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

FY03 Technology Evaluation for Chemical Demilitarization

Transpiring Wall-Supercritical Water Oxidation Technology Assessment

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

Final

Science Applications International Corporation

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NOTICE

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

EXECUTIVE SUMMARY

The United States Army has made significant investments over the past several years in the design, development, testing, and evaluation of supercritical water oxidation (SCWO) for the treatment of hydrolysates of chemical agents, energetics, and propellants as an alternative to incineration for chemical demilitarization. Two types of SCWO systems have been under investigation for the Assembled Chemical Weapons Assessment (ACWA) program: (1) solid wall (SW)-SCWO replaceable liner and (2) transpiring wall (TW)-SCWO liner. Both systems are down-flow vertical reactors; however, there are a number of differences in process, components, and equipment. General Atomics (GA) is the technology provider for the solid wall liner system, which has been tested by Program Manager for Assembled Chemical Weapons Assessment (PMACWA) for both Pueblo and Blue Grass (BG). Project Manager for Alternative Technologies and Approaches (PMATA) has also carried out significant work for the installation of a GA system (through Parsons as the lead contractor) at Newport Chemical Agent Disposal Facility (NECDF) for the secondary treatment of O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothiolate (VX) hydrolysate. The NECDF SCWO system has been put on hold while alternative options involving offsite shipment of hydrolysate to a commercial treatment, storage, and disposal facility (TSDF) are evaluated. Foster Wheeler is the technology provider for TW-SCWO, which is part of the Ecologic/Foster Wheeler Total Solution for BG proposed by a team consisting of ELI Eco Logic (Ecologic), Foster Wheeler, El Dorado Engineering, and Kvaerner Systems, with Ecologic as the lead contractor. The aim of this report is to provide a technical evaluation of the TW-SCWO system as tested under the ACWA program and proposed for full-scale treatment at BG. It also assesses the potential application of the TW-SCWO process for the treatment of VX hydrolysate at NECDF and for other chemical demilitarization wastes.

There is no fundamental basis for the scale-up of SCWO reactors for wastes as complex as chemical agent hydrolysates due to a lack of fundamental understanding of

a number of parameters including kinetics, mixing, fluid dynamics and flow characteristics, salt nucleation/precipitation, salt transport, and corrosion mechanisms. Considerable testing for both PMACWA and PMATA SCWO programs was therefore targeted at understanding and demonstrating the following key elements for scale-up:

a. High destruction removal efficiency (DRE) and oxidation stability including Schedule 2 compound destruction

b. Long-term operability

c. Corrosion of reactor and peripheral materials due to the severe reaction conditions, temperature, pressure, and corrosive/erosive environments—materials of construction

d. Plugging of reactors and downstream equipment—salt transport and management.

The TW-SCWO liner consists of overlapping platelets to create uniform orifices (pores) through which clean water (transpiration water) is metered along the length of the liner with the goal of protecting the liner from salt deposition and corrosion while providing a thermal and corrosion barrier for the pressure vessel. Extensive testing of TW-SCWO (at 100 to 500 pounds per hour [lb/hr] of hydrolysate feed) has occurred at Dugway Proving Ground over the 3 years (see table ES-1). The Engineering Design Study (EDS) II operability tests use oxygen as the oxidant.

A number of key successes were demonstrated in the EDS II operability tests including:

a. Effective destruction of Schedule 2 compounds

b. Overall availability of the TW-SCWO system was high (90.2 to 92.5 percent) for all three campaigns

Table ES-1. Summary of TW-SCWO Testing in the ACWA Program

Tests	Schedule	Total Hours of Testing
DEMO II Tests	7/2000-9/2000	231
EDS II Optimization Tests	3/2001-4/2001	137
EDS II GB Operability Test	10/2001-12/2001	504
EDS II VX Operability Test	2/2002-3/2002	503
EDS II H Operability Test	3/2002-4/2002	500

c. The TW-SCWO liner appeared to allow for effective salt transport within the reactor

d. Although liner mechanical stability was a significant issue in earlier tests, EDS II tests demonstrated that the liner was mechanically stable except for one instance when cracking and deformation were observed, but appears to be a manageable issue.

e. Liner corrosion appears to be manageable for both sarin (GB) and VX; however, significantly more corrosion was observed in the 500-hour mustard (H) tests, indicating that monitoring of the liner and other components will be required.

f. Oxygen was demonstrated to be a viable oxidant for the TW-SCWO process.

g. Reliability in the full-scale system is addressed by means of a strategy of redundancy, that is, five parallel reactors with one being an "on-line spare." The use of smaller multiple reactors lowers the overall risk of scale-up and provides flexibility in processing without requiring large ranges of turndown capability that would be required for fewer, larger reactors. (It may, however, require more coordination of operations.)

h. The basis for scale-up from EDS II to BG is volumetric. The diameter will be scaled up by a factor of almost 2, and the volume by a factor 5.6. The aspect ratio of length over diameter (L/D) of the full-scale reactor is higher than the EDS II system. The hydrolysate feed rate is scaled up by a factor of 5.6; however, the amount of transpiration water is scaled up by only a factor of 3.2, so the total amount of feed (that is, “Total Feed In” in section 4) is scaled up by a factor of 3.85 from 2,717 lb/hr at EDS II to 8,190 lb/hr in a full-scale BG reactor. This means that the total amount of water relative to the amount of salt is less for the full-scale system. The ratio of hydrolysate to total hydraulic feed is 0.24 in the full-scale system, compared to 0.17 for the EDS II reactor.

A number of problems or issues were observed during EDS II. While some of these are significant, they appear to be manageable at full-scale given sufficient time for shakedown, systemization, and pilot-scale testing at BG:

a. Problems with maintaining the oxidation stability as indicated by the occurrence of periodic spikes in the concentrations of carbon monoxide (CO) and volatile hydrocarbons (HCs) in the gas effluent

b. A number of changes were made during operability testing in EDS II to attempt to alleviate the HC/CO spikes including: changes in feed composition and preparation, feed rates, feed strainer size, quench water flow, and configuration of reactor outlet plumbing. Overall, reducing the feed rates of hydrolysate had the biggest impact decreasing the frequency of the HC/CO spiking. Using excess oxygen to attempt to improve mixing below the injector appears to help alleviate the problem as well. (Note: In the H test report [Foster Wheeler 2002c], the technology providers state that they do not intend to increase the excess oxygen in the BG system.)

c. Spiking in subsequent VX and H campaigns was considerably less than in the GB run. There are two issues arising from the observation of oxidation stability (HC/CO spikes):

   1. Treatment of the SCWO off-gas prior to release will likely be required, but this should be manageable and may require additional permitting.

   2. Not understanding the root cause of the HC/CO spikes increases the uncertainties associated with TW-SCWO system scale-up.

d. Feed rates for all three agent hydrolysates were reduced from design values to 350 lb/hr for VX and GB and to 210 lb/hr for H for EDS II testing, which prompted the technology providers to modify the feed rates for the full-scale TW-SCWO process at BG (Ecologic, 2002). The proposed revised feed limits require an availability of 95.5 percent for all campaigns, including H, to maintain the EDP proposed total schedule for each agent campaign and therefore add no additional time to the operations phase of the plant (Ecologic, 2002). Such a high availability for the full-scale system seems overly optimistic, particularly in light of all the remaining scale-up uncertainties and the lack of any operation of a fully integrated system. The overall processing schedule seems very tight and does not allow for much flexibility.

e. A number of issues for the other SCWO equipment was observed during the EDS II tests for which some design or operational changes have been recommended (for example, redundancy), but others may still need to be resolved in the full-scale system:

   1. Erosion of the injectors was observed for all three EDS II operability campaigns; however, the vendor claims, based on DRE, that the injectors continued to perform throughout the tests. As described in

section 4, injectors are critical for adequate mixing and reactor performance. Monitoring, and potentially change out, may be required at full-scale because it is unclear when erosion could lead to deterioration of performance in the full-scale system.

2. There were some problems with plugging or fouling of the feed system upstream of the SCWO reactor.

3. PCV wear and erosion appeared in all tests with some evidence of solids deposition or plugging/dislodging.

4. The effluent slurry cooler performance deteriorated steadily as witnessed by a gradual temperature increase from 80° to 120°F. Foster Wheeler suggests that their observation of occasional fouling may require change in the heat exchanger design for BG such as allowing for modularity for periodic isolation and cleaning.

5. A number of other problems and operational issues were experienced during testing which is to be expected for a pilot-scale operation of a new technology. These were corrected during the test program.

Based on available information and the EDS II test results, it appears that TW-SCWO can be made to work at full-scale at BG. All of the technical and programmatic risks associated with scale-up cannot be eliminated, so additional time for shakedown, systemization and testing of the full-scale system will likely be necessary and may need to be accommodated in the schedule. Integration of SCWO with all of the other unit operations within the Ecologic-Foster Wheeler total solution was not evaluated.

Because no proposal for using TW-SCWO at NECDF is available, it is not possible to assess the schedule or costs of implementing TW-SCWO at NECDF relative to those proposed for implementation of the GA SW-SCWO process. Furthermore, it is not possible to rule in favor of one SCWO process or the other given the unquantifiable uncertainties for scaling up either system. Based on this technical evaluation of available information for the TW-SCWO system and the lack of any identifiable or quantifiable significant advantage of TW-SCWO over the current NECDF SCWO process, it is recommended that the TW-SCWO process not be further considered for implementation at NECDF. A rating of “3” is given to this technology at this time, per the numerical ratings within the Program Manager for Chemical Demilitarization program (that is, no immediate need; could be useful and has sound fundamentals, but no need foreseen in immediate plans; revisit if need arises). If offsite shipment of VX hydrolysate and the GA NECDF SCWO system both are deemed to be unworkable, then this technology should be revisited.

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SECTION 1
INTRODUCTION

1.1 Introduction

The United States (U.S.) Army has made significant investments over the past several years in the design, development, testing, and evaluation of supercritical water oxidation (SCWO) for the treatment of hydrolysates of chemical agents, energetics, and propellants as an alternative to incineration for chemical demilitarization. This report provides a technical evaluation of the transpiring wall (TW)-SCWO technology as advanced by Foster Wheeler for implementation at Blue Grass (BG) as part of the Assembled Chemical Weapons Assessment (ACWA) program. It also assesses the potential application of the TW-SCWO process for the treatment of O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothiolate (VX) hydrolysate at Newport Chemical Agent Disposal Facility (NECDF) and for other chemical demilitarization wastes.

Chemical neutralization or hydrolysis using caustic for VX and sarin (GB) or water followed by caustic for mustard (H) and distilled mustard (HD) has been demonstrated to destroy chemical agents as an alternative to incineration. In several reports the National Research Council (NRC) is on record as stating that, "hydrolysis of chemical agents with water or caustic is capable of destroying 99.9999 percent of the chemical agent" (NRC, 2002b). Hydrolysis leads to the production of liquid hydrolysate streams, which have greatly reduced toxicity but require further treatment (secondary treatment) to destroy Schedule 2 compounds per the Chemical Weapons Convention (CWC) treaty, as well as other hazardous organics. Onsite treatment options and offsite shipment to a commercial treatment, storage, and disposal facility (TSDF) are being considered by the U.S. Army for secondary treatment. SCWO has been under development as an onsite secondary treatment for two distinct programs, the Program Manager for Assembled Chemical Weapons Assessment (PMACWA) and the Project

Manager for Alternative Technologies and Approaches (PMATA). Alternative technologies for the ACWA sites also must destroy hydrolysates of energetics.

Two types of SCWO systems have been under investigation for the ACWA program: (1) solid wall (SW)-SCWO replaceable liner and (2) TW-SCWO liner. Both systems are down-flow vertical reactors; however, there are a number of differences in process, components, and equipment. General Atomics (GA) is the technology provider for the solid wall liner system, which has been tested by PMACWA for both Pueblo and BG. PMATA has also carried out significant work for the installation of a GA system (through Parsons as the lead contractor) at NECDF for the secondary treatment of VX hydrolysate. As described in section 5, the NECDF SCWO system has been put on hold while alternative options involving offsite shipment of hydrolysate to a commercial TSDF are evaluated. Foster Wheeler is the technology provider for TW-SCWO, which is part of the ELI Eco Logic (Ecologic)/Foster Wheeler Total Solution for BG proposed by a team consisting of Ecologic, Foster Wheeler, El Dorado Engineering, and Kvaerner Systems, with Ecologic as the lead contractor. The aim of the present report is to provide a technical evaluation of the TW-SCWO system as tested under the ACWA program and proposed for full-scale treatment at BG. Evaluation of the GA SCWO system is outside the scope of this report; however, relevant findings from the large number of reports on extensive testing, development, and evaluation programs for GA SCWO systems are provided where appropriate.

1.2 Background

SCWO involves the destruction of aqueous organic wastes through rapid oxidation and hydrolysis by heating and pressurizing wastes, oxidant (either air, oxygen, or hydrogen peroxide) and if necessary, auxiliary fuel, above the critical point of water (374°C, 3,204 psi) to convert them to carbon dioxide (CO_2), water, and inorganic salts. The process takes advantage of the properties of supercritical water, including high miscibility of gases such as oxygen. Thermal oxidation rates are high so destruction removal efficiencies (DRE) higher than 99.99 percent are possible with reactor residence times of only seconds to less than a minute. Both radical and ionic mechanisms can be involved depending on the fluid density.

The dielectric constant, density, and solvent properties of water depend on temperature. At high temperatures above the critical point, the dielectric constant decreases significantly to the point where nonpolar organics are soluble and salts are poorly dissolved, and essentially undissociated and insoluble. This creates the potential for salt precipitation and reactor or component plugging for any salt-containing waste or wastes that generate salt upon oxidation. Significant laboratory-scale work has demonstrated that nitrogen in organic wastes can be converted to mostly nitrogen and small amounts of nitrous oxides (N_2O, NO_x). On the other hand, other heteroatoms such as sulfur and phosphorous are converted to sulfuric and phosphoric acid, or in the presence of excess base to sulfate and phosphate salts. Halogens such as chlorine or fluorine are converted to hydrochloric and hydrofluoric acid respectively, or to their halide salts. These acids or salts provide a highly corrosive and erosive environment within the SCWO reactor. Because salt solubility and ion activity vary with temperature, corrosion is often found to be more significant in the heat-up or cool-down sections of the reactor. While the literature discusses gas miscibility and organic solubility leading to homogeneous reaction environments for dilute or simple organic wastes, the phase behavior of complex, salt-producing or salt-containing wastes can be complex and involve multiple phases of compressed gas, supercritical fluids, concentrated salt solutions, and solid and/or molten salts. R.W. Shaw from the Army Research Office has provided an elegant review of the development of SCWO for commercial and defense applications up to 2000 (Shaw, 2000a,b). Included in this review are brief discussions on GA's SCWO systems and the TW-SCWO concept. He also describes development efforts at national laboratories and in Europe and Japan.

For aggressive feeds, a lined reactor is preferred to isolate the processing environment from the pressure vessel. The pressure drop across the liner is not very large (several hundred pounds per square inch [psi] or less at maximum). The liner may consist of transpiring wall platelets (TW-SCWO or a removable, replaceable SW corrosion resistant barrier [SW-SCWO]). Dimensions of the liner and reactor must allow for removal and replacement. The liner designs must consider both corrosion and erosion. Both types of liner can reduce the pressure vessel temperature. A number of materials of construction (MOCs) have been tested. The liner MOC must be chosen to meet the requirements of the SCWO feed.

TW-SCWO has been advanced as an alternative to the SW-SCWO reactor design. The general concept of the TW reactor as developed by Aerojet/GenCorp and Foster Wheeler is to use a porous inner wall as a liner to allow for a continuous transpiration of deionized water to form a thin film of clean water uniformly along the liner. The TW liner is placed concentrically within a pressure vessel. It capitalizes on technology originally developed by Aerojet/GenCorp for aerospace applications including high-pressure rocket engines. A schematic of the Foster Wheeler TW-SCWO liner is presented in figure 1-1. It is constructed of overlapping platelets to create uniform orifices (pores) through which clean water (transpiration water) is metered along the length of the liner with the goal of protecting the liner from salt deposition and corrosion, while providing a thermal and corrosion barrier for the pressure vessel. The intent is to reduce the contact between the SCWO reaction medium and the reactor wall. The reactor wall is kept cooler than the center of the reaction mixture with transpiration water (inlet temperature of the transpiration water is approximately 315°C), which the technology providers claim allows for higher operating temperatures and therefore shorter residence times. Wastes (feed) and oxidant (air or oxygen) are fed into the top of the reactor through injectors designed for mixing. The temperature profile is purported to decrease radially from approximately 815°C at the center of the to approximately 590°C. Transpiration water is added along entire length of reactor so the temperature decreases from 815°C at the top of the reactor to approximately 595°C at the bottom. The reaction is quenched at the bottom of the reactor through the addition of more water to cool it below the critical temperature of water and allow most of the product salts to redissolve. The quenched reactor effluent is let down from approximately 24 methylphosphonic acid (MPA) (3,500 psi) to approximately 30 pounds per square inch gauge (psig) through a pressure control valve (PCV). Five parallel reactors are proposed for BG with three or four in operation at any one time. The combined effluent

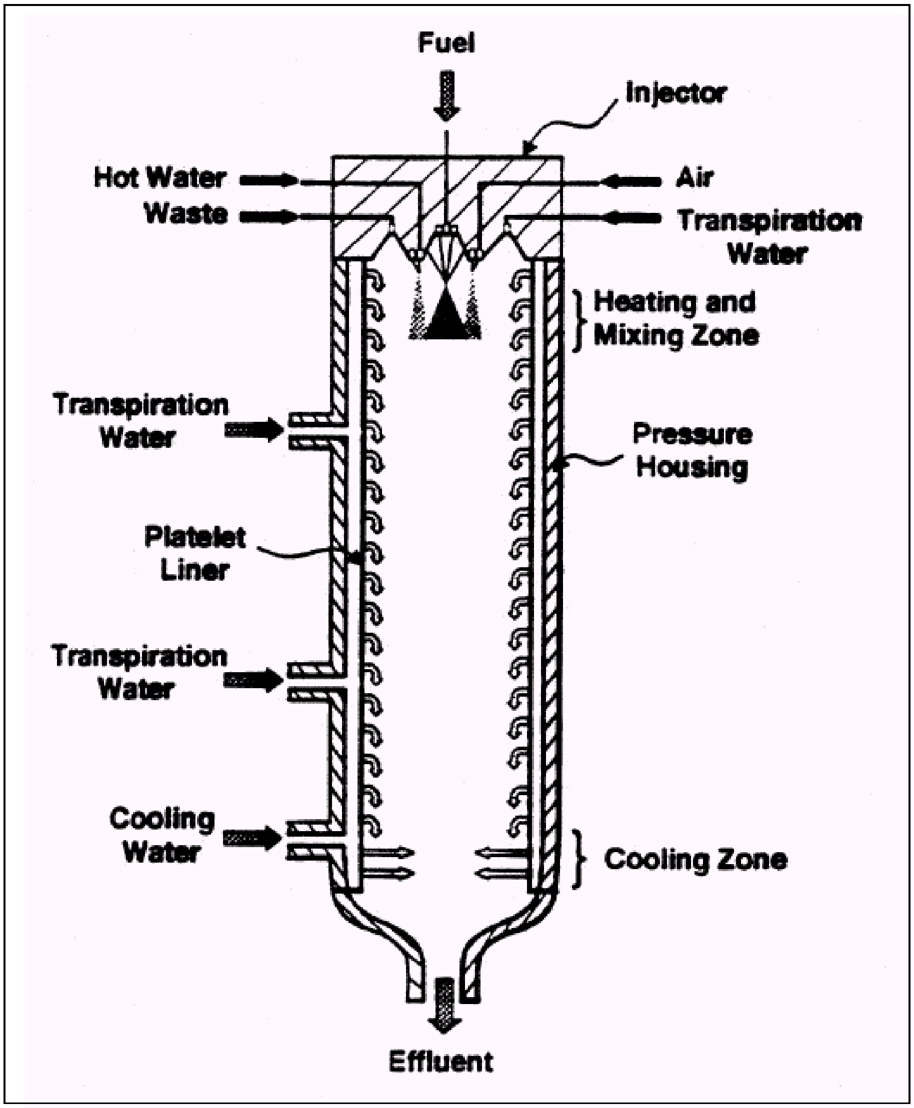

Figure 1-1. Schematic of TW-SCWO Reactor (Source: Ecologic, 14 December 2001)

from the SCWO reactors are to be fed to the venturi scrubber and the effluent knockout drum where the liquid slurry and vapor are separated (gas-liquid [G/L] separator).

The gas effluent will be scrubbed, monitored, and released to the atmosphere through carbon filters. Plans call for the liquid slurry effluent to be sent to an evaporator/crystallizer, which will produce salts for disposal and water for recycle. Early bench-scale tests of the TW-SCWO reactor were carried out by Sandia National Laboratories (SNL) on a 1.1-inch internal diameter (ID) prototype. As described in section 3, two other programs investigated the TW-SCWO system: (1) Army/Pine Bluff Arsenal (PBA) and 2) Navy/Defense Advanced Research Projects Agency (DARPA) shipboard wastes.

There is no fundamental basis for scale-up of SCWO reactors for wastes as complex as chemical agent hydrolysates due to a lack of fundamental understanding of a number of parameters including kinetics, mixing, fluid dynamics and flow characteristics, salt nucleation/precipitation, salt transport, and corrosion mechanisms. Considerable testing for both PMACWA and PMATA SCWO programs was therefore targeted at understanding and demonstrating the following key elements for scale-up:

- High DRE and oxidation stability including Schedule 2 compound destruction
- Long-term operability
- Corrosion of reactor and peripheral materials due to the severe reaction conditions (temperature, pressure, and corrosive/erosive environments), MOCs
- Plugging of reactors and downstream equipment—salt transport and management.

Extensive testing of TW-SCWO has occurred at Dugway Proving Ground over the past 3 years. A demonstration test was carried out from July to September 2000 as part of the ACWA demonstration (DEMO) II program. Engineering Design Study (EDS) II testing was carried out in two distinct time frames. EDS II optimization tests were performed from March to April 2001. After fabrication of a new, improved SCWO reactor and installation of an oxygen system to switch from air to oxygen as the oxidant, EDS II operability testing was performed from October 2001 to April 2002. Test dates are summarized in table 1-1. The scale of the tests was at hydrolysate simulant feed rates of 100 to 500 lb/hr. This evaluation is focused on the EDS II Operability Tests because they more closely represent the operation conditions for the proposed full-scale BG system. Due to the limited amount of chemical agent hydrolysates, the tests were largely run with simulants that were designed to mimic the heating value and salt or salt-producing content (for example, heteroatom content) of the actual agents. Composition of the simulants used for testing is provided in appendix C. Most of the tests were run with agent and energetics hydrolysate simulants combined. Some tests also used actual chemical agent hydrolysates. An Engineering Design Package (EDP) was submitted by the Ecologic-led team in December 2001 (Ecologic, 2001) with some proposed modifications provided in April 2002 (Ecologic, 2002).

The NRC formed two Assembled Chemical Weapons (ACW) Committees that published several reports evaluating the results from the DEMO II tests (ACW I) and the EDS II tests (ACW II). These committees also published assessments of the results of the

Table 1-1. Summary of TW-SCWO Testing in the ACWA Program

Tests	Schedule	Total Hours of Testing
DEMO II Tests	July to September 2000	231
EDS II Optimization Tests	March and April 2001	137
EDS II GB Operability Test	October to December 2001	504
EDS II VX Operability Test	February and March 2002	503
EDS II H Operability Test	March and April 2002	500

GA's SCWO system in DEMO I and EDS testing, respectively. The NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (the Stockpile Committee) has evaluated the implementation of GA's SCWO technology for NECDF in two full reports (NRC, 1998, 2000) and a letter report (NRC, 2001b). Key findings and conclusions from all these reports along with test reports and the EDP submitted by the Ecologic/Foster Wheeler team provide a sound basis for this evaluation.

1.3 Report Purpose and Format

The purpose of this report is to provide an updated review of the advances in TW-SCWO development, testing, and design for the ACWA program, and assess the potential application of this technology for NECDF and other chemical demilitarization operations. The development and implementation of SCWO for NECDF using GA's SW replaceable liner-based technology has been the subject of a number of recent reports and assessments, so it is not specifically assessed in this report. This technical evaluation focuses only on the TW-SCWO component of the Ecologic/Foster Wheeler total solution for BG. Integration of SCWO into the total solution will be critical for implementation at BG, but the intent here is to provide a stand-alone assessment of the stand-alone TW-SCWO technology rather than an evaluation of any integrated total solution. A summary of prior evaluations of SCWO for chemical demilitarization, particularly a large number of NRC reports, is provided in section 2. Section 3 presents a brief history of Program Manager for Chemical Demilitarization (PMCD) SCWO development and an update of recent test programs for TW-SCWO for ACWA as well as other Department of Defense (DoD) programs. A summary of a recent conference (August 2001) on the status of SCWO is also provided, and the executive and panel summaries are provided in appendix D. A review of key test results and findings are provided in the technical evaluation in section 4. Issues concerning the potential application of TW-SCWO to the treatment of VX hydrolysate at NECDF and to the destruction of other chemical demilitarization wastes are presented in section 5. Finally, key findings and conclusions are summarized in section 6 of this report.

SECTION 2
SUMMARY OF PRIOR EVALUATIONS

SCWO for the treatment of chemical agent hydrolysates has been extensively examined in a number of NRC reports that chronicle and provide thorough evaluations of SCWO development activities. Key reports and their findings and recommendations are summarized in the following paragraphs along with other PMACWA reports evaluating TW-SCWO. All planned pilot-scale tests for the application of TW-SCWO for the treatment of chemical agent and energetics hydrolysates have been completed, and all these tests have been evaluated by the NRC ACWA committees (ACW I and ACW II) in their full reports and letter reports. It is not intended for this report to track the numerous recommendations in the NRC reports nor to report on their status. Nonetheless, these prior evaluations, along with information provided by the technology providers through their formal test reports and EDP, provide the basis for this technical evaluation. A large body of reports, written under contract to PMATA, evaluates many aspects of the development and implementation of the GA SW-SCWO system at NECDF. These reports are not included in this section, but can be found in the bibliographies of several recent reports in this area (SAIC, 2001).

In their early reports, the NRC ACW I (NRC, 1999a) and Stockpile Committees both conclude that SCWO can be made to be an effective treatment capable of completing destruction of agent hydrolysates; however, they call out a number of key development issues and the need for significant testing at pilot-scale. The NRC has provided guidance and recommendations for most of the SCWO testing funded by PMATA and PMACWA.

In several reports, NRC is on record as stating that, “hydrolysis of chemical agents with water or caustic is capable of destroying 99.9999 percent of the chemical agent and, in combination with secondary treatments, 99.999 percent of the energetic materials” (NRC, 2002b). SCWO, or other secondary treatment technologies, including offsite shipment to a commercial TSDF, is required to destroy Schedule 2 compounds per the CWC treaty as well as other hazardous components of the hydrolysates.

2.1 Prior PMACWA Evaluations

Stone and Webster Engineering Corporation (SWEC), under their Technology Evaluation contract to PMATA, evaluated the draft study plans for ACWA DEMO II testing. The Army has reported to Congress on an annual basis on the status of the ACWA program since 1997, as required by public law (PL).

2.1.1 Evaluation of ACWA Draft Study Plans (SWEC, 2000). This report was prepared by SWEC for PMATA as an evaluation of the study plans for ACWA DEMO II testing submitted by the technology providers. These plans were also evaluated relative to NRC recommendations (see below) for SCWO processing. SWEC pointed out that DEMO II testing is essentially a proof of concept and that further Engineering Design Study (EDS) testing is required to produce engineering design data. A number of recommendations to the proposed study plans were made. SWEC states that "the feeds to be tested are specific to a narrow application (mixed hydrolysates) and would have limited applicability to other potential SCWO operations." The purpose of DEMO II was to validate the effectiveness of the TW-SCWO system for treatment of combined hydrolysates of agents, energetics, and aluminum hydroxide.

2.1.2 Assembled Chemical Weapons Assessment Program Annual Report to Congress, December 2001. As required by PL 104-208, which initiated the ACWA program, the Army has submitted annual reports to Congress describing program activities and accomplishments since 1997 (ACWA 1997, 1998, 1999, 2000, 2001a, 2001b). The December 2001 document reports that EDS I testing, including GA's SCWO testing of the SW reactor concept, was completed and an EDP was developed by GA for Pueblo Chemical Agent Disposal Facility and Blue Grass Chemical Agent Disposal Facility. This report also defines the EDS II testing for TW-SCWO. Optimization testing would establish throughput design basis for application to both the EDS reactor and the full-scale reactor. This report explains why optimization testing was carried out from March 2001 to April 2001 on the TW-SCWO equipment that was used for DEMO II testing. Modifications were then made to the existing system to more closely represent the full-scale design for BG. Metrics for long-term operability (that is, the 500-hour operability EDS II tests) are defined. This report also summarizes acquisition and environmental (permitting) activities.

2.2 NRC Technical Reports

A summary of the NRC reports that assess SCWO implementation for the treatment of chemical agent hydrolysates is provided in table 2-1. It should be noted that the NRC carries out technical evaluations and assessments, but does not compare the technologies nor make a recommendation as to the "best" technology. For example, as summarized in the NRC EDS II letter report (NRC, 2002b), the committees realize "that a technology decision for each depot must also be based on schedule, cost, and stakeholders' recommendations, and not only on the technical assessments and evaluations, it has neither compared the technologies with one another nor made a recommendation as to the 'best' technology." An excellent summary of ACWA testing and the corresponding NRC evaluations is provided in the introduction of the NRC's full report on EDS II (NRC, 2002a). Summaries of reports relevant to this technical evaluation along with key findings and recommendations pertaining to SCWO development and implementation are presented in the following paragraphs in chronological order.

2.2.1 Using SCWO to Treat Hydrolysate from VX Neutralization (NRC, 1998). This report provides an excellent introduction to SCWO and the issues associated with its use for treatment of VX hydrolysate at NECDF. It discusses the SCWO circa 1998, as well as a number of critical technical uncertainties, development needs, and potential program risk elements. This report recommended an Engineering Scale Test (EST) at 1/10th scale of the proposed full-scale NECDF system. This report also provides a detailed table summarizing and comparing the proposed NECDF system with other pilot testing and full-scale operation of SCWO treatment processes circa late 1997. A large number of findings center around the treatment of VX hydrolysate by SCWO being

Table 2-1. Summary of NRC Reports Relevant to SCWO Treatment of Chemical Agent Hydrolysates

Year	Committee[a]	Report Title	Test Results Evaluated
1998	Stockpile	Using Supercritical Water Oxidation to Treat Hydrolysate from VX Neutralization	SW-SCWO: GA confirmatory test (8-hour) for VX hydrolysate
1999a	ACW I	Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons	TW-SCWO & SW-SCWO: No test results. Evaluation of seven technology packages that passed DoD's initial screening for ACWA.
2000a	ACW I	Evaluation of Demonstration Test Results of Alternative Technologies for Demilitarization of Assembled Chemical Weapons, A Supplemental Review	SW-SCWO: DEMO I testing.
2000b	Stockpile	Integrated Design of Alternative Technologies for Bulk-Only Chemical Agent Disposal Facilities	SW-SCWO: Review of preliminary process design for NECDF, including SCWO of VX hydrolysate.
2001a	ACW II	Evaluation of Demonstration Test Results of Alternative Technologies for Demilitarization of Assembled Chemical Weapons, A Supplemental Review for Demonstration II	TW-SCWO: DEMO II testing.
2001b	Stockpile	Assessment of SCWO Technology Development for Treatment of VX Hydrolysate at NECDF, A Letter Report	SW-SCWO at NECDF including EST results
2001c	ACW II	Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Pueblo Chemical Depot	SW-SCWO: EDP and EDS I tests
2001d	ACW II	Update on the engineering design studies evaluated in the NRC report Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Pueblo Chemical Depot	SW-SCWO: EDS I tests
2002c	Non-Stockpile[b]	Systems and Technologies for the Treatment of Non-Stockpile Chemical Warfare Materiel	Batch SCWO processing
2002a	ACW II	Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Blue Grass Army Depot	TW-SCWO & SW-SCWO: Evaluation of results from EDS II Optimization tests and 500-hour GB long-term Operability tests and Engineering Design Package for Blue Grass

Table 2-1. Summary of NRC Reports Relevant to SCWO Treatment of Chemical Agent Hydrolysates (Continued)

Year	Committee[a]	Report Title	Test Results Evaluated
2002b	ACW II	Update on the Engineering Design Studies Evaluated in the NRC Report Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Blue Grass Army Depot. A Letter Report	TW-SCWO: Evaluation of all EDS II test results.

Notes:

[a] ACW I: Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons (1997-1999).
ACW II: Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons: Phase II (2000-2002).
Stockpile: Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program.

[b] Other reports from the Committee on Review and Evaluation of the Army Non-Stockpile Chemical Materiel (NSCM) Disposal Program (NRC, 1999b, 2001f, 2002d) are listed as references in appendix B.

ACW = Assembled Chemical Weapons
ACWA = Assembled Chemical Weapons Assessment
DEMO = Demonstration
DoD = Department of Defense
EDP = Engineering Drawing Package
EDS = Engineering Design Study
EST = Engineering Scale Test
GA = General Atomics
GB = sarin
NECDF = Newport Chemical Agent Disposal Facility
NRC = National Research Council
SCWO = supercritical water oxidation
SW-SCWO = solid wall-supercritical water oxidation
TW-SCWO = transpiring wall-supercritical water oxidation
VX = a chemical nerve agent, O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothiolate

significantly different and more complex than previous treatments using SCWO, particularly from a corrosion and salts transport/management perspective. In subsequent reports, the ACW and Stockpile committees state that all the findings of this NRC report apply to both GA and Foster Wheeler SCWO systems. Recommendations from this report are listed below:

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 letdown 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 letdown 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 rate 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 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.

2.2.2 Review and Evaluation of Alternative Technologies for Demilitarization of ACW (NRC, 1999a). This first report from the NRC ACWA Committee (ACW I) evaluates the seven complete technology packages for destroying assembled chemical munitions that passed the Department of Defense's (DoD's) initial screening. This NRC report was published in time for DoD to present its 1999 report to Congress (ACWA, 1999), so the evaluation was carried out prior to any testing and is based on technical information available before 15 March 1999. At that time, the Ecologic-Foster Wheeler Total Solution was called the Lockheed Martin Integrated Demilitarization System (LMIDS). Two of the three technologies initially chosen for demonstration testing (including the GA SW-SCWO process) were eventually carried forward to EDS I testing. Findings and recommendations relevant to the implementation of SCWO for ACWA include the following:

Steps Required for Implementation of Foster-Wheeler TW-SCWO:

Pilot-Scale Evaluation for SCWO.

a. Show that the SCWO reactor platelet wall can be constructed.

b. Demonstrate that the SCWO reactor can be operated for sufficient periods of time without excessive clogging or corrosion.

c. Fully characterize the SCWO gaseous effluent from mixed hydrolysates of agent and energetics.

d. Establish that the continuous monitoring of the SCWO gaseous effluent ensures against unacceptable releases of hazardous materials.

Finding LM-6. The SCWO process appears to be capable of completing the destruction of both agent and energetics in the hydrolysates. The key area of uncertainty in the technology provider's proposed application of SCWO is the use of its proprietary TW tubular reactor. The demonstration of this technology will be essential to proving the efficacy of this crucial step in the agent/energetics destruction process.

Finding LM-9. The gas stream from SCWO is not subjected to hold-test-release. Instead, the gas is scrubbed, monitored, and passed through activated carbon. This treatment appears to be appropriate for the anticipated composition of the SCWO off-gases.

Finding LM-12. All of the findings in the NRC report, *Using Supercritical Water to Treat Hydrolysate from VX Neutralization*, apply to the LMIDS SCWO system.

Steps Required for Implementation of GA SCWO for ACWA:

The following steps would have to be taken to implement the GA technology package:

a. Ascertain how well the SCWO process can handle high-solids materials (shredded dunnage).

b. Ascertain how well the SCWO system can treat hydrolysate containing large amounts of chlorides, sulfur, and phosphates on a continuing basis.

c. Determine erosion and corrosion behavior of the components of the SCWO system.

Finding GA-4. Shredding of dunnage and injection of the slurry directly into a SCWO system is a new and unproved process. While GA claims to have developed a proprietary pump capable of pumping the slurry at high pressures, it has not been tested under the intense solids loading anticipated. Furthermore, the injection of large amounts of solid material, including wood shreds, cut-up nails, and complex organic materials, such as pentachlorophenol and other wood preservatives, into the SCWO system has not been demonstrated. Considering the difficulty SCWO reactors have encountered with deposition of solids when liquids are treated, the committee believes that this application of SCWO may encounter significant difficulties. (At the time of this writing, processing of solids with SCWO was being performed as part of the ACWA demonstrations.)

Finding GA-5. All of the findings in the NRC report, *Using Supercritical Water to Treat Hydrolysate from VX Neutralization*, apply to the GA system.

Finding GA-7. No hold-test-release facilities are provided for gases from the hydrolysis reactors or the SCWO reactors. The gases will be scrubbed using activated carbon.

2.2.3 Integrated Design of Alternative Technologies for Bulk-Only Chemical Agent Disposal Facilities (NRC, 2000b). This report, which was written prior to the SCWO EST, evaluates the acquisition design packages for the Aberdeen Chemical Agent Disposal Facility (ABCDF) and NECDF. An ADP is an approximately 60-percent design used as a basis for competitive bids for completion of design, construction, commissioning and operation of each disposal facility. Chapter 3 of this report provides a summary of MOCs test results reported by SWEC and GA in 1999, along with other operational and safety issues. The report concludes that “the reliability of the integrated SCWO process step at NECDF is the only significant obstacle in terms of design and development.” An overview of the entire NECDF process is provided in appendix B of this report. Recommendations relevant to SCWO implementation at NECDF are as follows:

Recommendation 3-1a. The Army should develop criteria and a schedule for resolving design and operational issues raised in the 1998 report, *Using Supercritical Water Oxidation to Treat Hydrolysate from VX Neutralization*, that have not yet been resolved for SCWO operation at Newport. These issues include MOCs, fabrication methods, system plugging, pressure letdown, and the duration of successful continuous pilot-scale operations.

Recommendation 3-1b. The Army should pursue the testing of MOCs for treating VX hydrolysate by SCWO more aggressively to finalize materials selection, design, and fabrication methods for critical components, including the SCWO reactor, inlet, and pressure letdown system. This testing should clearly define mechanisms and rates of corrosion and erosion under the range of anticipated process conditions. An independent panel of experts in MOCs should evaluate testing to date and identify further needs to ensure that the reliability of the SCWO system is adequate to meet the processing objectives.

Recommendation 3-2. For worker protection and secondary containment, the final design package for the Newport facility must include the physical hazard controls (for example, protective barricades) common to industrial operations involving high pressure and stored energy. Systems must be designed to minimize leaks, plugging, and ruptures of the SCWO reactor and associated plumbing and protective barriers. Secondary containment equipment will also be necessary, including safety systems for handling high-purity oxygen at high pressure, such as protection against downstream fires and explosions caused by contact between combustible materials (for example, activated carbon) and oxygen-enriched gas streams under normal and process upset conditions.

Recommendation 4-1. The Army should evaluate offsite management of hydrolysates both for potential cost and schedule benefits and as a contingency plan in case difficulties arise during start-up and pilot testing of the onsite (postneutralization) process steps.

Outside of their formal recommendations, the committee also notes in this report that "off-site treatment of the hydrolysates would require that suitable treatment and disposal facilities be identified and that public acceptance be obtained."

2.2.4 Evaluation of Demonstration Test Results of Alternative Technologies for Demilitarization of Assembled Chemical Weapons, A Supplemental Review for Demonstration II (NRC, 2001a). This report is the first evaluation published by the NRC ACW II Committee, which was established to evaluate EDSs for Pueblo and BG. This report evaluates test results from DEMO II testing, which was the second round of demonstration testing for the ACWA program. The basis for this evaluation were PMACWA approved demonstration study plans and demonstration test reports produced by the ACWA technology providers and the associated responses of the providers to questions from PMACWA. DEMO II was aimed at demonstrating three technologies: (1) AEA Silver II, (2) Ecologic/Foster Wheeler total solution including a TW-SCWO system, and (3) Teledyne-Commodore solvated electron process. The NRC notes that the focus of EDS II should be demonstration of long-term operation of the modified TW-SCWO unit. Key findings and recommendations for the TW-SCWO system from this report are as follows:

Finding DII FEK-1. The proposed full-scale TW-SCWO has design and operating conditions significantly different from those tested in DEMO II. These include the temperature of the transpiration water at the inlet, pH of the feed, turbulence in the reactor, use of pure oxygen, not air, as the oxidant.

Finding DII FEK-2. The proposed full-scale design for the TW-SCWO system involves a scale-up in reactor cross sectional area by a factor of 2.25 from the DEMO II test unit and an increase in reactor throughput by a factor of 35. Performance under these full-scale design conditions has not been demonstrated.

Finding DII FEK-3. Aluminum present in hydrolysates, which could lead to the formation of slurries and plugging, could be a problem. The proposed changes for mitigating this problem (for example, changing operating conditions and/or removing aluminum during weapon disassembly) must be tested.

Finding DII FEK-5. All waste streams have been or can be characterized sufficiently for engineering design to proceed.

Finding DII FEK-10. The full-scale SCWO reactor design has not been tested and is different in size and in the flow rates of feed streams from those used in the DEMO II tests. The full-scale design treats hydrolysate at a rate per unit volume of reactor that is almost 10 times higher than those used in DEMO II tests. In addition, the ratio of flow rates of all other streams to flow rates of hydrolysate in the full-scale unit has decreased by an approximate factor of 10 from those used during DEMO II tests. These changes in hydrolysate processing per unit reactor volume and the reduction of other feed streams relative to the hydrolysate may reduce the efficacy of the SCWO reactor and may be expected to exacerbate problems of corrosion and plugging.

Finding DII FEK-11. The experience of multiple shutdowns during DEMO II testing resulted in thermal stresses and crack generation in the liner indicates a potential reliability issue, which must be significantly reduced or eliminated.

Recommendation DII FEK-1. Since the hydrolysate/total feed ratio and flow velocity used in DEMO II testing are so different from those of the proposed design, the TW-SCWO reactor must be tested at a hydrolysate/total feed ratio and flow velocities close to the proposed design conditions.

Recommendation DII FEK-2. Long-term testing of appropriately designed SCWO reactor liners under the new operating conditions for the proposed full-scale operation will be necessary to prove the reliability and effectiveness of the TW-SCWO unit.

Recommendation DII FEK-3. Long-term testing of the TW-SCWO unit should include feeds containing chlorine, phosphorus, and sulfur and should be at residence times and flow velocities close to the proposed design conditions.

(Note: As described in Section 4, the technology provider has proposed modifications of the feed rates for the full-scale BG TW-SCWO system based on EDS II testing [Ecologic, 2002].)

2.2.5 Assessment of SCWO Technology Development for Treatment of VX Hydrolysate at NECDF, A Letter Report (NRC, 2001b). This letter report was written as a response to the open items and unresolved issues observed during the EST contracted by PMATA for NECDF. It reiterated that MOCs and salt transport, as well as demonstration of a mechanically stable reactor liner, are among the issues that still have to be resolved for implementation of SCWO at NECDF. (Note: Although assessment of NECDF SCWO is not part of this current technical evaluation, the open issues have been worked extensively by PMATA, SWEC, Parsons, and GA, through design and further testing of SCWO processing of VX hydrolysate in a joint ACWA/PMATA test. A number of reports assessing the status of these issues and recommendations and potential solutions have been written subsequent to this report

[SAIC 2001].) The recommendations from this NRC report concerning SCWO were the following:

Recommendation 2. The Army should develop a realistic critical path schedule and decision process for implementing secondary treatment at NECDF, including the following steps:

a. The EST should be considered as a design and operating proof of the SCWO reactor system proposed for NECDF. The results to date should be viewed to determine whether a SCWO reactor can be made that will operate reliably at full capacity to meet the treaty schedule. The scope of the current EST should be upgraded or expanded to provide a broader basis for design scale-up of the SCWO reactor system, including the selection of optimal operating conditions, the prediction of the effects of corrosion, the deposition of salts in the reactor, and the erosion of the pressure letdown equipment.

b. The Army should immediately undertake a comparative evaluation of alternatives for treating and/or disposing of the VX hydrolysate produced at NECDF.

c. The critical path to complete NECDF disposal operations within the treaty requirements of the CWC should be identified.

The NRC Committee also recommended: (1) that the impacts on the disposal schedule caused by delays and difficulties be determined (NRC Recommendation 1), (2) criteria for a decision process should be developed (NRC Recommendation 3), and (3) stakeholders should be involved in its consideration of secondary treatment (NRC Recommendation 4).

2.2.6 Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Blue Grass Army Depot (NRC, 2002a). This full report on

EDS II testing for BG evaluates the EDP for TW-SCWO at BG submitted by the Ecologic-led technology provider team. This NRC report was written and reviewed prior to completion of the EDS II testing; therefore, submission of the final test reports by the technology provider. EDS II testing ended in April 2002. The data gathering cutoff for this NRC report was January 2002, so it could only include evaluations of the optimization testing and the 500-hour-long operability test for GB. The latter test was completed in December 2001, but only a draft test report was available for evaluation along with briefings by the technology provider to the committee. As described in the findings and recommendations below, significant spikes in the concentrations of carbon monoxide (CO) and hydrocarbons (HCs) were observed indicating problems with oxidation stability within the reactor and potential problems for scale-up. The NRC states that “the most significant need is to demonstrate that the SCWO reactor is ready to be commercialized. Effective and reliable operation over an extended period of time remains to be demonstrated.” A series of extensive general findings are provided in this report. Findings and recommendations pertaining to SCWO development and testing are as follows:

General Finding (Blue Grass) 5. Stable operation of the Ecologic/Foster Wheeler SCWO system at the design conditions has not yet been demonstrated. The SCWO system for treatment of hydrolysates in EDS II testing exhibited frequent spiking in HCs and CO concentrations in the off-gas. This issue must be resolved before implementing the Ecologic process at BG. If it is resolved, the committee believes that the Ecologic package could provide an effective and safe means for destroying the assembled chemical weapons. However, the following design feature still requires validation:

- Removal of aluminum from the feed to the SCWO reactor. At this time, Ecologic has not proposed an aluminum removal technology.

The Ecologic technology does accomplish the following:

- It destroys the hydrolysates and slurries that result from upstream processing by SCWO.

- It adequately treats the low volumes of off-gases produced in the process, including those from the SCWO reactors, through catalytic oxidation and activated carbon adsorption systems.

General Finding (Blue Grass) 7. As the ACW I Committee observed, the unit operations in any of the three technology packages have never been operated as total integrated processes. As a consequence, a prolonged period of systemization will be necessary to resolve integration issues for the selected technology as they arise, even from apparently straightforward unit operations.

Finding (Blue Grass) EFKE-1. The occurrence of frequent spikes in HC and CO emissions in the gaseous effluent from the TW-SCWO reactor is a serious problem that must be resolved before the Ecologic technology can be implemented.

Finding (Blue Grass) EFKE-5. To prevent scale buildup in the SCWO reactor due to the presence of aluminum in the hydrolysate feed, Ecologic must remove the aluminum from the feed stream to the SCWO reactor.

Ecologic intends to use a process that is based on the aluminum removal technology of GA. However, Ecologic does not have rights to the GA process and must obtain or develop such a technology. A 500-hour run with GB hydrolysate was completed, and a draft report was issued. To simulate the use of the GA process to remove aluminum from the hydrolysate, the concentration of aluminum was increased from zero to that expected from this process. This was done part way through the campaign and had no apparent adverse impact.

The NRC committee stated (NRC, 2002a), outside of a formal recommendation, that “overall, it is this committee’s opinion that problems remain with Foster Wheeler’s current transpiring wall SCWO system may prevent the application of this technology in a full-scale facility.” They also stated that the “SCWO reactor remains a significant and incompletely resolved problem” and “additional development on this operation is needed.”

2.2.7 Update on the Engineering Design Studies Evaluated in the NRC Report on Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Blue Grass Army Depot (September 2002). This Letter Report (NRC, 2002b) was written after all EDS II tests were complete. Final reports from EDS II testing were submitted in May 2002 with the GB 500-hour test report submitted in April 2002. The NRC ACWA II committee issued this letter report in September 2002 to review these final reports and provide a complete assessment of the EDS II tests. As described in their letter, they have additional findings for TW-SCWO, including a finding that they believe could impact scale up of any SCWO system at BG. Findings and recommendations from this report are listed in the following paragraphs:

Finding (Blue Grass Letter) 4. The technology provider has proposed several explanations for the spiking in HC and CO levels in the TW-SCWO reactor effluent, and it has made several changes that appear to have reduced the severity of the spiking but have not eliminated it. Based on the members' experience, the committee believes that these spikes are symptoms of an underlying instability that is not yet understood. The problem needs to be thoroughly understood and resolved before the TW-SCWO reactor is implemented in the larger size and at the increased throughput proposed for BG.

Recommendation (Blue Grass Letter) 2. Foster Wheeler should present convincing evidence that is has identified the root cause or causes of the spiking problem before scaling up the design of the TW-SCWO reactor.

(Note: It should be noted that while the EDP and the technology providers appear to claim that this issue is resolved, the NRC Committee "believes that Foster Wheeler has not clearly identified the root cause or causes of the problem" and "operability and permitting issues associated with spiking remain to be resolved." They also state that "the spiking problem will require additional testing." Most importantly, they conclude: "the lack of understanding of the cause or causes of the spiking problem raises questions about the use of the TW-SCWO reactors in the Eco Logic technology package at a BG facility, even if they are used at the size and throughput rates recently tested.")

Finding (Blue Grass Letter) 5. The results of the Foster Wheeler TW-SCWO reactor tests indicate that making changes in the design or operating conditions (such as flow rate of feed or choice of oxidant) of a SCWO reactor is not straightforward. Therefore, implementation of full-scale SCWO reactors with different operating conditions or designs may result in unexpected performance problems.

As another example, GA is planning to scale-up its SW reactor from a 3.5-inch diameter and 6-foot length to a full-scale 18-inch diameter and 18-foot length. This is a 3-fold linear scale-up, a 26-fold cross-sectional area scale-up, and an 81-fold volumetric scale-up. The committee believes that this degree of scale-up introduces uncertainties that could also lead to problems and instabilities other than or akin to those experienced by Foster Wheeler with the TW-SCWO reactor.

Finding (Blue Grass Letter) 6. Based on its experience and knowledge of permitting regulations, the committee believes that the HC and CO spiking may affect permitting of the SCWO process. The final permitting approach and the applicable and relevant rules can only be defined by the permitting authorities upon review of the permit application. The current performance may need to be improved to meet HC emissions standards if the hazardous waste combustor standards are invoked.

Recommendation (Blue Grass Letter) 3. Consideration should be given to establishing a performance standard for HC and CO emissions from any SCWO reactor system elected for implementation at BG. The basis for selection of these performance standards should be discussed with permit writers to ascertain likely permitting issues. While the committee first recognized this concern as a result of the Foster Wheeler EDS II testing, it is potentially a concern for any SCWO system or other oxidation system scaled up to a size appropriate for treatment of the BG stockpile.

Finding (Blue Grass Letter) 7. Significant corrosion of the lower liner was experienced during testing on HD hydrolysate but not during testing on GB and VX hydrolysates. This may be due to chlorine, which is present in the HD hydrolysate but not in the GB and VX hydrolysates. While the amount of H at BG is relatively small compared to the other agents, increased maintenance will be required during its destruction campaign.

All SCWO testing experience to date indicates that the operating environment associated with the SCWO reactions poses corrosion and material durability challenges per se, regardless of the SCWO process. Therefore, the committee believes the use of the SCWO process will require that the operator have an aggressive monitoring program in place to ensure planned completion schedules are not severely compromised by higher than expected maintenance and repairs.

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SECTION 3
TECHNOLOGY UPDATE

3.1 Introduction: SCWO Development and Testing

Considerable information on the development and implementation of SCWO processing of the hydrolysates of chemical agents and energetics has been garnered through significant testing programs. Table 3-1 summarizes the development history of SW-SCWO for NECDF, which PMATA funded.

A large number of technical evaluations as well as reports proposing and evaluating modifications and technical options for improvements of the NECDF SCWO system have been published. These reports provide valuable information on SCWO development, but are outside of the purview of this technical evaluation. A recent report entitled, *GA SCWO Development Summary Report*, was submitted to the U.S. Air Force by GA in September 2002. This report, which is scheduled for release within the next month or so, provides an excellent update on GA developments to date. It also includes an appendix on *Supercritical Water Oxidation for the Newport Chemical Agent Disposal Facility: A Status Report*, which summarizes recent developments in liner design for NECDF and Lessons Learned from joint PMACWA/PMATA testing on VX hydrolysate. Fewer technical evaluations are available for TW-SCWO (SWEC, 2000; ACWA, 1997 to 2001) aside from the NRC reports discussed in section 2. Table 3-2 provides an historical illustration of SCWO testing for ACWA, both SW- and TW-SCWO.

Past PMACWA test evaluation reports cover up to DEMO II testing. The reactor used for DEMO II was the same reactor used by Foster Wheeler for the Navy shipboard waste program (see paragraph 3.5.2). The liner was damaged during Navy testing so it was repaired for the DEMO II tests. The reactor was modified to deal with higher design temperature to resolve overheating problems that occurred when the system was tested for the Navy (SWEC, 2000). Air was used as the oxidant for DEMO II testing; whereas, oxygen is proposed for the full-scale BG system. The purpose of

Table 3-1. Chronology of Army SCWO Progress for NECDF[a]

1994	NRC makes recommendations for alternative neutralization technologies: Biological (stand alone), SCWO, wet air oxidation
1995	Commerce Business Daily solicitation for technologies
1996	Technology screening tests; SCWO selected (screening test, September/October)
1997	SCWO 8-hour confirmatory test with hydrolysate (February)
1998	NRC report for SCWO issued recommending materials of construction (MOC) testing and engineering scale test (EST) (NRC, 1998)
1998	MOC and EST solicitations
1999	MOC batch screening test at MIT; MOC flow test at Dugway Proving Ground
2000-2001	EST at Corpus Christi, Texas
2001	Independent Assessment Panel report on NECDF status and recommendations (SAIC, 2001)
2001	NRC letter report on concerns about delays and open issues for NECDF SCWO development (NRC, 2001b)
2001	NECDF SCWO design completion milestone scheduled. NRC letter report on proposed expedited disposal at NECDF (NRC, 2001d)
2002	Originally planned SCWO development test (SDT) canceled. SCWO implementation at NECDF and all development work put on hold. "Speedy SCWO" concept proposed by General Atomics. General Atomics 2002 GA SCWO Development Summary Report to Air Force along with updated status of NECDF SCWO development (General Atomics, 2002).
2002	RFP for commercial TSDFs for offsite treatment/disposal of VX hydrolysate issued.
2002	Final technology selection for treatment/disposal of VX hydrolysate pending.

Notes:

[a] Part of this table is adapted from SAIC 2001.

NECDF = Newport Chemical Agent Disposal
NRC = National Research Council
RFP = request for proposal
SAIC = Science Applications International Corporation
SCWO = supercritical water oxidation
TSDF = treatment, storage, and disposal facility

Table 3-2. History of SCWO Development for the ACWA Program

1996	ACWA Program established under Public Law 104-208
1997	RFP for total system solution for ACWA sites; NRC ACW I Committee formed
1998	Pine Bluff TW-SCWO system construction completed
1999	NRC ACWA full report (NRC, 1999a)
1999	DEMO I tests including GA SW-SCWO
2000	NRC ACW II Committee formed
2000	DEMO II TW-SCWO tests at Dugway Proving Ground
2000	Public Law 106-79 passed to “conduct evaluations of [the] three additional alternative technologies explored under the ACWA program” leading to DEMO II
2001	NRC DEMO II report (NRC, 2001a). NRC ACW II reports evaluating EDP for Pueblo (NRC, 2001c,d)
2001	PMACWA sponsored conference on Supercritical Water Oxidation: Achievements and Challenges in Commercial Applications, Alexandria, Virginia (VA 2001)
2001	Final EDP for Ecologic/Foster Wheeler Total Solution for BG submitted
2001-2002	EDS II TW-SCWO tests at Dugway Proving Ground
2002	NRC full and letter report evaluating EDS II (NRC, 2002a,b)
2003	Army decision for technology at BG pending

Notes:

ACW = Assembled Chemical Weapons
ACWA = Assembled Chemical Weapons Assessment
BG = Blue Grass
DEMO = Demonstration
EDP = Engineering Design Package
EDS = Engineering Design Study
GA = General Atomics
NRC = National Research Council
PMACWA = Program Manager for Assembled Chemical Weapons Assessment
RFP = request for proposal
SW-SCWO = solid wall supercritical water oxidation
TW-SCWO = transpiring wall supercritical water oxidation

DEMO II testing was to validate the effectiveness of the TW-SCWO system for the treatment of combined hydrolysates of agent and energetics, and aluminum hydroxide (SWEC, 2000). The objectives for DEMO II testing for TW-SCWO (NRC, 2001a) include:

a. Demonstrate the long-term continuous operability of the TW-SCWO unit with respect to salt plugging, corrosion, integrity of the platelet liner, and erosion of the PCV of the TW-SCWO reactor.

b. Determine if aluminum from the energetic hydrolysis process can be processed by the TW-SCWO reactor without plugging.

c. Demonstrate that the TW-SCWO can destroy CWC Schedule 2 compounds in the feed to below their detection limits.

d. Characterize the gas, liquid, and solid process streams from the TW-SCWO process for selected chemical constituents and physical parameters and the presence or absence of hazardous, toxic, agent, and CWC Schedule 2 compounds.

The NRC (NRC, 2001a) identified a number of open issues and concerns with the DEMO II test results, but they concluded that the DEMO II testing provided sufficient information to justify moving forward to additional pilot scale testing with reasonable probability of success for TW-SCWO (and also for Gas Phase Chemical Reduction [GPCR] for VX, GB, HD, and energetics). They also pointed out that the SCWO conditions employed during DEMO II were significantly different than that proposed for the full-scale BG system, including the temperature of transpiration water at the inlet, pH of the feed, mixing/turbulence in the reactor, and choice of oxidant. A summary of DEMO II testing is provided in table 3-3.

Table 3-3. Summary of DEMO II Testing

Campaign[a]	Total Hours	Start Date	Completion Date
VX/Hydrolysate Simulant	100	7/16/2000	7/31/2000
HD/Tetrytol/Aluminum/Hydrolysate and Simulant	55.28	8/29/2000	9/7/2000
GB/Comp B/Aluminum/Hydrolysate and Simulant	50	9/12/2000	9/17/2000
VX/Comp B/M28/Aluminum/Hydrolysate	25.67	9/25/2000	9/29/2000

Note:

[a] Simulant compositions are provided in appendix C.

3.2 EDS II Tests

A significant test program for TW-SCWO was carried out during the EDS II. This TW-SCWO testing was aimed at demonstration of long-term operability and resolution of open issues. There are no Army evaluations of EDS II testing, although as described in section 2, the NRC has evaluated these tests. This current report relies heavily on EDS II test results and the EDP submitted by the Ecologic-led team for BG. The purpose of the EDS II test was three-fold:

a. Support an request for proposal (RFP) for full-scale pilot facility

b. Provide supporting information for National Environmental Policy Act documentation and Resource Conservation and Recovery Act (RCRA) permit application

c. Certification that the "total solution" alternative is safe and cost-effective.

3.2.1 EDS II Test Objectives. In their December 2001 report to Congress (ACWA, 2001b), the Army identified the following goals for EDS II testing of the TW-SCWO system:

a. Verify long-term, continuous operability (that is, operation for the full length of the test without unintended shutdown) of the SCWO system as proposed for full-scale with no plugging. Long-term continuous operability includes, but is not limited to:

1. Operation with MOCs proposed for the full-scale system

2. Operation with all expected full-scale operating procedures (that is, any SCWO system flushing sequences at expected intervals

3. Operation with downstream solids separation units, new reactor, and oxygen

4. Operation without plugging/fouling upstream and downstream of the reactor

5. Operation without liner cracking/deformation

6. Operation without feed port plugging

7. Operation with minimal or no corrosion of the SCWO liner

8. Operation without plugging of the SCWO reactor

9. Operation without erosion of the PCV

10. Destruction of Schedule 2 compounds.

b. Characterize all operability issues to determine their causes and impact on the full-scale design.

c. Confirm and supplement DEMO II process effluent characterization.

d. Improve the monitoring of effluent quality and develop an effective control strategy with respect to Schedule 2 compounds and organic carbon destruction.

3.2.2 EDS II Test Summary. All tests were carried out at DPG. The EDS II tests in two parts were carried out in two distinct time frames: (1) Optimization Tests and (2) Operability Tests. Optimization testing was aimed at establishing maximum feed throughput for the operability tests with three main objectives:

- Salt plugging
- Corrosion
- Consistency in organic destruction (DRE).

The optimization test consisted of six different feed campaigns, four with VX hydrolysate simulant, and one each for HD and GB hydrolysate simulants. The same reactor system used for DEMO II testing was employed in the optimization tests. Operability tests (500-hour tests) were carried out using a new oxygen-based reactor at feed throughputs for GB, VX, and HD derived from optimization tests.

The operability tests (500-hour tests) consisted of Foster Wheeler carrying out three long-duration tests for TW-SCWO using the new SCWO reactor configuration largely with simulants for GB, VX, and HD along with energetic hydrolysates. Simulants were necessary due to the limited availability of actual chemical agent hydrolysates. The composition of these simulants, which were intended to mimic the heat value as well as the heteroatom and salt content of the actual wastes, are listed in appendix C. Some actual agent hydrolysates were also employed. An availability goal of 80-percent availability was set. Several systemization tests (10 to 72 hours) preceded each 500-hour run. A number of modifications of the equipment and operations were incorporated into the operability tests in an effort to more closely represent the EDP full-scale design. Major changes (Crooker, 2002e) were:

a. New SCWO reactor (same length and diameter as DEMO II system):

   1. 900°F design temperature

   2. Oxygen-based design

   3. Increased transpiration water temperature.

b. New back-end system to process effluent slurry:

   1. Effluent venturi scrubber

   2. Upgraded pressure letdown valve and alternate capillary design

   3. Effluent slurry cooling using spiral exchangers.

c. Improved feed system.

Oxygen, from liquid oxygen, was used as the oxidant. While aluminum removal will be required for BG, no such system was tested during EDS II. Aluminum was added at approximately 300 ppm to mimic expected aluminum levels in the GB systems. Specific changes (NRC, 2002b) for each EDS II operability test campaign (GB/energetics, VX/energetics, H energetics) are listed in the following paragraphs.

a. Modifications to TW-SCWO reactor for GB testing include:

- Oxygen, rather than air, used as oxidant
- Design and construction of new SCWO reactor with 6-inch diameter and 61-inch length
- Modification of the piping in the reactor outlet to enable better solids transport
- Modifications to the reactor feed system
- New online analyzers for total organic carbon (TOC) and Schedule 2 compounds in the liquid effluent.

b. Additional changes to the SCWO reactor for VX testing include:

- Installation of a new upper reactor section with a TW liner, which contained three additional "dummy" platelet layers (0.172 inch total thickness)
- Replacement of the injector, which experienced some erosion (the injector from DEMO II and EDS II optimization testing was modified for oxygen use).

c. Additional changes to the SCWO reactor for HD testing:

- Use of the injector employed for GB testing
- Installation of degassing system in reactor outlet piping to enable accurate measurement of the effluent flow

- Installation of a static mixer in the liquid feed line to mix hydrolysate and propylene glycol fuel in an effort to mitigate spikes in HC and CO concentrations in gas effluent (Note: no discernible effect on HC/CO spiking was observed).

Key findings and conclusions from reports on these tests from the technology providers and relevant NRC evaluations are provided as part of the technology evaluation in section 4. TW-SCWO testing activities for ACWA are summarized in table 3-4.

3.3 Engineering Design Package

The EDP Final Submittal for the Ecologic-Foster Wheeler Total Solution (Ecologic, 2001) is a 10-volume document. The final package was submitted in

Table 3-4. EDS II TW-SCWO Test Conditions and Schedule[a]

Test	Feeds[b]	Feed rate (lb/hr)	Total Duration (hr)	Schedule	Final Report Date[c]
Optimization tests (6 runs)	VX, GB hydrolysates and simulants (with energetics hydrolysates	Varied, Up to 300	137	3/7/01 to 4/12/01	7/6/01
GB 500 hour test (1 run)	GB hydrolysate and simulant	250 for 184.5 hr 500 for 319.5 hr	504	10/23/01 to 12/16/01	3/14/02
VX 500 hour test (1 run)	VX hydrolysate and simulant, and hydrolysates of energetics and propellant	350	503	2/7/02 to 3/4/02	5/16/02
HD 500 hour test (1 run)	HD hydrolysate and simulant, and energetics	210	500	3/16/02 to 4/7/02	5/31/02

Notes:

[a] Adapted from NRC 2002b.
[b] Compositions of simulants in appendix C.
[c] Final Technology Provider Reports (Foster Wheeler 2001, 2002a to c).

hr = hour
lb/hr = pounds per hour

December 2001 and has been evaluated by the NRC (NRC, 2001a). The EDP (Ecologic, 2001) provides definition of the basic process design including equipment requirements, system integration, materials, utilities, products, waste streams, capital cost estimates (±20 percent), operating and maintenance staff and utility demand. A project schedule through decommissioning is also provided. TW-SCWO is discussed in a number of sections in each volume. The EDP contains the following volumes:

Volume I	Design Basis
Volume II	Process Design
Volume III	Utilities
Volume IV	Civil/Structural/Architectural
Volume V	Piping
Volume VI	Electrical and Control Systems
Volume VII	Preliminary Hazard Analysis
Volume VIII	Life Cycle Schedule
Volume IX	Life Cycle Cost
Volume X	Proprietary Drawings.

Modifications to the EDP were issued in April 2002 (Ecologic, 2002), which call for reducing feed rates in the full-scale BG TW-SCWO system based on EDS II test results.

3.4 Conference on "Supercritical Water Oxidation: Achievements and Challenges in Commercial Applications" (ONR and PMACWA, August 2001)

A conference, which was sponsored by ONR and PMACWA, was held in Arlington, Virginia (ONR and PMACWA, August 2001), to discuss the status of development needs for SCWO. This conference included many of the leading researchers and developers of SCWO technology from the United States and Europe (both academia and companies), as well as providers of SCWO technology. Presentations and their summaries are available on the Web at:
http://www.aro.army.mil/chemb/people/shaw.htm.

The status of the four key areas for SCWO development were the topic of panel discussions:

- Economics and full-scale applications
- Salt precipitation and plugging
- Safety
- Corrosion.

Executive summaries taken from the Web site for these panel discussions in the last three areas are provided in appendix D because they are germane to TW-SCWO and SCWO processing of chemical agents in general.

3.5 Other Foster Wheeler TW-SCWO Test Programs

The DoD has funded a number of SCWO development programs for dealing with a variety of wastes. The Army, through the U.S. Army Armament Research, Development and Engineering Center with oversight by U.S. Army Defense Ammunition Center, sponsored implementation of a TW-SCWO system for the destruction of smokes, dyes, and explosives at PBA in Arkansas. The Air Force has sponsored GA SW-SCWO development work. GA's summary report for the Air Force program provides an appendix on SCWO development status at NECDF. The DARPA and the Office of Naval Research (ONR) funded both GA SW-SCWO and Foster Wheeler TW-SCWO work for the treatment of shipboard wastes. Some of this work provided the foundation and equipment design concepts as well as materials and equipment for the SCWO tests funded by PMATA and PMACWA. For example, reactor systems from the Navy programs of both vendors have been used in chemical agent SCWO testing. The Foster Wheeler Navy SCWO reactor was shipped to DPG for DEMO II testing.

It is important to note that while considerable development work on SCWO has been progressing for several years, there are still very few papers in the referred literature that describe these efforts and key results. Likely, this situation is due to technology providers considering many of their concepts, developments, and lessons proprietary. In fact, outside of the PMCD work, it is difficult to find any complete reports on pilot-scale or full-scale SCWO studies in the public domain. A search of the Web yields many links to sites with some information, but no complete reports are available in the public domain. A number of reports have been made available by the technology providers on other systems to PMCD and the NRC. In addition, there have been a number of presentations at conferences over the past several years; however, complete presentation materials are not available in many cases.

An overview of work up until 2000 on TW-SCWO reactors for DARPA/ONR and Army Pine Bluff programs was published in the open literature by Foster Wheeler personnel in 2000 (Crooker, 2000). While elements of these two systems were presented, no dimensions or details of the reactors were provided. Information on the TW-SCWO systems and testing for Pine Bluff and the Navy gleaned from the available sources, although certainly not complete, is summarized below.

3.5.1 PBA TW-SCWO. PBA has 104 tons of smoke and dye compounds containing high levels of salts (up to 35 percent salt), which must be destroyed. SNL-Livermore was the formal lead for the project, and provided basic and design research/technical support. The Pine Bluff TW-SCWO system was designed to process 145 kilograms per hour (kg/hr), at 575° to 750°C; 26.3 MPA using oxygen as the oxidant. It was based on bench-scale tests using a 1.1-inch diameter prototype reactor at SNL with Aerojet/GenCorp and Foster Wheeler. The bench-scale experiments were used to develop operating parameters and evaluate design issues for the pilot plant operation at PBA. Foster Wheeler was responsible for construction of this SCWO unit.

Construction of the Pine Bluff system was completed in 1998 and the system was fully commissioned in 1999. Validation testing was planned for 4Q 2000 with operation afterwards, but there are no reports describing these tests in the public domain. A complete report for Pine Bluff was issued to DoD in May 2002, but was not available at the time of this evaluation. While no complete reports are available in the public domain, it is clear from various briefings, notes, and reports that there were a number of operational problems with the Pine Bluff system, including liner deformation and stability problems. This system is currently not being operated at Pine Bluff.

3.5.2 DARPA/ONR Navy TW-SCWO System. The Navy system consisted of a 6-inch diameter reactor with feed rates of 100 to 200 lb/hr. DREs of 99.99 percent were observed with residence times of 6 to 7 seconds. The only published data for the TW-SCWO Navy reactor that could be found for this report were from the EDP (Ecologic, 2001, Volume 2, page 220), Foster Wheeler's 2000 publication (Crooker, 2000), and the conference presentations found on the Web (Ahluwalia, 2001a,b). No other information was available.

Waste feed rates of 45 to 95 kg/hr were used with compressed air as the oxidant. As illustrated in table 3-5 (Crooker, 2000), several corrosive wastes, including photographic solution simulants and chlorinated solvents that produce salts, were investigated. Operating conditions were 24.1 MPA at 594° to 816°C. Preliminary results (Crooker, 2000) demonstrated DREs better than 99.99 percent with CO levels in the effluent below 100 ppm. It should be noted that the highest CO levels were observed for the waste stream that produced/contained the largest amount of salts. Ahluwalia (Ahluwalia, 2001b) claims that the Navy system tested for 71 hours with feed material containing chlorine and fluorine without corrosion or plugging.

Two safety incidents for the Pine Bluff TW-SCWO system were described in Crane Robinson's presentation at the August 2001 SCWO Conference in Virginia (Robinson, 2001). These are discussed in more detail in section 4 of this report.

Table 3-5. Results from Navy Shipboard TW-SCWO Validation Testing

Feed	Hours	Feed Rate (kg/h)	Pressure (MPA)	Outlet Temp (°C)	DRE (%)	CO (ppm)	NO_x (ppm)	TOC (ppm)
Kerosene	N/A	36.3	24.0	307	>99.98	0-84	0-1	2.8
PCTFE[b]	23	36.3	24.0	310	>99.99	1-20	1-2	1.4
TCE[b]	32	46.4	24.2	316	>99.99	0-2	7-13	3.3
Photo	16	46.9	25.0	307	>99.99	50-100	4-25	1.3

Notes:

[a] Adapted from Crooker, 2000.
[b] Diluted with kerosene.

CO = carbon monoxide
DRE = destruction removal efficiency
kg/h = kilograms per hour
MPA = methylphosphonic acid
N/A = not applicable
NO_x = nitrous oxide
PCTFE = polychlorotrifluoroethylene
ppm = parts per million
TCE = trichloroethane
TOC = total organic carbon

3.6 Other SCWO Systems

Two companies, Chematur (Sweden) and Hydroprocessing (Texas), have been developing systems for municipal sewage sludge treatment. The general consensus in the SCWO community is that systems such as these for processing relatively non-corrosive or benign wastes are evolving differently than those for very aggressive or hostile waste streams such as most military wastes including chemical demilitarization wastes (ONR and PMACWA, August 2001, appendix D). Chematur has been collaborating with EcoWaste Technologies and purchased exclusive rights to their technology in 1999. At the August 2001 SCWO Conference (ONR and PMACWA, August 2001), Chematur presented that they have been developing a demonstration plant (based on a tubular SCWO reactor) at feeds up to 250 kg/hr since 1998, and that a large plant at Shinko Pantec at feeds up to 1,100 kg/hr was commissioned in the summer of 2000.

ONR-and PMACWA-sponsored researchers in Germany and Switzerland (Abeln, 2001) are also investigating TW-SCWO reactors. Bench scale plants at waste feeds of 50 kg/h have been described (Kritzer and Dinjus, 2001). Both pipe reactor and TW reactors investigated using relatively simple waste (ethanol), as well as wastes from pharmaceutical, chemical, and paper industries, and municipal sewage sludge at pressures of 27 MPA and temperatures greater than 550°C. Up to 5 percent solid material was present in the feed. They state that from their experience, the most promising solution to the salt problem is a TW reactor consisting of a pressure vessel with a concentric porous inner pipe inside. No details on the porous inner liner were provided. Long-term operation with ethanol and sodium sulfate (5 weight percent), led to high DRE (99.8 percent) and no plugging of the reactor for an 8-hour run; however, salt accumulated in the reactor.

SECTION 4
TECHNICAL EVALUATION

The Ecologic-Foster Wheeler total solution for BG involves weapon disassembly, caustic hydrolysis of agents and energetics, SCWO treatment of hydrolysates using TW-SCWO reactors, and gas phase GPCR to eliminate organic contaminants on decontaminated metal parts and dunnage. This report provides a technical evaluation for the TW-SCWO component of this technology package, which is slated for destruction of hydrolysates of agents and energetics (VX, GB, HD, energetics).

4.1 Technology Overview

4.1.1 Technology Provider. Ecologic is the prime contractor for the total solution team, which also consists of Foster Wheeler, El Dorado Engineering, and Kvaerner Systems. Foster Wheeler is responsible for the TW-SCWO system.

4.1.2 Process. TW-SCWO is one of four primary technologies that are part of the total solution proposed by Ecologic, et al. for BG (Ecologic, 2001). A schematic for the total solution is provided in figure 4.1. The process is divided into six areas:

Area 100	Reverse Assembly/Munitions Access/Continuous Indexing Neutralization System
Area 200	Neutralization and Deactivation
Area 300	SCWO and Brine Separation
Area 400	GPCR
Area 500	Utilities
Area 600	Materials Handling.

Area 300 houses the TW-SCWO operations and the evaporator/crystallizer. For BG, agent hydrolysates are combined with energetics hydrolysates. The complete technology package for BG is composed of many unit operations and is more complex

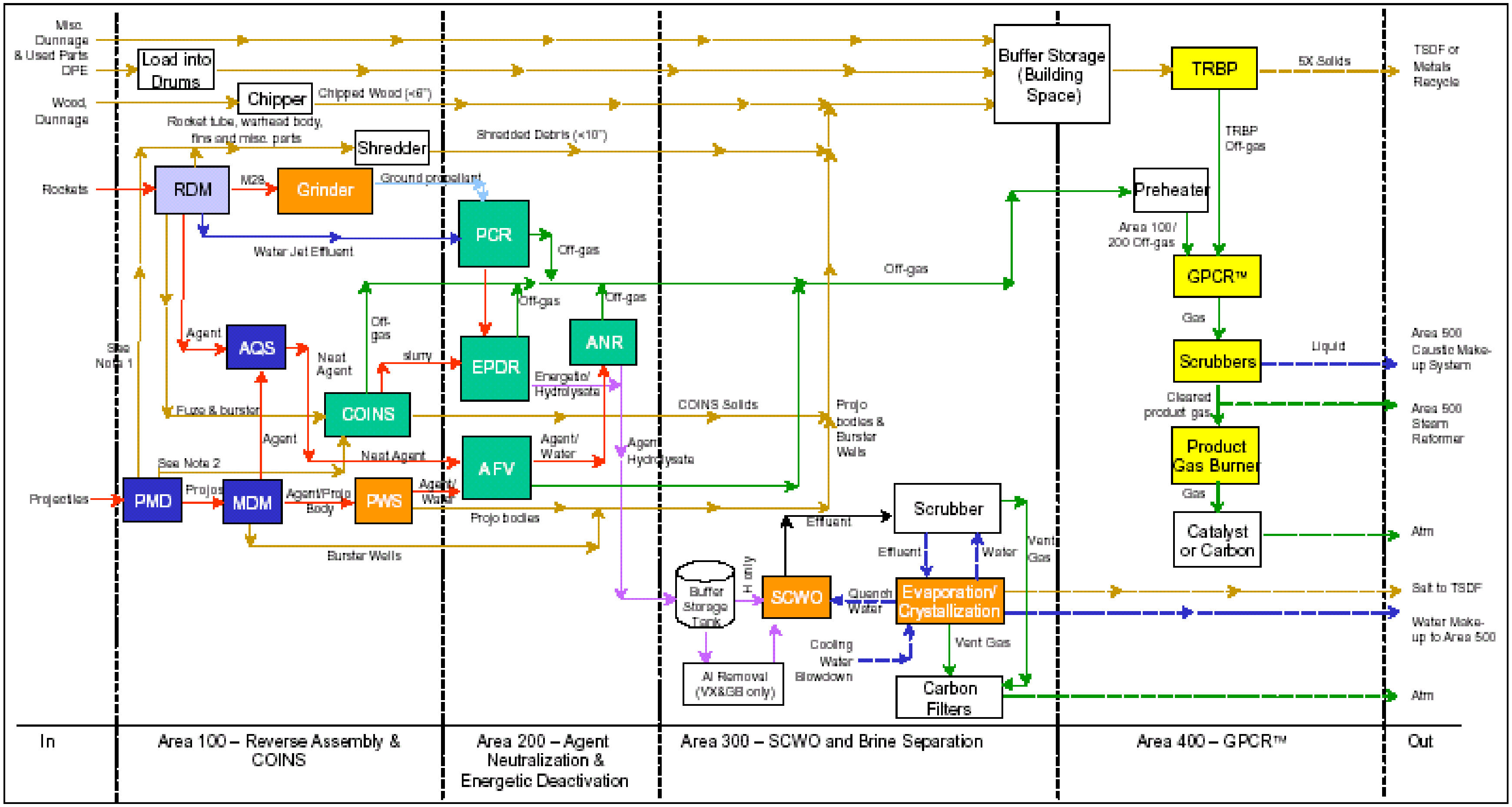

Figure 4-1. Block Schematic of Ecologic-Foster Wheeler Total Solution for BG (Source: Ecologic, 2001)

than NECDF because it must treat all three agents (VX, GB, and HD) in munitions (many contain energetics as well) rather than one agent (VX) in bulk storage in ton containers. The hydrolysates contain a complex aqueous mixture of organic compounds, including Schedule 2 compounds. DEMO II tests demonstrated that the TW-SCWO system cannot tolerate high levels of aluminum hydroxide (Al) in the feed (derived from energetics hydrolysis) so Al removal to levels less than 500 ppm is essential. The technology provider plans to use pH reduction, but the NRC (NRC, 2002a) points out that Ecologic does not possess and has not developed this technology.

The EDP for BG calls for the following:

- Five parallel reactors trains installed and one warehoused spare train, spare sections, liners, and other parts

- All campaigns using three or four reactors for sustained operation with a standby spare reactor available at all times

- Each reactor-train to include an installed spare PCV for automatic online switchover and isolation

- Full-load operating times of 3,700, 1,100, and 700 hours proposed for GB, VX, and H campaigns, respectively

- Operations for GB and H campaigns are planned to require one section changeover.

The stockpiles are to be destroyed using a series of three agent campaigns, where discrete agent types are processed together. Once a campaign is completed, the processing facilities are shut down, decontaminated, and serviced. All agent sensors will be recalibrated to the agent relevant to the next campaign prior to startup and processing.

Four changes to the EDP were proposed to accommodate for lower than expected processing rates in EDS II (Ecologic, 2002):

a. Reactor diameter increased from 11 inches to 11.6 inches (suggested to be less than a $2 million total impact on equipment costs)

b. Three reactors for VX sustained operations, but four for sprint operation

c. Small rate adjustments for GB campaign to avoid using the fifth spare reactor

d. Hydrolysate feed rates to SCWO for H campaign reduced from 100 percent throughput to 90 percent.

It was noted that these changes affect the EDP Total Operations Plan Munitions Draw Down and Campaign Ramp-up Charts as well.

4.1.3 Basis of Evaluation. This technical evaluation is based on the EDS II test reports and the EDP submitted by the technology providers, as well as a number of NRC reports that evaluate SCWO development, EDS II test results, and the EDP as described in section 2. Copies of the presentations given by the technology provider to the NRC (Foster Wheeler 2002d,e) were also available for this assessment.

4.2 Process Efficacy

4.2.1 Process Description. A schematic of the EDS II test reactor is shown in figure 4-2. The full-scale SCWO reactor proposed for BG is shown in figure 4-3. The SCWO equipment can be separated into the following key elements:

- Feed system and pumps

- Injectors

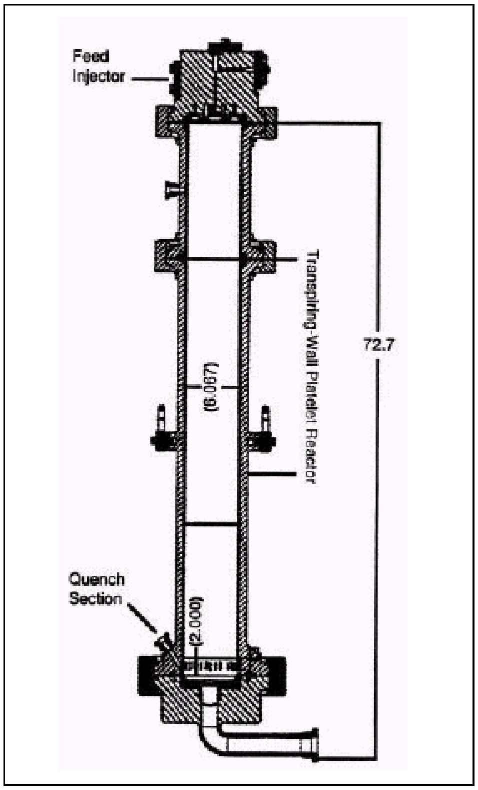

Figure 4-2. EDS II SCWO Reactor (Source: Ecologic, 2001)

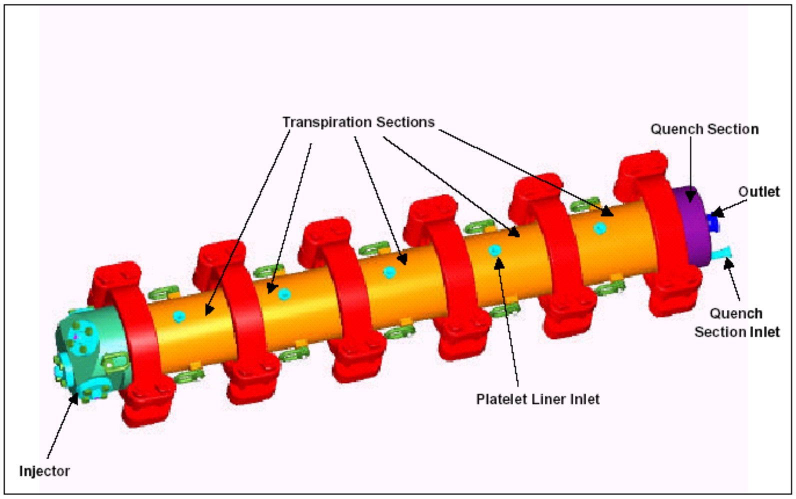

Figure 4-3. BG TW-SCWO Reactor (Source: Ecologic, 2001)

- Reactor and TW liner
- Quench zone
- Pressure letdown system
- Gas/liquid separator
- Heat exchanger.

The reactor and liner are described in the following paragraphs. Other critical components are described along with an assessment of their performance in EDS II testing and their development status in paragraph 4.2.4.

The SCWO reactor consists of a top section that contains the injectors, a pressure vessel, a full-length transpiring platelet liner, and provisions at the bottom of the reactor for adding quench water. Separate nozzles in the injector face at the top of the reactor are used for feeding oxygen, hot water, and a hydrolysate/fuel mixture. A slight stoichiometric excess of oxygen is used. The TW liner is fabricated from Inconel 600 and is assembled in sheets to form platelets to produce pores for transpiration. A schematic of the TW reactor is shown in figure 1-1. The EDS II upper and lower liners were 0.16-inch-thick and were constructed from diffusion bonding of 15 photo-etched platelets. The plan for the full-scale system is to bond a few dummy platelets at the inner diameter of the upper liner for BG to prolong the liner life. A 0.172-inch-thick liner with three additional 0.004-inch-thick “dummy” platelets was used for VX and H testing and is planned for the H campaign for BG. The liner life is estimated by Foster Wheeler to be at least 1,500 hours, which implies the need to change the upper liner at least once at full-scale.

The technology providers state that the liners have a predictable pressure drop as a function of transpiration water flow characteristics. (Note: As described in the following paragraphs, monitoring of this pressure drop provides an indicator of liner performance [for example, mechanical stability and salt build up].) The uppermost liner section has larger pores to allow for higher flows of transpiration water. The operating limit for the pressure drop across the TW liner is 300 psi with desired values from 50 to 150 psi.

The internal dimensions of the proposed full-scale BG reactors are 11.6 inches in diameter and 7.5 feet long. Each full-scale SCWO reactor consists of five 18-inch-long independent reactor sections connected by Grayloc® flanges. Each section is self-contained with its own supply of transpiration water and the housing/liner assembly. The top section, which is distinct from the other four identical sections, is connected to the injector head by a Grayloc® flange. The bottom section is connected to a quench assembly by a Grayloc® flange. The top section is designed for greater transpiration protection. The four bottom sections are identical and interchangeable to allow for replacement of any damaged liner sections. The EDS II reactor, which was 6 inches in diameter and 61 inches long, was comprised of two sections: a top 16-inch section and a bottom 48-inch section. These sections were also connected by a Grayloc® flange. Grayloc® flanges were also used to connect the reactor/liner sections to the injector head and quench area. Table 4-1 lists the size of the equipment used for the DEMO II and EDS II tests in comparison with the proposed BG reactor.

The overall SCWO process proposed for BG is depicted in figure 4-4. A mixture of propylene glycol (auxiliary fuel) and caustic added to agent and energetics hydrolysates are pumped to the feed injection ports of the SCWO reactor. Oxygen or an oxygen/nitrogen blend is fed to the reactor at high pressure through other injectors at the top of the SCWO reactor. A slight excess of oxygen is maintained. For startup and shut-down, a nitrogen-to-oxygen ratio of 4:1 or greater is provided to ensure that high oxygen concentrations will not break through the reactor. Deionized water is preheated (to approximately 590°C), then pumped to high pressure and fed through injectors to mix with the fuel and air at the top of the reactor to initiate the reaction. If sufficient fuel is provided, the temperature increases quickly and the reaction becomes self-sustaining. (Note: Kerosene was used for startup in EDS II, but propylene glycol appears to be proposed for the full-scale system.) Preheated deionized water is also pumped to the internal face of the TW liner in each reactor section. The TW liner is

Table 4-1. Comparison of Pilot-Scale and Full-Scale Systems for ACWA TW-SCWO

Parameter	DEMO II	EDS II Operability 500-hour tests	BG TW-SCWO Reactor
Reactor ID (inches)	6.0	6.0	11.6
Transpiration Water Temperature (°C)	21	150	150
Top Temperature (°C)	747	832	815
Number of Liner Sections	2	2	5
Number of Injectors	4	4	18
Bottom Temperature (°C)	403	533	595
Reactor Average Velocity (ft/s)	0.7	0.65	0.67
Residence Time (s)	6.6	8.0	12.0
Reactor Length (feet)	5	5	7.5
Reactor L/D (in/ft)	6/5	6/5	11.6/7.5

Notes:

BG = Blue Grass
DEMO II = Demonstration II
EDS = Engineering Design Study
ft/s = feet per second
ID = internal diameter
in/ft = inches per foot
L/D = length over diameter
TW-SCWO = transpiring wall-supercritical water oxidation

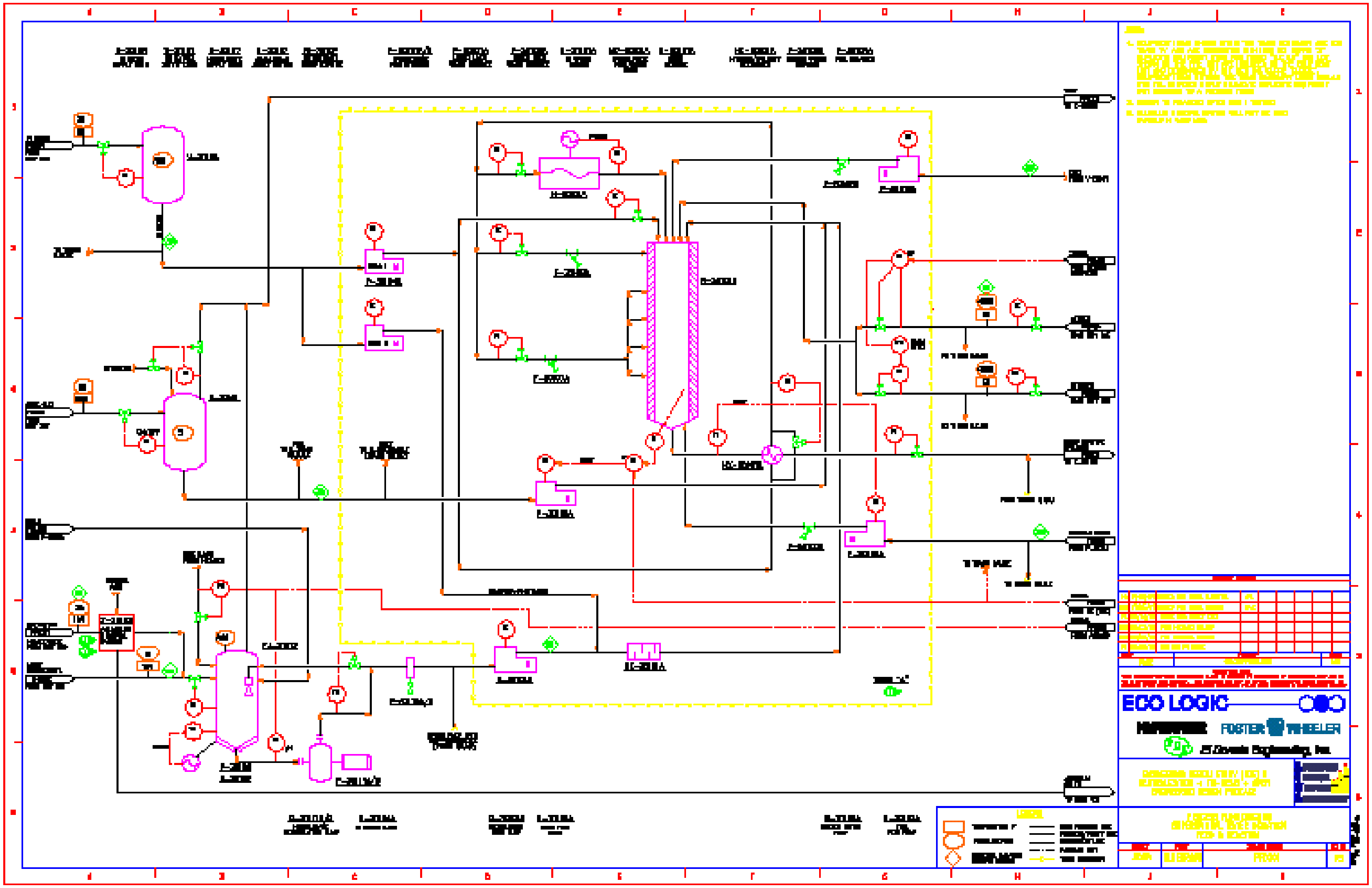

Figure 4-4. Flow Diagram of TW-SCWO Process for BG (Source: Ecologic, 2001)

used to protect the reactor walls from corrosion and salt deposition. Water is also added to the top of the reactor to protect the injector surface from corrosion and salt deposition. Separate pumps are used for feed, auxiliary fuel, oxygen, and deionized water. Flow rates are set to allow for a residence time of approximately 12 seconds in the full-scale BG reactors. The upper end of the reactor reaction zone is targeted to be approximately 815°C and 23.5 MPA. The temperature profile decreases radially from approximately 815°C at the center to approximately 590°C. Transpiration water is added along the entire length of the reactor so the temperature decreases from 815°C at the top of the reactor to approximately 595°C at the bottom. At the bottom of the reactor (quench zone), additional water is added to quench the reaction mixture and cool it below water's critical point to approximately 315°C where most of the product salts redissolve. The quenched reactor effluent is let down to approximately 30 psig through a pressure control valve. The combined effluent from all the SCWO reactors are fed to a venturi scrubber and an effluent knockout drum where the liquid slurry and vapor are separated (G/L separator). The overhead from the effluent knockout drum is separated and cooled to approximately 50°C by the vent condenser using cooling water. The gas effluent from SCWO is scrubbed, monitored, and filtered through activated carbon before release. The liquid slurry is also cooled to 50°C in the effluent cooler before being sent to one of three effluent surge drums, which are used to feed the evaporator/crystallizer that produces water for recycle and solid waste salts. Total remote operation is proposed for the full-scale BG system. The gas effluent is continuously monitored for CO, CO_2, NO_x, N_2O, and O_2. The liquid effluent is continuously monitored for TOC.

4.2.2 Operating Conditions. The operating parameters for the DEMO II, EDS II (Operability 500-hour tests), and proposed full-scale BG systems are compared in table 4-2. The volume and hydrolysate feed of a BG reactor are scaled up by a factor of 5.6 from the EDS II reactor; however, the volume of total transpiration water is scaled up by a factor of 3.2 from EDS II and the total hydraulic feed (total feed in) is scaled up by a factor of 3.85. The ratio of hydrolysate feed rate to the total hydraulic feed rate is 0.17 in EDS II and 0.24 in the BG system. This suggests that overall, there will be less

Table 4-2. Comparison of Operating Conditions for VX/Energetics Hydrolysate

Parameter	DEMO II	EDS II Operability 500-hour Tests	BG TW-SCWO Reactor[b]
Hydrolysate Feed Rate (lb/hr)	65	350	1,960
Hydrolysate/Total Flow	0.024	0.17	0.24
Hydrolysate Flow/Reactor Volume (lb/hr/ft^3)	65	350	350
Oxidant	Air	Oxygen	Oxygen
Additional Fuel (lb/hr)	73	140	500
Diluent (lb/hr)	167	0	0
Face Water (lb/hr)	19	100	300
NaOH (20 percent, lb/hr)	13	80	450
Oxidant (lb/hr)	1,508	400	1,570
Upper Transpiration Water (lb/hr)	402	425	1,100
Lower Transpiration Water (lb/hr)	470	440	1,650
Total Feed Inches (lb/hr)	2,717	2,125	8,190
Reactor L/D	10/1	10/1	7.8/1
Reactor Residence Time(s)	7.6	8.0	12

Notes:

[a] Adapted from Foster Wheeler 2002e.
[b] Values for one full-scale SCWO reactor.

BG = Blue Grass
DEMO II = Demonstration II
EDS = Engineering Design Study
L/D = length over diameter
lb/hr = pounds per hour
lb/hr/ft^3 = pounds per hour per cubic foot
TW-SCWO = transpiring wall-supercritical water oxidation

water relative to salts in the full-scale system as compared to the EDS II system, which could result in differences in salt transport.

4.2.3 Reactor and Liner Performance. The performance of the reactor and its TW liner are at the heart of an effective TW-SCWO system. An evaluation of key performance requirements for the TW-SCWO system is provided in the following:

a. Reactor performance: DRE for Schedule 2 and other organic compounds, and oxidation stability (paragraph 4.2.3.1)

b. Liner mechanical stability, corrosion, and lifetime (paragraph 4.2.3.2)

c. Salts precipitation, transport, and plugging of reactor and upstream and downstream components (paragraph 4.2.3.3)

d. Performance of other critical SCWO equipment

    1. Feed system and pumping (paragraph 4.2.4.1)

    2. Injectors, feed nozzles (paragraph 4.2.4.2)

    3. Quench zone (paragraph 4.2.4.3)

    4. Plumbing upstream and downstream of SCWO reactor (paragraph 4.2.4.5)

    5. Pressure letdown system, PCV (paragraph 4.2.4.4)

    6. G/L separator (paragraph 4.2.4.4)

    7. Heat exchanger, slurry handling (paragraph 4.2.4.5).

e. Long-term operability, availability, reliability (paragraph 4.2.4.6)

f. Choice of oxidant (that is, air versus oxygen) (paragraph 4.2.4.7)

g. Basis for scale-up (paragraph 4.2.5).

A number of methods were used for monitoring overall performance scale-up and operability of the liner and the other SCWO equipment during EDS II testing:

a. Pressure drop across the TW liner

b. On-line conductivity measurements of SCWO effluent (salts transport)

c. Measurement of corrosion metals (nickel, iron, and chromium [Note: These measurements provide only a gross indicator of corrosion in the total system])

d. Post-test inspections (boroscopic examination, video record) of injector, liner, and quench zone and comparison with baseline pretest.

EDS II testing was carried out using agent/energetic hydrolysate simulants and some actual hydrolysates. The composition of simulants used in the testing program is provided in appendix C. Summaries of the optimization test and the 500-hour operability tests for each agent (GB, VX, and H) are provided in tables 4-3 to 4-6.

4.2.3.1 Reactor Performance: Oxidation Stability and DRE. High DREs of Schedule 2 and other organic compounds, as well as overall reactor performance, require the ability to initiate and maintain effective oxidative destruction reactions in the SCWO reactor (that is, oxidation stability). The ability to maintain oxidation stability depends on a number of critical factors including temperature, temperature profile, pressure, fluid density, mixing, flow velocities, flow characteristics, residence time, feed rate, heating value of the feed, as well as oxidant and the overall performance of the reactor, liner,

Table 4-3. Summary of EDS II Optimization Testing

Feed of Hydrolysate Simulant[a]	Feed Rate (lb/hr)	Test Duration (hr)	Reactor Liner Plugging	Reactor Corrosion	Average TOC in Liquid Effluent (ppm)
VX	150	10			6.4
VX	200	10			3.1
VX	250	10			1.36
VX	300	10	No, but increase in lower liner DP indicating some salt deposition	Minor corrosion in upper liner[b]	3.55
HD[c]	100	25	No, but increase in lower liner DP indicating some salt deposition	Minor in lower liner	3.0
GB (with energetics simulant)	300	68[d]	High DP[e]	Minor in upper liner	2.5

Notes:

[a] Compositions of feeds reported in Foster Wheeler Optimization Study Report (Foster Wheeler, 2001).
[b] Determined by post-test inspection.
[c] HD test was originally planned to include energetics hydrolysate; however, undissolved solids in the feed led to plugging problems in feed line within 4 hours, so HD was tested without energetics hydrolysate simulant.
[d] GB/energetics simulant test was performed in three segments of 45, 5, and 18 hours duration. After 45 hours of operation, the feed strainer plugged. A power failure occurred after 5 hours in the second segment of operation. The last 18-hour run was terminated by an operator-initiated shutdown due to a high-pressure drop across the lower liner (>250 psi, see Note “e”).
[e] Attributed to malfunction of deionized water supply system for transpiration water, which led to salt deposition in transpiration pores.

DP = differential pressure
hr = hours
lb/hr = pounds per hour
ppm = parts per million
TOC = total organic carbon

Table 4-4. Summary of EDS II 500-Hour GB SCWO Test

Hydrolysate Feed Rate (lb/hr)	Continuous Operating Time (hours)	Reactor Plugging	Reactor Corrosion	Liner Deformation	Cumulative Operating Time (hours)
250[a]	59[b]	No	Not inspected	Not inspected	59
250[a]	64.5[c]	No	Not inspected	Not inspected	123.5
250[d]	61[e]	No	No	No	184.5
500	316.5	No	Not inspected	Not inspected	501
500[f]	3[g]	No	0.008-inch corrosion in upper liner	5-inch region of upper liner[h]	504

Notes:

[a] Without lead or aluminum
[b] Effluent blockage
[c] Strainer problem
[d] Without aluminum
[e] Oxygen pump trip
[f] With actual GB hydrolysate
[g] Limited supply of actual hydrolysate
[h] Three bump-like deformations and pin-holes.

lb/hr = pounds per hour

Table 4-5. 500-Hour VX EDS II TW-SCWO Test Summary

Hydrolysate Feed Rate (lb/hr)	Continuous Operating Time (hours)	Reactor Plugging	Reactor Corrosion	Liner Deformation	Cumulative Operating Time (hours)
VX/energetic simulant 350 lb/hr	18[a]	No	No		18
"	126.3[b]	No	No		144.3
"	141.17[c]	No	No		285.5
"	35.8[d]	No	No		320.3
"	179.7[e]				500
Actual VX hydrolysate (350 lb/hr)	3[f]				503
Feed rate 350 lb/hr for entire test					

Notes:

[a] Power failure
[b] Main breaker trip
[c] Pressure control valve leak
[d] Power failure
[e] End of test
[f] Limited supply of actual VX hydrolysate

lb/hr = pounds per hour

Table 4-6. Summary of 500-Hour H Campaign for EDS II TW-SCWO Test

Hydrolysate Feed Rate (lb/hr)	Continuous Operating Time (hours)	Reactor Plugging	Reactor Corrosion	Liner Deformation	Cumulative Operating Time (hours)
210	176.9[a]	No	0.012-inch in lower liner	No[b]	176.9
210	91.6[c]	No	0.012-inch in region in lower liner	No	268.5
210	231.5[d]	No	0.042-inch corrosion in lower liner	No	500

Notes:

[a] Liner pressure differential; power failure
[b] Upper liner was replaced after 176-hour inspection due to low (<10 psi) pressure differential across liner. This was believed to be due to a crack or deformation; however, no crack or deformation was observed upon inspection. Cause of low-pressure differential was not identified.
[c] PCV gasket leak
[d] End of test

lb/hr = pounds per hour

feed nozzles (injectors), effective quenching, and downstream processing zones. As discussed in paragraphs 4.2.3.2 and 4.2.4.2, controlling hot spots or high temperature excursions is also important for mitigating heat stress and degradation of the liner, injectors, and other equipment.

The 500-hour EDS II tests demonstrated that TW-SCWO is effective at destroying Schedule 2 compounds. For the GB and VX test, no Schedule 2 compounds were detected (above their detection limits) in any of the liquid effluent samples analyzed (7 samples for GB and 12 samples for VX). Out of 23 liquid effluent samples analyzed for the HD 500-hour test, three showed detectable amounts of thiodiglycol at levels of 10.96 ppm, 66.27 ppm, and 80.84 ppm for the samples taken at 75, 200, and 450 hours, respectively. The technology provider (Foster Wheeler, 2002d) stated that reanalysis of these samples (split samples) led to detection of thiodiglycol at only 0.0113 ppm, 0.0232 ppm, and 0.424 ppm, respectively. No Schedule 2 compounds were detected in the gas samples for GB and VX; however, tributylamine was detected in several samples. Tributylamine was detected only in the 200 and 350 hour samples at levels of 23 milligrams per cubic meter (mg/m^3) and 2.45 mg/m^3, respectively, for GB out of a total of four samples. Out of four VX gas effluent samples, TBA was detected at low levels in only two. The technology vendor claims that the low levels of TBA detected are acceptable, considering TBA is not listed as a hazardous air pollutant. Thiodiglycol was detected in only one of four gas effluent samples for the H campaign; however, the technology provider indicated that thiodiglycol was present in the gas sampling apparatus. Earlier test results demonstrated that loss of power that causes lower temperatures in the reactor can lead to incomplete destruction of compounds containing carbon-phosphorus bonds (for example, MPA, IMPA), so maintaining the oxidation stability and reaction temperatures is critical to the destruction of Schedule 2 compounds.

Observations during EDS II tests indicated problems with maintaining the oxidation stability. The most significant issue was the occurrence of periodic spikes in the concentrations of CO and volatile HCs in the gas effluent. The frequency and intensity of these spikes were greatest for the GB test, but were observed in all three campaigns. As shown in figure 4-5 for the 500-hour GB test, the concentrations for CO were normally 50 to 100 ppm, but spiked to 500 to 1,000 ppm at 5 to 15 minute intervals, with each spike lasting about a minute. The magnitude and frequency of these spikes increased with increasing flow rate (that is, from 250 lb/hr to 500 lb/hr). A number of changes to the operation were made in an effort to alleviate these CO/HC concentration spikes in the gas effluent (NRC, 2002b):

a. Increased quench water flow by 50 percent

b. Co-fed hot water (80 lb/hr) and kerosene (12 lb/hr) during normal operation

c. Increased nitrogen flow to improve system stability and purging

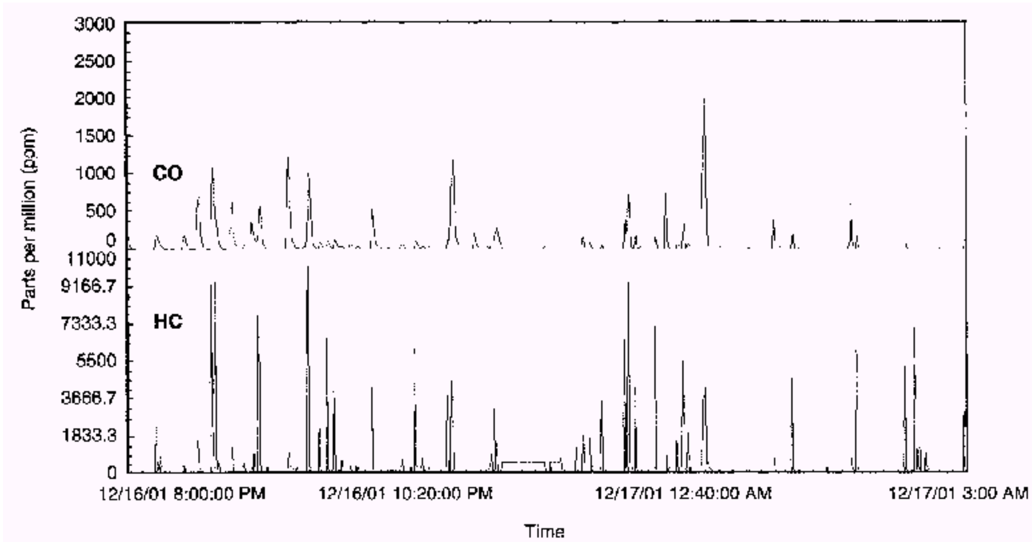

Figure 4-5. Profile of HC and CO Spikes Observed During GB 500-Hour Test (Source: NRC, 2002a)

d. Mixed some propylene glycol (PG) with hydrolysate feed prior to injection into the reactor (no effect observed)

e. Substituted hexylene glycol for PG (no effect observed).

Increasing the quench water flow appeared to reduce the spiking problem. Understanding and reducing the spiking observed during the GB tests were a major objective of subsequent 500-hour tests (VX and H).

The feed rate for the VX campaign was lowered from 500 lb/hr to 350 lb/hr because less spiking was observed at the lower feed rate during the workup run. Several additional changes were made for the VX campaign:

a. Reduced the quench water flow back to the design value

b. Increased size of the feed strainer

c. Decreased the diameter of piping from reactor outlet to pressure control valve

d. Increased nitrogen flow to increase flow velocity in piping.

For the VX 500-hour test, periodic spikes in HC concentrations were observed up to 5,000 ppm. (Note: Spikes above 5,000 ppm were observed, but were interpreted as being caused by instrument calibration or startup/shutdown transients.) Concurrent spikes in CO concentration were observed, but were about one-tenth to one-fifteenth as high as the HC spikes. One-hour rolling averages of HC concentration were below 100 ppm, except for occasional excursions between 100 and 200 ppm. CO concentrations were mostly below 50 ppm with spikes in the 50 to 150 ppm range. In general, the spiking was reported to be less than that observed in the GB tests.

Additional changes for the HD campaign were as follows:

a. Reduced feed rate from design value of 300 lb/hr to 210 lb/hr

b. Increased amount of excess oxygen

c. Installed a static mixer upstream of the reactor for HD test (no effect observed).

Increasing the oxygen in the H campaign reduced the HC spikes after the first 100 hours of operation. Foster Wheeler claims that operators were making adjustments during the first 72 hours. Foster Wheeler also claims that “with few exceptions, the large HC and CO emission spikes in the last 400 hours of test operation are attributable to instrument calibrations, and startup and shutdown transients from the two outages” (Foster Wheeler, 2002c). The 10-hour rolling average of HC spikes was only a few hundred ppm, including these transients.

Several potential explanations were offered by the technology providers as the cause of the HC/CO spikes (Foster Wheeler, 2002e):

a. The EDS II downstream plumbing configuration results in unsteady salt transport downstream of the reactor causing pressure oscillations in the reactor leading to oxidation stability problems (that is, salt formation and periodic sloughing off of salt from downstream piping)

b. Oxidation stability just under the injector (potentially related to #1 above)

c. Inadequate mixing of hydrolysate and PG upstream of the reactor (no effect on premixing observed)

d. Relatively low reactivity of PG.

(Note: It is possible that multiple hydroxylated fuels such as PG are not ideal for start up. Other SCWO testing programs have observed that sugars are a poor fuel for startup. GA has used both kerosene and isopropyl alcohol [IPA] effectively.) It is also possible that pressure oscillations could create flow patterns where organic materials could flow down the colder portion along the liner walls.

The NRC letter report on EDS II (NRC, 2002b) provides an excellent synopsis of the issues associated with the observed spikes in concentrations of hydrocarbons and CO, as well as attempts during testing by the technology providers to alleviate these spikes. In summary, a number of changes were made during operability testing in EDS II to attempt to alleviate the HC/CO spikes, including: changes in feed composition and preparation, feed rates, feed strainer size, quench water flow, and configuration of reactor outlet plumbing. Overall, reducing the feed rates of hydrolysate had the biggest impact decreasing the frequency of the HC/CO spiking. Using excess oxygen to attempt to improve mixing below the injector appears to help alleviate the problem as well. (Note: In the H test report [Foster Wheeler, 2002c], the technology providers state that they do not intend to increase the excess oxygen in the BG system.) The technology providers also state that this problem is manageable at full-scale and have proposed to add a catalytic oxidation unit to treat the gas effluent for permitting reasons. While the spiking in VX and H campaigns was considerably less than in the GB run, the NRC is on record (NRC, 2002b) as stating that “the committee believes that the operability and permitting issues associated with spiking remain to be resolved.” They further conclude “that Foster Wheeler has not clearly identified the root cause of the problem” and that the “cause may lie within the TW-SCWO reactor itself,” that is, “overall the problem appears to have been inadequately resolved”.

In essence, there are two issues arising from the observation of the HC/CO spikes. The first centers around whether the higher HC/CO levels can be managed from a permitting perspective. Treatment of the SCWO off-gas prior to release will likely be required, but this should be manageable. The second concern is the lack of understanding of the root cause of the HC/CO spikes and potential ramifications for and uncertainties about understanding scale-up of the TW-SCWO system. (Note: CO is often used in SCWO testing as an indicator of destruction efficiency or to help monitor proper oxygen input to the system [that is, CO versus CO_2 production].) Many changes were made to optimize the performance of the reactor system at EDS II scale. It is unlikely that everything will scale up exactly the same way, so, at the very least, further optimization will be needed at full-scale work. The HC/CO levels are likely manageable at full-scale via off-gas treatment. Lastly, as discussed in paragraph 4.2.4.6, the necessity of lowering the feed rates in EDS II has implications for full-scale throughput rates (Ecologic, 2002).

4.2.3.2 Liner Mechanical Stability. Observations of liner cracking and deformation as well as corrosion in DEMO II tests (Foster Wheeler, 2000 and NRC, 2001a) raised concerns about the mechanical stability and corrosion-resistance of the TW liner, and therefore, the effectiveness of the transpiration water to provide a protective barrier. (Note: The technology provider also states [Ecologic, 2001, Volume 2] that “a crack at the uppermost row of transpiration pores was observed in the lower liner section of the 6-inch Navy SCWO reactor at the end of the shipboard waste tests.” This crack was repaired and the same liner was used for DEMO II testing.) A number of explanations were offered by the technology providers. Thermal stresses from differential thermal expansion of the liner and its housing are a likely cause. Foster Wheeler's reports on DEMO II and the EDP (Ecologic, 2001) discuss a finite element stress analysis of the liner-to-housing junctions for both liner sections. It was found that the temperature differential can range from 50° to up to 400°C. The full-scale reactor will use sufficient (and hotter) transpiration water to keep the temperature differential below 200°C. SCWO is a high-temperature, high-pressure process, so its continuous operation is preferred to heat-up and cool-down on a daily basis. Effective start-up and shut-down operations are critical as well, since these cause more thermal stresses on equipment and metal fatigue over time. Excessive startup and shutdown operations could thermally stress materials unnecessarily. The EDP also calls out modified shutdown procedures to improve fatigue life. The EDS II operability reactor was fabricated with better quality control. A key goal of EDS II was the demonstration of liner performance with respect to mechanical stability and corrosion.

Some deformation of the liner was observed in the 500-hour GB tests (NRC, 2002a and Foster Wheeler, 2002a). No corrosion or erosion was observed after the 184.5-hour test at 250 lb/hr; however, after the 500 lb/hr test, the top 5 inches of the upper liner had three bump-like deformations and general corrosion. In each deformation, a bulge gradually protruded inward with peak protrusion at the bulge center. There were three pinhole-size leaks at the bottom of one of the bumps. General corrosion of approximately 0.008 inches was observed in this region as well. No deformations below the top 5 inches of the upper liner were observed; however, some patches of general corrosion were observed. No corrosion or deformation was observed in the lower liner. The deformations are believed by the technology vendor to have occurred due to lack of oxidation stability as also indicated by spiking in HC/CO concentrations (previously discussed). Problems with oxidation stability near the injectors could cause high temperatures or high-temperature differentials resulting in thermal stresses. As discussed in the following paragraphs, some erosion of the injector was also observed, which could be indicative of higher than expected temperatures or temperature gradients causing thermal stresses and/or different flow patterns. The NRC Committee (NRC, 2002a) "sees this discovery of deformations and tiny leaks as an issue, but not one so serious as to preclude implementation of the Foster Wheeler SCWO in a full-scale plant." The upper liner was replaced with a new section for VX and H tests.

No cracks or liner deformation was observed during the VX 500-hour test based on monitoring of the pressure drop across both liner sections and visual (boroscopic) inspection. During the 500-hour H test, the upper liner pressure differential fluctuated, dropping to less than 10 psi at one point. The upper liner was replaced (after 176 hours of testing) and no further significant pressure drops were observed during H testing. The technology providers stated that inspection of the liner after 176 hours of testing did not show any indication of a liner crack and no specific cause of the upper liner pressure differential fluctuation was identified.

The reactor sections are held together by Grayloc® flanges in the DEMO II and EDS II reactors as well as the proposed full-scale system. Not much information is provided on the performance of these seals expect that during DEMO II testing, the Grayloc® flanges were removed, and spare sections were installed and rebolted several times. No issues with the seals between sections were reported for the tests.

The operating limit for the pressure differential across the TW liner is 300 psi. For the NECDF program, there was considerable discussion on whether the SW liner should be able to withstand a rapid depressurization or if such an event would just trigger replacement of the liner. A rapid depressurization occurred during EST testing. There was no discussion of rapid depressurization for the TW-SCWO system. No such depressurizations were reported in the test reports. Presumably, the liner could not withstand a rapid depressurization, but the probability, while non-zero, is likely low. The use of parallel reactor systems, rather than one larger reactor, helps reduce schedule risk from such an event.

In summary, although liner mechanical stability was a significant issue in earlier tests, EDS II tests demonstrate that the improvements in the TW-SCWO system allow for liner cracking and deformation to be a manageable issue as long as a degree of oxidation stability can be maintained within the reactor.

4.2.3.3 Liner Corrosion. The observations of corrosion in the upper liner for the GB 500-hour test were summarized in the previous paragraphs. Foster Wheeler claimed that "once the liner deformation issue is resolved, the upper liner is expected to provide significantly longer life than tested" and "Inconel 600 is considered satisfactory for the Blue Grass design." The NRC concurs with Foster Wheeler (NRC, 2002a) that general corrosion of the upper liner at this level would lead to a liner life of at least 500 hours. The test report for VX (Foster Wheeler, 2002b) states that "the upper and lower liner surfaces appeared clean and corrosion-free during post-test inspections." While liner corrosion appears to be manageable for both GB and VX, significantly more corrosion was observed in the 500-hour H tests. The corrosion pattern was significantly different from that observed in the GB tests with the corrosion more prevalent at the bottom of the upper liner and at the top of the lower liner. The levels of corrosion observed in the H test are summarized in table 4-7.

The TW liner is constructed of a set of overlapping platelets. As described by Foster Wheeler and the NRC, the key platelet in the TW liner stack is the metering platelet that ensures uniform transpiration water flow distribution through the liner. This platelet is separated from the liner inner surface by five 0.010-inch thick platelets and three innermost 0.004-inch "dummy" platelets. Transpiration effectiveness begins to deteriorate if liner corrosion approaches the metering platelet. The level of corrosion observed after 500 hours of testing leaves only a 0.020-inch margin of corrosion before the critical metering platelet would become exposed. Foster Wheeler has proposed that they would prefer a margin of 0.030, so they propose adding three more dummy

Table 4-7. Summary of Corrosion Observations During 500-Hour EDS II H Test

Test Time	Corrosion (inches)	Comments
176 hours	0.012	All three "dummy" platelets corroded away
268 hours	0.012	Corrosion spread
500 hours	0.042	Corrosion heaviest near top of lower liner

platelets to the full-scale liner inner diameter. Foster Wheeler has proposed a 500-hour liner life and a liner changeout after approximately 400 hours of operation for the full-scale H campaign. Modularization of the liner to the proposed 18-inch sections should facilitate liner changeout. The NRC is on record as stating that “this seems like a reasonable strategy if corrosion during the disposal operations at Blue Grass proves to be at about the same level as experienced in the test run. However, given the unknown factors that affect corrosion rate, scale-up of the reactor could increase this corrosion rate further, exacerbating the maintenance requirements” (NRC, 2002b). While corrosion appears to be manageable, it is clear that the TW does not provide complete protection from the aggressive SCWO reaction environment. Monitoring of the liner and other components will be required at full-scale along with a maintenance and changeout program.

4.2.3.4 Salts Precipitation, Transport, and Plugging in the TW-SCWO Reactor. No incidence of reactor plugging was observed during all of the EDS II testing. Furthermore, no buildup of salt or salt deposits was discovered during post-test inspection. Conductivity measurements on the SCWO effluent fluctuated to some extent during all three 500-hour tests, which was taken as an indication of some salt buildup in the SCWO reactor or in the plumbing downstream of the reactor. The pressure differential across the liner (DP) exhibited some oscillations further indicating some salt build up on the reactor liner wall. The upper liner pressure drop was typically approximately 100 to 150 psi. For the VX 500-hour test (as well as the VX optimization test), DP rose slowly and steadily suggesting some salt deposition.

In summary, the TW-SCWO liner appeared to allow for effective salt transport within the reactor throughout the EDS II tests. Issues with salt holdup or precipitation downstream of the reactor are discussed in the following paragraphs.

4.2.4 Other Equipment and Long-Term Operability. A number of other critical components of the TW-SCWO process must perform well for an effective treatment. Other equipment vital to the TW-SCWO operation is further evaluated based on its performance during EDS II testing and recommendations for the full-scale design.

4.2.4.1 Feed and Pumping. The front-end of the SCWO system comprises the feed tanks and the pumps to deliver the hydrolysate feed and other chemicals (for example, oxygen, auxiliary fuel) along with clean water. Reliable pumping of fluids is essential for operation of the SCWO system. A number of fluids including deionized water must be pumped to high pressure by the TW-SCWO system. There were some problems with plugging or fouling of the feed system upstream of the SCWO reactor. The strainer plugged in the 250 lb/hr GB test. The technology provider claims the belief that this was due to solids in the feed from improper preparation of the simulant and that these solids would not be present in actual GB. The plugging was removable by flushing with water. Fluctuations were observed in the pressure drop across the feed strainer in the 500-hour VX test, which Foster Wheeler claims was caused by solids precipitation due to the presence of lead (undissolved lead stearate in the simulant). Nonetheless, it is clear that the feed system cannot tolerate many solids in the feed and it is critical to remove solids prior to processing through the feed system. At full-scale, solids are filtered upstream of TW-SCWO hydrolysate feed tanks (filtered solids are slated for treatment in the GPCR at full-scale).

4.2.4.2 Injectors. The injectors are designed for rapid mixing to initiate oxidation. Separate nozzles are used for feeding oxygen, hot water, and the hydrolysate/fuel mixture. Per Foster Wheeler, "the SCWO injector is an array of carefully machined ports in a solid metal mass that produce the correct points of entry and turbulent mixing for each input." The injector face is constructed of Inconel 625. Figure 4-6 provides a schematic of the injector systems used in the EDS II reactor and proposed for the BG system. Scale up of the injector is done by adding more parallel injectors of similar dimensions (orifice diameter, flow rate, injection velocity and pressure drop across the orifice), that is, the flow rate in the full-scale system is accommodated by increasing the quantity of injectors rather than increasing the size of the injectors. The goal is to have the reactants mix at approximately the same distance from the top of the reactor in both systems. The scaled up system goes from four injectors in the EDS II system to a total of 18 (6 in an inner row and 12 in the outer row) on each BG reactor injector face.

Volume II Figure 70 EDS II and Blue Grass Injector Design Comparison

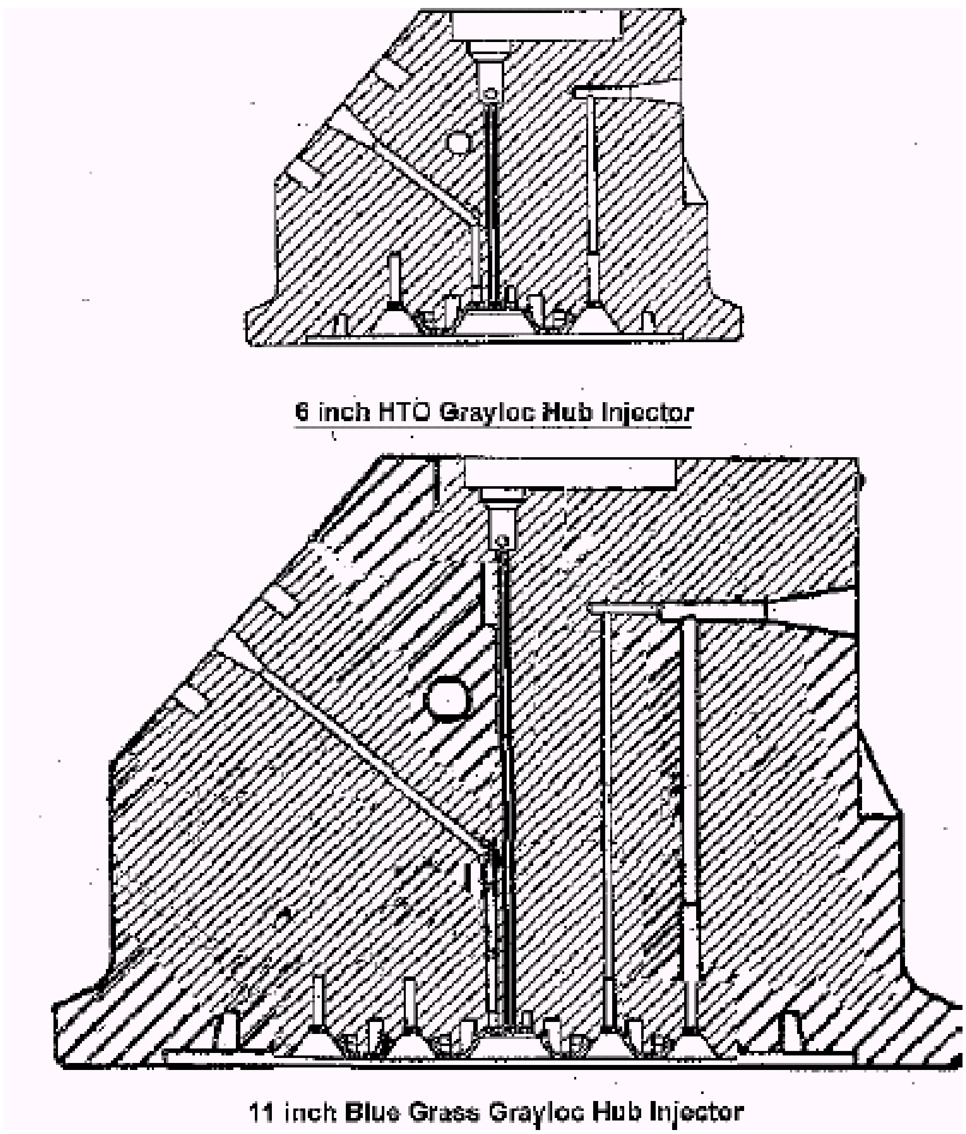

Figure 4-6. Illustration of Injectors for EDS II and BG

(Note: Drawing from EDP [Ecologic, 2001] for 11 inches. Presumably 11.6-inch head would be similar.)

The GB Operability Test Report (Foster Wheeler, 2002a) indicates that erosion of the injector face was observed in one instance with loss of material in two areas of the injector. Erosion less than 1/64th of an inch was observed in one area and 1/32nd of an inch erosion was observed near the oxygen ports. The injector face is approximately 1/8-inch thick. Foster Wheeler states that the injector will function satisfactorily for several hundred additional hours and the MOCs are sufficient. Post-test inspection after the VX and H tests demonstrated that the feed injector underwent some surface corrosion and the hydrolysate orifices had enlarged during operation. Foster Wheeler claims that "on-line indicators and analytical results do not suggest any deterioration in injector performance for the 500-hour H test."

Feed nozzles were an open issue from the Engineering Scale Test (EST in NECDF program) for the GA SW-SCWO system where significant degradation was observed. It is speculated that nozzle degradation was likely due to the non-dispersed two-phase flow of fuel and water combined with the use of pure oxygen as the oxidant, which resulted in significantly higher temperatures at the nozzle. The EST reactor system continued to provide acceptable DRE with a degraded nozzle. Plans were changed to use a water-soluble fuel, isopropyl alcohol, as a startup fuel instead of kerosene. The EDP originally proposed propylene glycol as the supplemental fuel, but kerosene was also used in the EDS II operability tests. Kerosene is not water-soluble. Problems with feeding multiphase system and water insoluble fuels were believed to be responsible for hot spots in the nozzle degradation observed in GA's EST testing.

The exact mixing characteristics of the nozzle or injectors in SCWO systems is not well-characterized nor understood; however, it is clear that the entry points of feed and effective mixing are critical to reactor performance. Any significant deterioration in injector performance would impact reactor performance, oxidation stability, and DRE. Significant in homogeneities in mixing could lead to hot spots, thermal stresses, or poor oxidation stability. While no other reported data are available for this evaluation and the NRC did not raise any specific concerns with respect to injectors, the observation of erosion in EDS II testing does raise the issue of injector material stability, reactor performance, and oxidation stability.

4.2.4.3 Quench Zone. The reaction mixture is cooled to 315°C, which is below the critical point of water, by the addition of clean water at the bottom of the reactor (the quench zone). In addition to cooling the fluid, the intent is to redissolve most, if not all, of the salts. The environment in the quench zone is much different than in the reaction zone. In the quench zone, where the density of water is considerably higher, conductivity increases as do the solubility and ion product of salts; therefore, corrosion mechanisms can be different than those in the reaction zone and are often found to be higher. (Note: It is believed that chloride is more corrosive at sub-critical temperatures than in less dense water considerably above its critical point.) In the quench zone it is not possible to protect the walls with transpiration water. The volume of the quench water used in EDS II or proposed for BG is not explicitly called out in the test reports or the EDP. Scale up of the quench zone may be straightforward, but there is no discussion of this issue. The test reports did not discuss any monitoring of the quench zone per se; however, no problems were explicitly called out. In addition, no problems with the Grayloc® seal between the last reactor section and the reactor bottom were noted. The ability to remove and replace the bottom of the reactor could reduce scale-up risks for the TW-SCWO system. (Note: Considerable work has gone into investigating and modifying the quench zone geometry and MOCs for the SW-SCWO reactor in GA's ACWA testing of VX hydrolysate to handle high amounts of corrosive salts for a removable C-276 liner. It is unclear if any parallels can be drawn between this work and the TW-SCWO system regarding the quench zone, because the reactor contents of the TW-SCWO system contain considerably more water due to the addition of transpiration water.)

4.2.4.4 Pressure Letdown and G/L Separation. Pressure letdown was called out by the NRC as one of the critical elements of SCWO processing of VX hydrolysate at NECDF (NRC, 1998). Pressure letdown of complex, salt-containing SCWO effluents is not straightforward and cannot be considered a conventional chemical industry process. The TW-SCWO system reduces the pressure of the SCWO effluent through a PCV prior to G/L separation (as shown in figure 4-4). The reactor effluent reduced from 24.2 MPA to less than 350 kPa (45 to 50 psig) through a PCV. Early testing (DEMO II) indicated that significant amounts of aluminum hydroxide in the feed caused excessive erosion of the PCV. This observation was one of the drivers for removing most of the aluminum prior to SCWO processing.

The position of the PCV was monitored during the 500-hour tests. Some erosion and valve wear were observed during post-test inspections for all the tests. In addition, changes in the valve position (that is, percent open) occurred with time; however, in general, no deterioration in the ability to control pressure for 500 hours of cumulative operation was observed. During the GB test, the valve opening changed from 23 to 65 percent during the two segments of the 184.5-hour run, but this behavior was not observed in the third segment of this run. Foster Wheeler states that “the experience for the remainder of the 500-hour run was very satisfactory.” The PCV trims (stem and seat) were replaced at each of the two shutdowns (176,268 hours) during the H test as routine maintenance. The observed valve wear did not affect valve performance; the valve opening did not reduce appreciably. It did appear, however, that solids were deposited in the beginning of each run but were dislodged later in the run. Processing in the VX campaign witnessed the most problems with the PCV. The valve position varied considerably during the VX tests: (1) from 15 to 35 percent during the first 126-hour segment of the 500-hour test and (2) from 60 to 80 percent after the valve trim was changed during the second long segment (141 hour run) and from 60 to 70 percent during the third long segment. The technology provider believes these valve changes are caused by periodic deposition and dislodging of solids in the valve opening. In one instance during the VX test (at 285 hours), the gasket of the PCV leaked. This caused a shutdown. Some deposits were observed on the valve during inspection after the shutdown at hour 285. These deposits could be readily washed off, but no analysis of the deposit was reported. It is planned to have an installed on-line spare PCV for each reactor in the full-scale system. The dimensions of the PCVs for the full-scale system will be larger than the EDS II system. While this perhaps suggests less opportunity for plugging, erosion will likely still be an issue that will require monitoring and maintenance.

(Note: Another strategy for pressure letdown is to do a G/L separation at high pressure and let down the gas and liquid through different PCVs. This method provides for a lower velocity for the denser liquid phase and removal of solids from the higher velocity gas letdown system.)

After pressure letdown through the PCV, the effluents from all reactors in the full-scale system are to be combined and sent to a venturi scrubber and knockout drum where a liquid slurry will be separated from the gas effluent.

4.2.4.5 Heat Exchanger for Slurry Cool-Down. For the continuous long-term test runs, the effluent heat exchanger was replaced by a scrubber system where a slurry cooler was used. The flow rate and temperature of the effluent is measured at the cooler exit. Increases in the temperature indicate plugging problems with the heat exchanger. Except for one run segment in the GB tests, Foster Wheeler states that “the effluent temperature had some minor fluctuations; however, the overall temperature remained relatively constant,” which “implies no fouling during the run.” In one segment the effluent temperature gradually increased from 82° to 120°F, indicating fouling of the cooler. (Note: The observed temperature increases are still below the design temperature of the heat exchanger.) Examination of the heat transfer surface revealed a “thin coating of a powdery substance.” Similar behavior was observed in the VX and H runs. For example, over the 500-hour operation of the VX test, the effluent slurry cooler performance deteriorated steadily as witnessed by a gradual temperature increase from 80° to 120°F. Foster Wheeler’s observation suggests that occasional fouling may require change in the heat exchanger design for BG such as allowing for modularity for periodic isolation and cleaning.

The back-end of the SCWO system is downstream of the reactor and must manage effluent from approximately 600°F and 35,00 psi to separated gas and liquid slurry streams at near atmospheric pressure and lower temperatures. Observations of fouling upstream (paragraph 4.2.4.1) and downstream of the reactor demonstrate the importance of being able to handle salts and avoid plugging in all the SCWO system piping. The HC/CO spiking (oxidation stability) may also be affected by downstream salt transport. Periodic maintenance and provisions for redundancy and isolation of components that could potentially plug will be required for the full-scale operation.

4.2.4.6 Long-Term Operability, Availability, Reliability. Long-term operability was a key metric for EDS II testing. None of the operability tests were run continuously for 500 hours. Reasons for intermittent shutdown or termination are provided in the footnotes of the tables summarizing the EDS II testing and have been discussed by both the NRC and the technology providers. A number of other operating problems were also experienced during EDS II testing, some of which are listed in the following paragraphs. Nonetheless, the availability of the TW-SCWO system was high. A.D. Little (ADL) has provided a brief report to PMACWA (A.D. Little, 2002) on the availability of the TW-SCWO system during EDS II operability tests. The availability for the 500-hour GB test was validated to be 90.2 percent including the first shutdown event, which ADL recognizes did not involve the SCWO reactor or related critical equipment (95.5 percent excluding first shutdown). The availability for the VX 500-hour test was 92.5 percent (Ecologic, 2002), while the availability calculated for the H 500-hour test was 91.7 percent (Foster Wheeler, 2002c). The Army set a goal of 75-percent overall plant availability (through identification of 98 "non-working" days by PMACWA including 28 non-plant days due to unanticipated plant shutdowns). The proposed revised feed limits require an availability of 95.5 percent for all campaigns, including H, to maintain the EDP-proposed total schedule for each agent campaign and therefore add no additional time to the operations phase of the plant (Ecologic, 2002). This availability still allows for the fifth SCWO reactor to be an on-line spare. Such a high availability for the full-scale system seems overly optimistic, particularly in light of all the remaining scale-up uncertainties and the lack of any operation of a fully integrated system. It is clear that corrosion needs to be managed for at least the H campaign, and potentially for the other campaigns, so the schedule and operations will need to accommodate liner replacement. The risks to the processing schedule at reduced feed rates should be further investigated along with mechanisms to accommodate lower system availability.

The EDP proposes that the full-scale SCWO plant will be operated 24 hours, 7 days a week. The intended operational life of the total solution is 5 years. The design life of all the equipment has been set to exceed the 5-year minimum. Area 300 poses challenges to reliability particularly due to high-pressure operations and scale-up uncertainties in the SCWO process. Reliability in the full-scale system is also handled with strategy of redundancy approach, that is, five parallel reactors with one being an “on-line spare.” The use of smaller multiple reactors lowers the overall risk of scale-up and provides flexibility in processing without requiring large ranges of turndown capability that would be required for fewer, larger reactors. In the full-scale design, provisions for storage (approximately 1 day) are provided between the SCWO process in Area 300 and hydrolysis/neutralization in Area 200, allowing for some uncoupling of the two processes.

Commercial production data for SCWO is very limited. The EDP claims Ecowaste’s Huntsman facility achieves more than 80 percent availability, but this waste contains no solids or salt-producing materials so it is a much simpler, less corrosive waste.

A number of other operational problems were encountered, the following are examples (not a complete list):

a. During early tests in the GB operability tests, there were problems initiating the SCWO reaction with propylene glycol. Kerosene was subsequently used as the initiating fuel.

b. Loss of reaction was experienced in several cases during workup runs for the GB test, which was resolved by continuing flows of kerosene during the testing.

c. Piping leak occurred near the PCV that was readily fixed but resulted in 1 day of downtime.

d. Seal leak occurred in the condensate pump.

e. The pressure relief valve actuated several times while diagnosing oxidation stability problems in the GB test, which resulted in periods of downtime.

f. Lost deionized water supply during a workup test and an electrical circuit overloaded due to an instrument air compressor malfunction.

g. Experienced a leak in the flange between the injector and the upper reactor during a VX systemization run due to "certain scarring of the sealing surface of the upper housing" (Foster Wheeler, 2002b).

h. The hydrolysate flow meter malfunctioned.

i. Several pipe joints leaked, which were associated with the "tight pipe routing in the pilot plant design" (Foster Wheeler, 2002b).

j. A computer control malfunctioned, which occurred during a power failure.

k. The effluent flow meter malfunctioned.

Many of these issues are what might be commonly expected to be encountered in pilot-scale studies. Most were rectified during testing. Nonetheless, some additional work during systemization and pilot-scale testing of the full-scale system will likely be required.

4.2.4.7 Oxidant: Air versus Oxygen. Discussions on the use of air versus oxygen as an oxidant for SCWO processing of chemical agent hydrolysates has been part of several reports in PMATA's NECDF SCWO program. Oxygen allows for higher processing rates because there is no need to accommodate all of the nitrogen present in air. The NRC has cautioned about downstream safety issues with enriched oxygen. They also discuss general problems anticipated in switching from air to oxygen in the GA's NECDF system (NRC, 2000). Foster Wheeler plans to blend in nitrogen for startup and shutdown. Both the GA EST and the Foster Wheeler Pine Bluff testing programs had problems with the commercial oxygen supply systems. Foster Wheeler did not experience these problems in the EDS tests, after the system was upgraded by the supplier. The oxygen/nitrogen system caused major problems during early phases of the GB operability test, but once these were corrected, the system supported testing without a single incident. The EDS II testing had over 2,000 hours of test operation with oxygen. Foster Wheeler states that there was no loss of oxygen system availability during these tests. They do call out the need for on-line maintenance to the cold-end of the pump and an installed spare.

The NRC noted that "assuming the instability problems encountered when operating on oxygen can be resolved, oxygen generated from liquid oxygen appears to be a suitable oxidant" (NRC, 2002a). Foster Wheeler claims that the oxygen system is lower in capital cost and that it is less expensive to pump liquid oxygen than compress air. They further noted that the chemical process industry has significant experience with liquid oxygen systems.

4.2.5 Basis for Scale-Up. The problem of reactor scale-up may be summarized as follows: Given a successful experiment conducted in small-scale equipment, specify a design that will operate equally as well (or better) at full scale. The EDP (Ecologic, 2001, 2002) describes that the basis for scale up from EDS II to BG is based on three criteria:

- Destruction of Schedule 2 compounds
- Long-term operability with respect to plugging
- Long-term operability with respect to corrosion.

While scale-up from pilot-scale testing and operations is a standard engineering practice (and scale-up factors are usually much larger), there is still a general lack of fundamental understanding of the SCWO processing parameters including kinetics, flow characteristics and mixing, and salt transport. This situation, coupled with lack of experience at larger scales, has required a significant testing program to develop a basis for scale-up, and some technical and programmatic risks for scale-up of SCWO remain. For example, without a fundamental understanding of the fluid dynamics and salt transport, one cannot, a priori, predict how salt transport will scale.

The basis for scale-up of the EDS II system to the full-scale BG system is volumetric, with the intent of providing the same (or lower) hydrolysate flow-per-unit reactor volume for the BG system, as demonstrated in EDS II. The proposed feed rates are equal to the EDS feed rates multiplied by the ratio of volumes of a BG reactor and the EDS reactor. The ratio of the volume of a single proposed BG reactor to the EDS II reactor is 5.6. The intent of Foster Wheeler's scale-up strategy is to ensure equal (or greater) residence time for the full-scale reactors, as compared to the EDS reactor. This strategy assumes that DRE scales with volume. While this is likely, the full-scale system should provide some flexibility in processing rates. The current proposed schedule (see paragraph 4.2.4.6) is very tight. The EDP also claims that the injector configuration for the full-scale system should ensure mixing of reactants similar to that in EDS II. ASPEN simulation modeling was used to understand the axial temperature profile in both the EDS II and BG systems. The EDS II system operated with a temperature profile of approximately 815°C to 510°C and a residence time of 9 seconds. The BG system is designed to provide a temperature profile of 815°C to 535°C and a residence time of greater than 10 seconds.

The EDP (Ecologic, 2001) also discusses an "Effectiveness Factor" for efficiency of protection of the liner by transpiration water. References to presentations at conferences are provided, but no more details or reports in the public domain are given. The EDP claims that "using the calculation of the effectiveness factor as a basis of comparison, the operational parameters of the 'scaled' reactor can be developed from the known operational parameters of the demonstration EDS II reactor." A table was provided in the EDP where the model indicates a "higher" wall protection in the BG reactor than the tested EDS II system.

In summary, Foster Wheeler claims that volumetric scale-up also ensures an equal (or smaller) plugging and corrosive load. They also state that they have considerable scale-up experience in the utility industry. The TW liner is designed and constructed by

Aerojet, which has over 40 years of platelet technology experience in the defense and civilian space programs. It was stated that they have used design models for decades.

Foster Wheeler has scaled up the 6-inch U.S. Navy SCWO reactor for shipboard wastes at up to 300 lb/hr feed from a 1.1-inch TW reactor at 4 to 8 lb/hr throughput, which represents a scale-up factor of 5.5 OD and 38 to 75 on throughput. Aside from preliminary results published in 2000 (Crooker, 2000a) and the information provided in the EDP, no detailed reports on this system were available for this technical evaluation.

Foster Wheeler also claims the following regarding scale-up:

a. The proposed pumps, Grayloc® fittings, valves, exchangers, tanks, outside reactor vessel are well within known ASME design bounds.

b. Increasing the reactor size does not change the transpiration effect function since the flow rates are modeled and increased in the full scale system to provide the same pressure and flow per unit area. (Note: The total water flow relative to salts, for example, hydrolysate is less in the full-scale system; the ratio of hydrolysate feed to total water flow is 0.24 in BG and 0.17 in EDS II.)

c. As long as the injectors provide the same mixture of the increased flows, they believe DREs should be within design limits.

d. Increasing the injector size and flow rates is within Aerojet's proven prior experience in injector design.

e. The transpiration water flow needs to be increased to the larger full-scale system. Due to success with transpiration in going from a 1.1-inch to a 6-inch diameter in the Navy system, this scale-up is considered well within normal engineering practices for flow design and pressure control.

Note: An independent assessment panel that evaluated PMATA's funded SCWO development by GA for NECDF stated that they were confident that the basis for scaling up the SCWO system for NECDF was sound (SAIC, 2001) from a processing standpoint. The key scale-up risk for the NECDF SCWO program was identified by the panel to be fabricability and mechanical stability.

4.2.6 Maturity of Technology. While the TW-SCWO and SW-SCWO technologies proposed for chemical agent hydrolysate treatment have evolved considerably during the Army testing programs, SCWO cannot be considered a mature technology, particularly for complex, corrosive wastes. Many improvements have been made, and a number of the problems observed during testing have been resolved. As described in the EDP (Ecologic, 2001), "the transpiring wall reactor is a unique piece of equipment in the chemical process industry." No systems larger than those tested in the PMACWA have been employed to process highly corrosive, high salt containing waste as complex as chemical agent hydrolysates, so the technology cannot be considered mature from a scale-up standpoint. The total solution for BG requires integration of all of the unit operations, including SCWO. To date, testing has focused on operation of the individual unit operations, and no integrated system has been constructed nor operated. A key problem with technology maturity is that no unit that mimics a full-scale system has been run.

4.2.7 Process Monitoring and Control. The EDP describes a Distribution Control System (DCS) that monitors and controls all aspects of the SCWO process including the reactor pressure, the reactor time-temperature profile, the TW, the effluent system, and the evaporator/crystallizer system. Each of these control functions is accomplished using a network of pressure, flow, temperature, and analytical sensors linked to control valves through the DCS control loops. The following parameters were automatically monitored during EDS II and recorded by the computer control system:

- Hydrolysate Feed Rate
- Feed Temperature

- Feed pH
- Oxidant Flow Rate
- Nitrogen Flow Rate
- Oxidant Temperature
- Start-up Fuel Feed Rate
- Start-Up Water Flow Rate
- Upper Transpiration Water Flow Rate
- Upper Transpiration Water Supply Temperature
- Lower Transpiration Water Flow Rate
- Lower Transpiration Water Supply Temperature
- Diluent Water Flow Rate
- Caustic Feed Rate
- Spike Fuel Feed Rate
- Quench Water Flow Rate
- Reactor Exit Temperature
- System Pressure

- Upper Liner Pressure Drop
- Lower Liner Pressure Drop
- Oxygen in Gas Effluent
- CO_2 in Gas Effluent
- CO in Gas Effluent
- N_2O in Gas Effluent
- HC in Gas Effluent
- TOC in Liquid Effluent
- Effluent Conductivity
- pH of Liquid Effluent.

In the full-scale system, the following materials will be pumped to the SCWO system under flow control using high pressure pumps:

- Hydrolysate feed
- Start-up fuel
- Spike (auxiliary) fuel
- Oxygen
- Deionized water.

Propylene glycol is added to the hydrolysate feed/water mixture by a spike feed pump as a spiking agent (that is, auxiliary fuel) to maintain a constant heat release in the reactor and for control of the reactor outlet temperature.

Quench water will be pumped under temperature control; the flow rate is to be adjusted based on the particular hydrolysate being processed. Pressure will be controlled with a PCV.

Effluents are monitored. Brine from the venturi scrubber is monitored for pH, conductivity, and TOC. Detection of organic carbon above the design level would trigger diverting the stream to the off-specification vessel. A system is needed to condition the brine sample to the TOC analyzer to avoid interferences from inorganic carbon. Vent gas in the stack is monitored for oxygen, CO_2, hydrogen, CO, NO_x and N_2O. Laboratory analytical testing (both onsite and offsite laboratory work) is planned to validate and supplement the continuous process monitoring.

Local interlocks are provided to prevent pumps and rotating agitators from running dry. Table 4-8 summarizes instrument interlocks (for one SCWO train) as described in the EDP (Ecologic, 2001), which also states that the interlocks can be provided either through the DCS or will be routed through the dedicated hard-wired Safety Interlock System, as necessary.

In addition to monitoring the performance and effluents, monitoring of the SCWO equipment and liners will be important. The NRC recommended in their EDS II letter report that "all SCWO testing experience to date indicates that the operating environment associated with the SCWO reactions poses corrosion and material durability challenges per se, regardless of the SCWO process. Therefore, the committee believes that use of the SCWO process will require that the operator have an aggressive monitoring program in place to ensure that planned completion schedules are not severely compromised by higher than expected maintenance and repairs."

Table 4-8. SCWO Instrument Interlocks from the EDP

P&ID No EDF-300	Instrument	Description	Action
101A	LSLL-0002	V-30102 hydrolysate low level	Shutdown P-30101A-E and shutdown all SCWO trains
101B	LSLL-0007	V-30106 DI water low level	Shutdown P=30104A-E and shutdown all SCWO trains
101B	LSLL-0008	V-30101 spike/fuel low level	Showdown P-30102A-E, P-30103A-E and shutdown all SWO trains
102A	PSLL-0016	Low oxygen header pressure	Shutdown all SCWO trains
102A	PSLL-0019	Low nitrogen header pressure	Shutdown all SCWO trains
102A	FSLL-1001A	Low oxygen flow-train A	Shutdown SCWO train A
102B	FSLL-1001B and TSLL-1012	Low N_2/O_2 ration (startup) and reactor low outlet temp	Shutdown SCWO train A
102B	YL-1013	Loss of P-30101A	Shutdown SCWO train A
102B	PSHH-1011	P-30101A high disch pressure	Shutdown SCWO train A
102B	PSLL-1011	P-30101A low disch pressure	Shutdown SCWO train A
102B	YL-1014	Loss of P-30102A	Shutdown SCWO train A
102B	PSHH-1012	P-30102A high disch pressure	Shutdown SCWO train A
102B	PSLL-1012	P-30102A low disch pressure	Shutdown SCWO train A
102B	YL-1015	Loss of P-30103A	Shutdown SCWO train A
102B	PSHH-1013	P-30103A high disch pressure	Shutdown SCWO train A
102B	PSLL-1013	P-30103A low disch pressure	Shutdown SCWO train A
103A103A	TSHH-1009 TSHH-1010	H-30101A high temperature H-30101A high temperature	Shutdown SCWO train A Shutdown SCWO train A
103A	PDSLL-1040	R-30101A lower liner low dP	Shutdown SCWO train A
103A	PDSLL-1041	R-30101A upper liner low dP	Shutdown SCWO train A
103A	FSLL-1018	R-30101A upper liner low flow	Shutdown SCWO train A
103A	FSLL-1019	R-30301A lower liner low flow	Shutdown SCWO train A
103A	TSHH-1011	R-30101A high skin temperature	Shutdown SCWO train A
103A	TSHH-1013	R-30101A high quench temperature	Shutdown SCWO train A
103A	PSHH-1020	R-30101A high reactor pressure	Shutdown SCWO train A
103A	PSL-1019	P-30106A low disch pressure	Shutdown SCWO train A
103A	FSLL-1022	P-30106A low flow	Shutdown SCWO train A

Table 4-8. SCWO Instrument Interlocks from the EDP (Continued)

P&ID No EDF-300	Instrument	Description	Action
103B	PSH-1029	SCWO Train A high letdown pressure	Shutdown SCWO train A
103B	PSLL-1027	P-30104A Head 2 low disch pressure	Shutdown SCWO train A
103B	PSLL-1028	P-30104A Head 1 low disch press	Shutdown SCWO train A
103B	YL-	Loss of P-30104A Head 2	Shutdown SCWO train A
103B	YL-1027	Loss of P-30104A Head 1	Shutdown SCWO train A
110B	ASHH-0009	High oxygen in stack	Shutdown all SCWO trains
110B	LSHH-0021	V-30105 high level	Shutdown all SCWO trains
111	LSLL-0022	V-30210 recycle water low	Shutdown all SCWO trains
113	LSH-024/025	V-30217A high level	Shutdown all SCWO trains
113	LSH-026/027	V-30217B high level	Shutdown all SCWO trains
113	LSH-028/029	V-20317C high level	Shutdown all SCWO trains
114	LSH-1017	Full bin under X-30207A conveyor	Shutdown X-30207A
114	LSH-2017	Full bin under X-30207B conveyor	Shutdown X-30207B
114	ZS-1017A/B	X-30207A conveyor misalignment	Shutdown X-30207A
114	ZS-2017A/B	X-30207B conveyor misalignment	Shutdown X-30207B
116	TAHH-1020 thru 1033	R-30101A high skin temperature	Shutdown SCWO train A

Note:

Table for illustrative purposes adapted from EDP Table 54 in Volume II (Ecologic, 2001). Further description of interlocks can be found in the EDP.

P&ID = piping and instrumentation diagram
SCWO = supercritical water oxidation

4.2.8 Process Robustness. Process robustness refers to the system's ability to respond to changes in feed. As previously discussed, the EDS II tests revealed the potential for problems associated with oxidation stability in the TW-SCWO reactor. The NRC (NRC, 2002b) pointed out that the spikes of high concentrations of HCs and CO in the SCWO gas effluent raises concerns about understanding and controlling reactions in the SCWO, and particularly for scaled-up systems.

4.2.8.1 Turndown Capability. It is essential to maintain the oxidation reactions within the SCWO reactor (that is, maintain the reaction temperature). Optimization testing in EDS II demonstrated that the upper reaction zone temperature of the pilot-scale TW-SCWO must be 1,450°F (788°C) for a 5 to 7 second residence time. Lower temperatures (<1,300°F) can lead to some incomplete destruction of carbon-phosphorus bond containing compounds (for example, 42.5 ppm of MPA was observed in the effluent of one test) or require longer residence times for complete destruction. The reactor temperature depends on a number of parameters including mixing, oxidant concentration, and fuel value (heat content) of the feed. The residence time for the full-scale BG system is proposed to be 12 seconds as compared to only 7 to 8 seconds for the EDS II pilot system. EDS II tests demonstrated that lower feed rates for agent/simulant hydrolysates could be accommodated. The range of feed rates for EDS testing were:

- VX: 150-350 lb/hr
- GB: 250-500 lb/hr
- HD: 100-210 lb/hr.

In order to maintain the heating value of the total feed, decreases in the waste feed rate would require additional auxiliary (spike) fuel to maintain the reactor temperature and high DRE. The use of parallel reactors in the full-scale system allows another possibility for turndown capability, namely, utilization of fewer reactors for lower feeds.

4.2.8.2 Feed Concentration Ranges. The upper limits for feed rates of agent/energetics hydrolysate simulants was established at EDS II to be less than originally planned. Feed rates of 500 lb/hr were expected; however, the system operated effectively at feed rates of 350 lb/hr for the VX and GB 500-hour tests and only 210 lb/hr for HD. Revised feed rates for the full-scale BG were proposed as a modification to the EDP in April 2002 (Ecologic, 2002), based on these EDS II test results. Proposed modified values for the full-scale system are shown in table 4-9 along with actual feed rates for the EDS II tests.

4.2.9 Applicability. The TW-SCWO unit is designed to treat chemical agent hydrolysates where the chemical agent has been destroyed by neutralization (99.9999 percent destruction) prior to secondary treatment via SCWO. No testing with agent has been carried out for TW-SCWO. In several reports the NRC is on record stating that "hydrolysis of chemical agents with water or caustic is capable of destroying 99.9999 percent of the chemical agent" (NRC, 2002b).

4.2.10 Mobility. The non-stockpile chemical materiel (NSCM) program has investigated a number of potentially mobile or transportable destruction technologies

Table 4-9. Revised Feed Rates for Full-Scale BG TW-SCWO System[a]

Campaign	Planned EDS Feed Rate (lb/hr)	Actual EDS Feed Rate (lb/hr)	EDP Design For each BG Reactor (lb/hr)	Revised Feed Limit per BG Reactor (lb/hr)
VX	500	350	2,800	1,960
GB	500	350	2,800	1,960
H	500	210	2,800	1,176

Notes:

[a] Proposed by technology providers (Ecologic, 2002) based on EDS II test results.

BG = Blue Grass
EDP = Engineering Design Package
EDS = Engineering Design Study
lb/hr = pounds per hour

including a batch SCWO process. The TW-SCWO system in the EDP, which is designed for continuous operation, has no provisions for mobile operations.

4.3 Process Safety

The SCWO process poses challenges related to high-pressure and high-temperature operations. The EDP incorporates a five-reactor design where up to four reactors are operational with a fifth incorporated as an on-line spare. The EDP also states that careful attention must be given to the high-pressure injection pumps, but does not provide any additional information. The general safety issues associated with SCWO processing have been summarized by the panel discussion from the August 2001 conference (ONR and PMACWA, 2001, appendix D). This panel concluded that three methods of design analysis were critical to SCWO technology development: HAZOP, Systems Hazard Analysis, and failure modes and effects analysis (FMEA). The general consensus of the workshop attendees was that "hazards associated with SCWO technology could be properly managed and mitigated to an acceptable level. Standard non-destructive test methods should be employed to ensure reliability of materials and systems components." Two safety and operational issues for TW-SCWO processing at PBA were presented by Army personnel (Robinson in Virginia, 2001) at this conference:

a. Failure of oxygen flow control valve, which led to products of incomplete oxidation and their rapid reaction. During oxidation the oxygen flow control valve approached closure, the system was deprived of O_2 for approximately 1/2 hour, leading to incomplete oxidation products, when oxygen was restored, very rapid increase in pressure and gas temperature resulted from very fast oxidation reaction.

b. A vendor, not following proper procedures, had loosened a high-pressure fitting to bleed air from the system, which resulted in the fitting being expelled from the line at an "extremely high velocity."

The EDP contains a preliminary hazards analysis (PHA) led and documented by Safety Management Services Inc. (SMS) for the technology provider team. The PHA was performed based on process flow diagrams, piping and instrumentation diagrams (P&IDs), and PHA team meetings (held in Houston on 8 to 11 May 2001 and 27 to 29 August 2001), and was tailored to meet requirements and guidelines provided by PMACWA and MIL STD 882D, as well as OSHA 29 Code of Federal Regulations 1910.119 (Ecologic, 2001, Volume 1, page 55). A FMEA was performed on the process design and a qualitative risk assessment was performed. The technology provider claims that "the identified potential safety hazards have been addressed and the majority of them have either been designed out of the process or the process has been modified to include engineering control features for mitigation. Where it was not feasible to mitigate the identified hazard through engineering design or control modifications, recommendations have been included for consideration during the detailed design through construction and startup. These items are limited to administrative controls for incorporation into operating procedures and preventive maintenance programs or specific items to be considered during detailed design." In their full report on EDS II, the NRC ACW II Committee states that "the PHA appears to have been conducted in a satisfactory manner, although it will need to be updated as the design progresses." Key safety issues identified by the technology provider for the SCWO operation in Area 300 at BG are listed in table 4-10.

Table 4-10. Area 300 Issues and Resolutions[a]

Issue	Resolution
Location of discharge in the event of a reactor relief scenario	Incorporation of a relief collection system isolated from personnel access pathways
Concurrent operations while performing maintenance on SCWO reactors	Isolation of reactor trains through the use of barriers and placement of lines, pumps, and the reactors
Reactor quench zone fouling	Use of recycled water from the process evaporators rather than reliance on plant water

Note:

[a] Taken from Ecologic 2001.

Of course, a number of other issues concerning leaks and their detection and containment, as well as any other measures to protect workers will need to be addressed in more detailed hazard analyses.

4.3.1 Worker Safety. The NRC (NRC, 2000b) provided the following recommendation for SCWO safety at NECDF, which also applies to the TW-SCWO system:

Recommendation 3-2. For worker protection and secondary containment, the final design package for the Newport facility must include the physical hazard controls (for example, protective barricades) common to industrial operations involving high pressure and stored energy. Systems must be designed to minimize leaks, plugging, and ruptures of the SCWO reactor and associated plumbing and protective barriers. Secondary containment equipment will also be necessary, including safety systems for handling high-purity oxygen at high pressure, such as protection against downstream fires and explosions caused by contact between combustible materials (for example, activated carbon) and oxygen-enriched gas streams under normal and process upset conditions.

The change from air to oxygen as an oxidant could have an impact on safety. The NRC Committee states that although the committee knows of no previous accidents with TW-SCWO, it is on record as expressing general concern about the use of oxygen in SCWO reactors. They go on to state that the use of oxygen "will remain an area of concern for the committee until a detailed QRA shows the final design to be of very low risk." The plan for BG calls for oxygen dilution (nitrogen to oxygen blend in a ratio of 4:1) during startup and shutdown to avoid high oxygen concentrations in the downstream equipment.

Some key safety features proposed for the SCWO processing area at BG (Area 300) include:

a. Aluminum removal system on SCWO feedstock to minimize abrasive potential on SCWO pressure letdown valve

b. Divider walls to be installed between SCWO reactor trains for safe maintenance access while other reactors remain in operation

c. Pressure relief valves to release to a containment system

d. Total remote operation

e. Automatic shutdown of system in case of process upset.

Two additional safety features taken directly from the EDP are:

a. A concern of the SCWO unit layout is how to avoid problems associated with handling the slurry (solid/liquid) effluent that has been encountered during the DEMO II and EDS II pilot testing phases. The most obvious limitation of the pilot unit is that it had to be constructed in the confines of an existing facility. This has resulted in cases in which pockets exist in the slurry piping where solids can collect and plug the line. Sufficient space has been provided in the BG SCWO plot plan to allow for sloped lines for drainage.

b. The nature of the SCWO process involves the use of extremely high-pressure liquids and gases. Failure of any of the inlet lines to deliver the proper amounts of fluid at the proper pressure can lead to reactor releases or insufficient product purities. Personnel exposure potential would be increased for cleanup and maintenance during such events. The lines and pumps are designed with sufficient safety margins to easily handle the high pressure. Recommendations were issued to incorporate the SCWO system on a preventive maintenance program to detect and repair/replace damaged lines or damaged pumps. In addition, procedures should include inspection of the critical high-pressure lines and pumps on a periodic basis during operation.

The NRC also suggests that “as the design becomes more detailed, the PHA will have to emphasize the safety of maintenance workers.”

4.3.2 Material at Risk. The proposed TW-SCWO process handles hydrolysates of chemical agents and energetics, therefore, there is not any agent material at risk. Schedule 2 compounds and other hazardous materials are part of the SCWO feed, so measures for containment in the event of leaks would be required.

4.4 Environmental Impact

4.4.1 Waste Generation. The effluents from the proposed TW-SCWO process coupled with the evaporator/crystallizer are:

- Salts sent to a TSDF
- Recycled water, which is sent to Area 500
- SCWO gas effluent released to the atmosphere after scrubbing, monitoring, and carbon filtration.

The original NRC ACWA report (NRC, 1999) discusses an effluent management strategy for the total solution, which was called at that time LMIDS. The gas SCWO effluent is scrubbed, monitored, and filtered through activated carbon prior to release to the atmosphere. The SCWO off-gas will not be subjected to a hold-test-release.

Salt streams or aqueous effluent from the SCWO systems will require disposal. The current EDP calls for evaporation of the SCWO effluent in an evaporator/crystallizer to allow for water to recycle and produce a solid waste stream. Salts from the evaporated SCWO effluent will contain aluminum salts and sodium salts of fluoride, chloride, sulfate, phosphate, carbonate, and potentially nitrate and nitrite, along with potentially trace amounts of organics and metals from corrosion (that is, nickel, iron, chromium). They will likely be classified as hazardous waste. The salts will be verified to be agent-free before they are released for offsite shipment and disposal. The original plans for NECDF also called for evaporation of SCWO effluent; however, a decision was later made to ship the effluent directly to an offsite TSDF. Corrosion metals (for example, nickel and chromium) can play an important part in the classification of the waste or may require additional analysis. Brines from the air pollution control systems at Tooele are currently being shipped offsite for disposal by commercial waste management facilities.

4.4.2 Permitting History. There is no documented permitting history for TW-SCWO. A SCWO treatment unit would most likely be permitted as a miscellaneous treatment unit under RCRA Subpart X. In their letter report on EDS II (NRC, 2002b), the NRC raises some concern that the spikes of concentration of CO and HC in the SCWO gas effluent may impact the permitting of the TW-SCWO process and that current performance may need to be improved.

4.5 Schedule

A life cycle schedule for BG was provided in the EDP including a level 1, 2, and 3 schedule. The proposed schedule (table 4-11) calls for completion of construction in June 2008 with systemization and plant optimization to September 2009. A Gantt chart is provided in figure 4-7. Operations (that is, agent destruction), slated to begin in September 2009 with a completion date in June 2012, include shutdown and decommissioning.

The EDP claims that the schedule for agent destruction will end 10 months before the CWC treaty extension deadline of 27 April 2012. Three munition campaigns of 13, 30, and 9 weeks for VX, GB, and H treatment are proposed. As previously discussed, maintaining this schedule with the modified feed rates requires very high availability (95 percent), which seems overly optimistic. The proposed total length of the overall operations phase, including clean-up and changeover between campaigns, is 91 weeks. The overall operations plan provided in the EDP is summarized in table 4-12.

Table 4-11. Level 1 Schedule for BG

Activity	Early Start	Early Finish	Duration (weeks)
Contract Management	12/3/01	6/19/11	498
Design	3/3/03	7/18/04	72
Permits	6/3/02	7/25/04	112
Procurement	10/27/03	10/7/07	206
Construction	6/26/04	6/15/08	203
Systemization	6/18/08	9/20/09	66
Operations	9/21/09	6/19/11	91
Shutdown, Decommissioning, Closure	6/20/11	6/24/12	53

Source: Ecologic 2001, Volume VIII

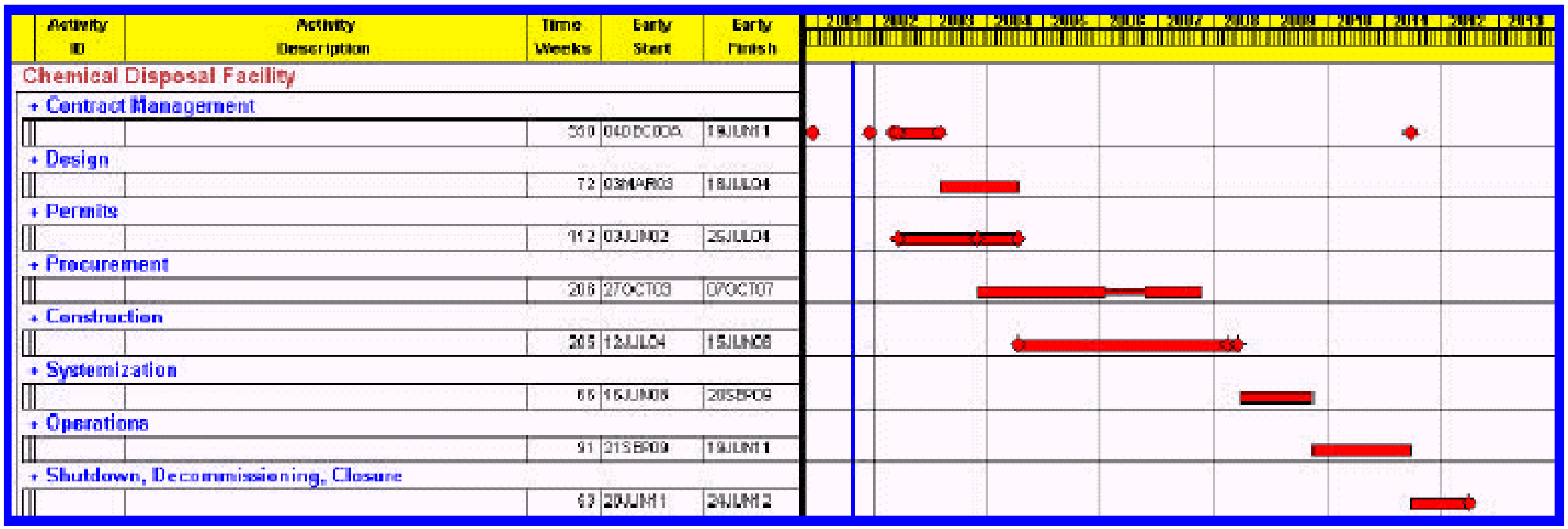

Figure 4-7. Gantt Chart for Level 1 Schedule for BG TW-SCWO (Source: Ecologic, 2001)

Table 4-12. Overall Operations Plan for BG

Activity	Duration (weeks)	Cumulative Time (weeks)
VX Campaign	13	13
VX Post-Treatment Cleanup	4	17
GB Changeover	13	30
GB Campaign	30	60
GB Post-Treatment Cleanup	5	65
H Changeover	13	78
H Campaign	9	87
H Post-Treatment Cleanup	4	91

Source: Ecologic 2001, Volume VIII

4.6 Life Cycle Costs

Cost information, as documented by the technology provider in the EDP, is presented in table 4-13. No attempt to evaluate or validate these costs was made for this technical evaluation. Capital costs for the proposed total solution at BG are summarized in table 4-13. The total capital cost, including indirect capital (18 percent flat rate of total installed cost for engineering and design) is $162.7 million. The $30.1 million for Area 300 provides all process equipment and complete installation of the SCWO and effluent evaporator/crystallizer operations. The SCWO equipment consists of five separate SCWO reactor trains. The evaporator/crystallizer consists of two 100-percent units. The cost of the evaporator/crystallizers is $8.5 million (total for both units). Each SCWO reactor is $1.4 million each with additional equipment costs of approximately $600K for other materials. The aluminum removal system is estimated at $1 million. The technology provider claims that the overall aggregated capital costs for the additions and modifications conform to a ±20 percent estimate accuracy range. No operating cost information was available for this report.

Table 4-13. Direct Capital Cost as Provided in the EDP

WBS Element Costed	Process Equipment ($)	Other Materials ($)	Installation Direct Labor ($)	Total ($)[a]
Site Infrastructure				
- Site Prep/Improvements	$1,903	$6,996	$7,125	$16,024
- Paving/Surfacing	($3,306)	($40,549)	($9,377)	($53,232)
- Exterior/Electrical		$100,000	$109,440	$209,440
- Water/Sewer/Gas		$75,000	$98,496	$173,496
- Storm Drainage	$7,542	$150,000	$137,467	$295,009
Interconnecting Pipe-racks	$50,799	$444,268	$946,685	$1,441,752
Area 500 Civils	$2,377	$66,123	$160,586	$229,086
MDB Modifications	$157,027	$4,182,006	$10,636,424	$14,975,458
Area 300 Building	$113,789	$1,316,695	$2,472,698	$3,903,183
Area 100	$9,464,128	$399,868	$1,971,117	$11,835,113
Area 200	$4,302,450	$4,317,575	$7,422,371	$16,042,396
Area 300	$18,165,880	$6,010,000	$5,961,452	$30,137,332
Area 400	$13,704,936	$6,616467	$11,500,168	$31,821,571
Area 500	$4,501,428	$1,087,141	$2,118,424	$8,066,994
Area 600	$4,577,209	$235,994	$1,177,974	$5,991,176
DCS/SIS	$482,035	$433,639	$658,433	$1,664,887
MDB Laboratory	$456,500	$35,000	$47,880	$539,380
Totals	$55,984,698	$25,436,223	$45,417,364	$127,289,065

Notes:

[a] Includes subcontracts of $360,000 for Area 500 and $90,780 for DCS/SIS.

MDB = munitions demilitarization building
WBS = Work Breakdown Structure

SECTION 5
EVALUATION OF POTENTIAL APPLICATION FOR NECDF

A brief summary of the SCWO development program for NECDF is provided in this section as a context for assessing the potential applicability of TW-SCWO to treatment of VX hydrolysate at Newport, Indiana. It is not the intent of this report to reevaluate the status of SCWO at NECDF nor the test results from the recent joint PMACWA/PMATA ACWA testing of the GA system for VX hydrolysate. Furthermore, no evaluation is implied of the more recent developments or recommendations from GA for SCWO implementation at NECDF.

The potential application of TW-SCWO processing to other chemical demilitarization wastes including secondary wastes, closure wastes, and the NSCM is also briefly discussed in this section.

5.1 Overview of NECDF Program

The Army currently stores 1,269 tons of the chemical nerve agent VX in 1,689 ton containers at Newport, Indiana. Groundbreaking on the construction of the disposal facility at NECDF occurred in April 2000 and the facility is now approximately 28 percent complete. The Army plans to destroy this VX through chemical neutralization (hydrolysis) within the CWC treaty schedule. As discussed previously, the NRC is on record as stating that hydrolysis destroys 99.9999 percent of the chemical agent and results in a VX hydrolysate with reduced toxicity, which contains Schedule 2 compounds and other hazardous organics. Further treatment and disposal of the VX hydrolysate is also planned. The original plans for NECDF, based on a contract awarded to Parsons Infrastructure and Technology Group, Inc., along with other industrial partners in 1999, was to destroy VX hydrolysate through onsite secondary treatment using SCWO. Parsons, Inc. is the Army's prime contractor for the construction, operation, and decommission of the chemical demilitarization operations at NECDF. GA is a sub-contractor and is responsible for the SCWO portion of the process. SWEC was responsible for oversight of a number of components of the program, including general oversight, and is the prime contractor for MOC testing and the EST.

The design for the full-scale SCWO process at NECDF calls for a straight down-flow reactor with an active length of 184 inches and an internal diameter of 10.2 inches. The Army planned to use two full-scale reactors. Each reactor was to be sized to 100 percent of the capacity needed to treat the VX hydrolysate on schedule. The 60-percent acquisition design package for NECDF was reviewed by the NRC Stockpile Committee in 2000 (NRC, 2000b). The original plans called for a removable platinum (Pt) liner, which was to be validated during an EST in 2000 through 2001. While the EST demonstrated that the corrosion rates were within expected limits and therefore manageable at NECDF, there were significant uncertainties around the mechanical stability and fabricability of the proposed full-scale Pt liner as well as several other open items unresolved at that time. The full-scale design for the NECDF SCWO liner was put on hold pending demonstration in a proposed SCWO Development Test (SDT).

The status, progress, and development issues associated with implementing SCWO at NECDF have been reviewed in a number of publications including several NRC reports (NRC, 1998, 2000b, 2001b). Table 3.1 of this report also summarizes the history of SCWO development for NECDF. Budget constraints, technical difficulties, and schedule delays prompted the Army to develop a new path forward for NECDF to ensure that VX will be chemically neutralized before the CWC treaty deadline. The new path forward for NECDF involved parallel evaluation, testing, and development of three options:

Option 1: SCWO processing of VX hydrolysate, followed by offsite shipment of SCWO effluent

Option 2: Offsite shipment of VX hydrolysate to a commercial TSDF

Option 3: Onsite pretreatment of VX hydrolysate prior to offsite shipment to a commercial TSDF.

This path forward is illustrated schematically in figure 5-1. A number of other developments ensued. A program for evaluating pretreatment of VX hydrolysate was initiated. A summary of the status, schedule, and path forward for secondary treatment of VX hydrolysate at NECDF up to August 2001 can be found in a report by an independent assessment panel (SAIC, 2001) as well as a number of other PMATA documents.

The events of 11 September 2001 prompted the Army to explore the potential of accelerating agent destruction at both ABCDF and NECDF. The NRC published letter reports (NRC, 2001e) evaluating the proposed accelerated programs for both sites. The SDT was canceled due to a number of developments in the program including results from a joint PMATA/PMACWA test on VX hydrolysate, which demonstrated that a replaceable C-276 liner could be a viable contingency. All SCWO development work for the full-scale system has been postponed and an active program to investigate

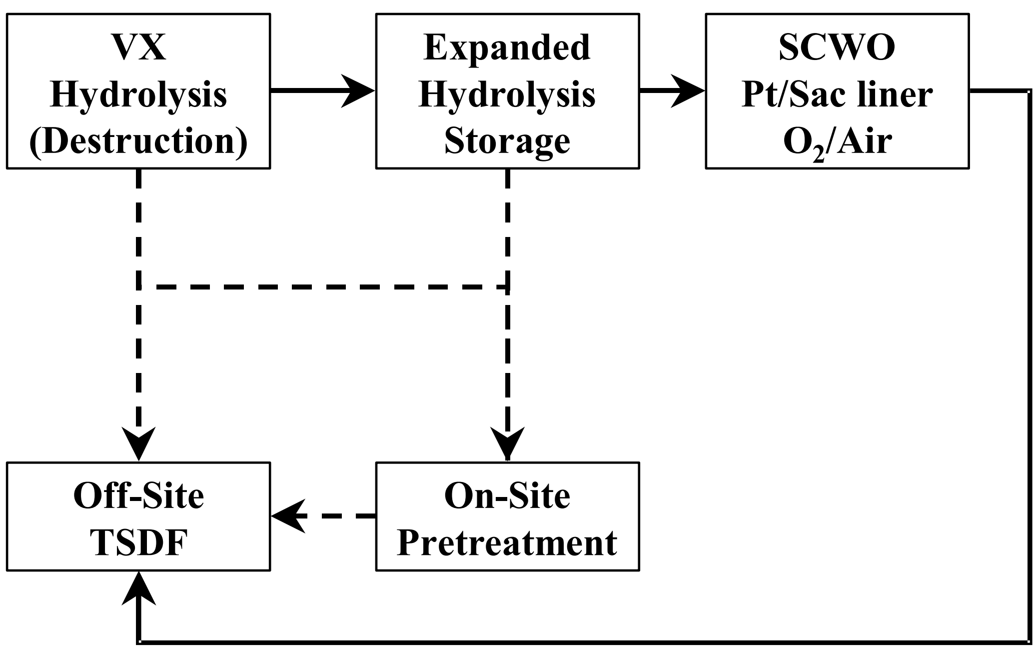

Figure 5-1. Schematic of Army's Path Forward for Treatment and Disposal of VX at NECDF (Source: SAIC, 2001)

offsite shipment to a commercial TSDF was initiated including identifying potential TSDFs that could accept VX hydrolysate with minimal (or no) pretreatment. The Army issued an RFP for offsite TSDFs in May 2002. A draft environmental impact statement (EIS) was written and public involvement meetings were held. A decision on the ultimate treatment of VX hydrolysate, whether onsite or offsite, is pending.

At the request of Parsons, Inc., GA prepared a proposal that would get SCWO online at NECDF within 12 months (the so-called speedy SCWO proposal). This proposal request was for the treatment of VX/H_2O (from *in situ* hydrolysis of VX by water rather than caustic); however, GA proposed the addition of caustic, so the proposal is also relevant to VX/NaOH. In their November 2001 speedy SCWO proposal, GA recommended construction and installation of four smaller SCWO units (each rated for 1,000 lb/hr of autogenic feed), which could process the VX hydrolysate within 6 to 12 months depending on availability during operation. Perceiving that an even faster implementation of SCWO would be desirable, GA submitted a revised speedy SCWO proposal (the S3 proposal) as an unsolicited document to Parsons and PMATA in February 2002. The S3 proposal recommended bringing up two smaller-scale units at NECDF, while a third and potentially a fourth unit of the same size as the SCWO systems proposed in November 2001 were being fabricated. The S3 proposal recommended using a removable high-pressure (HIP)-bonded Pt liner and a removable C-276 liner as backup.

GA has recently summarized their perspective of the status of the NECDF SCWO program in a report on SCWO development submitted to the Air Force (GA, 2002). Based on ACWA testing of replaceable C-276 liners and the development by GA of HIP bonding of platinum, it appears that the most likely candidate for NECDF would be a primary HIP-bonded Pt liner with a backup contingency being the use of replaceable C-276 liners. A HIP-bonded Pt liner has not been tested in a SCWO environment, but has been mechanically tested by GA.

It has been noted in past reports (SAIC, 2001) that VX hydrolysate is complex fluid that can separate into an organic rich layer (approximately 3 percent volume) above an aqueous layer that contains organics and salts. The ramifications of this phase behavior has impacts on a number of issues including storage, treatment, chemical analysis requirements, CWC treaty requirements, public acceptance, and other issues that must be managed in any new scenario where the generation of VX hydrolysate and its treatment are uncoupled. Very little is known about the properties of the organic phase as a separate entity, and a well-blended composite would be used as feed to the SCWO unit(s) at NECDF. It is important that this blending be maintained since any significant variation in phase ratio could result in different fuel values being feed to the reactor and different mixing, which could lead to a significant variation in reactor temperature that could result in a situation where there is insufficient oxygen to complete the destruction of organics.

5.2 Potential Application of TW-SCWO to NECDF

Although the final decision on secondary treatment of VX hydrolysate has not yet been made, the proposed GA SCWO process provides some context for considering the application of TW-SCWO to NECDF. There are no reports or proposals for the use of TW-SCWO at NECDF, so application to NECDF can only be assessed qualitatively by simple extrapolation of the processing rates and operations for the VX campaign proposed for BG in the EDP (Ecologic, 2001). In addition, there is no available information on schedule or costs for application of TW-SCWO at NECDF.

The chemical composition of VX hydrolysate is listed in table 5-1 (NRC, 1998).

As shown in table 5-2, the original plans for SCWO treatment at NECDF called for treating 2,100 pounds of VX hydrolysate per hour with a required total processing time of 6,760 hours (estimated to take approximately 10 months of total processing time). Each ton of VX corresponds to 8,368 pounds of VX hydrolysate, so a total of 10,619,000 pounds of VX hydrolysate must be treated. The steady-state operating conditions in the NECDF SCWO design are 1,150° to 1,200°F at 3,400 psi with a residence time of about 35 seconds. Since the VX at Newport, Indiana, is stored in ton

Table 5-1. VX Hydrolysate Constituents

Constituent	μg/L
Ethyl methylphosphonic 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(i-Pr2N)-3,4,7- trithianonane	1,700
Total Organic Carbon (TOC)	140,000
Sulfate	96.9
Phosphate	2.19
Total Sulfur (S)	38,400
Total Phosphorus (P)	37,700
Arsenic (As)	0.125
Barium (Ba)	0.236
Calcium (Ca)	121
Sodium (Na)	87,900

Note:

μg/L = micrograms per liter

Table 5-2. Parameters for GA SW-SCWO Processing of VX Hydrolysate at NECDF

-	1,269 tons VX in 1,689 ton containers
-	1 ton container = 8,368 pounds hydrolysate
-	2,100 pounds VX hydrolysate/hr; 6,760 hours
-	1,150-1,200°F, 3,400 pounds per square inch, ~35 seconds residence time
-	Start full-scale SCWO treatment 5/06 - End 3/07 (original schedule, delays will require a revised schedule)

containers with no munitions, there are no energetics hydrolysates that require treatment.

Each BG TW-SCWO reactor is proposed to process 1,960 lb/hr of VX/energetics hydrolysates, which is based on the feed rate of 350 lb/hr demonstrated in the EDS II reactor on largely simulants and some hydrolysate (from table 4-2). For the purpose of this analysis and comparison with the GA system, it is assumed that the TW-SCWO system can process VX hydrolysate with similar efficacy as observed for VX/energetics. While most of the tests were carried out with VX/energetics, the reactor was demonstrated to work on VX hydrolysate simulant as well. A comparison of the dimensions of the proposed full-scale GA reactor for NECDF and the TW-SCWO reactor proposed for full operation at BG is provided in table 5-3 along with proposed feed rates. Processing times are calculated for one reactor assuming 100 percent availability for comparison purposes only. These processing times do not take into account actual equipment availability or processing of additional aqueous wastes resulting from ton container washouts or other processes planned for NECDF. The TW-SCWO system processes considerably more water per unit time because of the higher volumetric input of water to supply the TW liner. From table 4-2, the hydrolysate feed comprises only approximately 25 percent of the total hydraulic load of the BG TW-SCWO reactor (1,960 lb/hr of hydrolysate in a total hydraulic feed of 8,190 lb/hr.) The shorter residence time (due to higher operating temperatures) of the TW-SCWO system compensates for the higher water loading, so the two systems are similar in overall processing rates (to within 10 percent) at the proposed sizes, assuming equal availability.

The simple comparison of processing rates and operation time in table 5-3 suggests that, given similar availabilities, the two systems could not be distinguished on processing schedule issues alone. There is no schedule available for implementation of a TW-SCWO system at NECDF since no proposals have been formulated for its application to NECDF. The schedule for BG of the Ecologic-Foster Wheeler total solution is likely more conservative than one for implementation at NECDF because many of the other treatment unit operations (and their integration) necessary for the

Table 5-3. Comparison of GA SW-SCWO for NECDF and Foster Wheeler TW-SCWO for BG

Parameter	GA SW-SCWO for NECDF	FW TW-SCWO for BG
ID (inches)	10.2	11.6
Length (inches)	184	90
Aspect Ratio (L/D)	18	7.8
Volume (ft^3)	8.97 (15,000 in^3)	5.50 (9,500 in^3)
Proposed VX Hydrolysate Feed Rate (lb/hr)	2,100	1,960
Hydrolysate Feed/Volume ($lb/hr/ft^3$)	234	356
Residence Time (seconds)	35	12
Temperature (°C)	620 to 650	815-595 (top to bottom)
Total Processing Time (hours)[a]	5,056	5,417

Notes:

[a] Assuming 100 percent availability. These processing times are for comparison purposes only and do not take into account equipment availability or processing of additional aqueous wastes resulting from ton container washouts or other processes planned for NECDF.

BG	=	Blue Grass
ft^3	=	cubic feet
FW	=	Foster Wheeler
GA	=	General Atomics
ID	=	internal diameter
in^3	=	cubic inch
L/D	=	length over diameter
$lb/hr/ft^3$	=	pounds per hour per cubic feet
NECDF	=	Newport Chemical Agent Disposal Facility
SW-SCWO	=	solid wall-supercritical water oxidation
TW-SCWO	=	transpiring wall-supercritical water oxidation

ACWA system would not be required for NECDF. A schedule for the GA SCWO system has been formulated, but it would need to be revised given that SCWO development and implementation is currently on hold. A more detailed analysis of the impact of the long-lead items for the GA system, as compared to those for the TW-SCWO system, could identify differences in the schedules.

The key technical risks for both the GA SW-SCWO and the TW-SCWO systems are associated with scale-up. Both technologies have been demonstrated at smaller scales. While there were a number of issues in the EST tests for the GA system, high DREs and reaction stability were demonstrated. Testing in ACWA at a smaller scale SW-SCWO system demonstrated high availabilities of greater than 80 percent for VX hydrolysate in the joint PMATA/PMACWA tests. The TW-SCWO system (6-inch diameter) had greater than 90 percent availability in the EDS II Operability tests. Nonetheless, there are technical risks associated with uncertainties involved in the scale-up of both systems. These uncertainties arise from the general lack of a fundamental basis for scaling up SCWO systems as well as from the fact that neither system has been built or operated at the proposed scales. An independent assessment panel (SAIC, 2001) determined that the basis for process scale up the GA system for NECDF was sound and low risk; however, there were significant uncertainties in scale-up regarding fabrication and mechanical stability of a Pt-based liner. Presumably, the demonstration of C-276 as a contingency as well as further (though unproven in a SCWO reactor) developments on HIP-bonding of Pt by GA reduces the risks arising from these uncertainties. On the other hand, the TW-SCWO reactor exhibited some problems with oxidation stability and for H corrosion. It is not certain how these factors would scale. In addition, Foster Wheeler provides a number of points on how protection of the liner by the transpiration water would scale up; however, these have, of course, not been demonstrated. In summary, it is not possible to rule in favor of one SCWO process or the other given the unquantifiable uncertainties for scaling up either system. It appears, however, that either system could be made to work given sufficient time for shakedown and systemization.

The schedule for implementation of the full-scale (that is, 100 percent) SCWO system at NECDF has experienced considerable slippage due to SCWO being put on hold, so it is unlikely that any full-scale SCWO system would be implemented at NECDF. As described, in the next section, implementation of smaller-scale SCWO reactors might still be installed within the schedule requirements although a more detailed analysis of the timeline proposed by GA would be required. It is unclear whether the full-scale TW-SCWO systems could fit within the remaining schedule for NECDF (further analysis would be required and would likely require a more formal process for soliciting a proposal from the technology providers).

5.3 Effluent Management and Offsite Shipment

The NRC and the Army have considered offsite shipment and disposal of hydrolysate as a potential treatment option since the mid-1990s (NRC, 1996). The Army decided to go forward then with implementation of onsite treatment at NECDF, ABCDF, and the ACWA sites. Due to a number of issues including budget constraints, delays in the SCWO development schedule, and the desire to accelerate agent destruction at the bulk-only sites, the Army is actively pursuing direct shipment of VX hydrolysate to an offsite commercial TSDF. An RFP for commercial TSDFs was released in May 2002, and a final decision for secondary treatment of VX hydrolysate is pending. PMCD has shipped wastes from chemical disposal facilities to offsite commercial TSDFs including brines from the Tooele Chemical Disposal Facility (TOCDF) and small amounts of hydrolysates sent to TSDFs during testing programs. The technical risks of offsite shipment have always appeared manageable, given that (1) provisions are made for the complex nature (that is, two layer) of VX hydrolysate with respect to handling, transfer, storage, analysis, and surety and (2) mechanisms for obtaining commitments from TSDFs can be developed. If costs for disposal of VX hydrolysate are similar to other hazardous wastes, it is difficult to imagine onsite treatment technology that must be constructed from the ground up could compete on economics along with offsite shipment to a TSDF. While there may be some technical issues such as analytical or certification, greater risks with offsite shipment of VX hydrolysate are associated with mainly political and public perception. A public involvement program with the communities at both the chemical disposal facilities and the TSDFs is planned.

The costs of any particular technology option for treating VX hydrolysate at NECDF depends strongly on the disposal costs of the effluents, which in turn depend on a number of factors including volume of effluent and classification (that is, hazardous or nonhazardous). For example, offsite shipment of SCWO effluent as hazardous waste to a TSDF would be considerably more expensive than its disposal to a POTW as a non-hazardous waste. The current NECDF SCWO design implies that the SCWO effluent would be nonhazardous (as long as corrosion metals from a C-276 liner were below hazardous limits); however, delisting and permitting issues would be required. The original plans called for an evaporator/crystallizer to produce a lower volume solid salt waste and water for recycle (analogous to the concept proposed by Ecologic/Foster Wheeler for BG). The final disposition of effluents could significantly impact decisions based on economics. As an extreme example, if both the SCWO effluent and VX hydrolysate were classified as hazardous waste with similar disposal costs, then disposal of the SCWO effluent, which is of considerably higher volume, would be considerably more expensive even though the hazardous organics were destroyed to high levels.

5.4 Potential Application for Secondary Wastes or Decommissioning and Closure Wastes

A large number of secondary wastes (for example, dunnage and nonprocess wastes) will be generated from operations at chemical weapons stockpile disposal facilities. In addition, decommissioning and closure of the facilities after operations are complete will lead to a significant amount of wastes that must be managed and sent for ultimate disposal. The Army has already developed or, in the case of some closure wastes, is developing methods for managing these waste streams. For example, granular activated carbon (GAC) generated is to be sent offsite to a commercial incinerator or a regeneration facility. Examples of wastes from both categories include:

- Dunnage (for example, wood)
- Personnel protective suits (DPE suits)
- GAC.

No plans were developed to consider employing SCWO for treatment of any of these types of wastes for NECDF operations. In the General Atomics Total Solution (GATS) for BG, however, GA plans to separate, shred, and grind dunnage and nonprocess waste so that it can be fed as a slurry to a SCWO reactor for treatment. Although evaluation of the GA system is outside the scope of this report, the NRC's position on treating secondary waste with SCWO in the GATS system is presented in the following paragraphs. While there were earlier concerns and issues (NRC, 1999a) with pumping and feeding wastes with high solids content, improvements in processing have been made and these wastes appear to be manageable by the GATS SCWO system. The NRC lists recent developments and improvements in its full report on EDS II (NRC, 2002a). Successful processing of slurried carbon was demonstrated for 153 hours using a SCWO reactor modified with internal baffles to ensure sufficient residence time. This report provides the following findings:

Finding (Blue Grass) GA-1. The GATS process appears to have reached a level of maturity sufficient for construction of a full-scale facility at BG, notwithstanding the issues raised in subsequent findings.

The testing that has been conducted has shown that the GA SCWO system is a high-maintenance operation; however, the level of maintenance that is required for the application of the SCWO system in particular, and the GATS process in general in a BG facility, is not beyond the ability of well-trained operators and maintenance personnel.

Finding (Blue Grass) GA-2. In the committee's opinion, the number of SCWO reactor liner changes required to process the stockpile at BG, while high, is manageable.

Finding (Blue Grass) GA-3. The committee still has some concerns about possible problems when scaling up from the existing GATS SCWO reactor to the full-scale design.

In EDS II testing, Foster Wheeler was not able to demonstrate that the TW-SCWO system was capable of handling significant amounts of solids in the feed, so it cannot be considered applicable to this type of waste. Based on current EDS II experiences, issues would likely arise with plugging of the TW-SCWO system upstream and potentially even downstream of the reactor. Given all the unforeseen problems and many Lessons Learned at pilot scale testing for chemical agent hydrolysates in the PMCD-funded SCWO programs (and for energetic hydrolysates in ACWA), treatment of any other type of waste (particularly complex waste containing solids) should require a significant testing program. It is unlikely that a new testing program could be put in place within current schedules.

5.5 Potential Application to NSCM

NSCM, which includes buried munitions, old production facilities, empty ton containers, chemical munitions, binary chemical warfare materiel components, chemical sample containers, chemical agent identification sets (CAIS) is much more diverse than the stockpile chemical weapons materiel. The latter four pose the greatest challenge to the program. Furthermore, NSCM is much more dispersed; at least 168 potential burial sites have been located. The Army has been developing a set of semipermanent and mobile facilities to destroy recovered NSCM. Future plans could also include use of stockpile disposal facilities (where appropriate and allowed) as well as experimental facilities that have long been used to destroy chemical agents (that is, the Chemical Transfer Facility [CTF] at Aberdeen Proving Ground in Maryland and the Chemical Agent Munitions Disposal System [CAMDS] in Utah). Construction of facilities at sites with significant NSCM is another potential component of the solution (for example, Pine Bluff, Arkansas).

The NRC Committee on Review and Evaluation of the Army NSCM Disposal Program has published four reports (NRC, 1999b, 2001f, 2002c,d) evaluating treatment technologies for treating neutralents (that is, agent hydrolysates of varying composition). Their 2001 report (NRC, 2001f) provides a summary of their ratings for SCWO against a set of criteria based on results from SCWO testing in ACWA and PMATA. In a subsequent report (NRC, 2002c), which supplements this report to include wastes produced by the Army's EDS, the NRC evaluated a batch SCWO concept that could interface with the EDS. The findings and recommendations from this report are not relevant to continuous SCWO processing at BG or NECDF, but do speak to application of continuous SCWO processes to NCSM. This report provides a short discussion on the use of batch SCWO to treat liquid secondary waste streams from the EDS. Four bench-scale tests were conducted at SNL-Livermore with H and GB hydrolysate simulants as well as an experiment to test the feasibility of destroying CAIS vials, which contain chloroform as well. Preliminary results "appear promising." The NRC concluded that "much more testing and scale-up work must be done" and "several years of development and scale-up are required." Key development areas include the stability of SCWO reaction in a large-diameter vessel, choice of MOCs, salts management, and the impact of repeated explosions followed by thermal and pressure cycles on the EDS and SCWO reactor. Recommendations from this report relevant to batch SCWO treatment of NSCM included:

Recommendation 2-11. The Army should continue research and development on batch SCWO only if it can demonstrate that the technology is more cost-effective than alternatives and that the number of non-stockpile items it will dispose of justifies the cost of technology development.

Recommendation 2-12b. Consistent with the committee's earlier analyses, there should be no further funding for the development of biological treatments, electrochemical oxidation, gas-phase chemical reduction, solvated electron technology, and continuous SCWO technologies for the treatment of neutralents and rinsates. PMNSCM should monitor progress in technologies being developed under the ACWA program but should evaluate ACWA technologies for the treatment of non-stockpile neutralents and rinsates only if no additional investment is required.

In summary, the NRC's position is that continuous SCWO processing is not as applicable to NSCM waste processing as other technologies. A wide range of treatment options is available (NRC, 2002d). Nonetheless, application of continuous SCWO processing, whether an SW or a TW system, would likely require the ability to handle a variety of feeds at a range of feed rates and potentially a higher frequency of startup and shutdown. While additional development would be required, one could draw from experience with the Navy SCWO system development programs for shipboard wastes.

5.6 Conclusions

Based on EDS II test results and extrapolation of the proposed BG processing rates to the quantities of VX hydrolysate that require treatment at NECDF, the following qualitative conclusions can be made:

a. Given the availability during operation, the processing time for the proposed full-scale BG TW-SCWO reactor and the full-scale GA SW-SCWO NECDF system are similar (within 10 percent).

b. While it appears that either full-scale system could be made to work at NECDF, both systems have risks associated with uncertainties related to scale-up. Neither proposed full-scale SCWO system has been constructed nor operated. The risk elements for the TW-SCWO and SW-SCWO systems are somewhat different. Provisions would need to be made for a significant period of shakedown, systemization, and testing of either system at full-scale.

c. Given the significant delays in implementation of SCWO at NECDF, it is unclear whether either technology could be implemented using the proposed full-scale systems within the current NECDF schedule.

d. Because no proposal for using TW-SCWO at NECDF is available, it is not possible to assess the schedule or costs of implementing TW-SCWO at NECDF relative to those proposed for implementation of the GA SW-SCWO process.

e. It is not possible to rule in favor of one SCWO process or the other given the unquantifiable uncertainties for scaling up either system.

f. The economics of technology options for treatment of VX hydrolysate at NECDF depend strongly on where the effluents are disposed of (that is, whether as hazardous or non-hazardous waste).

g. Offsite shipment of VX hydrolysate at NECDF has low technical risks given that issues associated with the complex behavior (that is, two layer) of VX hydrolysate can be managed with respect to analysis, surety, storage, and transfer (SAIC, 2001). PMCD currently ships wastes from chemical disposal facilities to commercial TSDFs. The risks associated with offsite shipment arise more from potential issues with public perception and mechanisms for obtaining commitments from TSDFs.

h. While SCWO processing of secondary wastes has been demonstrated for the GATS, the TW-SCWO system has not been demonstrated to handle significant solids in the feed, so it is not applicable to these types of wastes.

i. SCWO has been considered for treatment of neutralents in the NSCM program; however, the NRC's current position (NRC, 2002d) is that other technologies are more applicable and require less development.

SECTION 6
CONCLUSIONS

6.1 Conclusions from TW-SCWO Evaluation

All planned pilot-scale tests for the application of TW-SCWO for the treatment of chemical agent and energetics hydrolysates have been completed and all these tests have been evaluated by the NRC ACWA committees (ACW I and ACW II) in their full reports and letter reports. The findings and conclusions from this technical evaluation are presented below. A number of key successes were demonstrated in the EDS II tests including:

a. The 500-hour EDS II operability tests demonstrated that TW-SCWO is effective at destroying Schedule 2 compounds.

b. Although all of the 500-hour tests were not run continuously, overall availability of the TW-SCWO system was high. The availability for the 500-hour GB, VX, and H tests was 90.2, 92.5, and 91.7 percent, respectively. It is unclear whether these high availabilities will hold for the full-scale system at BG.

c. The TW-SCWO liner appeared to allow for effective salt transport within the reactor throughout the EDS II tests.

d. Although liner mechanical stability was a significant issue in earlier tests, EDS II tests demonstrated that the improvements in the TW-SCWO system allow for liner cracking and deformation to be a manageable issue as long as a degree of oxidation stability can be maintained within the reactor. Some deformation and pin-hole leaks were observed in the GB 500-hour test, which likely arose from problems with oxidation stability near the injectors, and could cause high temperatures or high-temperature differentials resulting in thermal stresses. The NRC "sees this discovery of deformations and tiny leaks as an issue, but not one so serious as to preclude implementation of the Foster Wheeler SCWO in a full-scale plant" (NRC, 2002a). No deformation was observed in a replaced liner for VX or H processing.

e. Liner corrosion appears to be manageable for both GB and VX; however, significantly more corrosion was observed in the 500-hour H tests. It is clear that the TW does not provide complete protection from the aggressive SCWO reaction environment. Monitoring of the liner and other components will be required at full-scale along with a maintenance and changeout program.

f. Oxygen was demonstrated to be a viable oxidant for the TW-SCWO process. The EDS II testing had over 2,000 hours of test operation with oxygen. Foster Wheeler states that there was no loss of oxygen system availability during these tests.

g. Reliability in the full-scale system is handled by a strategy of redundancy approach, that is, five parallel reactors with one being an "on-line spare." The use of smaller multiple reactors lowers the overall risk of scale-up and provides flexibility in processing without requiring large ranges of turndown capability that would be required for fewer, larger reactors. (It may, however, require more coordination of operations.)

h. The basis for scale-up from EDS II to BG is volumetric. The diameter will be scaled up by a factor of almost 2, and the volume by a factor of 5.6. The aspect ratio (L/D) of the full-scale reactor is lower than the EDS II system. The hydrolysate feed rate is scaled up by a factor of 5.6; however, the amount of transpiration water is scaled up by a factor of only 3.2, so the total hydraulic feed is scaled up by a factor of 3.85. This means that the total amount of water relative to the amount of salt is less for the full-scale system. The ratio of hydrolysate to total hydraulic feed is 0.24 in the full-scale system, compared to 0.17 for the EDS II reactor. It is unclear how higher salt concentrations in the full-scale system would impact corrosion rates, plugging, and overall reactor performance. Whether higher concentrations can be tolerated will need to be resolved at shakedown and testing of the full-scale system. If not, lower feed rates, and therefore longer processing schedules, will be necessary.

i. Scale-up is based on three criteria:

   1. Destruction of Schedule 2 compounds

   2. Long-term operability with respect to plugging

   3. Long-term operability with respect to corrosion.

A number of problems or issues were observed during EDS II. While some of these are significant, they appear to be manageable at full-scale given sufficient time for shakedown, systemization, and pilot-scale testing at BG:

a. Observations during EDS II tests indicated problems with maintaining the oxidation stability. The most significant issue was the occurrence of periodic spikes in the concentrations of CO and volatile HCs in the gas effluent. The frequency and intensity of these spikes were greatest for the GB test, but were observed in all three campaigns.

b. A number of changes were made during operability testing in EDS II to attempt to alleviate the HC/CO spikes including: changes in feed composition and preparation, feed rates, feed strainer size, quench water flow, and configuration of reactor outlet plumbing. Overall, reducing the feed rates of hydrolysate had the biggest impact decreasing the frequency and intensity of the HC/CO spiking. Using excess oxygen to attempt to improve mixing below the injector appears to help alleviate the problem as well. (Note: In the H test report [Foster Wheeler, 2002c], the technology providers state that they do not intend to increase the excess oxygen in the BG system.)

c. While the spikes in the VX and H campaigns were considerably less than in the GB run, the NRC is on record (NRC, 2002b) as stating that “the committee believes that the operability and permitting issue associated with spikes remains to be resolved.” They further conclude “that Foster Wheeler has not clearly identified the root cause of the problem” and that the “cause may lie within the TW-SCWO reactor itself” (that is, “overall the problem appears to have been inadequately resolved”).

d. There are two issues arising from the observation of lack of oxidation stability (HC/CO spikes):

   1. Treatment of the SCWO off-gas prior to release will likely be required; this should be manageable, but may require additional permitting.

   2. The lack of understanding of the root cause of the HC/CO spikes increases the uncertainties associated with scale-up of the TW-SCWO system.

e. A number of issues for the other SCWO equipment were observed during the EDS II tests:

   1. Erosion of the injectors was observed for all three EDS II operability campaigns; however, the injectors continued to perform throughout the tests.

2. There were some problems with plugging or fouling of the feed system upstream of the SCWO reactor. It is clear that the feed system cannot tolerate many solids in the feed and it is critical to remove solids prior to processing through the feed system.

3. PCV wear and erosion appears in all tests with some evidence of solids deposition or plugging/dislodging. The technology providers plan to install a parallel backup system for each reactor at full-scale.

4. The effluent slurry cooler performance deteriorated steadily as witnessed by a gradual temperature increase from 80° to 120°F. Foster Wheeler suggests that their observation of occasional fouling may require change in the heat exchanger design for BG such as allowing for modularity for periodic isolation and cleaning.

5. A number of other problems and operational issues were experienced during testing, which is to be expected for a pilot-scale operation of a new technology. These were corrected during the test program.

f. Controlling hot spots or high-temperature excursions is important for mitigating heat stress and degradation of the liner, injectors, and other equipment.

g. Feed rates for all three agent hydrolysates were reduced from design values of 500 to 350 lb/hr for VX and GB and to 210 lb/hr for H for EDS II testing, which prompted the technology providers to modify the feed rates for the full-scale TW-SCWO process at BG (Ecologic, 2002). The proposed revised feed limits require an availability of 95.5 percent for all campaigns, including H, to maintain the EDP proposed total schedule for each agent campaign and therefore add no additional time to the operations phase of the plant (Ecologic, 2002). This availability still allows for the fifth SCWO reactor to be an on-line spare. Such a high availability for the full-scale system seems overly optimistic, particularly in light of all the remaining scale-up uncertainties and the lack of any operation of a fully integrated system. The overall processing schedule seems very tight and does not allow for much flexibility.

6.2 Conclusions for Potential Application of TW-SCWO to NECDF and Other Chemical Demilitarization Wastes

Based on EDS II test results and extrapolation of the proposed BG processing rates to the quantities of VX hydrolysate that require treatment at NECDF, the following qualitative conclusions can be made:

a. Given the same availability during operation, the processing time that would be required for one proposed full-scale BG TW-SCWO reactor and the full-scale GA SW-SCWO NECDF reactor are similar (within 10 percent). The systems have different residence times, concentrations, and temperature profiles.

b. While it appears that either full-scale system could be made to work at NECDF, both systems have risks associated with uncertainties related to scale-up. Neither proposed full-scale SCWO system has been constructed nor operated. The risk elements for the TW-SCWO and SW-SCWO systems are somewhat different. Provisions would need to be made for a significant period of shakedown, systemization, and testing of either system at full-scale.

c. Given the significant delays in implementation of SCWO at NECDF, it is unclear whether either technology could be implemented using the proposed full-scale systems within the current NECDF schedule. A significant modification to the schedule would likely be required. A set of smaller-scale SCWO reactors could have merit due to reduced scale-up risks and faster implementation; however, a more detailed proposal and its analysis would be required.

d. Because no proposal for using TW-SCWO at NECDF is available, it is not possible to assess the schedule or costs of implementing TW-SCWO at NECDF relative to those proposed for implementation of the GA SW-SCWO process.

e. It is not possible to rule in favor of one SCWO process or the other given the unquantifiable uncertainties for scaling up either system.

f. The economics of technology options for treatment of VX hydrolysate at NECDF depend strongly on where and how the effluents are disposed of (that is, whether as hazardous or non-hazardous waste).

g. Offsite shipment of VX hydrolysate at NECDF has low technical risks given that issues associated with the complex behavior (that is, two layer) of VX hydrolysate can be managed with respect to analysis, surety, storage and transfer (SAIC, 2001). PMCD currently ships wastes from chemical disposal facilities to commercial TSDFs. The risks associated with offsite shipment arise more from potential issues with public perception and mechanisms for obtaining commitments from TSDFs.

h. While SCWO processing of secondary wastes has been demonstrated for the GATS, the TW-SCWO system has not been demonstrated to handle significant solids in the feed, so it is not applicable to these types of wastes.

i. SCWO has been considered for treatment of neutralents in the NSCM program; however, the NRC's current position (NRC, 2002d) is that other technologies are more applicable and require less development.

6.3 Path Forward

In summary, based on available information and the EDS II test results, it appears that TW-SCWO can be made to work at full-scale at BG. All of the technical and programmatic risks associated with scale-up cannot be eliminated, so sufficient time for shakedown, systemization, and pilot-scale testing of the full-scale system should be ensured. Integration of SCWO with all of the other unit operations within the Ecologic-Foster Wheeler total solution was not evaluated.

Because no proposal for using TW-SCWO at NECDF is available, it is not possible to assess the schedule or costs of implementing TW-SCWO at NECDF relative to those proposed for implementation of the GA SW-SCWO process. Furthermore, it is not possible to rule in favor of one SCWO process or the other given the unquantifiable uncertainties for scaling up either system. Based on this technical evaluation of available information for the TW-SCWO system and the lack of any identifiable or quantifiable significant advantage of TW-SCWO over the current NECDF SCWO process, it is recommended that the TW-SCWO process not be further considered for implementation at NECDF. A rating of “3” is given to this technology at this time, per the numerical ratings within the PMCD program (that is, no immediate need; could be useful and has sound fundamentals, but no need foreseen in immediate plans; revisit if need arises). If offsite shipment of VX hydrolysate and the GA NECDF SCWO system are both deemed unworkable, then this technology should be revisited.

APPENDIX A
ACRONYMS/ABBREVIATIONS

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ACRONYMS/ABBREVIATIONS

ABCDF	Aberdeen Chemical Agent Disposal Facility
ACWA	Assembled Chemical Weapons Assessment
ADL	A.D. Little
Al	aluminum
BG	Blue Grass
CO	carbon monoxide
CO_2	carbon dioxide
DARPA	Defense Advanced Research Projects Agency
DCS	Distribution Control System
DI	deionized
DMMP	dimethyl methylphosphonate
DoD	Department of Defense
DPE	demilitarization protective ensemble
DRE	destruction and removal efficiency
EDP	Engineering Design Package
EDS	Engineering Design Studies
EMPA	ethyl methylphosphonic acid
EST	Engineering Scale Test
FMEA	failure modes and effects analysis
G/L	gas-liquid
GA	General Atomics
GAC	granular activated carbon

GATS	General Atomics Total Solution
GB	sarin, a chemical nerve agent
GPCR	gas phase chemical reduction (Ecologic)
H	mustard, a blister agent
HAZOP	hazard and operability analysis
HC	hydrocarbon
HD	distilled mustard, a blister agent
HIP	high-pressure bonding
ID	internal diameter
IPA	isopropyl alcohol
kg/hr	kilograms per hour
L/D	aspect ration of length over diameter
lb/hr	pound per hour
LMIDS	Lockheed Martin Integrated Demilitarization System
mg/m^3	milligrams per cubic meter
MOC	materials of construction
MPA	methylphosphonic acid
N_2O	nitrogen
NECDF	Newport Chemical Disposal Facility
NO_x	nitrous oxide
NRC	National Research Council
NSCM	non-stockpile chemical materiel
O_2	oxygen
ONR	Office of Naval Research

PCV	pressure control valve
PG	propylene glycol
PHA	preliminary hazards analysis
PMACWA	Program Manager for Assembled Chemical Weapons Assessment
PMATA	Project Manager for Alternative Technologies and Approaches
PMCD	Program Manager for Chemical Demilitarization
ppm	parts per million
Pt	platinum
RCRA	Resource Conservation Recovery Act
RFP	request for proposal
S3	speedy speedy SCWO
SAIC	Science Applications International Corporation
SCWO	supercritical water oxidation
SDT	SCWO development test
SNL	Sandia National Laboratories
SW	solid wall
SWEC	Stone and Webster Engineering Company
SW-SCWO	solid wall-supercritical water oxidation
TBA	tributylamine
TOC	total organic carbon
TSDF	treatment, storage, and disposal facility
TW-SCWO	transpiring wall-supercritical water oxidation
TW	transpiring wall
VX	a chemical nerve agent, O-ethyl-S-(2-diiospropylaminoethyl)methylphosphonothiolate

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APPENDIX B
REFERENCES

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REFERENCES

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APPENDIX C

COMPOSITION OF SCWO FEEDS FOR DEMO II AND EDS II TESTS

APPENDIX C

COMPOSITION OF SCWO FEEDS FOR DEMO II AND EDS II TESTS

The chemical compositions of the hydrolysate simulants used in DEMO II and EDS II testing are provided in the following:

Substance	Weight percent
GB Hydrolysate Simulant	
DMMP	6.37
Sodium Fluoride	2.15
Sodium Hydroxide	2.60
Isopropyl Alcohol	1.03
Tri-n-butylamine	0.77
Deionized Water	87.08
GB Hydrolysate/Energetic Feed Composition[a]	
GB Hydrolysate Simulant	39.06
Explosive Hydrolysate	26.51
Propellant Hydrolysate	32.46
Deionized Water	1.9
Sodium Aluminate	0.03
Lead Hydroxide	0.04
VX Hydrolysate Simulant	
DMMP	13.2
Sodium Isethienate	15.3
Sodium Hydroxide	9.0
Isopropyl Alcohol	2.2
Diethanolamine	9.8
Deionized Water	50.5

Substance	Weight percent
VX/Energetic Hydrolysate[b]	
VX Hydrolysate Simulant	22.00
Explosive Hydrolysate	1.94 (5.62)
Propellant Hydrolysate	9.34 (18.46)
Deionized Water	56.61 (44.11)
Sodium Aluminate	0.12 (0.12)
Lead Hydroxide	0.05 (0.05)
Sodium Hydroxide	9.94 (9.64)
H Hydrolysate Simulant	
Thiodiglycol	9.97
Sodium Chloride	7.91
Sodium Hydroxide	0.27
Deionized Water	82.85
H/Energetic Hydrolysate Simulant	
H Hydrolysate Simulant	63.7
Explosives Hydrolysate	1.16
Sodium Hydroxide	7.34
Sodium Aluminate	0.11
Deionized Water	27.9

Notes:

H/Energetics Hydrolysate (210 pounds per hour) premixed with propylene glycol (35 pounds per hour)

a Energetic hydrolysates obtained from PMACWA

b The first composition was used for first 275 hours of testing. The numbers in parentheses used for testing from 275th hour to end of test.

APPENDIX D

SUMMARY OF AUGUST 2001 SCWO CONFERENCE

APPENDIX D

SUMMARY OF AUGUST 2001 SCWO CONFERENCE

The executive summary and panel summaries on salt precipitation/plugging, safety and corrosion from the Conference on Supercritical Water Oxidation: Achievements and Challenges in Commercial Applications" held in Arlington, VA in August 2001 (VA 2001) are provided below:

Executive Summary

This workshop brought together some of the world's experts from the US DOD, DOE and NIST; commercial developers from the US, Europe, and Japan; and academia. This expert group discussed the current state of development of Supercritical Water Oxidation (SCWO) reactors for real-world applications and solutions to remaining challenges.

Following one day of presentations, four panels led discussion on the following topics: Salt Precipitation and Plugging, Safety, Economics of Full-Scale Application, and Corrosion. The presentations and panel discussions, included in this report, provide the best current indicators (to our knowledge) of the state of SCWO technology and considerable informed advice about how to move the technology forward. Some of the principal points made during the workshop follow:

- There are two main groups of SCWO applications currently being pursued: 1) military wastes, which are extremely challenging with respect to corrosion and salt plugging, and 2) commercial industrial wastes and wastewater sludge, which are relatively benign with respect to corrosion and salt plugging. Companies pursuing the former include General Atomics and Foster Wheeler, while examples of companies pursuing the latter are Chematur and HydroProcessing. The more challenging feeds require more elaborate SCWO designs or operating techniques to manage the associated corrosion and salt plugging problems.

- All commercial firms have developed different and unique ways of dealing with corrosion and salt plugging, which in fact often characterize their designs and distinguish one from another. While some developed approaches are more optimized and mature than others, all have been able to demonstrate viable operation with a wide range of feeds.

- The type of waste processed (i.e., challenging or benign) significantly affects one's perception of processing characteristics and difficulties. Examples discussed at the Workshop include:
    - the nature of precipitated salts ("sticky" or not)
    - the degree of salt precipitation avoidance/removal required (e.g., whether high fluid velocity is sufficient or a more elaborate means is necessary)
    - cost of the SCWO process and whether it is competitive with other technologies
- Processing sludge through SCWO is very different from processing feeds with high salt concentrations, primarily with respect to solids behavior and its control.
- Going to extremely high-pressure operation to avoid salt precipitation and plugging problems may not be viable in practical applications.
- SCWO must prove long-term reliability and be economically competitive to be attractive to the private sector. This is already the case for processes designed for benign wastes. SCWO designs for high corrosion and salt generating feeds are still fairly expensive and do not yet appear to be competitive for private sector applications.
- While military applications are most challenging and currently driving the development of SCWO, the wider and long term market for SCWO is in the private sector handling less challenging feeds.
- Stricter regulatory conditions in Europe make SCWO (and new technologies in general) more attractive there than in the United States.
- While there have been many incidents of equipment damage over the years in SCWO processes (e.g., titanium fires, oxygen fires, liner breakthroughs), there has been no catastrophic failure of a SCWO system to date.
- There appears to be no universal corrosion-resistant material for all SCWO feeds and operating conditions.
- For benign wastes, a simple tubular reactor is adequate. For corrosive feeds, a liner and/or some feed chemistry control is needed. For high salt feeds, active control of scale buildup (e.g., transpiring water, feed additives, mechanical scraping) is required.

Panel 1: Salt Precipitation/Plugging Session
Jefferson W. Tester and Glenn T. Hong, Chairs

1. Nature of the problem of salt/solids precipitation, scale-buildup, and plugging

The problem of salt precipitation is multivariate, dependent on at least the following parameters:

1. Temperature – affects density and solid salt behavior such as melting
2. Pressure – affects density
3. Density – affects water properties and interaction of salts with water
4. Composition – different salts have dramatically different behaviors, e.g. NaCl vs. Na_2SO_4, Na_2CO_3, or $CaSO_4$.
5. Time – salt morphology can be affected by time both in the initial precipitation as well as in the aging of salt deposits. Salt precipitation problems are frequently localized to a region where a rapid drop in salt solubility occurs.
6. Geometry – reactor geometry, diameter expansions and contractions, and condition of surfaces can play a significant role in the accumulation of salt deposits.
7. Fluid dynamics – velocity and flow patterns play a significant role in the accumulation of salt deposits. For example, rapid changes in velocity in sudden expansions or contractions can be important in increasing susceptibility to both scaling and erosion.

Both homogeneous and heterogeneous nucleation occur in SCWO. The properties of the fluid phase prior to precipitation influence the solid phase nucleation, growth and morphology. The presence of particulate inert solids such as inorganic oxides can provide nucleation sites for the deposition of salts, allowing transport through SCWO systems.

2. Generalizations regarding susceptibility to scaling/deposition

The appropriate method of dealing with scaling deposition varies with the waste and the chosen reactor configuration. Current approaches are largely bounded by numerous constraints, typified by the statement, "for these feed compositions and this reactor type at these temperature, pressure/density and residence time conditions salt deposition was not a problem." Nonetheless, an ever-increasing database of SCWO operating experience has demonstrated successful management of solids for various feeds, reactor types, preheaters, cooldown heat exchangers, and letdown systems.

There are at least 3 broad categories of feeds or wastes for SCWO treatment applications:

1. Military wastes – chemical agents, munitions, energetics, smokes and dyes. Typically high salt or corrosive content.
2. Sludges with "inert" solids such as oxides and lower salt content than concentrated halogenated waste streams.

3. Specific chemical wastes and sludges from a variety of industrial sources. Important elements affecting susceptibility to scaling and plugging include: TOC, BOD/COD, water content, heteroatom concentrations (Cl, F, Br, P, S, Ca, etc.), the presence of inorganic, "inert" matter (oxides, ...), and the gross condition of the feed that specifies the extent of pre-treatment for pumpability.

3. Operating experience at a process level

Mike Modell spoke about his experience with $CaSO_4$ scale deposition in preheater tubes and with solids settling and scale buildup in horizontal small-diameter tubular reactors. A fundamental approach was taken to understand what mechanisms were important to solids deposition, including nucleation, particle adhesion to solid walls, and growth of scale.

Glenn Hong, Mike Modell, and others debated what is actually meant by classifying solids as "sticky" or "nonsticky." Important issues include the presence of secondary particles (oxides) in the feed such as in sludges, the actual salts that are present, wall roughness, flow velocity and changes in flow velocity, and time between precipitation and contact with the wall. Ron Latanision suggested that some of the "stickiness" may be due to corrosion reactions between the salts and the wall.

Bill Killilea cited the lack of deposition of solids for VX hydrolysate SCWO treatment in a vessel reactor. The phosphorus content of the VX is believed to play a key role. Al (K.S.) Ahluwalia and Crane Robinson discussed the positive results with respect to avoiding scale buildup or plugging in transpiring wall reactors. Although the details of internal conditions are not well known and early CFD modeling results from the CFDRC/OLI/MIT study reported by Ning Zhou suggest that transpiration may not be that effective in reducing or eliminating scale buildup, recent operating experience has generally only experienced scaling problems in equipment downstream of the reactor. In one case with GB hydrolysate, a reactor flush was carried out.

For sludge wastes, heatup and cooldown steps are more susceptible to solids deposition than is the reactor itself, based on the experience of Chematur, MODEC and Hydroprocessing. Organo (Akira Suzuki) has not experienced scale deposition problems in treating PCBs or TCE in their vessel reactors or letdown systems. For neutralized TCE SCWO treatment, 95 percent of the salts are redissolved in the brine and removed, while the remaining 5 percent is entrained in the overhead stream and redissolved by quenching. The lack of salt adherence to the wall may be due to the wall temperature being lower than the bulk temperature.

Hydroprocessing (Will Wofford) with both municipal and industrial sludges reported successful handling of solids deposition and plugging. Control of the point at which oxidation or precipitation is initiated may be helpful in avoiding scale. When oxygen was added upstream of the preheater, char and salt deposition in the preheater were a problem. Similarly, Chematur (Lars Stenmark) has not experienced plugging or solids deposition with sludges, although occasional descaling with an acid wash will be used if necessary.

Assisted hydrothermal oxidation appears to avoid salt deposition by the low operating temperature (380°C) and the reaction of HCl with the low solubility Na_2CO_3. Use of high pressure to mitigate salt precipitation may be prohibitive in practical applications.

4. Cleaning and mitigation approaches

A broad range of solids deposition and control methods were mentioned during the discussion. These included:

1. Control of precipitation/reaction zone, e.g., keep precipitation away from wall.
2. Utilize inert solids as nucleation sites to avoid wall deposition.
3. Utilize inert solids to scour wall deposits.
4. Take advantage of favorable regions of phase equilibrium, e.g., use high pressure or relatively low temperature to keep salts in solution.
5. Carry out continuous (e.g. transpiring wall) or intermittent flushing.
6. Control feed chemistry to yield transportable solids.
7. Use high velocity to reduce deposition.
8. Use acid washing for occasional descaling.
9. Use quenching to redissolve salts at the reactor exit or brine zone.
10. Control temperature profile to have higher salt solubility at the wall,
11. Mechanical filtration of hot solids.
12. Use of mechanical cleaning devices for periodic or continuous removal of scale buildup, e.g. the Conco cleaners that M. Modell discussed and showed people or the scraping devices that appear in the patent literature.

In summary, a variety of practical engineering approaches have proven to successfully handle solids deposition problems in SCWO systems. This is certainly good news for the potential expansion of SCWO into the private sector for treating municipal and industrial sludges as well as other industrial organic wastes.

Panel 3: Safety

Crane Robinson and Michael Spritzer, Chairs

The Safety Workshop was Chaired by Mr. Crane Robinson, US Army TACOM-ARDEC and Co-chaired by Mr. Michael Spritzer, General Atomics (GA). Mr. Robinson opened the Workshop with a series of slides regarding the mitigation of SCWO process hazards and the importance of utilizing ASME/ANSI Code guidelines in the design of system hardware to reduce hazards to an acceptable level of risk. Incorporation of system hardware such as the high-pressure process safety valves (PSV's), rupture discs, adequate shielding to protect operations personnel, and the possibility of implementing remote operation as well as the implementation of an adequate safety interlock strategy should be considered early during the system design phase. The importance of utilizing the correct materials of construction for the process conditions was also discussed. Three methods of design analysis which are critical to the SCWO technology development initiatives were briefly summarized: included are the Systems Hazards and

Operability Study (HAZOP Review), Systems Hazard Analysis and a Failure Modes and Effects Analysis.

Formal periodic classroom training for engineering and operations personnel as well as onsite plant training are essential activities in maintaining an effective safety program. The potential for human error can be minimized by making personnel cognizant of all process hazards, which are primarily attributed to the utilization of high pressure in combination with elevated temperatures. The importance of identifying all hazards and their associated consequences must be considered during the hazard mitigation process.

Mr. Robinson briefly discussed experiences in SCWO process operations relative to safety during process operations at the U.S Army's Pine Bluff Arsenal. An incident involving the failure of the oxygen flow control valve which lead to the formation of products of incomplete oxidation and their rapid reaction was discussed. It was mentioned that during oxidation the valve position of the oxygen flow control valve approached the closed position while the valve was set to be open remotely from the distributed process control system (DCS). The action resulted in the system being deprived from oxygen for a period of approximately ½ hour. The improper action of the valve, believed to be attributed to icing, resulted in an inadequate concentration of oxygen in the reactor and the formation of products of incomplete oxidation. When oxygen flow was restored to normal a very rapid reaction occurred which resulted in a very rapid increase in pressure and gas temperature. As a result of the incident, it was determined that a feedback indicator would be required to show the valve's actual position at any point in time. This parameter should be tracked along with the output signal (which controls valve position) from the DCS to ensure the valve's proper operation. As a result of the incident it was recommended that this feature should be incorporated into the control system design. It was also recommended that a low oxygen flow alarm be incorporated into the systems safety interlock strategy.

Another incident that occurred involved the loosening of a high pressure fitting during a training exercise in which a high pressure air compressor was being commissioned and tested. The air compressor was being utilized to supply the required start-up gas for system pressurization. It was mentioned that during the training activity in which operations personnel were present, the vendor had loosened a high pressure fitting to bleed air from the system, which resulted in the fitting being expelled from the line at an extremely high velocity. Fortunately there were no injuries as a result of the incident. It was mentioned that the vendor did not follow the proper bleed down procedures on the unit, which would have eliminated the possibility of the incident occurring.

Following Mr. Robinson's presentation, Mr. Spritzer presented a series of slides depicting General Atomics (GA) approach to Process Safety. Mr. Spritzer mentioned that GA's approach is structured into 4 main layers, which include the prevention of system upsets which could lead to failure, the ability to recover safely if an upset does occur, prevention of loss of the pressure containment system in the event of a serious upset, and finally to prevent personnel injury and further equipment damage if a compromise of the pressure containment system occurs. Follow-on conditions that have caused upset conditions in GA's SCWO systems were discussed. It was mentioned that the only major incidents that have occurred to date have involved the use of titanium lined reactors when air was employed as the oxidizer. It was mentioned to the participants that GA has extensive experience with titanium and would be happy to enter into more detailed discussions with any of the Workshop attendees if desired. Mr. Spritizer mentioned that as a result of GA's testing they do not recommend the use of oxygen as an oxidizer when employing titanium lined reactors.

Detailed discussions ensued with workshop attendees regarding their experiences relative to SCWO operational safety. It was mentioned by Dr. Steve Buelow of Los Alamos National Laboratories, where testing is performed to support destruction of organic contaminants in mixed wastes, that they have purposely created detonations in SCW to ensure the reliability of their containment system during processing. These tests were performed to insure that even if a detonation were to occur that the safety containment system, which would house the SCWO reactor and its associated high pressure components, could not be compromised. This evidence was required by the Department of Energy in order for a small scale SCWO system to be tested and utilized in an area where mixed wastes would be stored. Workshop attendees mentioned that they have experienced ruptures during small scale testing in high pressure tubing, but the energy liberated was contained by the safety containment system.

Methods to monitor and analyze the quality of the effluent gases were considered as being important from a safety perspective so that the extent of oxidation could be monitored on a continuous basis. It was also felt that if the carbon monoxide generation was sufficiently low that generally the oxidation of the organic contaminant was proceeding satisfactorily.

As a general consensus the Workshop attendees felt that the hazards associated with SCWO Technology could be properly managed and mitigated to an acceptable level. Standard non-destructive test methods should be employed to ensure reliability of materials and system components.

Panel 4: Corrosion

Ronald Latanision and William Killilea, Chairs

The workshop session was divided into 3 principal topics:
- System design for corrosion control and mitigation
- Materials of construction and
- Water (waste) chemistry control

This summary presents the consensus views of the workshop participants.

System Design for Corrosion/Mitigation

For benign SCWO feeds, meaning with respect to corrosiveness, salt or solids loading and ease of transport through the system, a tubular reactor is preferred. This reactor configuration will provide the lowest capital cost. For aggressive feeds, a lined vessel reactor is preferred. The liner isolates the processing environment from the pressure boundary. The liner may consist of alternatively transpiring wall platelets or a removable/replaceable solid wall corrosion resistant barrier. The aspect ratio of the vessel reactor must be suitable for practical, mechanical incorporation of the liner.

Liner designs must consider both corrosion and erosion phenomena. Unexpected liner erosion was observed in recent SCWO VX hydrolysate, solid wall, platinum liner testing. This experience confirms the need for post-test, destructive, metallurgical analysis.

Materials of Construction

Pressure Boundaries

For tubular reactors, nickel alloys are preferred as pressure boundaries due to their high strength at SCWO temperatures. For vessel reactors, nickel alloys have been also been used extensively although less exotic alloys are being used and proposed. These less exotic alloys take advantage of the reduced pressure boundary wall temperature created by use of the transpiring wall or insulated solid wall liners.

Liners

There is no universal material of construction for solid wall liners to meet the requirements of all SCWO feeds. Liner MOCs must be chosen to suit the processing environment of those feeds. Alloy 600 has been successfully used without corrosion for transpiring wall platelets for several hundred hours of operation on chemical demilitarization feeds. A longer term operational history is needed for confirmation.

Water (Waste) Chemistry Control

Water or waste chemistry control can be beneficial in producing a processing environment more conducive to improved material performance. There was concurrence that Pourbaix diagrams (potential as a function of pH) should be used to guide adjustments to water chemistry/waste feed chemistry for this purpose. Assisted hydrothermal oxidation technology developers have made use of such diagrams in choosing their mild (near critical temperature) operating conditions.

At SCWO's higher operating temperatures, however, Pourbaix diagrams are not available. Favorable processing conditions for materials must continue to be determined experimentally. For the longer term and in parallel with experimental efforts, development of appropriate instrumentation techniques and data collection for the generation of Pourbaix diagrams for materials of construction at higher temperatures were recommended.