubilize salts that were insoluble at reactor conditions,

is added at the exit end of vertical cylindrical reactors and transpiring wall reactors. However, less water is needed at the exit of a transpiring wall reactor because water has been added to the process through the reactor wall to maintain the surface boundary layer. Subsequent heat exchange is accomplished either with or without heat recovery. The materials of construction for pressure reduction valves must be carefully selected because of the corrosivity and erosivity (from residual entrained solids) associated with the process stream. Pressure reduction capillaries consist of long lengths (e.g., 3 to 25 m) of parallel narrow diameter (about 1.0 to 1.4 mm internal diameter) tubing sized so that wall friction and other frictional losses result in sufficient pressure reduction. A model for the design of capillaries for two-phase (liquid and gas) flow has been validated for SCWO application (General Atomics, 1995).

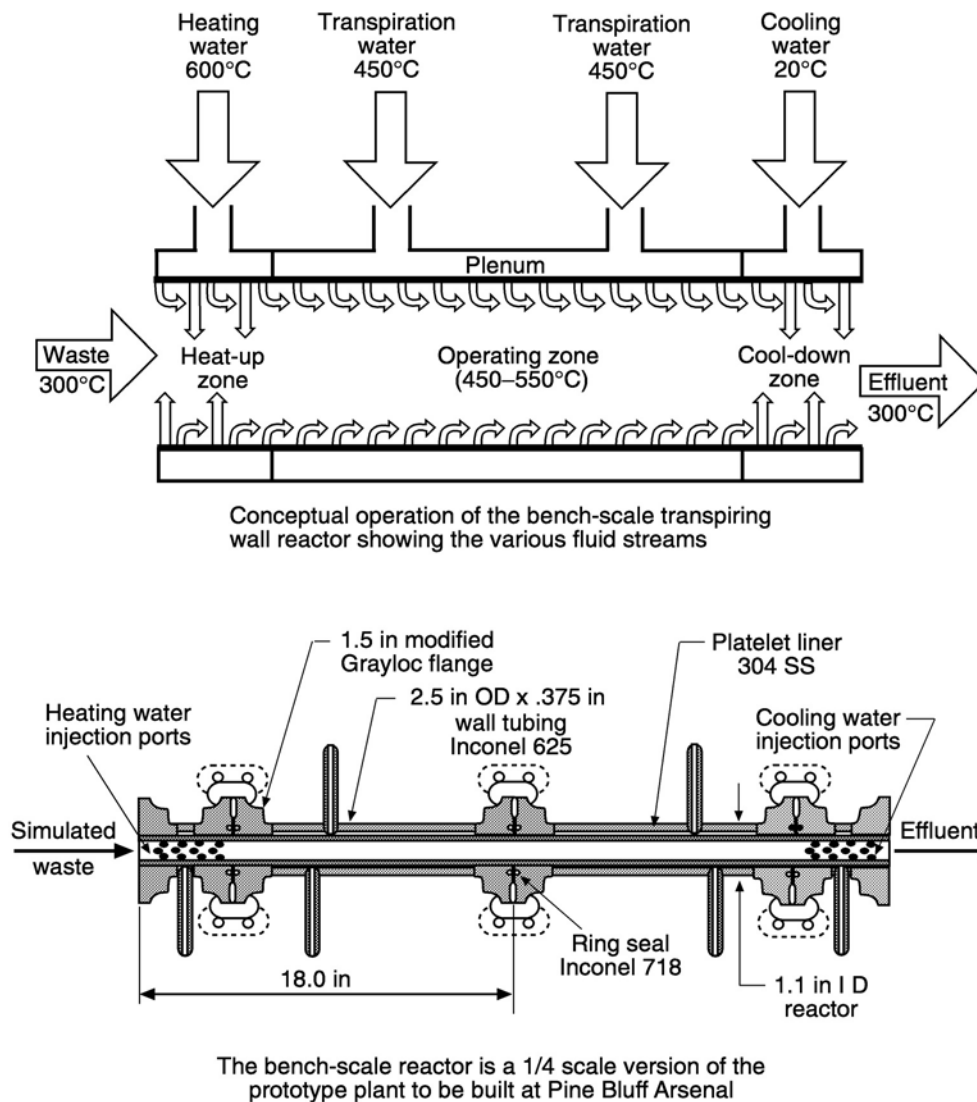


FIGURE 3-1 Schematic diagram of a transpiring wall reactor. Source: Adapted from Haroldsen et al., 1996.

Table 3-1 and Table 3-2 present a summary of the waste types and operational characteristics of prior, current, and planned uses of SCWO technology at pilot scale or larger. The majority of testing to date at pilot scale has been for limited technology demonstration intervals. Primary distinguishing features of each facility or demonstration are waste composition, process scale, reactor design, (tubular, vertical cylindrical, or transpiring wall), oxidant (air, oxygen or hydrogen peroxide), and pressure let-down system (valves or capillaries). Most experience to date has been with tubular and vertical cylindrical reactors. Only a single set of tests have been carried out with a transpiring wall reactor. These tests were carried out for a maximum three hour duration with a simulant solution feed to the one-inch diameter reactor. Only one commercial facility (Huntsman Chemical) currently uses SCWO technology for waste treatment. This facility uses a tubular reactor to treat five to eight gal/min of aqueous waste containing alcohols, amines, and relatively low salt content. So far, none of the pilot-scale testing or full-scale applications for other programs include the pH range or salt composition that will be present during treatment of VX hydrolysate. However, the treatment of a waste stream with high solids content (up to ca. 5.9 wt. percent solids) has been successfully scaled up to pilot scale using a vertical cylindrical reactor for the treatment of solid rocket propellants (General Atomics, 1995).

TABLE 3-1 Summary and Comparison of the Newport Chemical Agent Disposal Facility (NECDF) with Pilot Testing and Full-Scale Operation of SCWO Treatment Processes to Date

Project name	NECDF Projected Characteristics	Hydrolysate Test GA Vertical Reactor	Surrogate Test Vertical Reactor	Air Force Propellant Test	Industrial Wet Oxidation (SCWO) for Waste and Low Grade Fuels
Sponsor	PMATA ^a	PMATA	PMATA	Air Force	U.S. DOE
Waste characterization	hydrolysate, pH 14, 2,500 Btu/lb, Na salts of EMPA, MPA, thiols	drained agent hydrolysate, pH 14, 4,300 Btu/lb, Na salts of EMPA, MPA, thiols	ethanol, kerosene, DMMP, MPA, 11.6–15.1 wt% Na ₂ SO ₃ , 8.8–11.5 wt% NaHPO ₄ CH ₂ O	hydrolyzed class 1.1 rocket propellant, 0.1–6 wt% slurry	synthesized waste of chlorinated hydrocarbon, NaCl, Na ₂ SO ₄ , isopropyl alcohol, NaOH added to neutralize acid
Flow of waste	4 gal/min, 2,092 lb/h	equivalent to 0.15 gal/min of 2,500 Btu/lb; 44 lb/h of 4,300 Btu/lb drained hydrolysate	0.08–0.17 gal/min	0.3–0.38 gal/min	0.22 gal/min
Oxidant	oxygen	air	air	oxygen	air
Oxidation heat release	5 million Btu/h	0.19 million Btu/h	0.19 million Btu/h	0.1 million Btu/h	160,000 Btu/h
Salt characteristic in reactor	Na ₂ SO ₄ NaH ₂ PO ₄ NaH ₂ PO ₄	Na ₂ SO ₄ NaH ₂ PO ₄	Na ₂ SO ₄ NaH ₂ PO ₄	Predominantly AlOOH and NH ₄ Cl, approx. 1 wt%	NaCl, Na ₂ SO ₄ 2 wt%
Salt throughput	360 lb/h	14.6 lb/h	12–17.5 lb/h	9.9 lb/h	2.2 lb/h
Principal corrosion issue	high pH due to free NaOH	high pH due to free NaOH	no NaOH in these tests	high pH due to NH ₃ , 2,000–7,000 ppm Cl	chlorides, low pH
Approach to corrosion	corrosion resistant liner Pt or ceramic	corrosion resistant liner Ti for test; Pt or ceramic liner for use in NECDF	corrosion resistant Ti	corrosion resistant Ti liner	alloy 625 reactor, some nozzle failures
Reactor type	TBD	downflow cylindrical vertical vessel 4 in x 6 ft	downflow cylindrical vertical vessel 4 in x 6 ft	downflow cylindrical vertical vessel 3.4 in x 6 ft	reversing flow cylindrical vertical vessel 10 in x 40 in
Reactor nominal dimensions (diameter x length)	TBD	vertical vessel 4 in x 6 ft	vertical vessel 4 in x 6 ft	vertical vessel 3.4 in x 6 ft	vertical vessel 10 in x 40 in
Operating conditions, T,P	1,200°F, 3,500 psig	1,112–1,184°F, 3,400 psig	1,112–1,256°F, 3,400–3,800 psig	842–1,076°F, 4,000 psig	1,085°F, 3,400 psig
Pressure let-down, approach to erosion	vendor to specify, redundancy is required	erosion resistant, redundant valve and capillaries	erosion resistant, redundant valve and capillaries	erosion resistant capillaries	redundant valves
Project status	conceptual design	complete	complete	complete	complete
Hours continuously run without plugging	not yet operated	hydrolysate treatability test: 8 hours	4 tests, 7+ hours	25 hrs	102 hrs but reactor retained 15.8 % of the input salt
Destruction removal efficiency (DRE) or effluent quality (mg TOC/L) achieved	require < 15 mg TOC/L	99.98% DRE based on TOC 99.97% DRE based on MPA	98.8–99.9% DRE for TOC > 99.3–99.7 % DRE for MPA	> 99.9% DRE based on TOC	99.97% DRE 1 mg TOC/L
References, reports	Stone and Webster, 1997a	General Atomics, 1997b	General Atomics, 1997a	General Atomics, 1995	General Atomics, 1994

Project Name	SCWO Data Acquisition Testing	Huntsman Chemical	University of Texas Pilot Plant	PNNL ^b	Sandia National Laboratory
Sponsor	U.S. DOE	Huntsman Chemical	University of Texas	Battelle PNNL	U.S. DOE & U.S. Army ARDEC
Waste characterization	synthesized waste of chlorinated, sulfonated cutting oil, metal acetates of Ca, Fe, Pb, Zn, Ce, NaOH added to neutralize acid	amines, long chain alcohols (MW 2,000), methanol, 10 wt% methanol equivalent	thick sludges, amines, ammonia mixtures, pH 12-13, no halogens	high pH, organics with Na salts, Hanford tank wastes	3 wt % Na ₂ SO ₄ , 5.15 wt% red dye
Flow of waste	0.044 gal/min	5-8 gal/min	0.5-1 gal/min	0.13-0.17 gal/min; smaller unit: 0.0044 gal/min	0.033 gal/min
Oxidant	air	oxygen	oxygen	none, nitrate in waste	hydrogen peroxide decomposed to O ₂
Oxidation heat release	approx. 90,000 Btu/h	2 million Btu/h	0.4 million Btu/h	minimal, feed/effluent heat exchanger required	approx. 3,000 Btu/h
Salt characteristic in reactor	NaCl, Na ₂ SO ₄ , metallic chlorides	some trials with Na ₂ SO ₄ , Na ₃ PO ₄ , 1 wt%	oxides from industrial sludges, some trials with Na ₂ SO ₄ , Na ₂ CO ₃ 1-2 wt%	NaOH becomes carbonates NaNO ₃ (also the oxidant)	3 wt % Na ₂ SO ₄ , 1.6 wt% equiv. salt in dye test
Salt throughput	1.5 lb/h	approx. 25 lb/h, some scaling	approx. 2.5 lb/h, some scaling	approx. 10% 7 lb/h	0.63-1.6 lb/h for salt only test
Principal corrosion issue	chlorides, salts, metallic chlorides	confidential to vendor	variable since many wastes run through this pilot unit	high pH due to free NaOH; stainless steel sufficient when exposed to reaction products, 200 h in batch autoclave	salt on wall, effl pH 3.3-5, corrosion of Ni, Mo by salt, O ₂ observed in stainless steel
Approach to corrosion	ceramic coated Ti liner; some delamination but performed better than metallic Ti	confidential to vendor	Ni alloy tubing	replaceable inner shell vessel made of stainless steel	radial fluid flow to keep corrosives off reactor wall (i.e., transpiring wall)
Reactor type	reversing flow vessel	tubular	tubular	dual shell, vertical cylinder	transpiring wall
Reactor nominal dimensions (diameter x length)	10 in x 40 in	diam confidential to vendor, length several hundred ft	1 in x 120 ft	1 in ID x 6 ft	1.1 in x 36 in
Operating conditions, T,P	1,112-1,148°F; 3,400 psig	up to 930°F; 4,000 psig	up to 1,150-1,200°F; 4,000 psig	662°F; 2,500 psig	932°F; 3,800 psig, 8-9 sec res time
Pressure let-down, approach to erosion	redundant valves	up valve, erosion resistant	valve, and patented method with capillaries	staged, multiple drops	single valve in small system
Project status	complete	in commercial operation 3 years	in operation, various wastes	complete	testing completed
Hours continuously run without plugging	94 hrs total; full reactor rinses (with feed off) req'd at 40 and 80 hrs ~ 13 lb of NaCl remained in reactor	one week	hours	0.15 gal/min 24 hrs; smaller scale several days	3 hrs, salt deposits can be removed in <10 min below 662°F
Destruction removal efficiency (DRE) ^c or effluent quality (mg TOC/L) achieved	99.97% DRE, 2 mg TOC/L	10 mg TOC/L	< 10 mg TOC/L	99% DRE based on TOC 1-10 mg TOC/L	> 90% DRE based on TOC 100% destroyed for the dye
References, reports	Stone and Webster, 1996	Weismantel, 1996, and pers. com. Roy McBrayer, EWT, 11/6/97	plant tour in Austin, Texas (Wade, 1997, and Chowdhury, 1996)	Battelle, 1996	Sandia Report, 1996

^aPMATA = Product Manager for Alternative Technologies and Approaches

^bPNNL = Pacific Northwest National Laboratory

^cDRE = destruction removal efficiency

Source: Adapted from Stone and Webster, 1997c.

TABLE 3-2 Summary and Comparison of Full-scale SCWO Treatment Processes Planned or under Construction as of December 1997

Project Name	Hydrothermal Oxidation	Hydrothermal Oxidation	Pine Bluff	University of British Columbia
Sponsor	U.S. Navy	U.S. Navy	U.S. Army ARDEC	Noram Engineerings
Waste characterization	excess hazardous matls., fuels, lubricants, high Btu/lb, mostly non-sticky solids, chlorides	excess hazardous matls., fuels, lubricants, high Btu/lb, mostly non-sticky solids, chlorides	80 lb/h of dye, 240 lb/h of water	plans for pulp mill waste
Flow of waste	100 lb/h 0.2gal/min	100 lb/h 0.2gal/min	0.64 gal/min of slurry	0.044 gal/min
Oxidant	air	air	oxygen	oxygen
Oxidation heat release	2 million Btu/h	2 million Btu/h	800,000 Btu/hr	TBD (to be determined)
Salt characteristic in reactor	primary non-sticky paint pigments, MoO ₂	primary non-sticky paint pigments, MoO ₂	Na ₂ SO ₄	TBD
Salt throughput	25 lb/h max	25 lb/h max	50.4 lb/h	max amount to be a few %
Principal corrosion issue	Cl present in some wastes	Cl present in some waste	salt on wall	TBD
Approach to corrosion	radial fluid flow to keep corrosives off reactor wall (i.e., transpiring wall), Inconel 600 wall material	Ti corrosion resistant liner	Inconel 600 platelet, radial fluid flow to keep corrosives off reactor wall	confidential to vendor
Reactor type	transpiring wall	cylindrical, vertical	transpiring wall	tubular
Reactor nominal dimensions (diameter × length)	4.8 in × 7.5 ft	7.25 in × 5 ft	4.8 in × 7.5 ft	volume 150 in ³ , dimensions TBD
Operating conditions, T,P	top 1,350°F; bottom 1,050°F, 3,800 psig, 10 sec res time	1,157°F, 3,400 psig	top 1,350°F; bottom 1,050°F, 3,800 psig, 10 sec res time	slightly above critical conditions
Pressure let-down, approach to erosion	valve redundancy	stages pressure let-down valves	valve redundancy	pressure regulator
Project status	units under construction by Foster Wheeler and General Atomics not yet operated	units under construction by Foster Wheeler and General Atomics not yet operated	under construction, operational April 1998	scheduled operational date is summer 1998
Hours continuously run without plugging			rinse planned every 1–2 weeks	not yet operated
Destruction removal efficiency (DRE [®]) or effluent quality (mg TOC/L) achieved	project requirement is 99.99% DRE based on TOC	project requirement is 99.99% DRE based on TOC	99.99% DRE	TBD
References, reports	LaJeunesse et al., 1997	Teleconference	LaJeunesse et al., 1997	no reports, info based on Oct 23 and Nov 21, 1997, teleconferences

Currently, three prototype systems are under construction. The Office of Naval Research (U.S. Navy) has sponsored a direct comparison of two vendor systems (a Foster Wheeler transpiring wall reactor and a General Atomics downflow cylindrical reactor) for the treatment of shipboard waste (LaJeunesse et al., 1997; Stone and Webster, 1997c), and the U.S. Armament Research, Development, and Engineering Center (U.S. Army) has selected a system with a transpiring wall reactor for the treatment of pyrotechnic munitions at the Pine Bluff Arsenal (Stoddard, 1997). None of these systems is currently operational.

The use of SCWO for the treatment of VX hydrolysate presents significant challenges. To destroy the carbon-phosphorus bond in EMPA and MPA, operating conditions (temperature, pressure, and residence time), combined with a transition from alkaline to acidic composition during oxidation of hydrolysate components, will put severe requirements on the materials of construction to prevent corrosion. In addition, the large amount of inorganic salt-producing elements (phosphorus and sulfur) present in the original VX and sodium (as NaOH) added during the neutralization process means that a high solids content fluid will have to be managed in and downstream of the SCWO reactor. Salts that are insoluble in the SCWO reactor fluid phase have shown a propensity to adhere to the reactor walls causing reactor plugging and eroding the components of pressure let-down systems. These problems have been overcome for other wastes, but the composition of VX hydrolysate is significantly different because of its high solids-producing content and its pH range during treatment. Therefore, a development program specifically for the application of SCWO to VX hydrolysate will be required before the full-scale application of SCWO.

DEVELOPMENT PROGRAM FOR APPLICATION TO VX HYDROLYSATE

Testing SCWO technology specifically for the treatment of VX hydrolysate has been carried out at laboratory scale and pilot scale.¹ Laboratory-scale testing has focused on clarifying the destruction removal efficiency (DRE) for the oxidation of MPA, which is considered the most refractory hydrolysate constituent and is also an intermediate formed during oxidation of EMPA (Gloyna and Li, 1997). Pilot-scale testing has been carried out using a vertical cylindrical reactor for intervals of a few hours using both surrogates for hydrolysate and actual VX hydrolysate produced by neutralizing VX from the stockpile at the process design conditions specified for the Newport facility. The objectives of the pilot-scale testing were (1) to demonstrate DREs at larger than bench scale, (2) to test salt management within the reactor, and (3) to identify potential operational difficulties and problems with mechanical equipment. The following specific tests were carried out to address these objectives (General Atomics, 1997a, b):

- two campaigns (1.5 hours and 8.25 hours) processing solutions expected to have salt-handling characteristics similar to those of oxidized hydrolysate (August 1996)
- two campaigns (1.5 hours each) processing VX hydrolysate (August 1996)
- two campaigns (3 hours each) processing salt simulants (February 1997)
- one campaign (9.25 hours) processing VX hydrolysate (February 1997)

The results from these testing programs are discussed below.

¹The distinction between “laboratory scale” and “pilot scale” used in this report is based on the processing rate of hydrolysate (or surrogate feed) relative to the full-scale design. Laboratory-scale or “bench-scale” and pilot-scale testing had processing rates 0.2 percent and 4 percent of full scale, respectively.

Laboratory-Scale Tests to Establish Methylphosphonic Acid DREs

Bench-scale studies of SCWO for the treatment of VX simulants have indicated that the destruction of MPA is the rate-limiting reaction for the complete oxidation of VX degradation products (Gloyna and Li, 1997). The destruction of MPA is also anticipated to be the rate-limiting reaction for SCWO treatment of VX hydrolysate because the neutralization of VX produces constituents in the hydrolysate that are similar to the initial intermediates formed during SCWO treatment of VX. Thus, bench-scale testing to establish reaction conditions for the treatment of VX hydrolysate focused on the kinetics for the oxidation of MPA.

The specific objectives of bench-scale testing of MPA destruction by SCWO were (1) to determine the DRE for the oxidation of MPA, (2) to evaluate the effect of sodium hydroxide on MPA oxidation, and (3) to develop kinetic correlations for up to 99 percent MPA DRE as a function of process temperature, oxygen content based on the stoichiometric requirement for complete MPA oxidation, and residence time. Pure oxygen was used as the oxidant. Twenty nine cases, 17 without and 12 with sodium hydroxide, were tested. Process temperatures and oxygen contents were 400, 500, 550, and 594°C, and 110, 150, and 200 percent of stoichiometric, respectively. Residence time was varied from 3 to 80 seconds by varying reactor length with a constant feed rate. For test cases with sodium hydroxide, a sodium hydroxide to MPA molar ratio of 2:1 was used, which results in a salt loading of approximately 0.2 wt. percent. This ratio was selected to balance the carbonate ions derived from the oxidation of MPA. Fixed conditions included MPA feed concentration of 1,000 mg/l, feed flow rate of 25 g/min, and operating pressure of 276 bar (4,000 psi). Feed streams were preheated separately to reactor conditions before being mixed so that reaction times were well established; temperature control was maintained by using a small diameter reactor immersed in a fluid sand bed for rapid heat transfer. The Reynolds number in the reactor varied from 3,900 to 5,600.

Sample test results showing MPA DRE without sodium hydroxide and at 200 percent stoichiometric oxygen as a function of temperature and residence time are presented in Figure 3-2 (Gloyna and Li, 1997). DREs greater than 99.9 percent were achieved at 550°C and a residence time of about 15 seconds. The same DRE (> 99.9 percent) was observed with 50 percent excess oxygen content and the same residence time; however, at 10 percent excess oxygen, the conversion decreased to 92 percent. As expected, increased reaction rates were observed with increased temperature. The addition of NaOH to produce alkali reaction conditions yielded ambiguous results. At short residence times, which resulted in high residual MPA concentrations, conversion of MPA was greater when sodium hydroxide was added. However, high DREs were more difficult to achieve when sodium hydroxide was added because (1) the feed MPA concentration was limited by MPA solubility, and (2) MPA concentrations between 1 and 5 mg/l were persistent in the SCWO effluent. It was hypothesized that the low concentrations of MPA remaining in the effluent may have been caused by occlusion in salt particles during treatment.

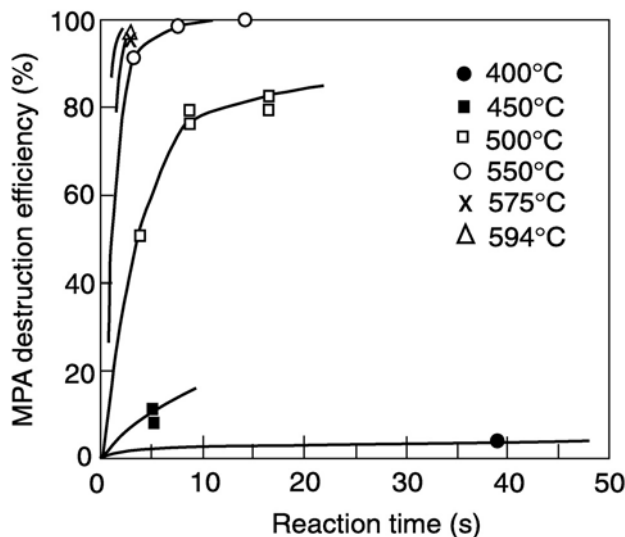


FIGURE 3-2 MPA DRE without sodium hydroxide and at 200 percent stoichiometric oxygen and 27.6 MPa as a function of temperature and residence time. Source: Adapted from Gloyna and Li, 1997.

Analysis of the off-gases produced during these tests indicated the presence of carbon monoxide (about 0.1 percent) and methane (2.1 to 12.3 percent), even when greater than 99.9 percent destruction of MPA was achieved. The presence of sodium hydroxide also appeared to result in greater concentrations of methane in the off-gas. The effect of oxygen concentration in the feed on methane content in the off-gas was not clear.

The presence of methane and carbon monoxide in the off-gas indicates incomplete oxidation and that these constituents are more refractory than MPA. These results suggest that higher temperatures or longer residence times may be required for the complete oxidation of hydrolysate constituents than would be required based on the destruction of MPA. They also suggest that monitoring of both carbon monoxide and methane in the off-gas from a SCWO process may be a sensitive indicator of the overall oxidation efficiency for organic constituents.

The conclusions from the laboratory-scale tests are that high destruction removal efficiency, over 99.9 percent, was possible at a temperature of 550°C or higher, with a residence time longer than 15 seconds and oxygen feed of at least 150 percent of the stoichiometric requirement. This destruction removal efficiency would probably be achievable in the absence or presence of NaOH and salts formed by the reaction. However, the occlusion of refractory intermediates in solids formed during treatment could limit overall DREs.

Pilot-Scale Testing with Surrogates and VX Hydrolysate

Initial VX Hydrolysate Treatability Studies and Testing with Salt Simulants (August 1996)

Pilot-scale testing with simulants and treatability studies with VX hydrolysate were carried out at the General Atomics pilot facility in August 1996. A flow plan of the pilot-scale reactor system as configured for the August 1996 tests is shown in Figure 3-3 (General Atomics, 1997a). The reactor was a vertical, titanium-lined cylindrical reactor of 10 cm (4 in) internal diameter and 1.8 m (6 ft) length. The pressurized waste feed was injected at the reactor top along with compressed air to ensure vigorous mixing at the top of the reactor. Diluent water and fuel were also injected, as needed, at the top of the reactor. The system was operated at a flow rate that provided approximately 30 seconds mean residence time (i.e., average linear velocity through the reactor of 0.06 m/s [12 ft/min]) although the mixing characteristics and

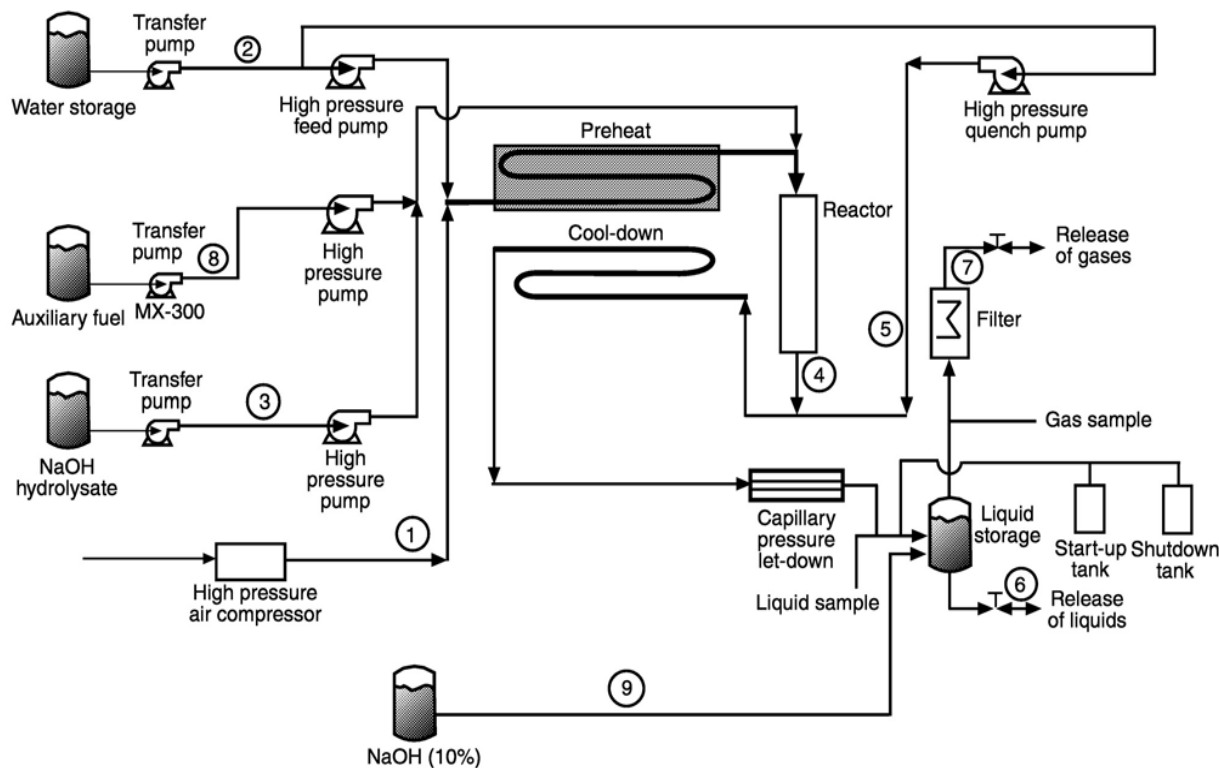


FIGURE 3-3 Simplified SCWO process flow diagram for pilot-scale testing with salt simulants and VX hydrolysate treatability studies (August 1996). Source: Adapted from General Atomics, 1997a.

residence time distribution in the reactor have not been determined. Temperature and pressure reduction after exiting from the reactor were achieved by quenching with 0.26 kg/min of clean water followed by cooling through a heat exchanger and then pressure let-down through capillaries.

The initial system demonstration was carried out using a heating value simulant (40 wt. percent ethanol) for one hour followed by an aqueous salt simulant (15.1 wt. percent Na_2SO_3 , 11.5 wt. percent $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, and ethanol added, as necessary, to maintain reactor temperature) for 1.5 hours. (Sodium sulfite was used to prepare the simulant solution because sulfate was not adequately soluble in the presence of high Na^+ concentrations. Sulfite was expected to be rapidly oxidized to sulfate in the reactor.) The total feed rate was 0.5 kg/min (135 g/min salt) with reactor operating conditions of 600°C and 247 bar (3,600 psig). No indications of salt plugging were observed.

After the initial system demonstration, two VX hydrolysate campaigns of 1.5 hours were carried out. During each campaign, steady-state operations with hydrolysate feed were achieved for about 30 minutes. The total feed rates for the first and second campaigns were 0.34 kg/min (116 g/min of 34 wt. percent salt) and 0.39 kg/min (133 g/min, of 34 wt. percent salt), respectively. Oxygen (200 percent stoichiometric) was provided using compressed air. The targeted reactor operating pressures were 254 bar (3,700 psig) and 261 bar (3,800 psig) during the first and second campaigns, respectively. During the second campaign, a back pressure control valve was added to the quench water supply to reduce pressure fluctuations. Maximum internal temperatures were 640°C (at the top of the reactor), with wall temperatures and average bulk fluid temperatures of 550 to 600°C for both campaigns.

During the two hydrolysate campaigns, samples of liquid and gaseous effluents were collected for analysis at 5 and 10 minute intervals, respectively. Liquid samples representative of baseline (effluent composition prior to hydrolysate feed) and steady-state conditions during hydrolysate treatment were analyzed for EMPA, MPA, VX, thiols, anions, TOC (total organic carbon), COD (chemical oxygen demand), and metals. Gas samples were analyzed for O_2 , N_2 , CO_2 , NO_x , SO_2 , H_2 , and volatile organic compounds (VOCs). No analysis for methane was performed. A summary of results and DREs for liquid effluent sampling reported by General Atomics is provided in [Table 3-3](#). DREs for the VX thiols exceeded 99.99 percent. DRE was lowest for MPA at 99.7 percent with residual MPA concentrations up to 53 mg/l. Results of off-gas testing during baseline operation (fuel only) and during steady-state operation are provided in [Table 3-4](#). Significantly lower concentrations of CO are reported than were observed during bench-scale testing for MPA destruction kinetics. Based on these results, operating conditions of 240 bar (3,500 psig) at 650°C with a ca. 45 second residence time were recommended for the full-scale system. Mass balance data indicated about 80 percent recovery of phosphorus and sulfur and 107 percent recovery of sodium; however, mass balance accuracy was limited by the experimental design. General Atomics reported that operational data and inspection of the system did not indicate a significant accumulation of salt.

An additional 8.25 hour campaign using a salt simulant (11.1 wt. percent Na_2SO_3 , 8.5 wt. percent $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) and ethanol as fuel was carried out after completion of the VX hydrolysate campaigns. The purpose of this campaign was to gather additional performance data on the management of salts within and downstream of the reactor. Previous testing with other feed streams had indicated that salt initially accumulated in the reactor to about 5 to 10 volume percent and that a steady-state condition was achieved where average salt influent and effluent rates were essentially equal. The total feed rate for this campaign was 0.75 kg/min (150 g/min salt) with reactor operating conditions the same as for earlier tests. Total salt content in the effluent was monitored through continuous measurements of conductivity.

Normalized results of salt transport through the reactor for the salt simulant campaigns and both VX hydrolysate campaigns are presented in [Figure 3-4](#). Results are normalized by dividing the rate of salt output from the reactor by the rate of salt input. These results indicate an accumulation of salt in the reactor during the initial hour of operation followed by an oscillatory pattern of salt accumulation and expulsion from the reactor. The apparent periodicity of the response is a reflection of the data sampling frequency.

Salt transport results over shorter time intervals indicate a random pattern of salt accumulation and expulsion that achieves a steady-state after initial start-up. This pattern is consistent with a mechanism whereby solids that adhere to internal reactor surfaces are intermittently removed by shear forces from a turbulent

fluid. However, it is not clear that the adhesion and transport properties of the salts produced during treatment of VX hydrolysate are the same as those observed using the salt simulants. This is because of the varying chemistry along the length of the reactor while the hydrolysate is oxidized. Thus, although there was no accumulation or blockage during the limited testing interval, the basis for the control of salt transport in the reactor is empirical. Reactor performance with different flow regimes (e.g., turbulence and shear stresses), varying salt composition as a function of reactor feed, and larger reactor scales has not been established.

TABLE 3-3 Liquid Effluent Concentrations of VX Hydrolysate Constituents and DREs Observed during Pilot-Scale Treatability Testing (August 13, 1996) a

Time sample removed ^b	TOC (mg/l)	EMPA (mg/l)	MPA (mg/l)	RSH (µg/g)	RSSR (µg/g)	RSR (µg/g)	RSRSSH (µg/g)	DIAE (µg/g)	MHA (µg/g)	EHHA (µg/g)
27 min	8.2	< 20	< 20	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	0.068
32 min	< 1	< 20	< 20	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008
37 min	3.8	< 20	< 20	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008
42 min	6.8	< 20	< 20	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008
47 min	16.6	< 20	53.9	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008
VX hydrolysate feed ^c	170,000	139,900	10,260	78,300	13,300	2,000	2,000	5,600	7,000	800
DRE (%)	99.9 to 99.995	> 99.89	99.7 to > 99.88	> 99.9999	> 99.9995	> 99.997	> 99.997	> 99.9988	> 99.999	> 99.97

^aConcentrations indicated as “<” reflect analytical detection limits; DREs indicated as “>” reflect that the calculated DRE was limited by the analytical detection limit for that constituent.

^bSamples removed at 5 minutes intervals while the system was at steady state.

^cNot corrected for dilution.

TOC = total organic carbon

EMPA = ethylmethyl phosphonic acid

MPA = methyl phosphonic acid

RSH = diisopropylaminoethane thiol

RSSR = bis (diisopropylaminoethyl) disulfide

RSR = bis diisopropylaminosulfide

RSRSSH = 1,9-bis (diisopropylamino)-3,4,7,-trithianonane

DIAE = other diisopropylaminoethane compounds

MHA = n,n'-methanetetrayl bis-cyclohexanamine

EHHA = mono (2-ethylhexyl) ester hexanedioic acid

Source: Adapted from General Atomics, 1997a.

TABLE 3-4 Composition of Off-Gas Produced during Pilot-Scale Treatability Testing (August 13, 1996)

Sample Number	O ₂ (%)	N ₂ (%)	CO (ppm)	CO ₂ (%)	NO _x (ppm)	SO ₂ (ppm)	H ₂ (ppm)	VOC ^b (ppm)
3	11.0	81.7	< 5.6	6.3	4.6	19	BDL ^a	< 1 or BDL
5	11.7	81.7	< 9.9	6.1	11.1	< 17	BDL	< 1 or BDL
7	11.9	82.3	< 5.2	6.0	6.7	< 11	BDL	< 1 or BDL

^aBDL = below detection limit

^bApproximately 50 different volatile organic compounds were measured

Source: Adapted from General Atomics, 1997a.

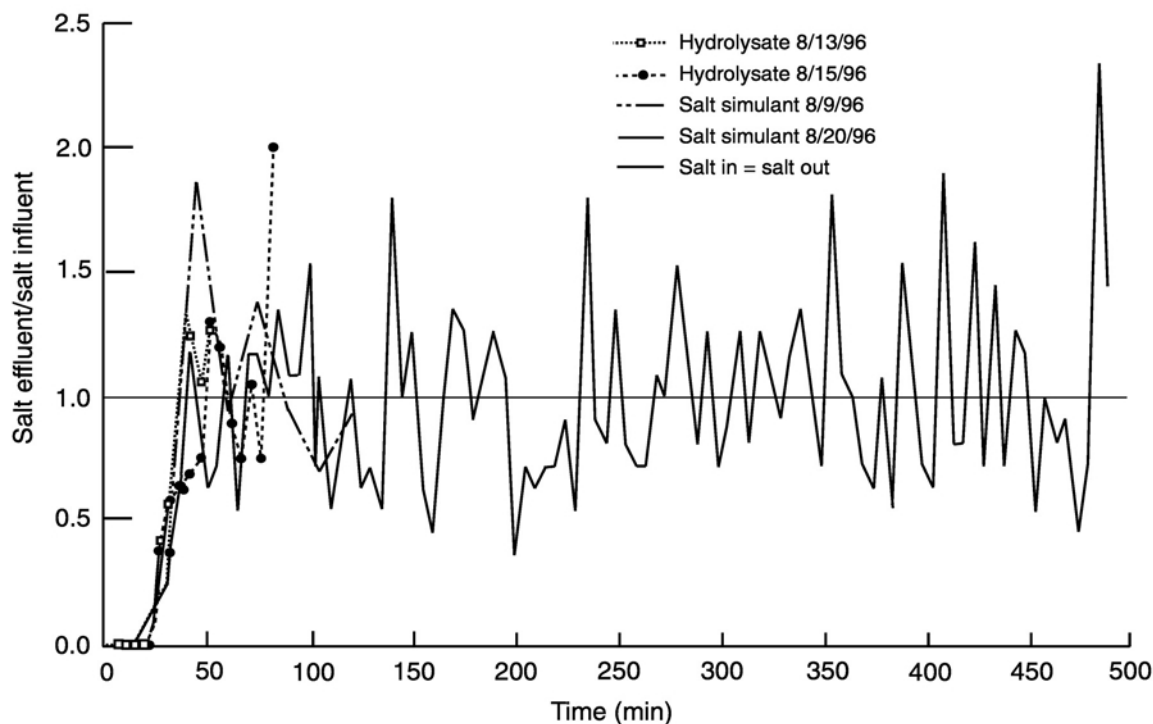


FIGURE 3-4 Normalized salt transport through the reactor during the pilot-scale treatability testing with salt simulants and with VX hydrolysate (August 1996). Source: Adapted from General Atomics, 1997a.

Confirmatory VX Hydrolysate Treatability Studies and Testing with Salt Simulants (February 1997)

Testing Program. A second set of pilot-scale tests was carried out during February 1997 with the following objectives (General Atomics, 1997b):

- demonstrate > 99 percent destruction of hydrolysate constituents with carbon-phosphorus bonds (e.g., EMPA and MPA), VX thiols, and TOC
- maintain continuous system operation for at least eight hours with VX hydrolysate feed
- demonstrate that salts from VX hydrolysate do not cause system plugging or interfere with organic destruction during the test interval
- demonstrate the basis for process control

The test program consisted of two three-hour campaigns with a surrogate as the feed followed by one eight-hour campaign with VX hydrolysate as the feed. The purpose of the two test campaigns with surrogate feed² was to verify system operations as configured and to verify DRE for MPA and TOC. For both campaigns, MPA was reduced to below analytical detection limits, and calculating the DRE was limited by a greater than anticipated analytical detection limit.³ Thus, only the test campaign with VX hydrolysate will be discussed.

The February 1997 tests used the same SCWO system as the August 1996 tests with slight modifications. The most significant system modification was the use of a back pressure control valve in the temperature and pressure reduction system. The valve was located after the quench and heat exchanger but before the capillary pressure let-down. The targeted steady-state operating conditions were VX hydrolysate feed rate of 0.33 kg/min, 233 bar (3,400 psig), and reactor wall temperature of 650°C. Dilution water was fed to the inlet of the reactor at a rate of 0.37 kg/min, and quench water was added at the reactor exit at a rate of 2.0 kg/min. The feed concentration of organic material in water was high enough that the feed was autogenic. However, reactor

²The surrogate feed consisted of 8.8 wt. percent monosodium phosphate hydrate, 11.6 wt. percent sodium sulfite, dimethyl methylphosphonate (DMMP) at 816 and 6,430 ppm on February 18, 1997, and February 19, 1997, respectively, and kerosene as auxiliary fuel.

³The detection limit was 5 or 10 mg/l (due to phosphate interference), depending on the specific sample analyzed. The calculated DREs were > 94 percent (February 18, 1997) and > 99 percent (February 19, 1997).

temperature control required a limited flow of diesel fuel during operations, as well as the addition of extra water because of the turn-down limitations of the water pump. The source of oxygen, which was required to fully oxidize all constituents in the hydrolysate, was compressed air supplied at about twice the stoichiometric amount.

In the course of the treatment campaign for VX hydrolysate, liquid effluent samples (about 150 ml) were collected at five minute intervals for pH, conductivity, and TOC analyses. Larger liquid samples (about 500 ml) were collected at 30 minute intervals for more detailed analyses (e.g., EMPA, MPA, VX thiols). Three additional liquid samples (about 3,000 ml) were collected to evaluate analytical precision and accuracy for TOC, MPA, and VX thiols. Two gaseous effluent samples were collected during hydrolysate feed operations at about three and six hours after the beginning of steady-state operations. Baseline samples for all sample types were obtained while the system was operating with kerosene feed only, prior to initiating the hydrolysate feed.

Test Results. The reactor wall temperature, pressure, and sampling history during the eight-hour hydrolysate test, as reported by General Atomics, are presented in [Figure 3-5](#). A significant decrease in operating pressure and temperature was observed from 2.25 to 2.75 hours into the test. Additional pressure fluctuations were observed at about four and six hours. These pressure fluctuations resulted from poor performance by the back pressure control valve, which necessitated the use of manual back pressure control after that time. There was no evidence of system plugging due to salt accumulation. The wall temperature fluctuated by as much as 50°C during the test campaign.

[Figure 3-6](#) presents the internal reactor temperature history for the uppermost region (feed end) of the reactor. A large temperature decrease at about 1.75 hours and subsequent temperature fluctuations of as much as 100°C were observed. Thus, the process control necessary to maintain consistent processing conditions over prolonged periods has not been demonstrated. In addition, the relationship between internal reactor temperatures and reactor wall temperatures and their relationship to process control are not clear.

Liquid effluent samples were odorless and clear, except for the presence of fine white salts that precipitated upon cooling. This contrasts with the VX hydrolysate, which has both aqueous and organic phases, is brown colored, and has an extremely strong offensive odor. The white salts most likely included titanium dioxide as a consequence of corrosion of the reactor liner.⁴

[Figure 3-7](#) presents the liquid effluent pH and salt balance⁵ history during the test campaign. Salt transport out of the reactor fluctuates at high frequency and is indicative of salt accumulation or adhesion followed by sloughing off in the reactor over short time intervals. Higher effluent pH values are associated with greater effluent salt concentration, reflecting buffering by carbonate salts when they are flushed intermittently from the reactor and then dissolved as the temperature and pressure are lowered.

Analyses of the feed and liquid effluent for specific hydrolysate constituents, TOC, and COD are presented in [Table 3-5](#). These results are not corrected for dilution from the additions of feed water and quench water. Nondetectable or very low concentrations of organic constituents remained in the process effluent, except for Sample No. 24, which was taken during the failure of the pressure control system between the first and second hour of the test (1100 and 1200 hours). Based on laboratory testing with MPA and results from other systems, some extremely low levels of partially oxidized organics should be expected, especially in a reactor with considerable internal mixing when some small degree of short circuiting through the reactor or constituent occlusion in solids can be expected. Samples were taken from the 55-gallon effluent drums (EFFDRUM); these samples can be considered to have average characteristics for the time interval during which the drum was filled.

Analytical precision and accuracy results are presented in [Table 3-6](#). Analytical reproducibility was good for all samples except the TOC analysis for Sample 60, in which the sample concentration was close to the detection limit. Analytical recovery was only fair (49 to 85 percent). Calculated DREs based on the liquid effluent samples are provided in [Table 3-7](#). DREs were greater than 99.9 percent for all organic analytes except (1) during failure of the pressure control system between 1100 and 1200 hours (Sample 24, 99.6 percent DRE),

⁴Titanium was not considered an appropriate reactor liner material for this application because of anticipated corrosion. However, this reactor was the only one available at the time.

⁵The salt balance was inferred from conductivity measurements.

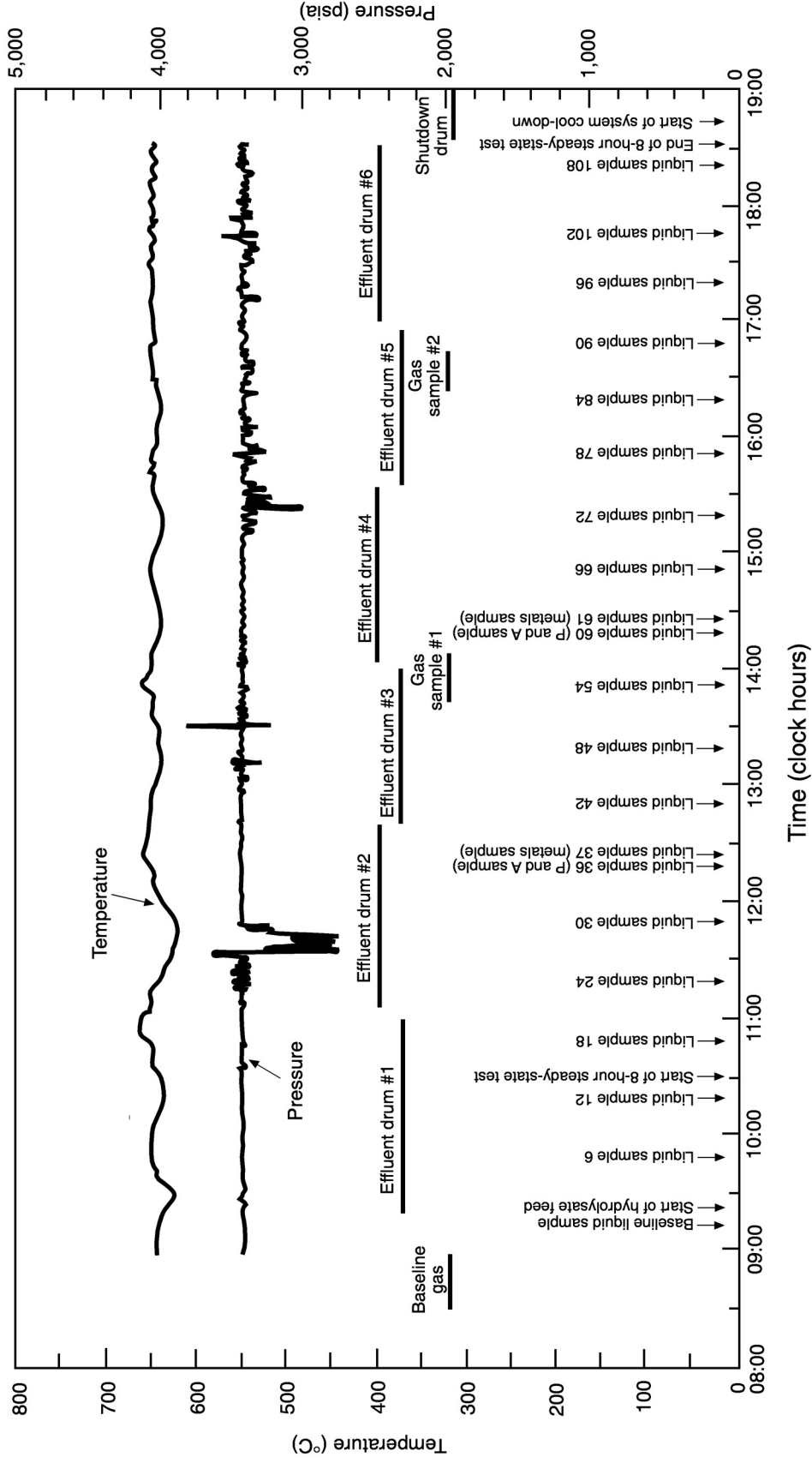


FIGURE 3-5 Reactor wall temperature, pressure, and sampling history during the eight-hour hydrolysate test. Source: Adapted from General Atomics, 1997b.

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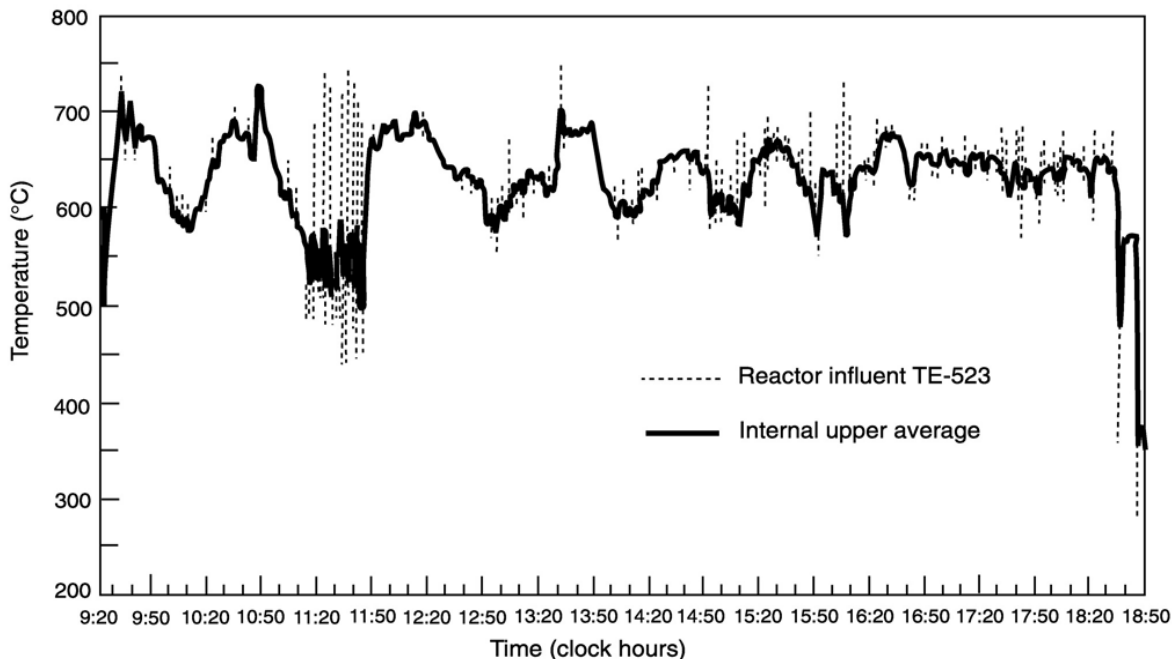


FIGURE 3-6 Internal reactor temperature for the uppermost region (feed end) of the reactor. Source: Adapted from General Atomics, 1997b.

and (2) MPA in Sample 54 (99.8 percent DRE). During both of these sampling intervals, short periods of out-of-specification operation allowed the reactor temperature to drop to about 550°C.

Effluent gas composition analytical results are presented in Table 3-8. Analysis for methane was not carried out. Effluent VOC concentrations were very low and should be easily removed by activated carbon filters during full-scale operation. No indicators of poor process performance were detected. Analyses of the effluent gas indicated significantly better performance, based on the much lower reported CO concentration, than was achieved during the bench-scale tests (Gloyna and Li, 1997). It appears that the higher temperature (650°C versus 550°C) was effective in completely oxidizing CO and VOCs.

At the conclusion of the hydrolysate test, a boroscope was used to examine the internal reactor surfaces for salt accumulation. Only a limited amount of salt accumulation was noted, mostly at the reactor top and bottom. Sampling and analysis of the accumulated salts indicated predominantly sodium sulfate and monosodium phosphate. No analysis was done for carbonate. Some unidentified organic constituents also were incorporated into the salt matrix, as indicated by TOC contents of 2,235 and 551 mg/kg in the salt at the top and bottom of the reactor, respectively. The salt sample from the bottom of the reactor also had high titanium content (about 7 wt. percent), indicative of corrosion of the reactor liner.

A steady-state mass balance for the process during the eight-hour hydrolysate campaign indicated good closure within measurement limits. Total recoveries of sodium, phosphorus, and sulfur were 93.1, 98.6, and 103.3 percent, respectively, excluding consideration of salts retained in the reactor.⁶ These results are consistent with a limited amount of salts being retained in the reactor.

Toxicity of the Liquid Effluent

Intravenous toxicity of the liquid effluent from the SCWO pilot testing was measured in mice (Manthei et al., 1997a). The test effluent used for toxicity testing was obtained during steady-state operations (Effluent Drum 4)

⁶Recoveries of greater than 100 percent reflect precision and accuracy limitations typical of mass balances for processes at this scale.

as part of the February 1997 test campaign with VX hydrolysate as feed. Both the clear supernatant from the effluent and homogenized samples of the supernatant with the fine white solids were tested. Dosages of SCWO effluent to individual mice were limited to about 10,000 mg/kg because of excessive total liquid dosage. The results of testing indicated no signs of agent toxicity, and all of the mice survived the received dosage. Observed effects included mild ataxia, temporary decreases in activity, and disorientation, most likely caused by the high salt content of the effluent. Thus, the dose that would result in 50 percent mortality in a test population (LD_{50}) was greater than 10,000 mg/kg, which represents a greater than 30-fold reduction in toxicity compared to VX hydrolysate (and the elimination of all signs of residual agent toxicity).

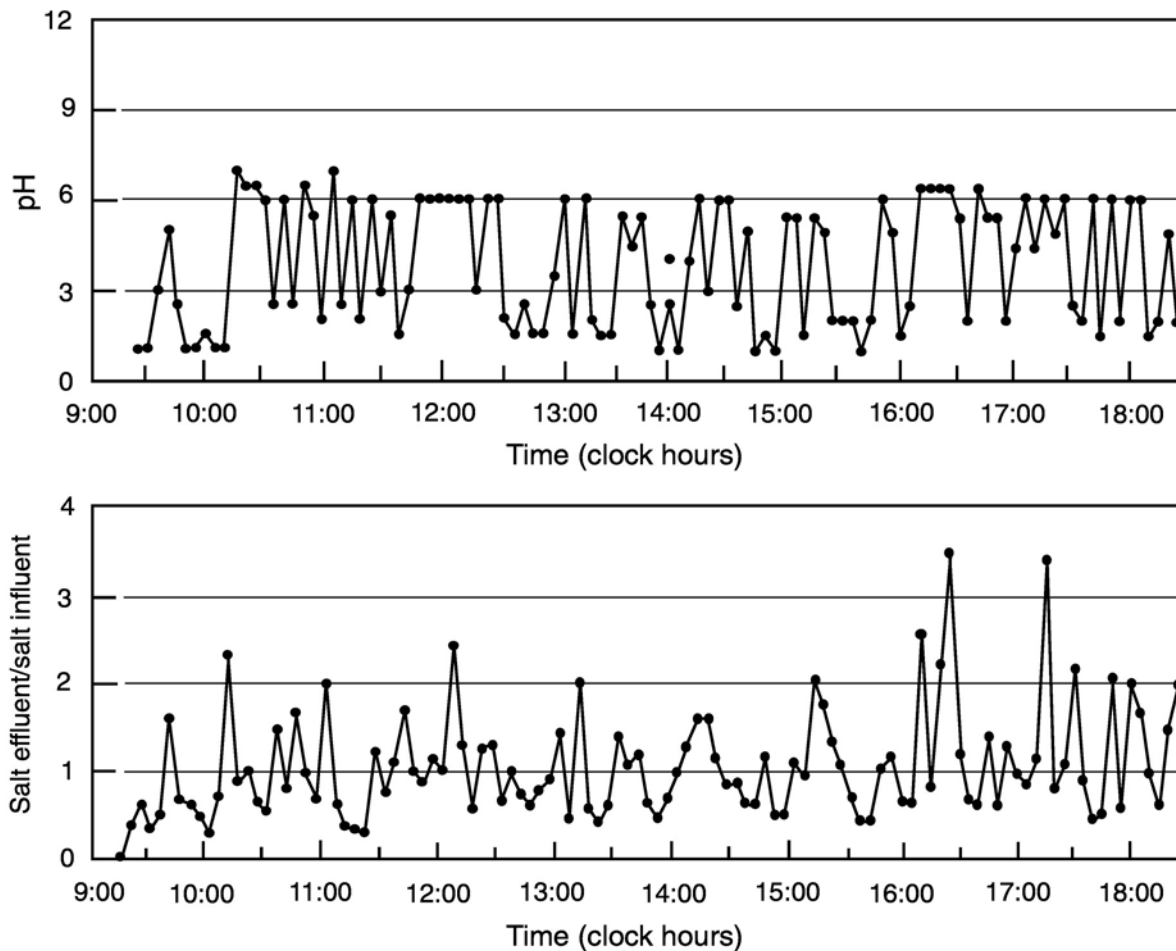


FIGURE 3-7 Liquid effluent pH and salt balance during the VX hydrolysate test campaign. Source: Adapted from General Atomics, 1997b.

Additional toxicity testing of the same liquid effluent carried out using U.S. Department of Transportation test procedures (Manthei et al., 1997b) evaluated oral exposure to rats and dermal exposure to rabbits. Both the clear supernatant and the supernatant homogenized with the fine white precipitate were tested. Oral exposure of 500 mg/kg by gavage caused no observed toxic effects for either sample during the 14-day observation period. Dermal exposure of direct contact for 24 hours caused no dermal irritation for either sample during the 13-day observation period.

Summary of Solids Management and System Performance

Results of the pilot tests clearly illustrate the potential problem of handling salts and indicate that salts management at full scale will require additional testing and development. The pilot-scale system was operated in a

TABLE 3-5 Analyses of Feed and Liquid Effluent for Specific Hydrolysate Constituents, TOC, and COD

Sample Number	Time ^a	Total VX									
		EMPA (mg/l)	MPA (mg/l)	Thiol (mg/l)	TOC (mg/l)	PO ₄ ⁻³ (mg/l) ^c	SO ₄ ⁻² (mg/l)	NO ₃ ⁻ (mg/l)	Na (mg/l)	P (mg/l)	S (mg/l)
Feed	N/A	152,673	13,348	175,670 ^b	140,000	2.19	96.9	—	87,900	37,700	38,400
Baseline	N/A	<1	<1	<0.266	<0.5	0.2	0.5	0.1	0.54	0.08	0.03
18	1050	<10	4.52	<0.266	0.98	7,868	21,210	16.5	15,400	7,730	7,300
EFFDRUM 1 ^c	0920-1100	—	—	—	6.1	—	—	—	—	—	—
24	1120	39.6	647	<0.266	75.2	1,951	5,130	91.8	3,480	1,670	1,790
30	1150	<5	5.77	<0.266	1.9	3,933	11,870	19.6	8,290	3,960	4,060
36	1220	<5	1.69	<0.266	<0.5	4,791	12,078	17.6	9,500	4,830	4,860
EFFDRUM 2 ^c	1105-1240	—	—	—	32.9	—	—	—	—	—	—
48	1320	<5	<1	<0.266	0.6	2,408	6,421	32.9	4,370	2,000	2,230
54	1350	<5	25.8	<0.266	2.8	2,970	7,102	25.0	4,880	2,390	2,440
EFFDRUM 3 ^c	1240-1400	—	—	—	4.3	—	—	—	—	—	—
60	1420	<5	<1	<0.266	<0.5	5,834	16,725	13.4	12,900	5,670	6,050
72	1520	<10	<1	<0.266	<0.5	7,634	20,224	16.1	15,000	7,340	7,170
EFFDRUM 4	1405-1535	<5	4.95	<0.266	4.1	4,810	13,857	14.4	9,800	4,450	4,750
84	1620	<10	<1	<0.266	<0.5	7,810	19,602	26.9	18,500	6,650	6,300
EFFDRUM 5 ^c	1535-1655	—	—	—	1.4	—	—	—	—	—	—
96	1720	<5	<1	<0.266	<0.5	2,534	7,055	43.1	4,840	2,010	2,350
102	1750	<10	<1	<0.266	<0.5	8,920	23,194	19.7	20,000	9,640	9,240
108	1820	<10	<1	<0.266	<0.5	5,797	15,378	23.5	11,500	5,120	5,290
EFFDRUM 6 ^c	1700-1830	—	—	—	1.2	—	—	—	—	—	—

^aThe start of steady state (i.e., start of the 8-hour continuous test period) was 1030 hours, although the start of hydrolysate feed was 0920 hours.

^bSum of 160,000 ppm RSH, 13,000 ppm RSSR, 970 ppm RSR, and 1,700 ppm RSRSSR. (See Table 3-3 for chemical names of those constituents.)

^cEffluent drums 1, 2, 3, 5, and 6 were analyzed for TOC only at D-TEK, a San Diego laboratory.

^dPO₄⁻³ expressed as phosphorus for effluent samples.

Source: Adapted from General Atomics, 1997b.

TABLE 3-6 Analytical Precision and Accuracy Testing Results for TOC, MPA, and VX Thiol a (sample identifiers correspond to sample intervals indicated in Figure 3-5)

Replicate	TOC (mg/l)		MPA (mg/l)		Total VX thiols (mg/l)	
	Sample 36	Sample 60	Sample 36	Sample 60	Sample 84	Effluent Drum 4
1	0.6245	0.8635	9.24	8.21	0.887	0.782
2	0.5535	0.7370	8.94	8.17	0.895	0.996
3	0.4690	0.5060	8.63	8.24	0.961	0.964
4	0.6220	0.7360	8.74	8.23	1.107	0.993
5	0.6370	0.4525	8.30	8.26	0.994	0.956
6	0.5345	0.5950	8.19	8.26	0.994	0.956
7	0.7335	0.3705	8.50	9.07	1.009	1.025
Average	0.6	0.6	8.65	8.48	0.979	0.964
Standard deviation	0.085	0.178	0.365	0.435	0.0751	0.0847
Minimum detection limit	0.269	0.559	1.15	1.37	0.236	0.266
Percent recovery ^b	60	60	74	84.8	50.1	49.4

^aAnalytical values presented are for a 99% confidence level for TOC, MPA, and VX thiols. For TOC analyses, samples were spiked with 1 ppm TOC. For MPA analyses, samples were spiked with 10 ppm MPA. For VX thiol analyses, samples were spiked with 1,953 ppm total VX thiols (1,640 ppm RSH and 0.313 ppm RSSR).

^bPercent recovery = average detected sample concentration divided by the SCWO effluent sample concentration + spike concentration and multiplied by 100. Samples below detection limits were calculated as zero (e.g., sample 36 TOC concentration at < 0.5 ppm were assumed to be zero for this calculation). For example, the recovered MPA concentration in spiked Sample 36 of 8.65 ppm divided by the SCWO effluent MPA concentration of 1.69 ppm plus 10 ppm spike concentration, then multiplied by 100, yields 74 percent recovery.

Source: Adapted from General Atomics, 1997b.

poorly understood, nonsteady-state manner, even though system performance was maintained, and significant salt accumulation did not occur. During the pilot-scale tests, the flow of materials out of the reactor was monitored by pH and conductivity measurements on the liquid effluent, as well as by system performance. The salt output fluctuated over short time intervals, varying considerably from minute to minute. Salt was obviously being held up in the reactor and then released; however, over an extended time interval (ca. 1 hour), the total salt in the effluent was approximately the amount expected. It appears that the solids flowed freely enough and that material did not stick to the walls tenaciously enough to cause plugging of the reactor. The precise mechanism of solids transport was not established. The optimistic outlook is that a reactor of this size and with these flow conditions can be operated over an extended period (certainly much longer than eight hours) without plugging. However, local flow velocities and shear stresses may not be replicated in the full-scale reactor.

Tests to date have not provided sufficient data on the performance of pressure let-down and control systems. Data on the anticipated problem of the erosion of valve seats and other control surfaces are inconclusive because of the relatively short intervals of system operation. Vendors have stated that they have solved the problems of valve seat erosion and related difficulties, but the data are proprietary and were not available to the committee.

The status of SCWO technology for treatment of VX-hydrolysate can be summed up as follows:

- Test data show that SCWO at a temperature of 600 to 650°C will oxidize VX hydrolysate to a satisfactorily high degree, with only parts per million of partially oxidized organic species remaining in the liquid and gas phases.
- Solid salts deposited during the reaction did not cause plugging of the reactor. The unsteady operation, with considerable fluctuations in the solids transported out of the reactor, is not ideal but appears to be workable.
- Based on intravenous testing in mice, the acute toxicity of SCWO effluent is negligible. Oral dosages in rats and dermal applications in rabbits also indicate negligible acute toxicity.

TABLE 3-7 Calculated DREs Based on Liquid Effluent Samples^{a,b}

Sample Number	TOC	EMPA	MPA	Total VX Thiol
18	99.994	> 99.95	99.97	> 99.998
EFFDRUM 1	99.96	—	—	—
24	99.6	99.8	96.0	> 99.998
30	99.99	> 99.97	99.96	> 99.998
36	> 99.997	> 99.97	99.99	> 99.998
EFFDRUM 2	99.8	—	—	—
48	99.996	> 99.97	> 99.994	> 99.998
54	99.98	> 99.97	99.8	> 99.998
EFFDRUM 3	99.97	—	—	—
60	> 99.997	> 99.97	> 99.994	> 99.998
72	> 99.997	> 99.95	> 99.994	> 99.998
EFFDRUM 4	99.98	> 99.97	99.97	> 99.998
84	> 99.997	> 99.95	> 99.994	> 99.998
EFFDRUM 5	99.992	—	—	—
96	> 99.997	> 99.97	> 99.994	> 99.998
102	> 99.997	> 99.95	> 99.994	> 99.998
108	> 99.997	> 99.95	> 99.994	> 99.998
EFFDRUM 6	99.993	—	—	—

^aCalculational procedure is shown below for Sample 24 for TOC, EMPA, MPA, and VX thiol. A dilution factor of 8.18 was used to correct the feed concentration to account for the addition of dilution water and quench water.

$DRE_x = [\text{feed concentration of X, corrected for dilution-effluent concentration of X}] / [\text{feed concentration of X, corrected for dilution}] \times 100\%$

$DRE_{\text{TOC}} = [(17,114.9-75.2)/17,114.9] \times 100\% = 99.6\%$

$DRE_{\text{EMPA}} = [(18,644.2-39.6)/18,664.2] \times 100\% = 99.8\%$

$DRE_{\text{MPA}} = [(16,081.5-647)/16,081.5] \times 100\% = 96.0\%$ (MPA feed concentration includes contribution from EMPA)

$DRE_{\text{VX thiol}} = [(21,476-.266)/21,476] \times 100\% = 99.9988\%$

^bSample numbers correspond to sampling intervals indicated in [Figure 3-5](#). Samples designated by “EFFDRUM” indicate a sample from the effluent drum, in which process effluent was collected during a prolonged interval (approximately 1.5 hr.). Source: Adapted from General Atomics, 1997b.

STATUS OF EVAPORATOR TECHNOLOGY

The evaporator and solids separation technique selected for the NECDF (Newport Chemical Agent Disposal

Facility) represents a well established, full-scale technology for similar applications (Solomon, 1997). Table 3-9 is a summary of similar evaporator process units. The proposed Newport facility is included for comparison.

TABLE 3-8 Composition of Effluent Gas

Sample Number	O ₂ (%)	N ₂ (%)	CO ₂ (%)	CO (ppm)	NO _x (ppm)	SO ₂ (ppm)	VOC (ppb)
Baseline ^b	10.8	76.9	7.9	< 3	0.35	< 8.6	9-16 ^a
1 ^c	8.8	78.0	8.5	< 3	6.9	< 9.2	7-28 ^a
2 ^d	12.4	77.2	6.0	< 3	4.0	< 9.9	14-41 ^a

^aAnalyses were conducted for approximately 50 different VOCs (volatile organic compounds). Of these, only five were detected, all at very low concentrations. Acetonitrile, acetone, 2-butanone, carbon disulfide, and vinyl acetate were detected in concentrations of 9 to 41 ppb. The most prominent volatile organic was acetone, which was present at 41 ppb in Sample 2.

^bBaseline gas sample was collected between 0831 and 0858 hours.

^cGas Sample 1 was collected between 1343 and 1405 hours (193 to 215 minutes after the start of steady state).

^dGas Sample 2 was collected between 1625 and 1643 hours (355 to 373 minutes after the start of steady state).

Source: Adapted from General Atomics, 1997b.

The proposed system includes a single evaporator big enough to process 125 percent of the SCWO aqueous effluent stream. Evaporation and crystallization take place in a single vessel at 107°C and at atmospheric pressure. Slurry containing precipitated salts is

TABLE 3-9 Summary of Evaporator Installations Similar to the Design Specifications for NECDF

Plant	Location	Facility	Flow (gal/gin)	MVR or Steam ^a	Solids Separation Device	Salts	Purge
Aerojet	California	chemical plant	15	MVR	centrifuge	Na ₂ SO ₄ , Na ₂ CO ₃ NaCl,	NaNO ₂ , organics
Auburndale	Florida	cogeneration	3	steam	pressure filter	CaSO ₄ , Na ₂ SO ₄ , 3Na ₂ SO ₄ Mg SO ₄ , NaCl	—
Cedar Bay	Florida	cogeneration	48	steam, thermoc compressor	centrifuge	CaSO ₄ , Na ₂ SO ₄ , NaCl	organics
Debiensko	Poland	coal mine	319	MVR	centrifuge	NaCl	MgCl ₂ , CaCl ₂
Doswell	Virginia	cogeneration	6	steam	pressure filter	CaSO ₄ , Na ₂ SO ₄ , NaCl	—
East Penn	Pennsylvania	chemical plant	16	MVR	pressure filter	NaSO ₄	—
Gordonsville	Virginia	cogeneration	3	steam	pressure filter	CaSO ₄ , Na ₂ SO ₄ , NaCl	—
Orlando	Florida	public utility	25	steam, thermoc compressor	centrifuge	CaSO ₄ , NaCl, 3Na ₂ SO ₄ MgSO ₄ , Na ₂ SO ₄ 2MgSO ₄ 5H ₂ O	—
Newport (proposed)	Indiana	NECDF	21.6	MVR	pressure filter	Na ₂ SO ₄ , Na ₂ HP O ₄	—

^aMechanical vapor recompression (MVR) or steam was used to add energy to the system and increase the temperature, via a recycle loop into the evaporator vessel.

Source: Adapted from Solomon, 1997.

recirculated from the evaporator vessel through a heat exchanger and back into the evaporator vessel. A portion of the recirculation stream flows through a filter press, where salt crystals are separated out by a vacuum belt-filtration process. Upon cooling, most of the remaining water, with separated salts, is taken up as water of hydration, resulting in a final stream that is about 70 wt. percent solids. System heating is provided by mechanical vapor compression in conjunction with condensation of recovered high purity water, which is recycled into the overall facility process. Flushing the system with water for cleaning (about 10 hours required) is anticipated to be necessary at intervals of two weeks to three months, depending on system performance.

Laboratory testing was carried out to specify design conditions for the evaporator process. The SCWO effluent used for testing was obtained during steady-state operations (EFFDRUM 4) during the February 1997 test campaign with VX hydrolysate as feed. Laboratory results indicated successful processing was possible if (1) the feed to the evaporator was adjusted to pH 9.6 to avoid nitrite carryover, and (2) the specific gravity of the slurry in the evaporator was maintained at less than 1.5 to keep solids from caking. The required specific gravity can be maintained by releasing a small purge stream from the evaporator. Based on laboratory tests, the purge stream will also solidify upon cooling.

Materials of construction will have to be carefully selected if the full-scale SCWO effluent contains the same concentration of chlorides as the pilot-test sample. However, the chloride content of the pilot-test sample may be anomalous because the use of chloride-free reagents was not specified. Full-scale process design should include specifications for maximum acceptable chloride content in all process feed streams.

4

Scale-Up, Stability, and Reliability

PROCESS SCALE-UP

Although significant research and development have been focused on using SCWO for the destruction of organic compounds (Shanableh and Gloyna, 1991; Tester et al., 1993; Modell, 1989), a number of technical challenges must still be overcome before widespread, full-scale implementation will be feasible. These include better management of salts/solids, better understanding of the phase behavior and kinetics/flow dynamics for scale-up, a better understanding of the corrosion characteristics of potential materials of construction, and the development of process monitoring and control regimes.

Because a fundamental understanding of the fluid dynamics, mixing processes, and reaction kinetics occurring in a SCWO reactor does not exist, process scale-up has been based on reactor residence time, engineering judgment, and significant pilot-scale testing. This empirical approach to scale-up is especially important for complex systems, like VX hydrolysate, that contain large quantities of salt and may have several phases. For example, mixing of materials in the reactor is important; cold feed must mix with hot product to bring the material to reaction temperature; solids condensed from the supercritical fluid will impinge on, and may stick to, the reactor walls or other surfaces. There is no good way to extrapolate these complex flow effects from smaller to larger scale.

Fundamental information on the number of phases and the phase behavior of VX hydrolysate, as well as the kinetics of destruction and related oxidant effects, mixing and fluid dynamics, salt nucleation and precipitation characteristics, and the handling of salts within and downstream of the reactor must be determined before equipment can be scaled up from bench-scale or limited pilot-scale testing. Unfortunately, the Army's schedule for VX destruction does not allow sufficient time for thorough development of a fundamental understanding. Therefore, significant pilot testing and development will be needed for designing the full-scale treatment unit. In addition, the full-scale design and testing protocol should be flexible enough to incorporate findings, as well as engineering and equipment changes to accommodate potential problems that may be encountered.

The key areas of concern for scale-up application of SCWO to VX hydrolysate are: (1) salts management and solids handling; (2) the impact of the oxidant (e.g., air versus oxygen) on mixing and heat balance; (3) corrosion of the materials of construction; and (4) reliability of pressure let-down systems. A better understanding of the design, engineering, and operational implications of these issues is also critical for demonstrating the stability and reliability of the full-scale process. The pilot testing on VX hydrolysate described in the previous chapter focused on demonstrating the destruction of VX and did not specifically address these issues, although it did reveal potential problems in all of the aforementioned areas. The design issues are discussed in more detail below. [Table 4-1](#) provides a comparison of the Army's full-scale design (described in detail in [Chapter 5](#)) with the pilot-scale designs.

SALT MANAGEMENT AND REACTOR DESIGN

Given the large quantities of salt generated by SCWO treatment of VX hydrolysate, it is clear that solids management, both within and downstream of the SCWO reactor, is a critical issue. In general, the separation of inorganic salts generated during SCWO can be problematic. At the low densities and solvent dielectric of typical SCWO systems (200 to 275 bar, 500 to 650°C), most inorganic salts dissociate very little and are essentially insoluble. These solids may adhere to the reactor walls or associated plumbing hardware (valves, inlets, feed and exit lines, etc.).

Precipitated salts can also clog pressure let-down systems. It may be possible to "unclog" reactor parts via cooling and flushing with water, which should lead to redissolution. However, this fix would require

considerable shutdown and start-up time and, depending on frequency, could result in additional thermal and pressure stresses on system components. Large quantities of precipitated salts left in a reactor could significantly reduce reactor volume, with commensurate shortening of residence times, thereby leading to reduced DREs (destruction removal efficiencies). These possibilities suggest that either the management of solids must be better understood or stringent monitoring of destruction removal efficiencies may be necessary. In addition, the effect of precipitated salt on mixing and fluid flow characteristics could be significant. Scale formation by carbonate generated from organic carbon oxidation may also present a problem and must be properly managed.

TABLE 4-1 Comparison of Full-Scale Design with Pilot-Scale Design Tested with VX Hydrolysate (February 1997)

Reactor Property	Pilot Scale	Full Scale
Reactor size	4.25 in ID × 6 ft long	10 in ID × 15 ft long
Operating conditions (T, P)	650°C, 4,000 psi	650°C, 4,000 psi
Oxidant and oxidant stoichiometry	air (100 percent excess)	oxygen (50 percent excess)
Maximum operating interval	8 hrs	undefined, TBD ^a
Feed composition	VX hydrolysate/H ₂ O; salt simulant	VX hydrolysate, ton container cleanout effluent, decontamination fluids
Mass flow rate	63.7 lb/min•ft ²	105.7 lb/min•ft ²
Residence time ^b	40 sec	60 sec
Heating flow rate	0.19 × 10 ⁶ Btu/hr	5 × 10 ⁶ Btu/hr
Linear velocity ^b	8.25 ft/min	13.7 ft/min
Pressure let-down system	valves	TBD
Materials of construction	titanium (corroded metals observed in effluent)	TBD (platinum suggested; more testing needed)

^aTBD = to be determined

^bEstimated based on exit condition

Source: Adapted from General Atomics, 1997b; Stone and Webster, 1997a.

Despite these potential difficulties, it appears, as described below, that engineering and mechanical equipment that would mitigate some of these problems are becoming available; however, further testing at appropriate scales to define the full-scale design is necessary.

Solid salts that could be expected to separate out in the reactor from the oxidation of VX hydrolysate in the presence of NaOH include sodium phosphates, sodium sulfate, and possibly sodium carbonate (depending on pH). Several research studies have focused on understanding the behavior of salts in subcritical and supercritical water, including the phase behavior of NaCl, NaSO₄, and phosphates (Broadbent et al., 1997; Tester et al., 1993; Martynova, 1976; Martynova and Smirnov, 1964; Ravich and Yastrebova, 1959). Although considerable progress has been made in understanding and measuring the solubility and phase behavior for simple systems, the behavior of salts in SCWO systems is a complex and poorly understood phenomenon that nevertheless must be managed for effective SCWO implementation.

Recently, a number of approaches have been investigated for managing salts more effectively. These include higher system pressures, solubilization with added NaOH, lower temperature catalyzed reactions at higher densities, and new reactor concepts (i.e., transpiring wall reactors). Although these approaches may be promising, none has been developed enough for full-scale treatment of VX hydrolysate. All of these approaches will require considerably more development and pilot-scale work than appears to be necessary for a vertical

cylindrical reactor operated at approximately 650°C and 275 bar.

Another alternative would be to increase the dilution of hydrolysate to reduce salt concentration. However, this approach would require continuous feed of supplemental fuel, and a proportionate scale-up of all process components after the neutralization process step; it would also potentially increase process complexity and substantially increase capital and operating costs. Therefore, this option should be considered only if additional pilot-scale testing indicates that SCWO operation at the currently specified hydrolysate concentration is not practical.

Higher Pressure Systems

At significantly higher pressures, the density of water can increase to the point that many salts become soluble again in supercritical water (Foy et al., 1994). This higher pressure SCWO system looks very promising; however, a good deal more development work would be needed to assess its potential for VX hydrolysate. Higher pressure systems could also increase the cost of equipment considerably, which would have to be weighed against other salt management issues.

Dissolution in Molten Sodium Hydroxide

Several researchers have investigated the concept of using high concentrations of NaOH to prevent carbonates and, presumably, a wide range of other salts from precipitating in SCWO reactors (Borovaya and Ravich, 1968). High loadings of NaOH can result in a separate molten NaOH phase under SCWO conditions, which has been demonstrated to dissolve significant quantities of carbonate and, presumably, a number of other salts. Unfortunately, strongly caustic high temperature water is very corrosive, and materials of construction then become a considerable concern.

Catalyzed Oxidation

Catalyzed oxidations at decreased temperatures result in higher densities and salt solubilities. At lower temperatures, ($\leq 350^\circ\text{C}$), salts can be considerably more soluble and thus kept in the reaction medium. The penalty of lower temperatures is significantly lower DREs. Several studies (Ding et al., 1995) have reported the use of homogeneous or heterogeneous catalysts, which flow through the reactor to enhance oxidation kinetics and increase DREs (e.g., metal systems, solid carbonate). Disadvantages of catalyzed reactions include that the catalyst activity and concomitant DRE must be closely monitored and that the catalyst most likely will have to be separated from SCWO effluent. Little is known about catalyst lifetime or about poisoning and attrition mechanisms.

Transpiring Wall Reactor

The recently developed transpiring wall platelet is claimed to overcome corrosion of the reactor wall and salt deposition by deposition of a thin film of clean (often much lower temperature) water uniformly along the reactor wall. Testing to date, however, indicates salt buildup in the reaction entrance region. Fabrication of the platelet may be complex if noble metals (e.g., platinum) are required for corrosion resistance (Shoenmann et al., 1997).

A liquid rocket engine type injection system has also been described, which can be used for rapid mixing at the reactor inlet. Although this technology is currently slated for full-scale treatment of Navy shipboard wastes and Army smokes and dyes, most, if not all, testing to date has been on bench-scale systems with tube diameters of about 7.6 cm.

Engineering Control

Several vendors have claimed that, through considerable testing, they should be able to design engineering controls (often proprietary) to manage salts in SCWO effluents more effectively. Although it may be possible to remove inorganic salts directly as dry solids or concentrated salt solutions or slurries, this would require pressure let-down at elevated temperatures. Instead, most scenarios involve pressure let-down after cooling (via the addition of extra water and/or heat exchange) to allow for redissolution of most, if not all, salts.

Conclusion

The first four options, although they may seem promising, are somewhat immature or underdeveloped, and

the fifth involves vendor-specific proprietary technology that may require larger scale testing. The Army has opted for a full-scale design that incorporates cooling of the SCWO effluent by adding cold water and heat exchange prior to depressurization. Salts are then recovered through evaporation.

CHOICE OF OXIDANT, MIXING, AND HEAT BALANCE

The pilot tests on VX hydrolysate used air as the oxidant at 100 percent stoichiometric excess. The full-scale design calls for pure oxygen at 50 percent stoichiometric excess. The substitution of pure oxygen for air could have significant implications for mixing and for the heat capacity of the waste stream.

The reduction in excess oxygen will probably not affect the destruction of hydrolysate constituents. The reaction has been demonstrated to be approximately zero order with respect to oxygen when sufficient excess oxygen is present. Bench-scale data on MPA oxidation showed essentially the same conversion at 50 percent and 100 percent excess oxygen, as would be expected for a zero order reaction (Gloyna and Li, 1997). A much smaller amount of excess oxygen (10 percent excess) resulted in reduced MPA conversion (92.1 percent versus 99.9). The residence time for the full-scale reactor will be longer than that of the laboratory unit. Pilot-scale testing completed to date has demonstrated greater conversion of hydrolysate constituents than anticipated based on laboratory testing with MPA. The volumetric flow rate of fluid through the reactor is reduced substantially by eliminating nitrogen (from air) and by using less excess oxidant. The molar flow rate is also reduced by about 50 percent. As a consequence, the residence time for the full-scale unit is calculated to be twofold greater than for the pilot-scale unit.

The use of air as an oxidant results in the addition of considerable quantities of nitrogen gas (up to about 50 percent by volume for the VX hydrolysate pilot test), which could result in different fluid phase characteristics within the reactor than when pure oxygen is the oxidant. Flow dynamics and mixing could be significantly different in a larger scale system if the phase behavior is significantly different. The most critical impact of changes in fluid dynamics could be on the transport of salts out of the reactor at reduced shear stresses, which may result in increased salt adhesion, reactor plugging, or lower conversion efficiencies. In the pilot-scale reactor, the solid salts were carried out by the flowing fluid intermittently with reasonable frequency (e.g., less than 30 seconds between peaks). The physical situation in the reactor is not well enough understood to predict whether added nitrogen and potentially added turbulence would be beneficial or detrimental to conversion efficiency and salt removal from the reactor. The effects of substituting oxygen for air cannot be determined confidently without some pilot-scale testing.

The presence or lack of a considerable amount of nitrogen can significantly affect the heat capacity for the process stream, as well as the heat balance for the full-scale design. By eliminating the nitrogen, the heat capacity of the material flowing through the reactor would be reduced more than twofold.

High levels of hydrolysate conversion in the reactor depend on rapid mixing to bring the relatively cold feed up to reaction temperature very quickly. Again, it is not clear how the reduced heat capacity and mixing of the fluid will affect the ability of the reactor to increase the temperature of the inlet feed stream.

Another effect of changing the oxidant from air to oxygen is that the exit gas from the SCWO reactor will be oxygen-rich. This characteristic raises the possibility of combustion of the carbon filter on the SCWO vent unless the exit gas is cooled or diluted. This question should be addressed in the final process design and quantitative risk assessment for the SCWO process.

Another change in the feed to the full-scale facility relative to pilot testing is that it will include the treatment of spent decontamination fluid/NaOH solution, with a small amount of organic material (presumably the same products found in the hydrolysate). The spent decontamination fluid is planned to be treated in combination with the effluent from ton container cleanout. The presence of these fluids will reduce the heat released in the reactor. Some auxiliary fuel (e.g., diesel) may be needed to maintain the reactor temperature at 650°C.

CORROSION AND THE MATERIALS OF CONSTRUCTION

Materials of construction that can withstand the extreme pressures, temperatures, and often corrosive conditions within a SCWO reactor remain one of the key challenges for the broad implementation of SCWO technology. This is particularly true for the treatment of wastes that contain heteroatoms and generate significant

quantities of oxyacids or their salts depending on the cations present in the system. Numerous studies have demonstrated that streams that contain chloride are especially corrosive. In general, it is believed (and some test results have corroborated) that salt solutions at intermediate temperatures (e.g., during pressure letdown or during heat-up, or near inlet or exit areas) can be much more corrosive than the supercritical fluid in the reactor. Erosion from precipitated salts at high velocities could also be an important issue. Materials of construction are an important consideration for the reactor inlet system, the reactor itself, and all hardware and plumbing downstream of the reactor (e.g., pressure let-down equipment and reactor exit plumbing).

Recent studies have demonstrated that corrosion is a critical issue for SCWO hazardous waste disposal systems. Test system materials have exhibited pitting, stress corrosion cracking, and accelerated general corrosion (Latanision, 1995; Latanision et al., 1997). The operational performance and reliability of SCWO will depend on mitigating corrosion under operating conditions (Latanision et al., 1997).

Highly caustic VX/NaOH hydrolysate (pH~14), combined with the relatively high temperature and high pressure of the SCWO process, produces highly corrosive and erosive mixtures of reactants, reaction intermediates, and products. Pilot-scale tests in a titanium reactor produced significant amounts of solid TiO_2 and other metal oxide corrosion products after only a few hours of operation (General Atomics, 1997a,b). Careful selection of internal materials of construction will be essential, or reactor lifetime will be short, and system efficiency will be compromised. Welds and other joints are often sites of severe corrosion, so the reactor should be designed with the minimum number of joints and welds necessary for structural integrity. Furthermore, the failure of reactor liner joints should be anticipated as a possible process failure mode.

Metal coupon tests sponsored by the Defense Advanced Research Projects Agency at General Atomics (General Atomics, 1997c), as well as analyses of the survivability of metallic thermocouples in Armsponsored tests (General Atomics, 1997b), indicate that noble metals, specifically platinum and gold, withstand the corrosive assault best, particularly under the caustic (high pH) conditions near the reactor inlet. Although noble metal reactors will clearly be expensive, they will probably still represent a small fraction of the overall cost of a SCWO system. System reliability may be enhanced and down time reduced by reactor designs that include replaceable internal sleeves in the reactor entrance section, which is exposed to caustic; parallel reactors; or systems in which spare reactors can easily be substituted.

Additional data on materials lifetimes and failure modes under SCWO conditions representative of those with VX/NaOH hydrolysate will be necessary for making informed selections of reactor construction materials and operating parameters. Current information is insufficient for the confident selection of materials. The Army recognizes that selecting the best materials of construction is a key issue and has embarked upon a materials testing program.

PRESSURE LET-DOWN SYSTEMS

Reliable and stable operation of the full-scale SCWO process will require a robust system for depressurization that is not subject to clogging by precipitated salts and is not vulnerable to significant corrosion. The pressure let-down system may be the weak link in the full-scale process chain. The pressure let-down system will probably have to handle some precipitated salts because all salts may not redissolve prior to depressurization. Furthermore, as described above, the depressurization system will be exposed to a fairly corrosive environment. Thus, materials of construction will have to be tested for corrosion and reliability. The full-scale design calls for the addition of cold water and for further cooling by a heat exchanger prior to pressure let-down. The pilot-scale test used back-pressure valves for heat exchange, which were not very reliable. The final fullscale design will be specified by the system contractor.

SUMMARY

The operating and reactor parameters for the fullscale design, as well as for the pilot-scale test, are summarized in [Table 4-1](#). The scale-up factor from pilot-scale test to full-scale design is about 25, in terms of the amount of VX hydrolysate to be treated (13,600 kg/day versus 545 kg/day). The operating temperature and pressure are designed to be the same (650°C, 275 bar). The pilot plant ran on air at 100 percent stoichiometric excess, while the full-scale design calls for pressurized oxygen at 50 percent excess. To date, pilot-scale testing has demonstrated a continuous operational time of only eight hours; the design time for

continuous on-line operations for the full-scale plant has not been established. The residence time for the full-scale reactor will be increased by a factor of about two relative to the pilot-scale test if oxygen rather than air is used. The feed to the full-scale reactor will include fluid from ton container cleanout and spent decontamination fluid in addition to VX hydrolysate. Additional fuel will be needed to make up for the decreased heating value of these two streams and maintain the reactor temperature at 650°C. The pressure let-down system and the materials of construction still must be determined through testing.

There is no strong fundamental basis for the scale-up of SCWO. Given that the Army's schedule does not permit substantial fundamental work on VX hydrolysate to identify and measure fundamental data (e.g., kinetics, reaction order, fluid dynamics and mixing, corrosion, and salt nucleation and precipitation), a substantial amount of pilot-scale work should be done to define the engineering parameters more confidently and to resolve the issues of scale-up and materials of construction discussed above. Furthermore, given that there will probably still be uncertainties for the full-scale plant, substantial start-up time may be necessary, and the plant may have to operate in a developmental mode for some time. Facility planning should provide for sufficient flexibility to take this into account, as well as to implement key lessons learned from full-scale or larger testing.

5

Full-Scale Process Design

PROCESS DESCRIPTION

Figure 5-1 is a block flow diagram of the integration of SCWO into the overall process for the treatment of VX at Newport, Indiana. The overall process consists of five primary operations in series:

- draining VX from ton containers and ton container cleanout operations (ton container cleanout)
- the neutralization of agent and ton-container cleanout fluids (neutralization)
- SCWO
- evaporation followed by condensation of water for recycling and filtration to recover crystallized salts for disposal (evaporation)
- disposal of all waste streams

More detailed process flow diagrams for the SCWO and evaporation process steps are provided in Appendix A . Supporting process steps are the process water system, which provides water for ton container cleanout and other operations; sodium hydroxide storage, where caustic materials are stored and prepared for the neutralization step and other necessary pH adjustments; the

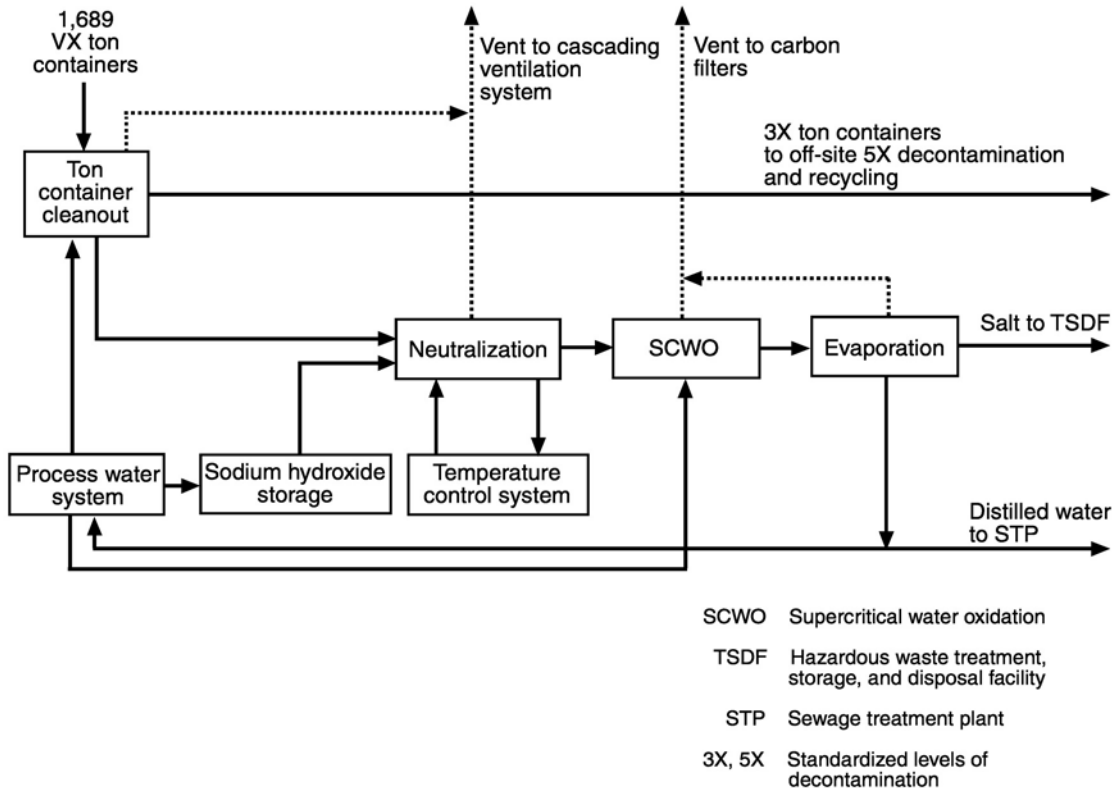


FIGURE 5-1 Overview of the disposal process for VX ton containers. Source: Adapted from U.S. Army, 1996b.

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temperature control system, which maintains process temperatures; and the ventilation filtration system (not shown), which filters vent gases and SCWO off-gas through activated carbon prior to release.

The first four primary process steps are separated by intermediate storage of the process streams. The storage tanks are big enough to permit up to 16 hours of operation of other process steps if one process step is shut down. Complete redundant process systems are provided for the ton container cleanout, neutralization, and SCWO process steps so that maintenance can be performed on a redundant system while the parallel system continues to operate. Redundant critical components (e.g., pumps and control valves) will also be installed in each parallel system. These features are designed to reduce reliance on intermediate storage capacity for maintaining overall operations and to facilitate scheduling maintenance for subsystems. No redundant system is provided for the evaporation step, however. To accommodate facility downtimes, the Army should consider providing storage for SCWO effluent and recycled water for more than 16 hours.

The overall process is planned to operate 24 hours per day, seven days per week, with a maximum of six ton containers of VX being processed per day, or approximately 4,500 kg (10,000 lbs) of VX per day. This will produce 13,600 kg/day (30,000 lbs/day) of hydrolysate; additional water from the ton container cleanout will increase the flow to the SCWO unit to 22,800 kg/day (50,200 lbs/day).

The SCWO process requires feeding hydrolysate (which may include ton container cleanout fluid or decontamination fluids), oxygen, and supplemental fuel (diesel) during start-up and during the processing of used decontamination fluids and excess effluent from ton container cleanout. The hydrolysate will be analyzed to ensure that VX and EA-2192 are not present at toxic levels prior to being transferred to the feed tanks for the SCWO process step. In addition, the hydrolysate will be diluted with water so that the resulting heating value is only slightly above the heating value required for the process to be autogenic. Hydrolysate will be pumped from one of four hydrolysate tanks to a water-cooled heat exchanger for temperature control to 38°C (100°F) prior to high pressure pumping.

The primary variable associated with hydrolysate feed is the heating value associated with each specific batch. The heating value determines (1) how the operating temperature of the SCWO reactor will be maintained, (2) the oxygen required, (3) the feed of supplemental cooling water, and (4) the feed of supplemental fuel, if necessary. Each hydrolysate tank will be filled sequentially, mixed well to avoid phase separation, and used as an individual batch for continuous feed for the SCWO reactor to ensure that feed properties remain constant during a given operating interval. The hydrolysate in each tank will be mixed during storage by in-tank mixers and a recirculation loop from the tank to the inlet of the high pressure pump. Each batch of hydrolysate will be analyzed on site for TOC (total organic carbon)—as a surrogate measure of heating value—prior to that batch being fed to the SCWO reactor. A high pressure pump (double diaphragm, positive displacement) will be used to increase the hydrolysate pressure to 240 bar. Water at 38°C and pumped to 240 bar using a positive displacement plunger pump will be mixed with the hydrolysate prior to feed to the SCWO reactor to maintain a constant heating value (1,700 Btu/lb) of the reactor feed at the inlet to the reactor. The full-scale reactor will be approximately 25 cm (10 in) internal diameter and 4.5 m (15 ft) long, with an internal volume of approximately 0.23 m³ (8.2 ft³).

Oxygen will be delivered to the site as a cryogenic liquid if pure O₂ is selected as the SCWO oxidant. A liquid pump will pressurize the oxygen to 276 bar (4,000 psig). The oxygen will be vaporized to gas in an ambient temperature, natural convection vaporizer. Oxygen gas at 276 bar will flow to accumulator bottles from which it will be metered by a control valve as it enters the hydrolysate stream prior to entering the SCWO reactor. The oxygen feed rate will be controlled to maintain excess oxidant, based on the oxygen content of the SCWO effluent gas. Oxygen feed is designed to be 150 percent of the stoichiometric requirement based on the heating value of the reactor fuel.

Once the hydrolysate and oxygen have entered the reactor, the mixture will be heated to 650°C. Once process start-up has been completed, the exothermic reaction through oxidation of the hydrolysate will be sufficient to maintain the reactor at 650°C without supplemental fuel or auxiliary heating. Within the reactor, organic constituents of the hydrolysate will be oxidized to their corresponding salts. The resulting inorganic salts will have low solubility in the supercritical fluid at 240 bar and 650°C and, therefore, will form a separate solid effluent phase, which will be transported out of the reactor with the fluid effluent.

Quench water at 38°C will be mixed with the reactor effluent to cool and condense the supercritical fluid mixture to a combined liquid aqueous mixture and

gaseous stream. Measurement of the quenched liquid stream temperature will be the basis for feedback control of the flow rate of the quench water. Subsequently, the combined gas, liquid, and solid stream will be cooled by an air-cooled heat exchanger followed by final cooling to 43°C (110°F) in a water-cooled, double pipe heat exchanger.

After cooling, the pressure on the combined liquid, solid, and gas stream will be reduced to 1.7 bar (25 psig), and the gas will be separated from the mixed liquid and solid phase. A bank of capillary tubes or control valves will be used to lower the pressure. After pressure reduction and phase separation, the gas stream will be passed through activated carbon filters and vented. The liquid stream with entrained solids will be monitored for TOC (as a surrogate for DRE) and pH. The TOC and pH of this stream are expected to be less than 10 mg/l and 6, respectively. Eighteen percent sodium hydroxide solution will be mixed with the stream of liquid and entrained solids to bring it to a pH of 9 before it enters an evaporator.

The evaporator will be used to evaporate water from the mixed liquid and solid stream, resulting in the formation of a salt slurry. Solid salts will be separated from the slurry using a filter press. The evaporator will operate at 106°C (223°F) and atmospheric pressure. The filter press output will solidify when cooled and form a solid about 70 wt. percent salt and 30 wt. percent water. Evaporated water will then be condensed and cooled to 38°C and subsequently used as process water. The resulting water is expected to have a conductivity of about 70 $\mu\text{mhos/cm}$ (micro siemens per centimeter) which is approximately 100 $\mu\text{g/l}$ TDS.

The complete SCWO reactor and evaporator system are anticipated to operate 24 hrs per day, seven days per week, excluding maintenance intervals. Operator training requirements are standard for chemical process industry operations. Two chemical operators per shift are anticipated.

PROCESS START-UP AND SHUTDOWN

The reactor will be started on auxiliary fuel (diesel fuel). System preheating to raise the process temperature and initiate the oxidation reaction will be provided by a 70 kW electric heater. Once the oxidation reaction has been initiated, the heat from oxidation of the auxiliary fuel reaction will further increase the reactor temperature to the desired process conditions. Hydrolysate should not be fed to the reactor until the temperature reaches the design temperature range of 635 to 650°C or if the pressure is lower than the design pressure for the reactor. Operating the reactor at a lower temperature will result in incomplete oxidation; the product will have to be reprocessed and some light organic species may volatilize into the gas phase. Start-up and shutdown procedures must be planned so that this requirement can be met.

Shutdown is accomplished by stopping hydrolysate feed and flushing the reactor with water, which results in system cooling. When the temperature drops below the design temperature, the hydrolysate flow should automatically stop, and auxiliary fuel should be used to bring the reactor back to design temperature. A decrease in DRE, indicated by organic species present in the effluent liquid phase, would also require that the hydrolysate feed be stopped. However, very rapid response instrumentation (near real time) does not appear to be available for this application. Measurement of CO in the effluent gas stream has been suggested for near realtime monitoring as a surrogate for DRE; however, more testing is needed to validate this approach.

As a final control of the reactor, the liquid product will be stored in tanks until analysis verifies the required destruction removal efficiency. If the material is off-specification, it can be reprocessed. Thus, the present control is based on maintaining the specified operating temperature and holding the product for analysis before release.

The final liquid stream, part of which is to be discharged, is the condensate from the evaporator. This will be monitored for electrical conductivity and pH as measures of salt and acid content, respectively. "Normal" conductivity is expected to be about 70 $\mu\text{mhos/cm}$ (corresponding to about 100 $\mu\text{g/l}$ TDS); any significant increase in conductivity would require that the condensate be returned to the evaporator feed tank and that the evaporator be taken off line for maintenance.

PROCESS MASS AND ENERGY BALANCES

A complete mass balance for the Newport Chemical Agent Disposal Facility process is presented in [Appendix B](#). The anticipated maximum process throughput corresponds to six ton containers, or approximately 4,500 kg (10,000 lbs) of VX per day. This results in ~22,800 kg (50,200 lbs) per day of hydrolysate and ton container cleanout fluid, which contains ~20 wt. percent organic constituents. Approximately 9,100 kg (20,000 lbs)

per day of additional water will be required to control the reactor's temperature.

The three major output flows from the proposed plant are a gas stream from the SCWO reactor and liquid and solid streams from the evaporator. The anticipated gas composition is described in the process mass balance in [Appendix B](#). The estimated compositions of the aqueous stream condensed from the evaporator (essentially distilled water) and the solid salts are provided in [Table 5-1](#).

The gas stream has been estimated to be ~8,850 kg (19,500 lbs) per day (0.39 kg per kg of hydrolysate; Stone and Webster, 1997a). The small N₂O content in the gas originates from nitrogen in the VX molecule. The quantity of organic compounds estimated to be present in the gas is greater than was observed in the off-gas during pilot-scale testing. The liquid water from the evaporator (7,070 kg/day or 15,600 lbs/day) is condensate from the vaporized steam and is expected to be of relatively high purity. The estimated composition of the aqueous phase presented in [Table 5-1](#) indicates that the largest impurities will be salts (Na₂SO₄ and Na₂HPO₄) that have been physically carried over from the boiling liquid during evaporation.

The solids produced will be approximately 6,160 kg/day (13,600 lbs/day) or 0.27 kg per kg of hydrolysate. In practice, the anhydrous salts (Na₂SO₄ and Na₂HPO₄) will be transformed to hydrates upon cooling and recrystallization. Trace quantities of incompletely oxidized organic compounds and trace metals from the SCWO reactor will be present as impurities in the solids.

The oxidation reaction occurring in the SCWO reactor is very exothermic, with approximately the same heat release as occurs during VX incineration.¹ The reactor temperature of 650°C, which is a critical control element, is achieved by taking advantage of the heat of reaction during oxidation. The temperature of the feed to the reactor is far below reactor temperatures but quickly reaches the required temperature by rapid mixing and reaction in the reactor. The size of the preheat mixing zone is not known. A measurement of the axial temperature profile would provide this information but does not appear to have been done. As a reasonable approximation, it seems likely that the preheat mixing zone would scale with the size of the inlet pipe, i.e., the diameter of the inlet gas jet. On this basis, the mixing zone would occupy approximately the same fraction of the reactor volume for both pilot-scale reactor and fullscale plant.

TABLE 5-1 Composition of the Post-Treatment SCWO Aqueous Effluent and the Solid Salt Streams

Constituent	Value	Units
Evaporator Condensate		
TDS	100 ^a	mg/L
Na ⁺	30 ^b	mg/L
SO ₄ ⁻²	40 ^b	mg/L
PO ₄ ⁻³	40 ^b	mg/L
NO ₃ ⁻	0.2 ^b	mg/L
NO ₂ ⁻	0.2 ^b	mg/L
Cl ⁻	0.3 ^b	mg/L
TOC	< 1 ^b	mg/L
MPA	< 1 ^b	mg/L
EMPA	< 1 ^b	mg/L
THIOL	< 1 ^b	mg/L
pH	6.8	standard units
Specific Metals ^c		
Arsenic	0.72 (8.3)	µg/L
Barium	0.003 (0.1)	µg/L
Calcium	0.003 (0.01)	µg/L
Chromium	0.13 (1.3)	µg/L
Copper	0.05 (0.7)	µg/L
Iron	0.002 (0.006)	µg/L
Lead	0.04 (0.7)	µg/L
Magnesium	0.0004 (0.007)	µg/L
Mercury	0.014 (0.1)	µg/L
Selenium	0.38 (4.7)	µg/L
Evaporator Solids		
Na ₂ SO ₄	35	wt %
Na ₂ HPO ₄	35	wt %
H ₂ O (fixed as water of hydration)	30	wt %
NaNO ₂	0.15	wt %
NaNO ₃	0.16	wt %
Total Metals (excluding Ca, Mg, Fe, Si)	11	mg/kg

^abased on conductivity measurement

^bbased on assuming limited carryover of feed constituents into the condensate

^caverage (maximum) values based on analysis of hydrolysate ([Table 1-1](#)) and the assumption of no processing loss

Source: Adapted from Resources Conservation Company, 1997.

¹Differences in the heat release observed during SCWO treatment of VX hydrolysate and direct incineration of VX will be a consequence of (1) the heat of reaction during the neutralization process step and (2) the heat release from the oxidation of supplemental fuel added during both processes

A heat release of 3,960 kJ/kg (1,700 Btu/lb) of hydrolysate is estimated to be sufficient to raise the feed to the reaction temperature of 650°C, based on operation using pure oxygen at 50 percent excess. The heating value of the hydrolysate has been estimated to be about 5,600 kJ/kg (2,400 Btu/lb). Thus, the heat release from treatment of the hydrolysate should exceed the autogenic value, and the reactor temperature can be maintained by dilution of the hydrolysate with water, as necessary. The planned addition of water is approximately 0.4 kg per kg of hydrolysate. The heat released by the oxidation process is removed from the system through a large water quench at the outlet of the reactor (~3.6 kg per kg of hydrolysate) and through an air-cooled heat exchanger between the reactor and the evaporator.

During normal operation, the evaporator will contain a slurry of precipitated salts in a saturated solution; the mixture will be at its boiling point. Heat is provided from two sources, (1) live steam at a temperature a little above 100°C, and (2) superheated vapor from the evaporator that has been compressed to raise its condensation temperature. (This vapor is superheated a few degrees as it leaves the boiling solution because of the high salt content of the solution; and it is superheated further by the compressor.) The heat from these two streams is provided to the evaporator indirectly; the heat is transferred to a pumped recirculation loop of evaporator liquid/slurry, via a heat exchanger. The hot liquid in the recirculation loop provides the heat required for evaporation. At the same time, the live steam and the compressed steam from the evaporator are condensed and discharged as fairly clean water.

The heat exchanger, which condenses the evaporator steam, has a vent to eliminate noncondensable gas. This is necessary to maintain efficiency. The vent is expected to be a very small stream of fixed gases (e.g., N₂ and O₂) that remained in solution from the SCWO reactor. Its exact composition is unknown at this time.

The design and operation of as complex a system as this requires some art. Laboratory-scale testing indicates that the evaporator operation should be satisfactory if the liquid specific gravity is maintained at less than 1.5, which can be achieved by withdrawing a small purge stream from the evaporator. This stream will be added directly to the salts that are recovered through filtration. Most water present will be bound as water of hydration as crystallization occurs during cooling of the mixture.

PROCESS MONITORING AND CONTROL

Monitoring chemical agents and the products of their incomplete destruction is a critical process component because monitoring systems ensure efficient operation, trigger alarms if there is a threat to worker or public safety, and guarantee that discharge levels are environmentally acceptable. In the baseline incineration system, the committee closely reviewed the instrumentation and method of deployment for the near real-time monitoring of potential agent releases (NRC, 1994b; NRC, 1996b). The use of a new technology, such as SCWO, as the final step for the destruction of VX hydrolysate requires the development of process monitoring and control strategies that are tailored for the new system. The safety, environmental release, and process monitors developed for the baseline incineration system will not always be applicable or optimal for the new system.

Because very little or no VX will be present in the hydrolysate fed to the SCWO system, monitoring for the destruction of the agent after a process stream is released from the toxics containment area is not a significant issue. Thus, the near real-time agent monitors deployed on the common stack of the baseline incinerators as process "end point" monitors are not applicable to the SCWO process, although they will be needed for vents associated with the upstream toxics containment area (e.g., ton container cleanout and agent neutralization operations). However, high levels of organic phosphonate compounds, especially EMPA (ethyl methylphosphonic acid) and MPA (methylphosphonic acid) and their sodium salts, will be present and must be efficiently destroyed (U.S. Army, 1997). Monitoring the DRE of these and related organic phosphonates is a critical challenge for the proposed SCWO system.

The current assumption is that other organic phosphonates decompose to MPA and that MPA is the most refractory phosphonate during SCWO processing. If this assumption is correct, monitoring the destruction of MPA will be extremely important. The Army has developed fairly sensitive ¹³C and ³¹P nuclear magnetic resonance (NMR) methods for monitoring EMPA, MPA, and related organic phosphonate species in solution (U.S. Army, 1997). Unfortunately, these methods require time consuming batch sampling procedures and

are not suited for real-time, or even near real-time, process control. Nevertheless, the Army plans to use NMR analytical facilities that have a projected time for a complete analysis of approximately two hours, which would be a workable time for testing SCWO effluent stored in intermediate tanks prior to subsequent processing. Ion chromatography may prove to be a sensitive and faster approach for monitoring EMPA and MPA in the aqueous phase. On-line chromatography could be studied for near real-time monitoring of liquid effluent from SCWO processing.

The kinetics of destruction for EMPA, MPA, and related organic phosphonates are sufficiently well known that high DREs can be obtained if the VX hydrolysate is maintained in the SCWO environment at design pressures and temperatures for a long enough time (Gloyna and Li, 1997; General Atomics, 1997a,b). Therefore, continuous monitoring of reactor temperature and pressure profiles, as well as of flow rates (which determine residence times), will clearly be necessary for SCWO process control. Pilot-scale SCWO demonstration studies on VX hydrolysate have clearly shown that failure to maintain design pressure and temperature will result in decreased destruction removal efficiency (General Atomics, 1997b). Reactor flow rates, pressure drops, and salt removal are critical because insoluble salts are typically formed from VX oxidation products (SO_4^{-2} , PO_4^{-3} and CO_3^{-2}), and Na^+ is formed from decontamination fluids and neutralization reagents. These salts may lower the DRE by partially or completely plugging the SCWO reactor and keeping organic constituents from reacting.

Continuous monitoring of CO in the off-gases separated from the SCWO output may serve as a near real-time monitor of SCWO process efficiency and has been used in pilot-scale studies (General Atomics, 1997b). However, laboratory studies show that MPA may be more refractory than CO under SCWO conditions, indicating that CO may not be a reliable surrogate for monitoring the destruction of MPA (Gloyna and Li, 1997). Laboratory-scale studies also suggest that methane in the off-gas may be a surrogate for measuring the DRE of organic compounds. Additional studies of the destruction kinetics of CO, CH_4 , and MPA at design SCWO conditions should be done to develop a reliable, near real time surrogate for overall destruction efficiency. In any case, CO levels in the off-gas should be continuously monitored because high levels of unprocessed CO will almost certainly signal that the reactor is not functioning as designed, even though low levels of CO will not guarantee the efficient destruction of MPA. Monitoring the level of CH_4 in the off-gas may serve a similar purpose.

The currently proposed design for the SCWO system allows for the storage of SCWO reactor liquid output for several hours before discharge (Stone & Webster, 1997a). This will allow enough time for slow batch sampling to monitor the destruction of EMPA and MPA and for the reprocessing of inadequately processed hydrolysate. However, real-time or near real-time monitoring of the DRE of these organic phosphonates or a demonstrated and reliable surrogate would be a much better design option.

One possible option to a real-time or near real-time monitor specific for MPA/EMPA in the liquid effluent stream would be a real-time or near real-time TOC detector. Sensitive, real-time, gas phase TOC monitors, usually based on flame ionization detectors, are well developed and are widely used for process control of systems with potential gas phase organic effluents, including the Army's baseline incineration system for chemical demilitarization. TOC detectors for aqueous waste streams are available with cycle times of approximately 10 minutes, but their reliability for testing aqueous streams with high levels of dissolved solids, phosphates, and alkalinity content has not been demonstrated.

MANAGING UPSETS AND MAINTENANCE

Components of the postneutralization process step that will be subject to standard process application conditions include high pressure pumps, heat exchangers, control valves, etc. The process design includes enough redundancy to minimize component changeouts and permit maintenance without affecting the overall process schedule.

Several critical systems and components, including the SCWO reactors and SCWO pressure let-down systems, have little history of operations under similar conditions. Therefore, planning maintenance requirements and schedules will be difficult. Corrosion, erosion, salt accumulation, and blockage are the primary considerations for maintenance of the SCWO reactor and pressure let-down systems. Scheduling maintenance for these components will be facilitated by the redundant full-scale SCWO system and a spare SCWO reactor liner. The principal remedy for salt accumulation will be reactor shutdown and flushing the system with

water. Severe erosion of the control valves for pressure let-down occurred during limited process testing, which required manual control of the valves. Intervals between maintenance operations have not been defined. Frequent cleaning or maintenance of the pressure let-down system may result in additional stresses from thermal and pressure cycling. Design information provided to date suggests that the minimum period of continuous operation between maintenance cycles should be at least one week. The design goal, however, should be for much longer periods of continuous operation.

The evaporator system will require periodic cleaning of salt entrainment and carryover to meet the requirements for water recycling. Cleaning will require flushing the system with clean water at near operating temperatures. In addition, salt accumulation and blockages can be anticipated in the brine slurry conveyance and filtration system. However, there is considerably more industrial process experience with this system, and therefore a reliable design basis exists for it. Performance specifications for this system should be equivalent to or exceed the intervals between maintenance operations specified for the overall SCWO system.

Maintenance operations for postneutralization processing will be greatly facilitated because the SCWO and evaporator systems will be located in a separate building. This building is classified for Hazard Category D, which does not require extensive personal protective equipment because the hydrolysate is significantly less toxic than the original VX. Maintenance will be further facilitated by separate interior rooms for each SCWO reactor designed to contain debris in case of a pressure containment failure. Thus, one SCWO reactor system can be serviced while the second unit is operational.

PROCESS SAFETY

Process safety requirements are based on the nature of process reagents and products and the potential for process failure modes that could result in harm to workers or the surrounding population. Process reagents for postneutralization processing are hydrolysate, oxygen (both as liquid oxygen and a high pressure gas), sodium hydroxide (18 percent aqueous solution), No. 2 fuel oil, and demineralized water.

The feed to the SCWO reactor is hydrolysate, not agent, which has already been detoxified in the batch neutralization process upstream. The facility design provides for holding reacted fluid in the neutralization reactors and analyzing them for agent prior to transferring them to the hydrolysate tanks from which they are fed to the SCWO system. A key feature of the design is certainty that the agent has been destroyed to the point that it no longer has military-unique toxicity before it is fed to the SCWO reactor. Agent and EA-2192 have not been detected in the hydrolysate at their analytical detection limits of 20 µg/l and 5 mg/l, respectively. Tests have shown that the hydrolysate has low toxicity relative to agent, although it does have a noxious odor (NRC, 1996a).

The main active components of the SCWO system and hydrolysate storage tanks will be located indoors, in dedicated areas that will not be inhabited during normal operations. The building that will house the SCWO unit will be fabricated to the same standards as other structures associated with the NECDF (Newport Chemical Agent Disposal Facility). Thus, the SCWO building will be designed for a seismic factor of 1.5, and the equipment will be supported to meet that criterion.

If hydrolysate is released from the storage tank room or the SCWO building, the release would be contained by the structure. Any vaporized hydrolysate would be swept away by the ventilation system, which will discharge to the exhaust system of the container handling building and will pass through the main filter farm before being discharged to the atmosphere. The ventilation for the SCWO equipment area within the SCWO building will also be equipped with a carbon filter. The release of hydrolysate liquids will be directed to a local sump and collected. This will act as a secondary containment to prevent community exposure.

The system is designed in accordance with the American Society of Mechanical Engineers' code for design pressure, and temperature conditions and operating limits will be set accordingly. As part of the construction process, verification of appropriate construction practices will be performed in accordance with code requirements. During operation, periodic maintenance and inspections will be conducted, as required by code, to verify continued system adequacy and operability, as part of a preventative maintenance program.

Components containing hydrolysate include the inlet piping, the check valve, the high pressure pump, and the reactor itself. The volume of material at high pressure is not large. Feed piping is nominally 0.5-inch internal diameter; its length will depend on the specific design but is not long, (e.g., 20 feet); the total volume is 0.027 ft³. The two stage high pressure pump is also small, with a volume estimated to be 0.01 ft³. The reactor volume at

SCWO densities (0.1 g/cm^3) contains approximately 0.8 ft^3 of fluid. Hence, the quantity of hydrolysate available for instantaneous release to a controlled area is limited. System shutdown, including the termination of feed, would follow the loss of system pressure, thereby limiting the quantity of hydrolysate that could potentially be released to the controlled area. Workers would be able to repair the system in a controlled fashion and under controlled conditions.

The adverse effects of exposure to hydrolysate are caused by its pH of 14. Toxicity testing has indicated that normal exposure control techniques, such as proper personal protective equipment and operating and maintenance practices, will keep exposure within acceptable limits (Manthei et al., 1997a). For example, systems will be purged of hydrolysate to reduce potential worker exposure. Finally, workers will be educated about the hazards of hydrolysate and trained to respond to incidents associated with the release of hydrolysate.

The primary process hazard is associated with high pressure fluids in the SCWO system. Failure of the pressure containment system (piping, SCWO reactor, postreactor air cooler, or pressure let-down system) could result in rapid depressurization and the dispersal of hot fluids and debris at high velocities. Similarly, failure of the pressure let-down system could result in a large pressure surge that could rupture equipment downstream. Protection from the failure of the pressure containment systems is provided by (1) an adequate safety margin in system specifications (e.g., piping and pressure vessels), (2) rupture disks or pressure relief valves to prevent overpressurization of the SCWO reactor and high pressure components, (3) rupture disks or pressure relief valves immediately downstream of the pressure let-down system, and (4) depressurization capacity in the secondary containment, in the event of a sudden release of pressure through relief valves on high pressure components.

The three other hazardous chemicals noted earlier (NaOH, oxygen, diesel fuel) are known entities that are commonly used in industry. The design approach related to these chemicals will be to implement known industry design and safety practices for handling and operations. The liquid oxygen and start-up feed will be stored outdoors away from the main SCWO process building. Caustic will be supplied from the caustic storage tank via a transfer pump.

Diesel fuel will be used as an auxiliary fuel for the SCWO process during start-up and shutdown and when supplemental fuel is required to process dilute solutions (e.g., decontamination fluids). Thus, the quantity of auxiliary fuel required for the SCWO process is limited. Standard safety practices will be applied to the handling, storage, and use of this fuel.

The caustic system will be used on demand to mix with the evaporator feed to control pH. The system would only be in service while the process is operational. Standard caustic exposure precautions will be required. Exposure to caustic would have the same health effects as expected for a worker in other areas of the plant where caustic is already being used.

The oxygen system requires established standard design features implementing the known precautions for industrial liquid (cryogenic) and gaseous oxygen systems.

Standard worker safety precautions promulgated by the Occupational Safety and Health Administration and code design standards should significantly reduce the hazards associated with the process chemicals noted above. Worker training will greatly reduce the potential for errors by operators or technician. Sources of release associated with these chemicals would be primarily via line breaks or tank failures. Each tank will be designed with secondary containment to confine liquids and minimize evaporative surfaces. Training of operators and technicians in the use of standard operating procedures, emergency response procedures, and coordination with the site emergency response team will ensure the fastest response possible to an incident. Emergency response equipment will be appropriately located.

While the integrated VX bulk agent destruction and disposal facility design is being completed (March 1999–April 2000), it is anticipated that additional process safety-related issues will arise (e.g., monitoring, process control, containment), which will have to be addressed. Once the design has been completed, a quantitative risk assessment will be prepared to evaluate the integrated process for accidents and failures that could affect worker or public safety.

PROCESS EFFLUENT REQUIREMENTS

Process effluents from the neutralization/SCWO facility include: vent gases from the neutralization, SCWO, and evaporator units; liquid effluent from the SCWO; and crystallized salts from the evaporator/ crystallization unit. These streams must meet regulatory requirements for disposal.

Gaseous effluents from the SCWO unit will be filtered and released; solid wastes from the evaporator will be disposed of in a licensed disposal facility. Most evaporator condensate will be recycled within the facility, but some may be discharged periodically to the NECDF sanitary sewer system.

The analyses of the gaseous effluent from the General Atomic eight-hour SCWO pilot-scale test (for which air was the oxidant) demonstrated that the primary constituents are O₂, N₂, and CO₂. Only five volatile organic compounds (acetonitrile, acetone, 2-butanone, carbon disulfide, and vinyl acetate) were detected in the gaseous effluent at levels of 7 to 28 ppb. These materials showed up in individual samples, not together, and the concentration levels were too low for concern. Nevertheless, as an added precaution, they will be filtered out when the SCWO vent is exhausted to an activated carbon filter.

The concentrations of TOC (total organic carbon) in the liquid effluent from the SCWO unit (evaporator condensate) were found to be below the detection limit (< 10 mg/l). The results of bench-scale evaporation tests (performed in a 500 ml Rotavap apparatus and a 1-liter standard boil-down apparatus) demonstrated that the condensate of the SCWO effluent has a conductivity of less than 70 µmhos/cm and should be suitable for recycling (Stone and Webster, 1997a). The analyses of metals (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Ti, and Zn) in the condensate confirmed that their concentrations were at or below the detection limits (Resources Conservation Company, 1997; SRI, 1997). These analyses indicate that excess condensate could be discharged to a sewage treatment plant. However, standards for condensate discharge must still be established.

The crystallized salts from the evaporation unit can be dewatered to form a cake for disposal that contains more than 70 wt. percent solids. The preliminary results of the toxicity characteristic leaching procedure for the solids showed that the concentrations of leached metals were well below the regulatory limits (40 CFR 261.24) (SRI, 1997). Testing for organics in the crystallized salts was not done.

A preliminary disposal survey was conducted to identify commercial facilities for receipt of the solid effluent. Based on the source of the effluent, the solid waste can be disposed of at a Subtitle C (hazardous waste) landfill. However, the permit requirements for disposal have not been finalized. The committee does not anticipate that this will present a problem.

Before contractors are asked to finalize the design of the operational SCWO reactor and its concomitant process and environmental control systems, the Army will have to specify both the not-to-be-exceeded limits on specific hydrolysate products or classes of products and the proven and acceptable analytical methods for measuring the amounts of these products in aqueous and salt matrices. Because gases emanating from the process will pass through activated carbon filters prior to venting to the atmosphere, no additional treatment requirements for process gas streams are anticipated.

Nonprocess wastes include disposable protective clothing (gloves, booties, tape, etc.) and filter media, such as carbon and high-efficiency particulate air cartridges. The proposed plan for the disposal of these items is to decontaminate them and ship them to an off-site hazardous waste facility. Prior to shipping, the waste will be stored in the solid waste storage building. The design of this building represents an estimate of space requirements to house solid waste packing and processing equipment, with more than adequate storage capacity.

The SCWO building areas will be washed down with demineralized water from the process water tank. Sumps will return wash-down water to the off-specification tank and back to the hydrolysate tank for sampling, analysis, and processing by SCWO.

TECHNOLOGY IMPLEMENTATION TIMELINE

The Army provided the committee with an internal working schedule (2/5/98) for technology implementation at NECDF (Stone and Webster, 1997a). The schedule includes timelines for the acquisition design package, environmental permit applications, system contract request for proposal and award, final facility design, equipment procurement, site preparation, construction, equipment installation, systemization, pilot testing, operations, and closure. The implementation timeline is shown in [Table 5-2](#).

Critical tasks in the schedule include environmental permitting, site preparation, construction and equipment installation, systemization, operations, and closure. A delay in any one of these will extend activities and operations associated with the proposed VX neutralization and SCWO facility at NECDF. The proposed schedule allows a maximum of two years for the Army to initiate and complete the required testing and to complete the final SCWO design (March 1998–April 2000).

TABLE 5-2 Technology Implementation Timeline at NECDF (as of February 5, 1998)

Task	Timeline
Acquisition of design package	11/6/96–2/23/98
Environmental permitting	5/21/97–12/8/99
System contract request for proposal and award	3/2/98–3/25/99
Final facility design	3/26/99–4/20/00
Equipment procurement, site preparation, construction, and equipment installation	6/23/99–9/6/02
Systemization	9/9/02–9/8/03
Pilot testing	9/9/03–4/23/04
Operations	4/23/04–12/31/04
Closure	12/31/04–7/10/06

Source: Adapted from Stone and Webster, 1997a.

ENVIRONMENTAL PERMIT REQUIREMENTS

Environmental permitting is scheduled to take approximately three years and is a critical task in the implementation schedule. The NECDF environmental requirements include:

- Resource Conservation and Recovery Act (RCRA) Part B Permit
- air permit
- water permit
- National Environmental Policy Act (NEPA) process

The RCRA permit specifies conditions for the handling and disposal of hazardous waste. The RCRA permit application is based on guidelines in the U.S. Code of Federal Regulations (40 CFR 270 Subpart B) and state specified guidelines and/or examples. Upon submission of the application to the state, a determination of completeness is made. If the application is complete, the state will review it and may issue Notices of Deficiency for specific items that require additional information, additional data, modifications of wording or approach to match guidelines (or the interpretation of guidelines in federal or state regulations), or an explanation of one or more aspects of the application. Following the Notice of Deficiency process, the state will develop a Draft Permit, which it provides for public scrutiny and comments. Following a minimum 45-day public comment period, the state responds to comments and usually issues a Final Permit, which allows the permittee to commence construction of the treatment, storage, and disposal facility (TSDF) or to initiate other actions regulated under 40 CFR. The RCRA permit application is scheduled to be submitted to Indiana regulators in the second quarter of FY98. The RCRA permit must be obtained prior to construction. The Army anticipates that the RCRA permit will be issued in the second quarter of FY00. Health risk assessments are required by Indiana law to be included with the RCRA application.

SCWO will be permitted under 40 CFR 264.600 (Subpart X-Miscellaneous Unit). Indiana is not authorized to administer 40 CFR 264.600 at this time and is not sure when that authority will be granted to the state. In the meantime, the U.S. Environmental Protection Agency (EPA) regional office will be involved in the permitting process, specifically with respect to Subpart X. The regulators have been notified that the permit application will ask for relatively broad operating ranges, so that the plant can begin operations and the integrated process shown to work without an unnecessarily restrictive demonstration test.

The NECDF air permit will provide quality standards for air emissions and facility operating conditions. Indiana has legal authority to administer the federal air pollution control regulations (Clean Air Act) through its State Implementation Plan (SIP). The SIP is routinely updated when new federal regulations are promulgated by EPA. The air permit application is also scheduled to be submitted to Indiana regulators in the second quarter of FY98, and the Army anticipates that the state will issue the permit in the second quarter of FY00. The air permit must also be obtained prior to construction.

The Clean Water Act provides quality standards for liquid effluent discharge. For disposal of agent-derived waste into navigable waters, a delisting petition is required, which is in preparation. The Army plans to submit a water permit request to Indiana regulators in the first quarter of FY98 and anticipates that the permit will be issued in the first quarter of FY00. The water permit is required 180 days before operations begin.

The NEPA process requires that federally funded projects undergo NEPA analysis. A notice of intent to proceed with the NECDF demilitarization facility was

published on May 23, 1997, and a scoping meeting was held on June 30, 1997. Minimal comments were received at the meeting. The completion of the environmental impact statement is scheduled for the third quarter of FY98, and a Record of Decision is expected by the fourth quarter of FY98. This decision action is required before a contract can be awarded.

Construction of the facility depends directly on the receipt of these permits. Public acceptance of the technology will facilitate the permitting process. To date, the neutralization and SCWO process for treating VX seems to have the necessary public support, or at least the committee heard no evidence from the contractors that there was public opposition. Review of news clippings from the Newport, Indiana, area by committee members also supports the opinion of the contractors that the public is not opposed to the proposed technology at this time.

6

Findings and Recommendations

Chemical neutralization of VX nerve agent results in the production of a liquid hydrolysate stream that has greatly reduced toxicity compared to the original nerve agent but requires further treatment to meet the requirements of the Chemical Weapons Convention and to be suitable for disposal. After considering several approaches, the U.S. Army has selected SCWO (supercritical water oxidation) as the primary process for treating the hydrolysate from VX neutralization prior to ultimate disposition. The integration of SCWO into the complete process for the destruction of VX stored at Newport, Indiana, also requires an evaporator system after SCWO treatment to allow water to be recycled back into the neutralization process. The evaporation system also produces a dry solid waste stream consisting of salts produced during the neutralization and SCWO treatment steps. Excess condensed water from the evaporator is expected to be of relatively high purity and suitable for discharge. The technology selected for the evaporation process step is mature with considerable full-scale design and operations experience. In contrast, treatment of the hydrolysate will be a new application for SCWO. Thus, the findings and recommendations presented here focus on the use of SCWO for the treatment of VX hydrolysate.

FINDINGS

Finding 1. Limited pilot-scale testing has demonstrated the ability of SCWO to achieve high destruction efficiencies for the organic constituents of VX hydrolysate. Effluent from SCWO treatment of VX hydrolysate has been shown to have negligible acute toxicity in intravenous testing in mice, gavage testing in rats, and dermal testing in rabbits. The separation of salts in the effluents from SCWO through an evaporator system should produce relatively pure water suitable for discharge and solid salts suitable for disposal. Treatment requirements for VX hydrolysate are less stringent than they are for VX because the hydrolysate has low toxicity relative to the agent. However, criteria for process destruction efficiency and final disposal standards have not been established.

Finding 2. Using SCWO to treat VX hydrolysate is significantly different and more complex than previous applications. SCWO systems on a pilot scale have been used to treat several other types of wastes, but SCWO is in commercial operation at only one site. There has been only limited pilot-scale or operational-scale experience with wastes that are similar to VX hydrolysate in being highly corrosive and salt-laden. Operation with VX hydrolysate or appropriate surrogates at design conditions, equipment configuration, or approximate scale for full-scale operations has not been demonstrated. A vertical cylindrical reactor is the only reactor configuration that has been successfully demonstrated to date at pilot scale for the treatment of VX hydrolysate and similar waste streams. Additional development and pilot-scale testing of SCWO technology will be necessary to ensure sustained, reliable operation of a full-scale integrated treatment system. Sufficient time appears to be available in the Army's implementation schedule for the Army to carry out development and testing for using SCWO at the Newport site, provided they are carried out expeditiously.

Finding 3. Pilot-scale operation of SCWO in a vertical cylindrical reactor at the temperature and pressure necessary for the effective destruction of hydrolysate constituents has been limited to one eight-hour and two less than two-hour tests. During pilot-scale testing with hydrolysate, the following factors were identified that could create difficulties in sustaining system performance:

- Large quantities of insoluble salts were produced, which must be effectively managed within, and downstream of, the SCWO reactor.

- Unexpected fluctuations were observed in temperature, pressure, and salt expulsion from the SCWO reactor.
- High levels of corrosion and erosion of materials of construction were observed in the reactor liner and pressure let-down valves.
- The sustained performance and reliability of the pressure let-down system was not demonstrated.

Although at this point in development the Stockpile Committee cannot be certain, it believes that a SCWO system for the treatment of VX hydrolysate with sufficient sustained performance can be achieved with additional development and testing.

Finding 4. Limited bench-scale and pilot-scale tests have demonstrated operating regimes under which SCWO can effectively destroy carbon-phosphorus bonds and oxidize the organic constituents present in VX hydrolysate. The demonstrated conditions for high levels of destruction (> 99 percent) include temperatures between 640°C and 730°C and pressures between 234 and 261 bar. At temperatures and pressures below this regime, effluent from SCWO processing may contain significant concentrations of residual organic species that are difficult to destroy, including constituents with carbon-phosphorus bonds.

A basis for the reliable scale-up and operation of SCWO technology for the treatment of VX hydrolysate has not yet been demonstrated. Fundamental knowledge about the following processes within the SCWO reactor is still not available:

- the number and characteristics of the physical phases, including large quantities of entrained and adhered solids and potentially liquid, gas, and supercritical fluid phases
- fluid dynamics and mixing processes complicated by relatively high loadings of insoluble salts
- heterogeneous and homogeneous reaction mechanisms and kinetics
- salt nucleation, particle growth, agglomeration and adhesion mechanisms, and kinetics

Because the understanding of fundamental processes is limited and the process operational data and experience are sparse, empirical design and engineering judgment will be required for the selection of a prudent scale for development prior to full-scale demonstration. This is common engineering practice.

Finding 5. Alkaline VX hydrolysate and its destruction products under SCWO reaction conditions create an extremely corrosive and erosive environment that requires the careful selection of materials of construction. Although preliminary data indicate that certain noble metals, such as platinum and gold, may have acceptable properties, the data currently available are insufficient for the selection of materials of construction. The Army has initiated further testing of materials of construction.

Finding 6. Process monitoring and control strategies for the management of salts within the SCWO reactor and the destruction of the organic constituents of the hydrolysate have not been demonstrated.

RECOMMENDATIONS

Recommendation 1. A pilot-scale SCWO process facility with the critical characteristics of the full-scale design should be constructed and operated to further define operating characteristics and demonstrate sustained continuous operation of the process. Objectives for process development and demonstration should include:

- operation with either hydrolysate or a suitable surrogate to demonstrate reliable operation for periods similar to full-scale design operating cycles
- the development and validation of process monitoring and control strategies for salt management and the destruction of organic constituents
- the definition of stable operating regimes, including the temperature, pressure, and the use of the oxidant (liquid oxygen or compressed air) selected for full-scale operation
- the definition of a basis for process scale-up, operation, and maintenance of a full-scale system
- the development and demonstration of a reliable pressure let-down system

Because the understanding of the fundamental process mechanisms and operating characteristics is limited, the committee recommends that the pilot-scale system be within an order of magnitude of the total mass and heating throughput of a full-scale design unit. Based on testing and reactor scale-ups to date, a vertical cylindrical reactor configuration is recommended as the system

that will probably require the least amount of additional development. Other reactor configurations may perform at required levels but would require significant additional development.

Recommendation 2. Testing of materials of construction should be carried out as necessary to finalize the selection of materials for critical components, including the SCWO reactor and the pressure let-down system. Additional pilot-scale testing indicated in Recommendation 1 should include fabrication with the materials of construction selected from testing smaller samples and evaluation of corrosion and erosion rates for critical components.

Recommendation 3. Flexibility and redundancy of critical components should be incorporated into the design of the full-scale system to allow for uncertainties about the basis for scale-up and operation. Trade-offs should be evaluated to establish an appropriate balance between two 100 percent capacity SCWO reactors or a greater number of smaller reactors. The analysis should consider performance uncertainties associated with process scale-up and complexity, as well as the reliability of operating several reactors in parallel.

Recommendation 4. The Army should make provisions for targeted research and development to resolve problems identified during pilot-scale testing and the full-scale implementation of SCWO technology.

Recommendation 5. Requirements for process destruction efficiencies and final disposal standards for all effluent streams from SCWO treatment should be clearly defined to ensure that the final design meets regulatory standards.

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Appendices

Appendix A

Process Flow Diagrams for the Supercritical Water Oxidation and Evaporation Process Steps

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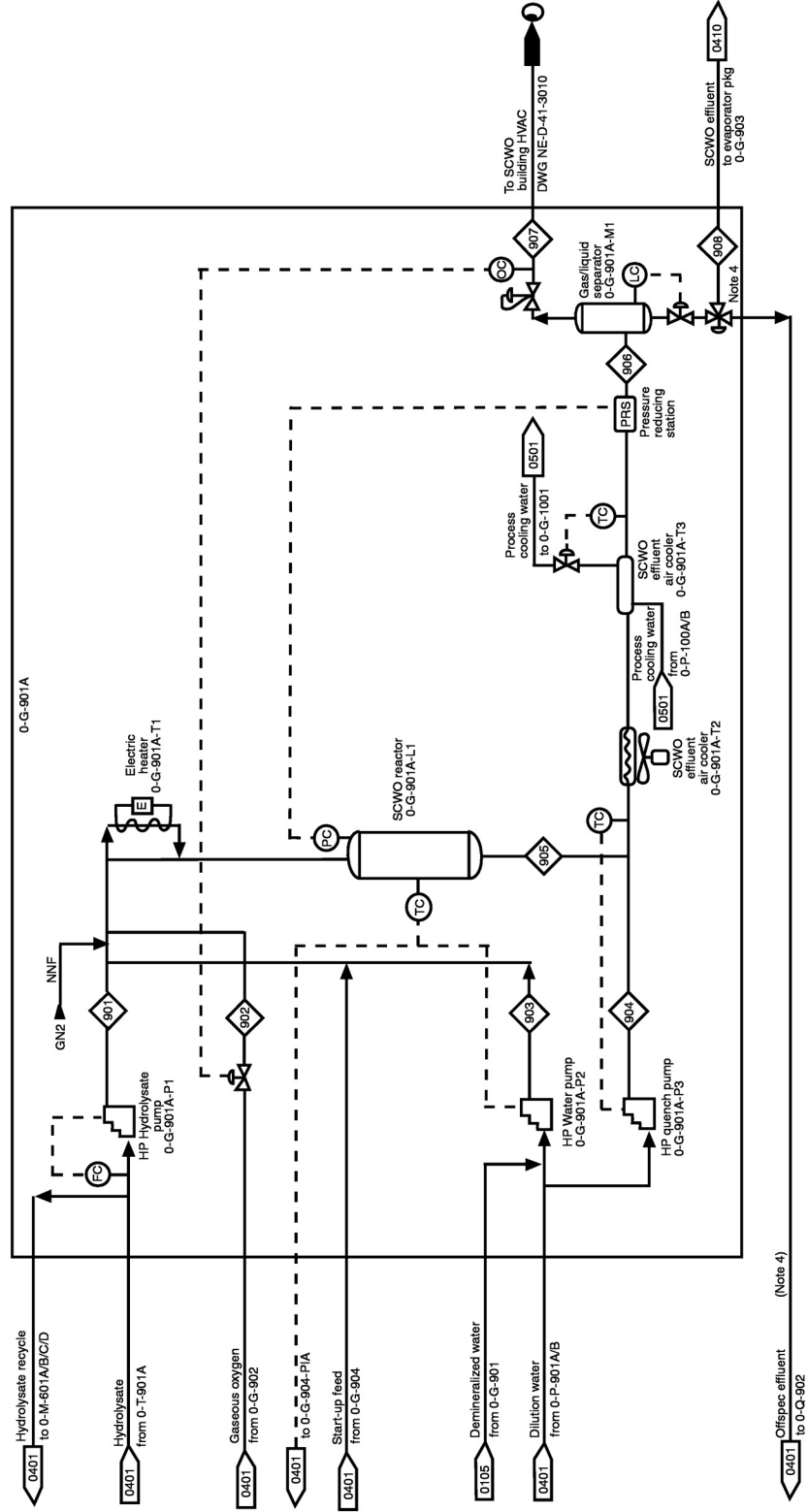


FIGURE A-1 Process flow diagram for the SCWO process step (design basis). Source: Stone and Webster, 1997b.

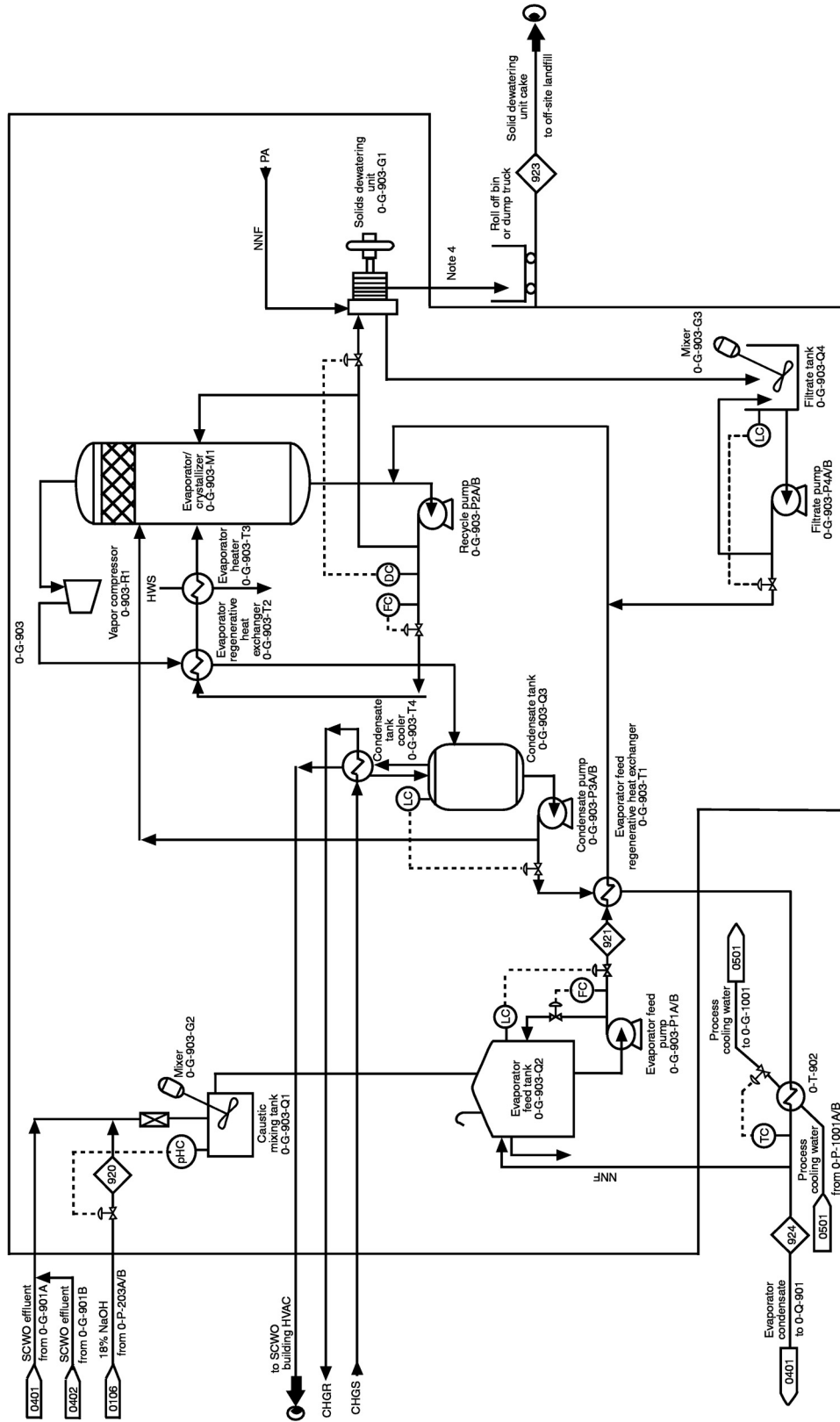


FIGURE A-2 Process flow diagram for the evaporation process step (design basis). Source: Stone and Webster, 1997b.

Appendix B

Mass Balance for the Newport Chemical Agent Disposal Facility (NECDF) Process

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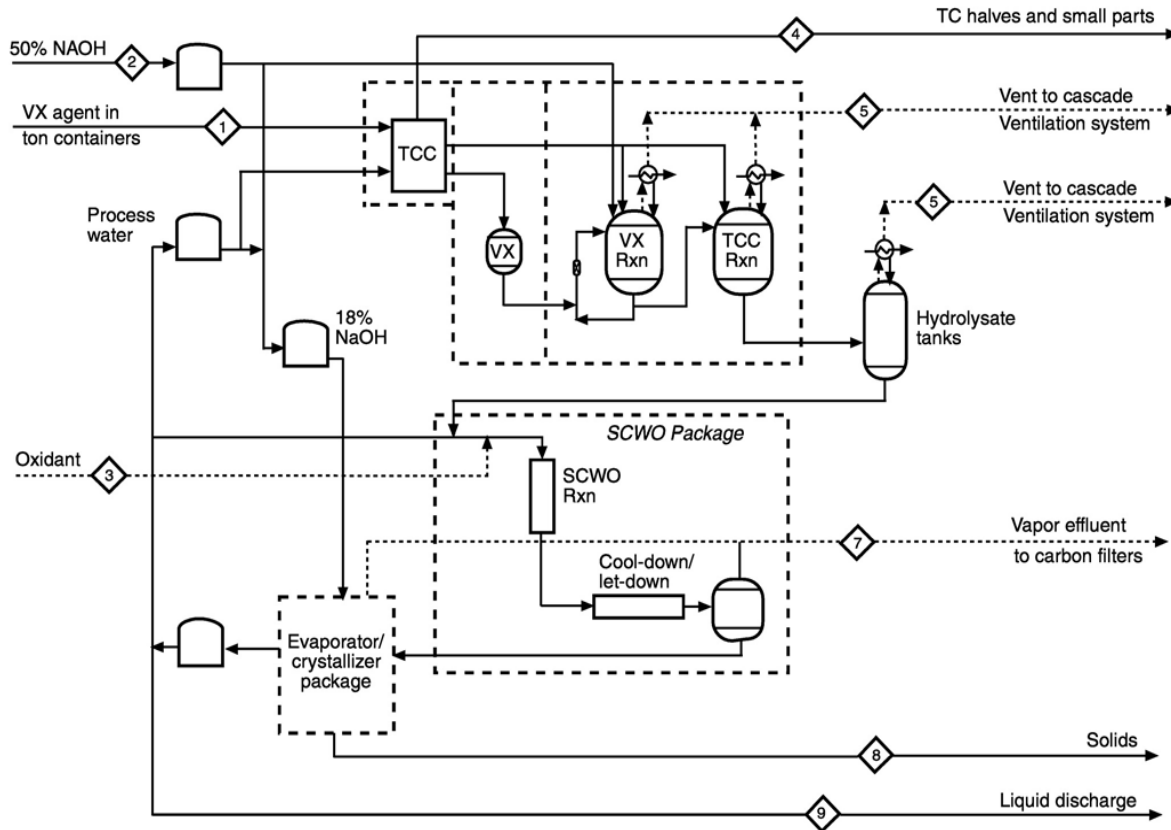


FIGURE B-1 Process flow diagram for the integrated NECDF process.

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TABLE B-1 NECDF Inputs for Process Mass Balance (stream numbers correspond to streams identified in Figure B-1)

Description	Process Inputs					
	Agent in Ton Containers	50% NaOH Solution	Oxidant to SCWO	Nitrogen to Neutralization Vessels	Process Air to TCC	Total Inputs
Stream Number	1	2	3	N/A	N/A	N/A
Total Flow (kg/1,000 kg agent)	1,000	1,195	3,500	7	5,667	11,369
Physical State	liquid	liquid	vapor	vapor	vapor	
temperature (°F)	70	80	70	70	70	
pressure (psig)	14.7	14.7	3,500	17.7	100	
Vapor Components						
oxygen (kg/1,000 kg agent)			3,500		1,190	4,690
nitrogen (kg/1,000 kg agent)				7	4,477	4,484
Liquid Components						
VX (kg/1,000 kg agent)	957					957
agent impurities (kg/1,000 kg agent)		44				44
NaOH (kg/1,000 kg agent)		598				598
Water (kg/1,000 kg agent)		598				598
Solid Components						
TC shells (no./1,000 kg agent)	1.5					1.5
TC valves (no./1,000 kg agent)	2.9					2.9
TC plugs (no./1,000 kg agent)	8.8					8.8

Source: Adapted from Stone and Webster, 1997b.

TABLE B-2 NECDF Outputs for Process Mass Balance (stream numbers correspond to streams identified in Figure B-1)

Description	Process Outputs		Neutralization Reactors Vent	Hydrolysate Tanks Vent	SCWO Vapor Effluent	Salt Solids to Disposal	Discharge to STP	Total Outputs
	Ton Container Parts	TCC Air Dry Vent						
Stream Number	4	N/A	5	6	7	8	9	
Total Flow (kg/1,000 kg agent)		5,667	6	1	3,121	1,531	1,043	11,369
Physical State	solid	vapor	vapor	vapor	vapor	solid	liquid	
temperature (°F)			46	40	80	95	100	
pressure (psig)			18	21	15	15	15	
Vapor Components								
oxygen (kg/1,000 kg agent)		1,190			1,803			2,993
nitrogen (kg/1,000 kg agent)		4,477	6	0.3				4,483.3
VOCs (kg/1,000 kg agent)			0.4		1,165			1,165.4
carbon dioxide (kg/1,000 kg agent)					82			82
nitrous oxide (kg/1,000 kg agent)					0.1			0.1
inorganic impurities (kg/1,000 kg agent)					10			10
Solid/Liquid Components								
Na ₂ SO ₄ (kg/1,000 kg agent)					70	451	1,043	1,574
Na ₂ HPO ₄ water (kg/1,000 kg agent)						530		530
TOC (kg/1,000 kg agent)						0.1		0.1
inorganic impurities (kg/1,000 kg agent)						10		10
TC shells (no./1,000 kg agent)	1.5	1.5						
TC valves (no./1,000 kg agent)	2.9	2.9						
TC plugs (no./1,000 kg agent)	8.8	8.8						

Source: Adapted from Stone and Webster, 1997b.

TABLE B-3 Water Formation Resulting from the Neutralization of VX and Oxidation of the Hydrolysate during the NECDF Process

Water is formed in the neutralization supercritical water oxidation (SCWO), and pre-evaporation pH adjustment processes. The following illustrates this water formation by showing that elemental hydrogen enters the process in water and other compounds but exits the process mostly as water.

The elemental hydrogen inputs to process are for 1,000 kg of agents.

Stream	Constituents	Hydrogen Content
Agent	1,000 kg VX	98 kg
50% NaOH solution	598 kg NaOH	15 kg
	598 kg H ₂ O	67 kg
Total	2,195 kg	180 kg

Notes: For simplification, the agent is assumed to be pure VX, with a molecular weight of 267 and a molecular formula of C₁₁H₂₆O₂NPS. The 50% NaOH solution flow shown here includes all caustic to the process, both for neutralization and for post-treatment.

The only product other than water that contains hydrogen is the phosphate salt in stream number 8, [Figure B-1](#), salt solids to disposal, which contains

530 kg Na₂HPO₄/1,000 kg of agent = 4 kg H/1,000 kg of agent

The balance of hydrogen:

180 - 4 = 176 kg H/1,000 kg of agent

is reacted with oxygen present throughout the process to form water.

The resulting water is found in the following output streams (per 1,000 kg of agent).

Stream	Water Content	Hydrogen Content
SCWO vapor effluent	70 kg H ₂ O	8 kg
Salt solids to disposal	461 kg H ₂ O	51 kg
Discharge to STP	1,043 kg H ₂ O	116 kg
Total	1,574 kg H ₂ O	175 kg

The total amount of water formed in the process is water out minus water in.

1,574

- 598

976 kg H₂O/1,000 kg of agent

Source: Stone and Webster, 1997b