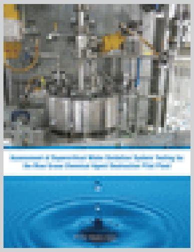

Assessment of Supercritical Water Oxidation System Testing for the Blue Grass Chemical Agent Destruction Pilot Plant

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COMMITTEE TO ASSESS SUPERCRITICAL WATER OXIDATION SYSTEM TESTING FOR THE BLUE GRASS CHEMICAL AGENT DESTRUCTION PILOT PLANT

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Preface

The United States joined the 1993 Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction (CWC) in April 1997. Under the CWC, the United States, along with 188 other states (as of 2012), agreed to eliminate their entire stockpiles of chemical weapons by April 2007. The CWC allowed for one 5-year extension to this mandate, and the U.S. availed itself of this extension. Thus, the deadline for full stockpile destruction was extended until April 2012. Over 90 percent of the U.S. stockpile of chemical agent and munitions had been disposed of by this extended deadline. Of the nine stockpile sites, seven have completed agent destruction and the disposal facilities are either closed or undergoing closure. The Pueblo Chemical Agent Destruction Pilot Plant, in Colorado, and the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP), in Kentucky, are being constructed at the time of this writing to dispose of the remainder of the U.S. stockpile.

Initially, the U.S. Army, following recommendations from the National Research Council (NRC), decided to use incineration as its destruction method at all sites. Citizens in some states with stockpile storage sites opposed incineration because they believed it was impossible to determine the exact nature of the effluents escaping from the incineration stacks. The Army pursued incineration at four of the eight storage sites in the continental United States. In response to growing public opposition to incineration, the Army developed alternative processes to neutralize chemical agents by hydrolysis. These processes were used to destroy the VX nerve agent at Newport, Indiana, and the mustard agent at Aberdeen, Maryland.

In 1996, public opposition to incineration in Kentucky and Colorado caused Congress to enact Public Law 104-201, which instructed the Department of Defense to "conduct an assessment of the chemical demilitarization program for destruction of assembled chemical munitions and of the alternative demilitarization technologies and processes (other than incineration) that could be used for the destruction of the lethal chemical agents that are associated with these munitions." The Army established a Program Manager for Assembled Chemical Weapons Assessment (PMACWA) to "identify and demonstrate not less than two alternatives to the baseline incineration process for the demilitarization of assembled chemical munitions."[1] Following a detailed selection process among proposed methods for destroying the weapons at Blue Grass Army Depot, PMACWA selected technologies using hydrolysis to destroy both agent and energetic streams. The products of hydrolysis, called hydrolysate, are no longer as acutely toxic as the chemical agents. At BGCAPP, the hydrolysates will be treated by supercritical water oxidation (SCWO) to further process them into environmentally benign products.

This report discusses the results of the first-of-a-kind testing of the SCWO system. It also discusses the BGCAPP response to the 2012 NRC report *The Blue Grass Chemical Agent Destruction Pilot Plant's Water Recovery System* and considers systemization of both the SCWO system itself and the water recovery system. Finally, the report presents findings and recommendations for systemization and testing of these combined process elements.

I wish to express my gratitude to the members of the Committee to Assess Supercritical Water Oxidation System Testing for the Blue Grass Chemical Agent Destruction Pilot Plant. All members served as volunteers, and all have given unselfishly of their time and knowledge. The committee members' expertise covered the needs of the project, although most had a steep learning curve to assimilate the background and applications to chemical agent demilitarization. The members attended plenary meetings, toured the first-of-a-kind testing facility at General Atomics in San Diego, California, toured the BGCAPP construction site, and

[1]PMACWA has since been renamed the Program Executive Office, ACWA.

studied the extensive literature, including engineering charts and diagrams, provided to the committee by the technology providers and the BGCAPP program staff.

The committee recognizes and appreciates the extensive support of the sponsor as well as the equipment contractors. The committee also appreciates the openness and cordiality of the representatives of the technology providers. I believe our relationship with the sponsor, his team, and support contractors has been effective and constructive and that the committee has been given the best available information to conduct this evaluation.

A study like this always requires extensive logistics support, and the committee is indebted to the NRC staff for their assistance. Meetings were arranged and run smoothly, and the committee was well cared for, in no small part due to the efforts of Deanna Sparger, the Program Administrative Coordinator for the Board on Army Science and Technology. I would like to acknowledge particularly the close working relationship I had with the NRC director for this study, James Myska. Working as a team in leading this study, we were in close communication.

John R. Howell, *Chair*
Committee to Assess Supercritical Water Oxidation System Testing for the Blue Grass Chemical Agent Destruction Pilot Plant

Acknowledgments

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's (NRC's) Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Robert A. Beaudet, Independent Consultant, Pasadena, California
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Andrew Brown, Jr., NAE, Delphi
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Frederick J. Krambeck, NAE, ReacTech, Inc.
Digby D. MacDonald, University of California at Berkeley
Baoxia Mi, University of Maryland
Michael Schrage, Massachusetts Institute of Technology

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations nor did they see the final draft of the report before its release. The review of this report was overseen by Hyla S. Napadensky, Napadensky Energetics Inc. (retired). Appointed by the National Research Council, she was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

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Acronyms and Abbreviations

ACWA	Assembled Chemical Weapons Alternatives
BGCAPP	Blue Grass Chemical Agent Destruction Pilot Plant
CN^-	cyanide
CWC	Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on Their Destruction
FOAK	first of a kind
GB	a nerve agent, also known as sarin
H	a blistering agent, also known as mustard
HCN	hydrogen cyanide
NRC	National Research Council
OWS	oil-water separator
QDP	quality data package
RO	reverse osmosis
SCWO	supercritical water oxidation
TDS	total dissolved solids
TOC	total organic carbon
VX	a nerve agent
WRS	water recovery system

Summary

The Army Element, Assembled Chemical Weapons Alternatives (ACWA), is responsible for managing the conduct of destruction operations for the remaining 10 percent of the nation's chemical agent stockpile, stored at the Blue Grass Army Depot (Kentucky) and the Pueblo Chemical Depot (Colorado). Facilities to destroy the agents and their associated munitions are currently being constructed at these sites. The Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) will destroy chemical agent and some associated energetic materials by a process of chemical neutralization known as hydrolysis. The resulting chemical waste stream is known as hydrolysate.

Among the first-of-a-kind (FOAK) equipment to be installed at BGCAPP are three supercritical water oxidation (SCWO) reactor systems. These will be used to further treat the agent and energetics hydrolysates generated by hydrolysis of sarin (GB) and VX nerve agent, possibly mustard blister agent, and the energetics associated with M55 rocket warheads and with various projectile munitions. The SCWO systems will subject the hydrolysate feeds to very high temperatures and pressures, breaking down their organic content into carbon dioxide, water, and salts. These particular hydrolysate feeds present unique non-agent-related challenges to subsequent processing via SCWO due to their caustic nature and issues of salt management.

The potential problems with corrosion and salt buildup prompted ACWA to require extensive FOAK testing of the SCWO process prior to shipment, installation, and systemization at BGCAPP. Ten months were allocated for testing SCWO Unit 1 to verify the full-scale design and to continue prior work in furtherance of mitigating performance risks. These tests used hydrolysate simulants representative of the actual agent and energetics hydrolysates that will be processed at BGCAPP. During this testing, not only were corrosion and salt buildup examined, but changes in chemical additives to the SCWO feed and in SCWO operating conditions were tested.

The Program Executive Office (PEO), ACWA, of the Department of Defense requested that the National Research Council (NRC) review and evaluate the results of the FOAK tests conducted on one of the SCWO units to be provided to BGCAPP. In addition, the NRC was asked to provide recommendations for systemization of the SCWO system, an assessment of actions taken in response to the 2012 NRC report *The Blue Grass Chemical Agent Destruction Pilot Plant's Water Recovery System* (Letter Report), and how systemization of the SCWO system and WRS might be affected by recommendations from that prior report.

To accomplish this task, the NRC established the Committee on Assessment of Supercritical Water Oxidation System Testing for the Blue Grass Chemical Agent Destruction Pilot Plant (the SCWO committee). This report presents the SCWO committee's background discussions, findings, and recommendations pursuant to these tasks. The committee's statement of task was as follows:

> The National Research Council will establish a committee for an assessment of First-Of-A-Kind factory acceptance test performance results of the General Atomics SCWO system design and recommendations for testing during systemization at BGCAPP:
>
> - Examine test reports and results as made available within the timeframe of this study with respect to verification of the functionality of tested SCWO system components, operability under normal and abnormal conditions, and performance in meeting throughput and other operational requirements;
> - Provide an evaluation of how well the test data supports conclusions reached;
> - Provide recommendations on SCWO systemization testing at BGCAPP inclusive of durability testing; and
> - Discuss systemization testing objectives and concepts in consideration of committee findings from the BGCAPP Water Recovery System (WRS) study.

After chemical neutralization in the main part of the BGCAPP plant, the agent and energetics hydrolysates will be sent to hydrolysate tanks, where they will be stored until they are blended for further processing in the SCWO reactors. Aluminum will also be removed from the energetics hydrolysate prior to blending. Also, chemical additives are added to allow the flow of salts through the reactors. In the SCWO reactors the blended hydrolysate will be mixed with supercritical water, air, and a fuel and exposed to conditions of roughly 1200°F and 3,400 psia. The resulting oxidation will convert elements to their most stable oxidized state. Thus, carbon is oxidized to carbon dioxide, hydrogen to water, sulfur to sulfates, and so on. However, salts such as sodium sulfate will not dissolve in supercritical water and can block outlet orifices and coat the walls if not properly managed.

The supercritical hydrolysate streams in the reactor can be very corrosive. Thus, a sacrificial titanium liner is inserted into the reactor to protect the outer pressure vessel walls. The titanium liners will have to be replaced periodically owing to corrosion. Sarin (GB) hydrolysate is the most corrosive and mustard hydrolysate is the least corrosive. After the SCWO process, the SCWO effluent will be cooled by quench water recycled from the WRS. This is to manage the salt buildup problem. Finally, the temperature and pressure are let down and the gaseous and liquid effluents are separated. At letdown, the salts dissolve into the water.

The liquid SCWO effluent, water with dissolved salts and possibly other solids (depending on the hydrolysate being processed), will be passed through a WRS for purification. Coagulant and prefilters will be used to remove solids from the effluent. The resulting salt-containing water will be passed through a reverse osmosis membrane to filter out the salts. At least 70 percent of the effluent will be passed through the membrane and emerge as permeate with a level of total dissolved solids of less than 500 mg/L. What does not pass through the membrane will become a concentrated brine that will have to be disposed of off-site. A portion of the permeate will be recycled to the SCWO reactors as described above. Figure S-1 depicts the combined SCWO and WRS systems.

The SCWO committee, after extensive study of test

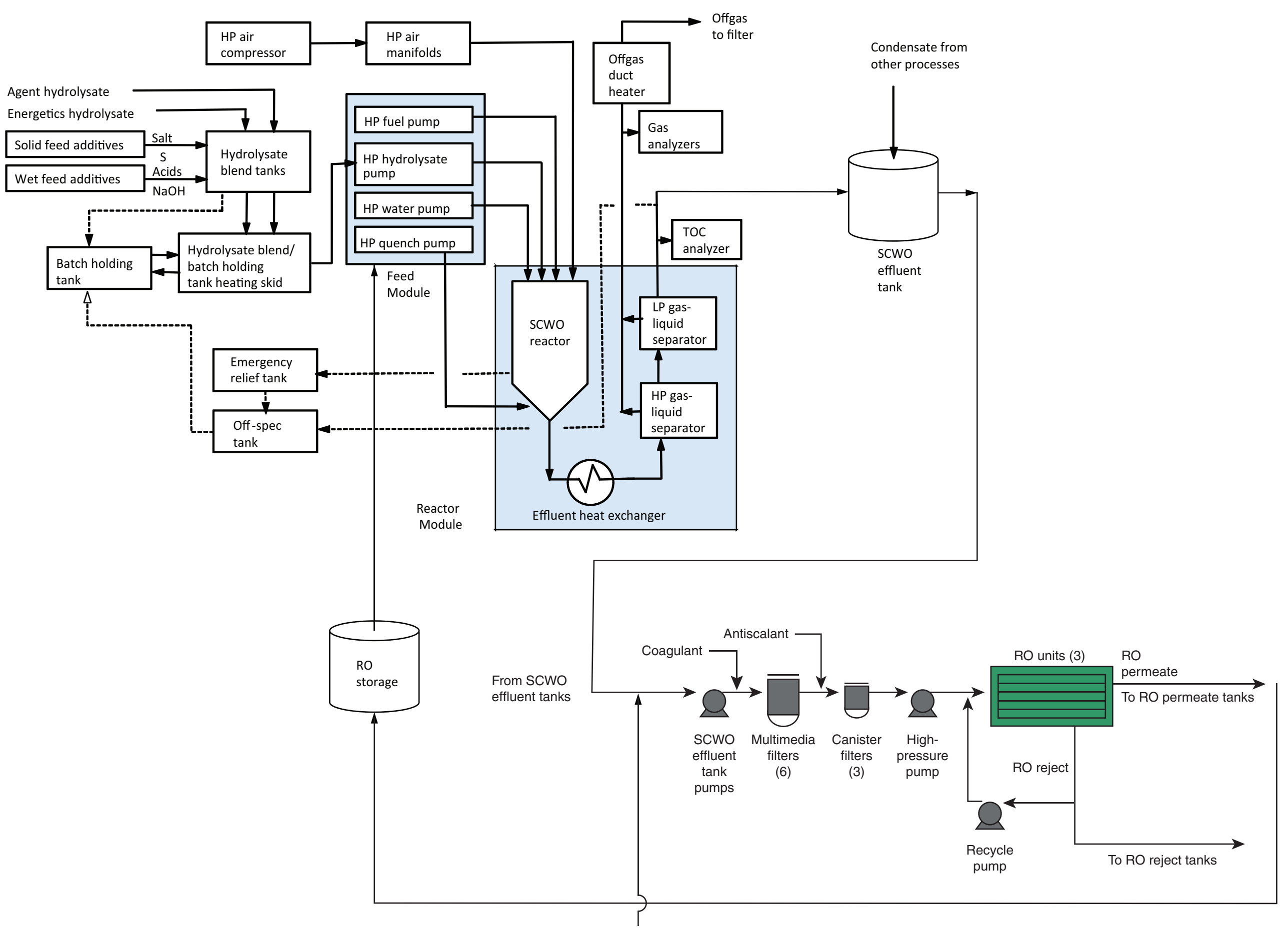

FIGURE S-1 Flow diagram of SCWO system and reverse osmosis WRS. SOURCE: Adapted from Dan Jensen, advanced process system program manager, General Atomics, "SCWO System Equipment and Layout," presentation to the committee, January 7, 2013; and NRC, 2012.

documents, briefings by contractor and BGCAPP staff, plant visits, and much deliberation arrived at the following findings and recommendations. They are arranged in the order in which the appear in the report.

FINDINGS AND RECOMMENDATIONS

Chapter 2 of this report reviews and assesses the results of FOAK testing. The committee had discussions with the BGCAPP project staff and the SCWO system contractor and reviewed a significant amount of information, including the preliminary FOAK test report. These are the findings and recommendations resulting from this.

Corrosion

Finding 2-1. The FOAK testing was adequate to establish the expected operating lifetime for the titanium liners. This expected operating lifetime is sufficient to enable continued safe operations and adequate operational throughput except for VX hydrolysate.

Finding 2-2. The 300-hr liner change-out interval recommended for the operational GB hydrolysate campaign is adequate if the operating temperature remains at the recommended 1150°F and the flow rate is 1,000 lb/hr. The 300-hr change-out interval is not adequate if a higher operating temperature (1200°F vs. 1150°F) is reached in the reactor for significant lengths of operation. It also may not be adequate for flow rates above 1,000 lb/hr.

Finding 2-3. The 400-hr liner change-out interval recommended for the VX nerve agent campaign is not supported by the worst-case corrosion data in the draft FOAK preliminary test report.

Recommendation 2-1. The Blue Grass Chemical Agent Destruction Pilot Plant staff should shorten the liner change-out period for VX processing from the 400 hr recommended in the test report until the corrosion rates under actual operating conditions are verified. Two hundred hours would be a better initial change-out period.

Finding 2-4. Corrosion thinning of the thermowells (accompanied by mechanical failure when minimal material remains) is a critical failure path for the reactors and is expected to be the most frequent maintenance issue associated with continuous operations.

Recommendation 2-2. The diameter of the thermowells should be increased to at least 0.75 in. from the current diameter of 0.50 in. by increasing the wall thickness. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should use existing corrosion data to estimate the lifetime of these new thermowells. This operation is a simple modification that would lengthen the thermowell life during operations and help minimize maintenance-related reactor shutdowns.

Finding 2-5. As noted above, the corrosion of thermowells is greater for higher feed velocities than for lower feed velocities. Another way to address the corrosion of thermowells could be by reducing the feed velocity.

Finding 2-6. Any new alloy used for the thermowells, or any coatings applied to the thermowells, would have to be qualified before use in the SCWO system. There is no guarantee that corrosion performance would improve. Using a lower processing temperature for sarin (GB) processing and using an alternative geometry for the titanium cap would likely necessitate further testing to ascertain whether these changes would affect SCWO processing operations.

Finding 2-7. Based on the test data, the committee believes that availability goals can be met with grade 2 titanium thermowells of appropriate wall thickness.

Recommendation 2-3. The corrosion issue with thermowells should not be resolved by attempting to qualify another material. Grade 2 titanium should be used as planned. Other potential strategies for extending thermowell life (i.e., coatings, alternative geometries, reduced operating temperature, and hardened titanium alloys) need not be explored since simply increasing the wall thickness of the thermowells will extend their operational life and thus reactor uptime.

Elemental Sulfur Additive

Finding 2-8. The elemental sulfur additive did not have any adverse impact on FOAK testing and successfully resolved the issues it was intended to.

Recommendation 2-4. Elemental sulfur additive should be used instead of sulfuric acid additive.

Variation in Feed Composition

Finding 2-9. The limited feed variations tested during FOAK testing did not result in any negative impacts to the SCWO process. Variations other than those tested during FOAK testing could be a concern and are addressed in Chapter 3.

Functionality During FOAK Testing

High-Pressure Air Compressor

Finding 2-10. There was a much higher failure rate for the high-pressure air compressor than would be expected from a mature system. These failures repeatedly interrupted FOAK testing. The multiple issues with the air compressor, which is a single, critical component of the SCWO system, are of concern to the committee.

Recommendation 2-5. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should review the maintenance and start-up plan for the air compressors so that they are maintained to industry standards. The project staff should use the time between compressor delivery and systemization to run the compressors, to discover any problems similar to those which occurred during FOAK testing, with the goal of obtaining reliability comparable to that of the supercritical water oxidation reactors.

Finding 2-11. The oil-water separator appears to present the risk of a critical single-point failure that could shut the entire SCWO process down.

Recommendation 2-6. In addition to the action recommended in Recommendation 2-5, the Blue Grass Chemical Agent Destruction Pilot Plant project staff should consider mitigation strategies such as having an additional oil-water separator (OWS) in parallel that could run should the main OWS require maintenance. Additionally, a spare OWS could be kept on hand.

High-Pressure Quench Water

Finding 2-12. The processing of the modified blended H hydrolysate simulant recipe at 1275°F proceeded smoothly with little corrosion and complete oxidation.

Recommendation 2-7. The Blue Grass Chemical Agent Destruction Pilot Plant supercritical water oxidation system test plan should ensure that the recipe for the blended H hydrolysate is the same as the recipe used in the FOAK tests.

High-Pressure Hydrolysate Feed

Finding 2-13. Particulates in the blended hydrolysate simulant, which was not filtered, caused the check valves to stick during testing.

Maintainability

Finding 2-14. The overall first-of-a-kind testing objectives for the supercritical water oxidation system to be used at the Blue Grass Chemical Agent Destruction Pilot Plant were met. The processes and subsystems, inclusive of maintenance activities, performed individually and collectively to meet test objectives and exceed the target of 76 percent availability.

Chapter 3 of the report considers systemization of the SCWO reactors at BGCAPP. In addition to the preliminary FOAK test report, the committee also reviewed the Systemization Implementation Plan and had extensive discussions with the BGCAPP project staff. The following findings and recommendations resulted from this work.

SCWO Feed Composition

Finding 3-1. Compositional variations within the energetics and agent feedstocks are dampened by the blending of multiple batches and post-hydrolysis neutralization to a common pH range. It is unclear, however, how the SCWO system would respond if it received a feed with a composition outside the range tested during FOAK testing.

Recommendation 3-1. The range of acceptable feed compositions for the SCWO unit, which must be achieved in the hydrolysate blend tank, should be clearly specified. These compositional parameters should be based on the range of compositions actually used and verified during testing of the SCWO unit.

Finding 3-2. There is uncertainty as to whether the agitation and heating methodologies used during FOAK testing accurately represent the conditions that will be present in the full-scale hydrolysate storage tanks.

Recommendation 3-2. The full-scale agitation/circulation system at the Blue Grass Chemical Agent Destruction Pilot Plant should be evaluated upon systemization. Care should be taken to avoid conditions where sulfur can melt on the heater surfaces, and vigorous agitation should be applied near the bottom of the tank. The blended sarin (GB) hydrolysate should be sampled to confirm that the agitation and heating conditions are sufficient to maintain uniform feed composition.

Safety

Maintenance

Finding 3-3. There is uncertainty regarding which parts of the SCWO system may have to shut down during parts (e.g., liner or thermowell) replacement. There are also concerns about worker safety since at least two SCWO units will be running simultaneously and they are located close to each other in the process building.

Finding 3-4. Current plans permit maintenance personnel to be in the SCWO bay while adjacent SCWO units are operating. The committee is concerned that existing safety planning and procedures may be inadequate for this situation. If current plans are implemented, the committee believes additional worker protection would be warranted.

Recommendation 3-3. The safety protocols used during first-of-a-kind testing need to be adapted and applied to operation and maintenance of the three parallel units at the Blue Grass Chemical Agent Destruction Pilot Plant. This includes not conducting maintenance adjacent to operating supercritical water oxidation reactors.

Recommendation 3-4. If the safety protocols used during first-of-a-kind testing are not adopted for SCWO operations and maintenance, the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) project staff should conduct detailed operational risk and safety analyses before allowing personnel to conduct maintenance activities in close proximity to operating SCWO reactors. BGCAPP staff should also investigate additional worker protection, such as supplemental barriers between workers and operating SCWO reactors, which could also capture debris.

Process Exhaust

Finding 3-5. The discharge of process gas effluents into the general atmosphere of a building is not a good design practice. Such discharge can pose any number of safety risks to personnel depending on the composition and volume of the gas effluent.

Recommendation 3-5. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should evaluate the SCWO process building design to ensure that the quality of the air inside the emergency relief tank room is safe for personnel. Remedial action could include the discharge of SCWO gas effluent through the appropriate offgas treatment system rather than to the atmosphere inside the building, air quality monitoring inside the emergency relief room with appropriate alarm settings, or other approaches that would ensure the room and building air quality is safe for personnel.

Recommendation 3-6. If process exhaust is to be not vented through the appropriate offgas treatment system, an operational risk and safety evaluation should be conducted on the venting of process exhaust into the SCWO process building.

Personnel Issues and Knowledge Transfer/Retention

Finding 3-6. The committee is concerned about how the know-how, knowledge, and experience obtained by the system contractor SCWO system operators and engineers, and by the Blue Grass Chemical Agent Destruction Pilot Plant staff who shadowed the system contractor operators, will be preserved during the multiyear hiatus between equipment delivery and systemization.

Recommendation 3-7. Plans should be made for periodically providing refresher training opportunities for SCWO plant operators and personnel during downtime and systemization activities. This training should include actual system operations to the extent possible. A manual should be developed for SCWO system operations and used routinely as part of training and maintaining the readiness of the plant personnel and the process equipment and systems throughout systemization. Such a manual is described more fully in a later section in Chapter 3.

Effects of Aging and Storage on Component Operability

Finding 3-7. Systemization will use equipment that is to be acquired years before its operation.

Recommendation 3-8. A detailed maintenance schedule should be created that leaves ample time to test and evaluate all subsystems of the SCWO system. The schedule should include ample training time for operators to familiarize themselves with the equipment.

Finding 3-8. SCWO system process equipment (e.g., reactor and peripherals, compressor, and pumps) will be shipped to the Blue Grass Chemical Agent Destruction Pilot Plant and remain in storage for several years prior to start-up of the SCWO process for systemization and eventually for operations. Additional extended periods of idleness are likely. The committee has concerns about whether the equipment, either as a working system or as individual components, will perform as designed and expected after sitting idle for such a long time.

Recommendation 3-9. In addition to planned systemization activities, plans should be made for regularly testing or operating the various SCWO and water recovery system components. These plans should be included in the interim SCWO operations manual for the interim period between delivery and operations, described in the next section.

SCWO Operations Manual for Interim Period

Finding 3-9. A manual is needed that addresses the concerns discussed above for the periods between equipment delivery and systemization, during systemization, and between systemization and operations, and including integrated SCWO and water recovery system operation. Creating the manual in electronic form would allow for maximum visibility across a wide range of information in a searchable framework on portable platforms such as tablet computers.

Recommendation 3-10. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should prepare a manual specifically to be used in the interim period preceding SCWO systemization, throughout the SCWO systemization time period, and during the time following SCWO systemization, prior to plant operation. This manual should also address integrated SCWO and water recovery system maintenance and operation during these periods and should address all the concerns discussed above. The manual should be prepared in electronic form.

Cyanide

Finding 3-10. Cyanide will be present in the energetics and blended hydrolysate streams. This must be managed to protect worker safety. The testing done to date shows that the SCWO process will destroy any HCN or CN^- present in the liquid hydrolysate feed to undetectable levels. A formal risk analysis would be needed to quantify the actual risks to workers.

Recommendation 3-11. If cyanide cannot be removed from the hydrolysate, affected personnel should be informed that if exposure to hydrolysate occurs in an off-normal situation, the hydrolysate could have contained up to approximately 7 ppm, or 300 μM, cyanide. Information about the possible presence of cyanide should also be included in emergency response manuals or other documentation so that first responders are aware of the potential risk. Workers should be trained in how to recognize exposure to cyanide and what should be done while awaiting first responders.

Recommendation 3-12. The Blue Grass Chemical Agent Destruction Pilot Plant project management should quantify the amount of HCN gas that vents from the aluminum filtration system and install an appropriate mitigation to avoid worker/public exposure if the concentrations are above the local air quality release limits. If cyanide cannot be removed from the hydrolysate, project management should conduct a risk and safety analysis to identify the risks and mitigation strategies.

Finding 3-11. Which methodology will be used to manage the cyanide problem has not yet been determined. Whatever methodology is used will change the chemistry of the SCWO system feed and could impact the performance of the system.

Recommendation 3-13. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should identify an effective cyanide management system that does not negatively impact the performance of the SCWO unit.

Overall System Operations and Computer Model

Finding 3-12. There is no computer simulation model that describes the integrated system operations, over time, of all SCWO system processes or of the entire SCWO/WRS. A model tailored for the SCWO and the integrated SCWO/WRS systems would permit system performance to be optimized.

Recommendation 3-14. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should consider investing in a simulation-optimization study where external experts can help develop a computerized simulation-optimization model that describes the operations, over time, for the entire combined supercritical water oxidation and water recovery system.

Chapter 4 discusses systemization of the WRS and integrated SCWO and WRS systems. It does so bearing in mind the 2012 NRC report *The Blue Grass Chemical Agent Destruction Pilot Plant's Water Recovery System*. The chapter also takes into account the results of the FOAK testing of the SCWO system and how possible changes in the makeup of the SCWO effluent from what was considered in the 2012 report might affect systemization of the WRS.

BGCAPP Actions in Response to the 2012 NRC Report

Pretreatment

Finding 4-1. Although stable, fouling-free performance cannot be guaranteed ahead of time, the Blue Grass Chemical Agent Destruction Pilot Plant project staff appear to have taken appropriate engineering design measures to safeguard the reverse osmosis membranes from excessive fouling conditions.

Reverse Osmosis Membranes

Finding 4-2. The WRS committee's concerns about the storage of the RO membranes between delivery and systemization and their chemical cleaning appear to have been adequately addressed.

Materials of Construction

Finding 4-3. The materials of construction planned for use in the WRS now appear to have been adequately tested in representative environments. It is now possible to have confidence that the planned materials will perform adequately for the amount of time that the water recovery system will operate and in the anticipated environments.

Systemization of the WRS

Reverse Osmosis Membrane Storage after Systemization

Finding 4-4. There is the potential for membrane degradation between systemization and full plant operation unless care is taken to preserve the membrane.

Recommendation 4-1. Blue Grass Chemical Agent Destruction Pilot Plant operators should obtain, review, and follow manufacturer recommendations for membrane preservation between systemization and start-up of plant operations.

Development of Water Balance

Finding 4-5. The operation of the WRS has not been optimized for use with the SCWO system.

Recommendation 4-2. Blue Grass Chemical Agent Destruction Pilot Plant staff should optimize permeate generation to match supercritical water oxidation system quench demand.

Impact of Water Recycling on the SCWO System

Finding 4-6. The committee foresees no problems with using the water recovered via reverse osmosis in the SCWO system other than slight changes that may need to be made to the monitoring parameters.

Recommendation 4-3. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should characterize the reverse osmosis effluent for each agent campaign. They should then reestablish normal operating conductivities when reverse osmosis permeate is injected (recycled) at the bottom of the SCWO reactor.

Integrated SCWO and WRS Operations

Finding 4-7. Since the final effluent total organic carbon (TOC) level will be based on permit levels, the WRS feed may have a considerably higher level of TOC than envisioned in previous reports, and this could lead to more rapid and severe fouling of the reverse osmosis membrane than originally envisioned in the WRS design. The main concern is the need for more frequent and extensive cleaning (ideally between campaigns), which could lead to rapid membrane degradation and call for premature replacement.

Recommendation 4-4. Blue Grass Chemical Agent Destruction Pilot Plant operators should monitor the reverse osmosis membranes and system during systemization testing to determine if there is any evidence of premature membrane degradation. If this is observed, then the membranes would need to be replaced sooner. This is a minor operational issue that can be handled by keeping a spare set of membranes on-site at all times.

REFERENCE

NRC (National Research Council). 2012. The Blue Grass Chemical Agent Destruction Pilot Plant's Water Recovery System (Letter Report). Washington, D.C.: The National Academies Press.

1

Introduction

The United States joined the 1993 Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction (CWC) in April 1997. Under the CWC the United States, along with 188 other states as of 2012, agreed to eliminate their entire stockpiles of chemical weapons. The terms of the CWC originally mandated destruction of the U.S. stockpile by April 2007. The CWC allowed for one 5-year extension to this mandate, and the U.S. availed itself of this extension. Thus, the deadline for full stockpile destruction was extended until April 2012. Over 90 percent of the U.S. stockpile of chemical agent and munitions had been disposed of by this extended deadline. Of nine stockpile sites, seven have completed agent destruction and the disposal facilities are either closed or undergoing closure.[1] As of the writing of this report, the Pueblo Chemical Agent Destruction Pilot Plant, in Colorado, and the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP), in Kentucky, are being constructed to dispose of the remainder of the U.S. stockpile.

Initially, the U.S. Army, following recommendations from the National Research Council (NRC), chose incineration as the destruction method at all sites. Citizens in some states with stockpile storage sites, however, opposed incineration because they believed it was impossible to determine the exact nature of the effluents from the exhaust stacks at the incineration plants. In the end, incineration was used at four of the eight storage sites in the continental United States.[2] The stockpiles at each of these four sites consisted of assembled munitions and bulk stored agent. In response to growing public opposition to incineration, the Army developed alternative processes to neutralize chemical agents by hydrolysis. These processes were used to destroy the VX nerve agent at Newport, Indiana, and the mustard agent at Aberdeen, Maryland. Only bulk stored agent was present at those two sites.

In 1996, public opposition to incineration in Kentucky and Colorado caused Congress to enact Public Law 104-201, which instructed the Department of Defense to

> conduct an assessment of the chemical demilitarization program for destruction of assembled chemical munitions and of the alternative demilitarization technologies and processes (other than incineration) that could be used for the destruction of the lethal chemical agents that are associated with these munitions. (PL 104-201, section 142)

As a result, the Program Manager for Assembled Chemical Weapons Assessment[3] was established to

> identify and demonstrate not less than two alternatives to the baseline incineration process for the demilitarization of assembled chemical munitions. (PL 104-208, section 8065)

Following a detailed selection process among proposed methods for destroying the weapons at Blue Grass Army Depot, Kentucky, the Program Manager for Assembled Chemical Weapons Assessment selected technologies using hydrolysis to destroy both agent and energetic material (propellant, fuzes, and bursters) streams (see NRC, 2002). Hydrolysis will destroy chemical agent to a permit-mandated 99.9 percent, and the resulting hydrolysates no longer exhibit the acute toxicity of the original chemical warfare agents.[4]

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[1]These sites were the Aberdeen Chemical Agent Disposal Facility (Aberdeen, Maryland); Anniston Chemical Agent Disposal Facility (Anniston, Alabama); Johnston Atoll Chemical Agent Disposal System (Johnston Atoll), Newport Chemical Agent Disposal Facility (Newport, Indiana); Pine Bluff Chemical Agent Disposal Facility (Pine Bluff, Arkansas); Tooele Chemical Agent Disposal Facility (Tooele, Utah); and the Umatilla Chemical Agent Disposal Facility (Umatilla, Oregon).

[2]Anniston, Alabama; Pine Bluff, Arkansas; Tooele, Utah; and Umatilla, Oregon.

[3]The Program Manager for Assembled Chemical Weapons Assessment has since been renamed the Program Manager for Assembled Chemical Weapons Alternatives, its current name.

[4]Personal communnication between Steven Mantooth, Blue Grass Chemical Agent Destruction Pilot Plant program office, and James Myska, NRC study director, on February 5, 2013.

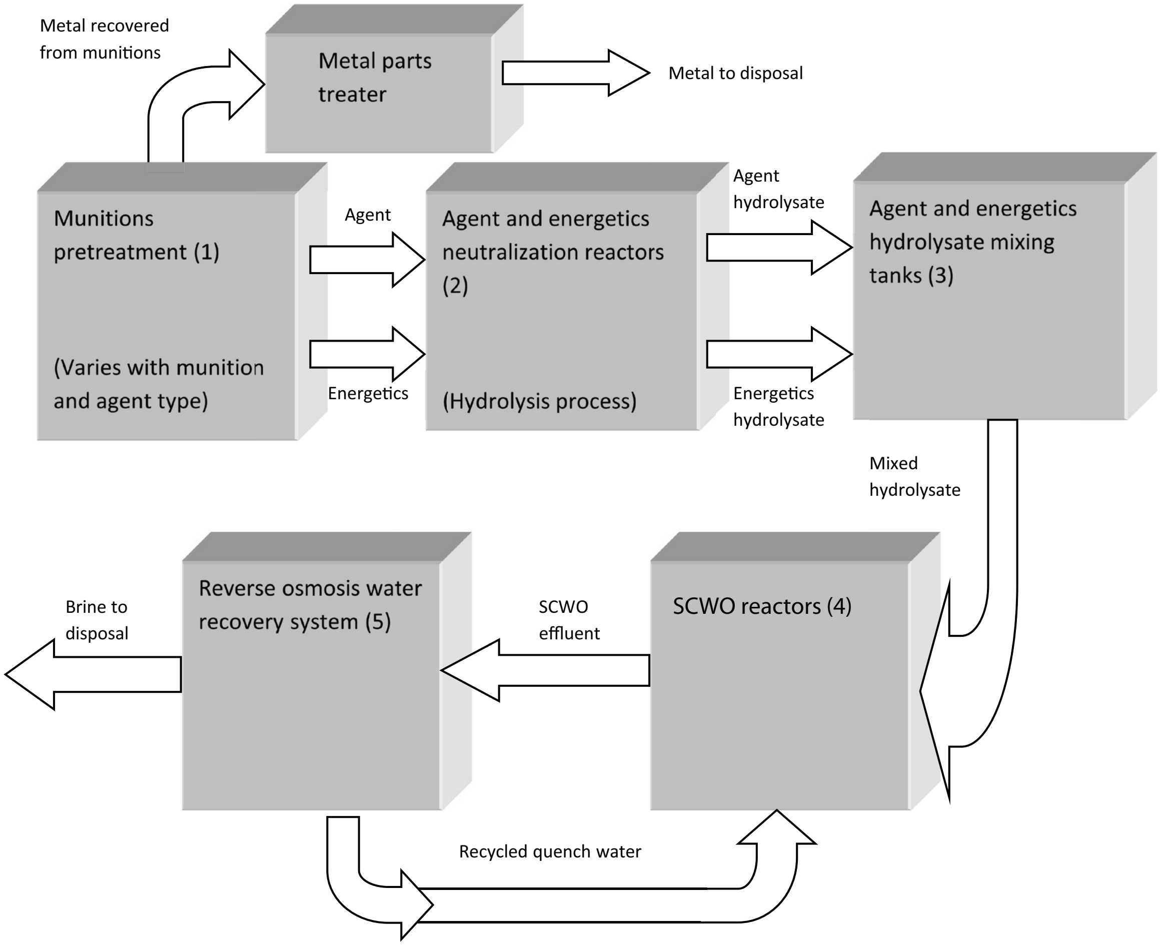

FIGURE 1-1 Simplified process diagram for the BGCAPP demilitarization process using hydrolysis followed by SCWO.

At BGCAPP, the blended agent and energetics hydrolysates will be treated by a supercritical water oxidation (SCWO) process to further process them into environmentally benign products. In total, roughly 6.1 million gallons of hydrolysate will have to be processed through the SCWO system.[5] The SCWO hardware has been built, tested, and is being shipped to BGCAPP as of this writing.

STOCKPILE CHARACTERISTICS

The stockpile to be processed at BGCAPP consists of 115-mm M55 rockets containing GB (sarin) or VX (69,479 total rounds); 155-mm M110 projectiles containing mustard agent (H) and 155-mm M121 projectiles containing VX (28,308 total rounds); and 3,977 8-in. M426 projectiles containing GB.[6,7] The VX and GB will be demilitarized using caustic hydrolysis. Any energetic materials disposed of at BGCAPP will also be treated by caustic hydrolysis. The mustard agent will be hydrolyzed using hot water, although at this writing an alternative process is being considered for the disposal of the mustard munitions because many of the mustard artillery rounds contain solidified or gelled mustard heels, which can be difficult to wash out.

OVERALL BGCAPP DEMILITARIZATION PLAN

A simplified diagram of the demilitarization process planned for use at BGCAPP, including hydrolysis and the SCWO and water recovery system (WRS) processes, is shown in Figure 1-1. Agent will be removed after mechanically breaching the munitions (1) using a sodium hydroxide

[5]John Barton, chief scientist, Bechtel Parsons Blue Grass Team, "BGCAPP Process Overview," presentation to the committee on January 7, 2013.

[6]Ibid.

[7]Conrad Whyne, Program Executive Officer, Assembled Chemical Weapons Alternatives, "Assembled Chemical Weapons Alternatives (ACWA) Program Update," presentation to the Committee on Chemical Demilitarization on December 4, 2012.

(or water in the case of mustard) washout process, then (2) producing hydrolysate that is still considered a toxic waste. The agent hydrolysate will be mixed with hydrolysate resulting from similar caustic treatment of the energetic materials removed from the munitions (3). This mixture will then be treated by the SCWO process (4) followed by a coupled reverse osmosis WRS for treating SCWO effluent (5). Some recovered water will be used as quench water in the SCWO units, and the remaining salt-containing WRS effluent will then be disposed of off-site.

At the time of this writing, the schedule for BGCAPP plant construction, systemization, and operation is not firmly set. The most recent schedule is shown in Figure 1-2.

This schedule shows that construction will be complete in mid-2017; systemization will proceed in parallel with construction and be complete by mid-2020. Agent processing operations will begin in mid-2020 and be completed by the end of 2023. Plant closure will then commence and be complete at the end of the first quarter of 2027. The BGCAPP project schedule is strikingly different from a typical industrial project schedule. This is a unique government project and is not subject to the usual schedule and budget constraints of a commercial operation. The schedule has slipped several times due to various budget issues and congressional actions. Also, the SCWO system is presently expected to operate for only 2-3 years, after which it then will be dismantled and disposed of.

DESCRIPTION OF THE SCWO PROCESS

The thermodynamic critical point for water is 704°F and 3,200 psia. Above these values, the water is described as being in a supercritical state, and its properties differ greatly from those observed under more familiar conditions. Figure 1-3 is a phase diagram for water and the conditions planned for the BGCAPP SCWO process. One important characteristic of supercritical water is that it behaves as a single-phase fluid throughout the supercritical region (i.e., it does not separate into discernible liquid and gaseous phases). However, at a given supercritical pressure its density (and other properties) can vary greatly as the temperature is varied over a relatively small range. Of interest for processing, water changes from a polar solvent at ambient conditions to a nonpolar solvent at supercritical states. It then becomes an excellent solvent for most nonpolar substances such as the organic materials present in the chemical agents stockpiled at BGCAPP. Conversely, at supercritical conditions water becomes a poor solvent for ionic materials such as salts.

If an organic compound is dissolved in supercritical water and excess oxygen is also introduced and dissolved, rapid and efficient oxidation of the organic compound can take place. This is the basis for the SCWO process. SCWO reactors have been proposed and built for many purposes such as sewage waste disposal and the destruction of undesirable pollutants such as polychlorinated biphenyls. A review of commercial-scale SCWO reactors and their performance is provided by Marrone (2012). He points out that many of the commercial SCWO installations have failed due to one of two factors: (1) unexpectedly high corrosion rates in the reactor or heat exchangers or (2) salt buildup in the reactor. Thus, modern SCWO designs carefully incorporate methods for sidestepping or mitigating these two factors.

The hydrolysates from the chemical neutralization of chemical agents and energetics contain organic components, making SCWO decomposition of them attractive. However, the hydrolysates also contain metallic components, which are converted into salts during hydrolysate processing. Thus, use of SCWO for agent destruction can be expected to face both of the problems inherent in the process: corrosion of the SCWO unit and heat exchangers, as well as solid salt buildup in the SCWO unit. First-of-a-kind (FOAK) testing of the BGCAPP SCWO units was meant to demonstrate that these potential problems have been successfully addressed in the SCWO system design to be used at BGCAPP.

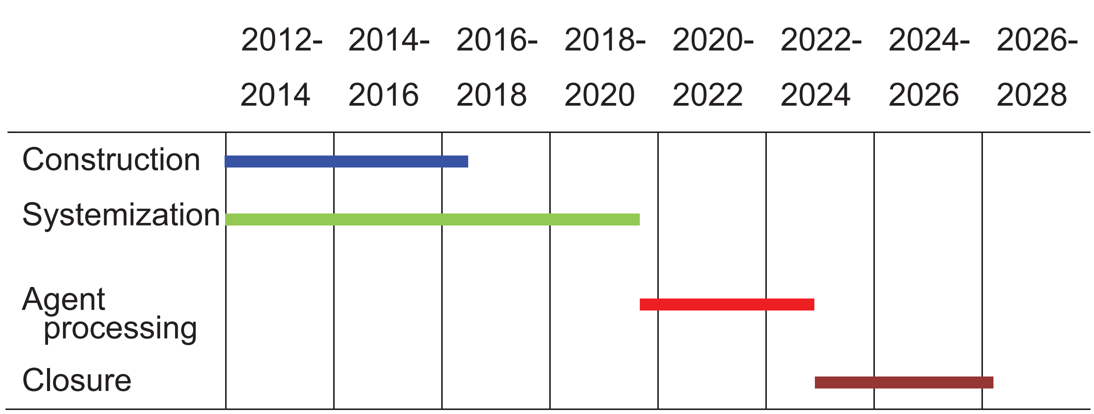

FIGURE 1-2 Program schedule for BGCAPP. SOURCE: Adapted from Joe Novad, Deputy Program Executive Officer, Assembled Chemical Weapons Alternatives, "Program Executive Office Assembled Chemical Weapons Alternatives Update," presentation to the Committee on Chemical Demilitarization, April 9, 2013.

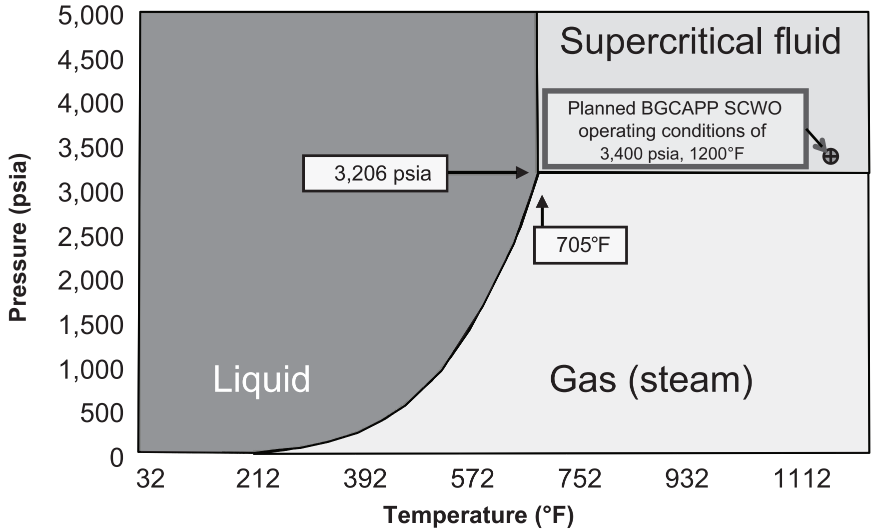

FIGURE 1-3 Phase diagram for water showing the operating conditions planned for the BGCAPP SCWO process. SOURCE: Adapted from John Barton, chief scientist, Bechtel Parsons Blue Grass Team, "BGCAPP Process Overview," presentation to the committee on January 7, 2013.

The SCWO reactor pressure vessel is made of Hastelloy C-276. A Hastelloy C-276 sleeve is placed inside the pressure vessel, and a sacrificial titanium liner is placed inside the sleeve to prevent corrosion of the sleeve and pressure vessel. This liner does not serve any structural purpose and does not need to do any more than support its own weight. The change-out periods for the liners are based on corrosion data from testing and set to ensure that the liner thickness is not corroded through prior to replacement. An air purge between the sleeve and the pressure vessel prevents reactor contents from entering the space between the liner and the pressure vessel. Material is introduced into the SCWO reactor through ports in the reactor head. Titanium thermowells also protrude into the reactor from the head. These thermowells hold thermocouples to monitor operating conditions. At the bottom of the reactor, quench water is used to cool the SCWO effluent. The materials have been chosen through a thorough series of assessments and tests to best handle the SCWO operational environment, and the design has matured over the course of more than a decade.

During operations, the SCWO reactor will first be brought to its operating temperature and pressure. The process streams, including the blended hydrolysate streams, will then be injected into the reactor and immediately subjected to supercritical conditions. Figure 1-4 shows the overall SCWO reactor. Figure 1-5 is a more detailed drawing of the reactor. It shows the major pieces of the reactor and how they are assembled, where the feed nozzle enters the reactor, where the thermowells are placed in the reactor, and the process outlet from the reactor.

FIGURE 1-4 Exterior view of the overall SCWO reactor. SOURCE: Personal communication between Steven Mantooth, Blue Grass Chemical Agent Destruction Pilot Plant program office, and James Myska, NRC study director, on August 1, 2013.

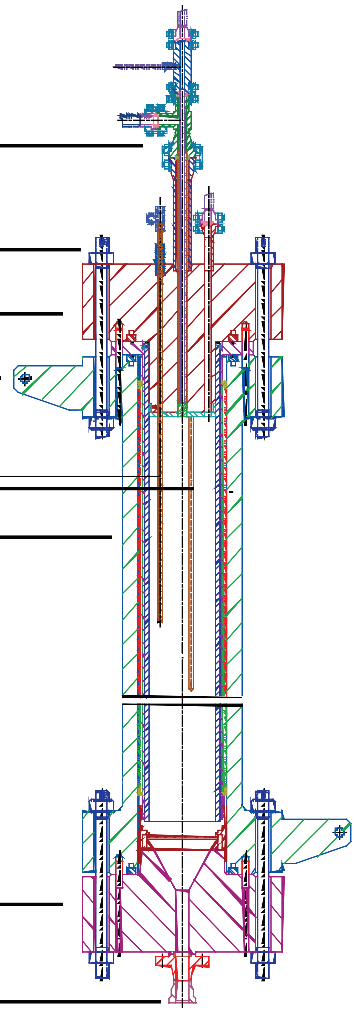

FIGURE 1-5 Detailed drawing of the reactor showing the main parts of the reactor and how they are assembled, where the feed nozzle enters the reactor, where the thermowells are placed in the reactor, and the process outlet from the reactor. SOURCE: Personal communication between Steven Mantooth, Blue Grass Chemical Agent Destruction Pilot Plant program office, and James Myska, NRC study director, on August 1, 2013.

THE INTEGRATED SCWO/WRS SYSTEM

This report is chiefly concerned with the SCWO system and with its interactions with the WRS. An equipment and flow diagram for this part of the BGCAPP installation is shown in more detail in Figure 1-6.

The effluent from the SCWO process will pass through the reverse osmosis water recovery system, where it will be separated into clean water (less than 500 mg/L of total dissolved solids) and a brine stream. A portion of the clean water will be recycled for use as a quench purge stream introduced near the outlet of the SCWO units to reduce the outlet temperature of the effluent stream and to dissolve the salts present in that stream. Any excess clean water from the WRS will be mixed with the brine stream and the mixture disposed of off-site.

SCWO SYSTEM DESIGN AND FOAK TEST OBJECTIVES

As stated above, the difficulties associated with SCWO processing—extreme corrosion conditions and potential salt buildup—require careful system design. The design of the SCWO system for BGCAPP is the result of a significant amount of prior assessment and testing that resulted in the choice of materials, design features, and processes to address these concerns.[8] The FOAK tests were to confirm that the full-scale production system would meet the operational requirements at BGCAPP. These tests used simulated hydrolysates that closely resembled the concentrations of all chemical species expected in the blended agent and energetic mixed feeds that will be processed at BGCAPP. Corrosion rates were measured under the flow rates and processing conditions expected at BGCAPP, including SCWO reactor start-up and shutdown. The system was also tested to determine whether modifications to operational conditions and chemical pretreatment of the blended hydrolysate simulants controlled salt buildup within acceptable limits.

The combined SCWO/WRS system was not tested as a coupled unit. This will be done during the BGCAPP systemization period.

STATEMENT OF TASK

The NRC will establish a committee for an assessment of FOAK factory acceptance test performance results of the General Atomics SCWO system design and recommendations for testing during systemization at BGCAPP:

- Examine test reports and results as made available within the time frame of this study with respect to verification of the functionality of tested SCWO system components, operability under normal and abnormal conditions, and performance in meeting throughput and other operational requirements;
- Provide an evaluation of how well the test data support conclusions reached;
- Provide recommendations on SCWO systemization testing at BGCAPP inclusive of durability testing; and
- Discuss systemization testing objectives and concepts in consideration of committee findings from the BGCAPP Water Recovery System (WRS) study report.

[8] See NRC, *Interim Design Assessment for the Blue Grass Chemical Agent Destruction Pilot Plant* (2005) and *Letter Report of Review and Assessment of the Proposals for Design and Operation of Designated Chemical Agent Destruction Pilot Plants (DCAPP-Blue Grass)* (2006); these two NRC reports addressed design.

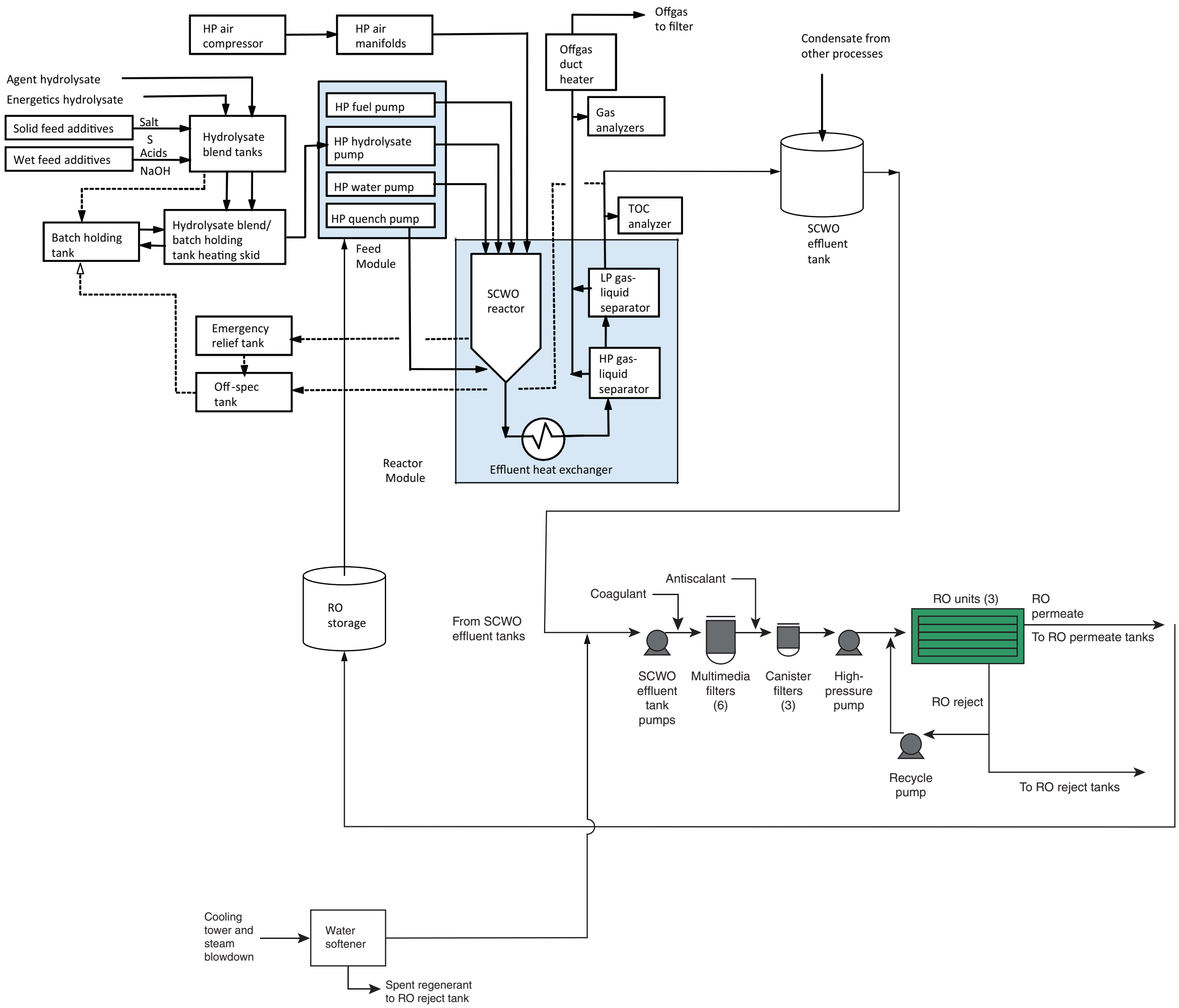

FIGURE 1-6 Flow diagram of SCWO system and reverse osmosis WRS. SOURCE: Adapted from Dan Jensen, advanced process system program manager, General Atomics, "SCWO System Equipment and Layout," presentation to the committee on January 7, 2013; and NRC, 2012.

REPORT OVERVIEW

This report addresses progress in the development, construction, and FOAK testing of the SCWO system. It also considers the interactions between the SCWO system and its associated reverse osmosis WRS. The report presents findings and recommendations for the systemization and preoperational testing of these combined process elements. It also addresses the adequacy of the BGCAPP response to findings and recommendations in the 2012 NRC report *The Blue Grass Chemical Agent Destruction Pilot Plant's Water Recovery System* (Letter Report).

SCWO is a mature technology with a strong scientific and engineering base underlying it. As noted in the preceding section, "SCWO System Design and FOAK Test Objectives," a significant amount of design work, laboratory work, and testing have been put into the current SCWO design. This has been addressed in previous NRC reports.[9] As can be seen from the statement of task, however, this committee was not charged to assess the design of the SCWO system to be used at BGCAPP or to address its scientific bases, and this report does not do so. The committee does not review the technical literature on SCWO but rather accepts the technology's

[9]For example, *Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Blue Grass Army Depot* (2002); *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 (Letter Report)* (2002); *Interim Design Assessment for the Blue Grass Chemical Agent Destruction Pilot Plant* (2005); and *Letter Report of Review and Assessment of the Proposals for Design and Operation of Designated Chemical Agent Destruction Pilot Plants (DCAPP-Blue Grass)* (2006).

maturity and focuses on its task of examining and evaluating a specific set of test data.

Accordingly, this report is confined to a review and assessment of the FOAK testing of the SCWO system hardware that will be used at BGCAPP, an assessment of the BGCAPP response to the 2012 NRC WRS report, and making recommendations for moving forward to systemization. In the course of its work, the committee made use of a broad range of sources of technical information, including the following:

- *Test Report for Supercritical Water Oxidation (SCWO) First-of-a-Kind (FOAK) Test*, April, Preliminary Draft (BPBGT, 2013);
- *Test Plan for Supercritical Water Oxidation (SCWO) First-of-a-Kind (FOAK) Test*, Rev. 1, July (BPBGT, 2012);
- *Supercritical Water Oxidation: Current Status of Full-Scale Commercial Activity for Waste Destruction* (Marrone, 2012);
- *Bench-Scale Evaluation of GB Hydrolysis*, TRRP #02a Phase II Test Report, Rev. 0 (Malloy et al., 2007);
- *Technical Risk Reduction Project (TRRP) 07 and 09 Report on Supercritical Water Oxidation Blended Feed Performance Tests*, Rev. 0 (BPBGT, 2005);
- Process flow diagrams for the SCWO system;
- Briefings from BGCAPP and system contractor staff;
- Rounds of technical questions and answers with the BGCAPP staff; and
- Detailed discussions with BGCAPP and contractor staff.

This report is organized into four chapters. Following the general introduction in Chapter 1, Chapter 2 reviews the FOAK test results and assesses whether the tests have adequately addressed concerns about corrosion rates and salt buildup and removal. Chapter 3 addresses the installation, scheduling, staffing, and testing envisioned for the SCWO units when delivered, installed, and systemized at BGCAPP and offers committee observations about the systemization process. Finally, Chapter 4 addresses the response to *The Blue Grass Chemical Agent Destruction Pilot Plant's Water Recovery System* (Letter Report) and discusses and makes recommendations for the systemization of the combined SCWO/WRS systems. In each chapter, findings and recommendations are set forth based on the observations of the review committee.

The statement of task only directs the committee to examine the FOAK testing results for the SCWO unit that was tested and the systemization of the coupled SCWO/WRS when installed at BGCAPP. Factors beyond those addressed in the FOAK testing are not examined unless the committee believed they could potentially affect the operation of the systemized SCWO/WRS.

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2

First-of-a-Kind Testing

INTEGRATED OPERATIONS

The committee's first task in this study was to determine whether the supercritical water oxidation (SCWO) system met its first-of-a-kind (FOAK) testing goals and whether the testing supports the systemization of the SCWO system at Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP). The FOAK testing involved integrated operation of one of the three SCWO reactor trains and was conducted at the system contractor's facility in San Diego, California.[1] The functionality, operability, performance, and maintainability testing were all completed. In summary, four test campaigns were completed: integrated operations (no simulant), blended simulants of sarin (GB) and energetics hydrolysates, blended simulants of VX nerve agent and energetics hydrolysates, and blended simulants of H and energetics hydrolysates. Simulants of the agent and energetics hydrolysates were blended at the system contractor's site to have chemical compositions as representative of the actual agent and energetics hydrolysates feeds as possible. Tables 2-1, 2-2, and 2-3 give the composition of the simulated blended hydrolysates. The chemical reactions that occur on the SCWO reactor are standard oxidation reactions. For the interested reader, a detailed listing of the SCWO effluents resulting from the processing of H, GB, and VX hydrolysates can be found in BPBGT, 2007.

In the final FOAK tests, each of these simulants was tested in aggregate for between 96 and 100 hr of operation at a feed rate of approximately 1,000 lb/hr. Stable and predictable temperature and pressure control was achieved during SCWO processing. Destruction of organics was confirmed to less than 10 ppm by measuring total organic carbon (TOC) in the effluent. Any salt buildup was sufficiently minimized so as to not affect system availability goals. Variations in a limited number of compositional and operational parameters were explored. These variations were tests of abnormal SCWO operating conditions; that is, variations from the planned normal operating conditions specific to each agent being processed. The abnormal operating conditions tested included off-normal flow rates, temperatures, and hydrolysate composition. These abnormal conditions and their impact on the system are addressed in more detail in the following sections of the report. Also, as discussed below in the section "Maintenance," errors were induced to test system response to abnormal operating conditions. Despite numerous minor maintenance issues, a system availability greater than the target of 76 percent was achieved. The availabilities achieved during the 100-hr tests were as follows: GB, 88.5 percent; VX, 96.5 percent; and H, 100 percent.[2]

Both the chemical processes in the SCWO reactor and the SCWO process equipment were reviewed to assess whether the objectives described in the SCWO FOAK testing presentation were met. Because various scheduled and unscheduled maintenance events are inevitable in such a complex system, the contractor expressed test success as achieving an overall system availability goal of 76 percent. The FOAK test objectives were to provide full-scale verification for H, GB, and VX blended hydrolysate simulant[3] feeds of the following items:

- Reactor rinsing requirements, if any;
- The replacement of sulfuric acid with elemental sulfur in the GB campaign;
- Variations in a limited number of feed compositions and flow rates;
- Reactor liner and thermowell corrosion; and
- Ability to meet 76 percent overall availability.[4]

[1]General Atomics is the system contractor for the SCWO systems that will be used at BGCAPP.

[2]Personal communication between Steven Mantooth, Blue Grass Chemical Agent Destruction Pilot Plant program office, and James Myska, NRC study director, on April 25, 2013.

[3]Blended hydrolysate consists of a mix of agent and energetics hydrolysate.

[4]Kevin Downey, advanced process system manager, General Atomics, "SCWO Factory Acceptance Testing," presentation to the committee on January 7, 2013.

TABLE 2-1 Simulated Blended GB and Energetics Hydrolysates

Constituent	Wt-%
Deionized water (H_2O)	80.64
Sodium sulfate (Na_2SO_4)	9.14
Sodium chloride (NaCl)	3.81
Sodium hydroxide (NaOH)	1.08
Dimethylmethyl phosphonate ($C_3H_9O_3P$)	1.66
35 percent Hydrochloric acid (HCl)	1.38
Sodium formate ($NaCHO_2$)	0.85
Sodium fluoride (NaF)	0.52
100 percent Isopropanol (C_3H_8O)	0.33
Sodium nitrite ($NaNO_2$)	0.28
Sulfur (S)	0.26
tri-n-Butylamine ($C_{12}H_{27}N$)	0.06

SOURCE: BPBGT, 2013.

TABLE 2-2 Simulated Blended VX and Energetics Hydrolysates

Constituent	Wt-%
Deionized water (H_2O)	74.18
Sodium sulfate (Na_2SO_4)	7.40
56 percent Sodium isethionate ($C_2H_5NaO_4S$)	4.34
Sodium hydroxide (NaOH)	1.77
Sodium chloride (NaCl)	4.00
85 percent Diethanolamine ($C_4H_{11}NO_2$)	2.15
Dimethylmethyl phosphonate ($C_3H_9O_3P$)	2.06
Denatured ethanol (C_2H_6O)	1.29
35 percent Hydrochloric acid (HCl)	1.25
Sodium formate ($NaCHO_2$)	0.68
98 percent Sulfuric acid (H_2SO_4)	0.65
Sodium nitrite ($NaNO_2$)	0.23

SOURCE: BPBGT, 2013.

TABLE 2-3 Simulated Blended H and Energetics Hydrolysates

Constituent	Wt-%
Deionized water (H_2O)	88.34
Sodium hydroxide (NaOH)	3.04
Thiodiglycol ($C_4H_{10}O_2S$)	2.52
Sodium chloride (NaCl)	1.38
Ferric chloride ($FeCl_3$)	2.92
Sodium sulfate (Na_2SO_4)	1.11
Sulfur (S)	0.43
Sodium formate ($NaCHO_2$)	0.18
Sodium bicarbonate ($NaHCO_3$)	0.09

SOURCE: BPBGT, 2013.

This report evaluates the results of the FOAK from two perspectives. First, the effectiveness of each step was assessed with respect to the individual operation of that step (e.g., Did the air compressor work?). Then, each step was evaluated with respect to any overall impact on the process (e.g., Did the reliability of the air compressor affect system availability goals?). The processes/subsystems evaluated include the following:

- Elemental sulfur additive;
- Limited variations in feed composition;
- High-pressure air compressor;
- High-pressure quench water;
- High-pressure hydrolysate feed, high-pressure fuel feed;
- Gas and liquid sampling and analyses;
- Temperature and pressure letdown and effluent;
- High-pressure water feed, preheater;
- Maintainability (seven anticipated maintenance activities were evaluated during FOAK testing); and
- Integrated operations.

OVERVIEW OF TEST RESULTS

This section discusses the test results that the committee believes to be the most significant. These are either areas of particular criticality to the overall SCWO process, or areas where significant challenges were encountered. This is not intended to be a comprehensive review of the FOAK test report, so not every aspect of the FOAK testing and results is discussed here. If something worked well or a particular challenge was judged by the committee to be minor based on its experience, it is not addressed here. The committee had access to a wide range of technical material while conducting its work, including test plans and reports, process flow diagrams, briefings, and discussions with BGCAPP and system contractor staff. Please see the list of this material in Chapter 1.

Corrosion

The severe conditions of the SCWO process and the generation of molten salts have a corrosive effect on the interior of the reactor. This corrosion requires a relatively inert metal for use in the reactor design. The committee assessed the ability of the titanium liners and thermowells to withstand the reaction conditions within the SCWO unit and evaluated whether the corrosion rates noted during testing support a SCWO availability of 76 percent or greater.

The liner of the SCWO reactor is 10 ft long, has an inner diameter of 7.625 in., and a wall thickness of 0.5 in. The material of construction is grade 2 titanium. The liner is not a pressure vessel but is contained in one with an annular space between the pressure vessel and the titanium liner. The liner mitigates the potential for penetration of the hydrolysate into the annular space and, thus, corrosion of the pressure vessel. Corrosion of the pressure vessel itself is not an issue since failure of the liner results in shutdown of the reactor. The liner and thermowells are subject to the highest temperatures and pressures of the components of the SCWO system.

Periodic reactor liner change-out is required because of corrosion. The highest liner corrosion occurs in the first several diameters from the top of the reactor and the high-

TABLE 2-4 Summary of Reported Maximum Average Corrosion Data Reported from FOAK Testing

Test Conditions	Maximum Average Liner Corrosion Rate (mil/hr)	Maximum Average Thermowell Corrosion Rate (mil/hr)
GB 24-hour low sulfur	1.6	1.9
GB 24-hour high sulfur	1.8	1.6
GB 8-hour +2 percent sulfur	1.0	1.5
GB 8-hour –2 percent sulfur	1.0	1.7
GB 24-hour low velocity (800 lb/hr)	0.56	0.55
GB 24-hour high velocity (1,200 lb/hr)	1.2	1.7
GB, 1,200°F	1.8	1.9
GB, 1,150°F	1.2	1.7
VX 8-hour +2 percent HCl	1.2	0.67
VX 8-hour +2 percent NaCl	1.0	0.67
VX 24-hour low velocity (800 lb/hr)	0.97	0.94
VX 24-hour high velocity (1,200 lb/hr)	0.95	1.2
H 24-hour high velocity (1,200 lb/hr)	0.01	0.04
GB performance test, 100-hr (1,000 lb/hr)	1.1	1.5
VX performance test, 100-hr (1,000 lb/hr)	0.82	1.1
H performance test, 100-hr (1,000 lb/hr)	0.006	0.09

SOURCE: BPBGT, 2013.

est thermowell corrosion measured occurs within the first 4.5 reactor diameters (4.5 × 7.625 in., or 34.3 in.) from the top of the reactor. The corrosion rates of the titanium liners were determined using ultrasonic measurements and comparing them to a baseline measurement. Corrosion rates for thermowells were determined by direct micrometer measurements of the disassembled components. Corrosion varied among the various FOAK tests as detailed in Tables 1-1 and 1-2 of the preliminary draft of the *Test Report for Supercritical Water Oxidation (SCWO) First-of-a-Kind (FOAK) Test* (BPBGT, 2013). The reported corrosion data are compiled in Table 2-4. The highest corrosion rate noted was 1.9 mil/hr for thermowells in the high-temperature GB test. The lowest corrosion rate noted was 0.01 mil/hr for the liner in the H tests. The maximum allowable corrosion is 67 percent of the initial wall thickness for the liners and 80 percent for the thermowells, and replacement intervals for liner and thermowell replacement were determined accordingly. Liner change-out requires a shutdown of the SCWO reactor for 10-12 hours while the liner is replaced. Thermowell change-out takes approximately 6 hours. While it is desirable to prevent the failure of thermowells, such a failure would not necessitate an immediate shutdown of the reactor because there are four redundant thermowells and they are internally pressurized to the working reactor pressure with compressed air to prevent the contents of the SCWO reactor from migrating up a ruptured thermowell. (A liner failure would, however, necessitate a shutdown.) During the performance test with simulated GB hydrolysate, thermowells did fail after 85 hours of operation and broke apart. The pieces were found at the bottom of the reactor after the test. The failure of the thermowell had no impact on operations.[5]

Corrosion rates for the reactor liners were measured during and following the nominal 100-hr FOAK tests. They were determined using ultrasonic measurements and comparing the measurements to a baseline measurement taken before the liner was first used. Either 320 or 328 measurements were made at each sampling, i.e., either 40 or 41 axial measurements and 8 circumferential locations, depending on the test. The corrosion rate for each individual liner was determined by dividing the change in liner thickness by the number of hours of hydrolysate operation. The maximum average corrosion rate for liners in a given test condition was the highest of the averaged 8 circumferential points for each liner at any distance along the length of the liner.

Thermowell corrosion was measured along the thermowell's thinnest orientation using a micrometer. Measurements were made at 1-in. intervals along the length of the thermowell. The difference in thickness between 0.50 in. (the original diameter of the thermowell) and the micrometer measurement was divided by 2. The maximum average corrosion rate was determined by using the highest of the average of corrosion rates measured at the same point along each of the thermowells and was determined by dividing the maximum average corrosion by the number of hours of simulated hydrolysate operation.

The maximum average corrosion rates for the liners across all the FOAK tests in simulated VX hydrolysate were

[5]Dan Jensen, advanced process system program manager, General Atomics, "SCWO System Testing and Lessons Learned," presentation to the Committee on Chemical Demilitarization on April 10, 2013.

1.2 mil/hr, similar to those predicted from the Technical Risk Reduction Project testing of 1.2 mil/hr (BPBGT, 2005 and 2013). The maximum average corrosion rates for the simulated GB hydrolysate varied as functions of flow velocity and temperature. In addition to testing at the 1,000 lb/hr flow rate planned for use at BGCAPP, tests were conducted for all simulated hydrolysates at a flow rate of 1,200 lb/hr, and also at 800 lb/hr for the simulated GB and VX hydrolysates. For the simulated GB hydrolysate, the high velocity nozzles/flow rates doubled the maximum average corrosion rate of the liner from 0.56 mil/hr to 1.2 mil/hr and tripled the maximum corrosion rate of the thermowell from 0.55 mil/hr to 1.7 mil/hr. Temperature also influenced corrosion rates in the case of GB testing. The highest maximum average corrosion rates during GB testing occurred when running the SCWO at 1200°F and was 1.8 mil/hr for the liner and 1.9 mil/hr for the thermowells. For the tests conducted at 1150°F, the maximum average corrosion rates were 1.2 mil/hr for the liner and 1.7 mil/hr for the thermowells (BPBGT, 2013). Visual examination of the liner after exposure to the hydrolysate simulant indicated that while the corrosion damage is localized, in the form of shallow rivulets extending longitudinally along the wall of the liner, there were no exceptionally severe areas of corrosion. The FOAK testing report recommended the following liner and thermowell change-out periods to achieve the desired SCWO reactor availability goal:

- GB: liners, 300 hr; thermowells, 75-100 hr;
- VX: liners, 400 hr; thermowells, 130 hr; and
- H: liners, no change-out required; thermowells, 1,600 hr (BPBGT, 2013).

According to the committee's calculation, a 400-hr change-out period for the liners during VX processing would result in the liners being almost entirely consumed. As noted above, the maximum average corrosion rate observed during VX simulant testing was 1.2 mil/hr (BPBGT, 2013). A change-out period of 400 hr at this corrosion rate would result in the loss of 480 mil, or 0.48 in., of titanium. That is 96 percent of the liner thickness. A shorter change-out period would seem to be called for by these data. A change-out period of 200 hr would result in only 240 mil, or 0.24 in., of the liner being consumed at the maximum average corrosion rate. At 1.2 mil/hr, the maximum allowable 67 percent corrosion for the liners would be reached in approximately 279 hours. Thus a 200 hour change-out period would be conservative until systemization and operational experience can be used to adjust that number.

Finding 2-1. The FOAK testing was adequate to establish the expected operating lifetime for the titanium liners. This expected operating lifetime is sufficient to enable continued safe operations and adequate operational throughput except for VX hydrolysate.

Finding 2-2. The 300-hr liner change-out interval recommended for the operational GB hydrolysate campaign is adequate if the operating temperature remains at the recommended 1150°F and the flow rate is 1,000 lb/hr. The 300-hr change-out interval is not adequate if a higher operating temperature (1200°F vs. 1150°F) is reached in the reactor for significant lengths of operation. It also may not be adequate for flow rates above 1,000 lb/hr.

Finding 2-3. The 400-hr liner change-out interval recommended for the VX nerve agent campaign is not supported by the worst-case corrosion data in the draft FOAK preliminary test report.

Recommendation 2-1. The Blue Grass Chemical Agent Destruction Pilot Plant staff should shorten the liner change-out period for VX processing from the 400 hr recommended in the test report until the corrosion rates under actual operating conditions are verified. Two hundred hours would be a better initial change-out period.

Corrosion of the thermowells is generally more severe than corrosion of the liners. The wall of one thermowell suffered full penetration (and accordingly failure) in approximately 76 hr during the GB simulant FOAK test.[6] The thermocouples contained in the thermowells provide critical process feedback and so it is obviously desirable that thermowell mechanical integrity be maintained.

Since the thermowell walls are about 180 mil thick, the measured maximum average corrosion rates will result in the near or actual penetration of the thermowell walls before 100 hours of operation at the higher corrosion rates measured. Mechanical stresses from the turbulent flow in the reactor will only further shorten the thermowell lifetime by causing mechanical failure when only small amounts of titanium remain. While the thermowells met availability requirements with their current material and design, BGCAPP has expressed a desire to increase the operating life of the thermowells to bring their change-out periods more in line with the change-out periods for the liners, thus increasing the availability of the SCWO system and reducing maintenance requirements.[7]

BPBGT (2013) suggested several alternatives to extend thermowell operating life, including evaluation of

- Reactor operation at <1150°F during GB blended feed processing;
- Other titanium materials, including hardened titanium alloys,

[6]BGCAPP project staff indicated that the thermowells had been exposed to various simulants for as many as 30 hours before the performance test was conducted.

[7]PEO ACWA, "Supercritical Water Oxidation Tech Review," briefing to the Program Executive Officer, Assembled Chemical Weapons Alternatives supercritical water oxidation technical review, April 22, 2013.

- Hastelloy or an alternative alloy;
- Increasing thermowell wall thickness by increasing the overall diameter to 0.75 in. from 0.5 in.;
- Application of coatings to the thermowells; and
- Alternative nozzle/insert geometries.

Also, the BGCAPP project staff indicated in discussions with the committee that redesign of the thermowells, by increasing the diameter of the thermowells to 0.75 in. from the current 0.5 in., would not be a major design change and even recommended the change. This would lengthen the thermowell change-out periods and thus increase the availability of the SCWO reactors. The project staff also raised the possibility that a more corrosion-resistant alloy could be selected for the thermowells. However, any new alloy that might be considered would have to be qualified for the corrosive environment of the SCWO reactor. There is no guarantee that changing alloys would result in improved thermowell performance. The application of coatings to the thermowells was also presented as an option, but this would meet the same challenges as selecting a new alloy. Processing GB at less than 1150°F would likely necessitate further testing to ensure that operations at the selected temperature would produce the required results, because it would represent a change in the operating conditions of the reactor. The use of alternative nozzle and insert geometries would also likely necessitate additional testing to ascertain whether they would affect SCWO processing operations since the reaction in the SCWO reactor is dependent to some extent on geometry (BPBGT, 2013).

Finding 2-4. Corrosion thinning of the thermowells (accompanied by mechanical failure when minimal material remains) is a critical failure path for the reactors and is expected to be the most frequent maintenance issue associated with continuous operations.

Recommendation 2-2. The diameter of the thermowells should be increased to at least 0.75 in. from the current diameter of 0.50 in. by increasing the wall thickness. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should use existing corrosion data to estimate the lifetime of these new thermowells. This operation is a simple modification that would lengthen the thermowell life during operations and help minimize maintenance-related reactor shutdowns.

Finding 2-5. As noted above, the corrosion of thermowells is greater for higher feed velocities than for lower feed velocities. Another way to address the corrosion of thermowells could be by reducing the feed velocity.

Finding 2-6. Any new alloy used for the thermowells, or any coatings applied to the thermowells, would have to be qualified before use in the SCWO system. There is no guarantee that corrosion performance would improve. Using a lower processing temperature for sarin (GB) processing and using an alternative geometry for the titanium cap would likely necessitate further testing to ascertain whether these changes would affect SCWO processing operations.

Finding 2-7. Based on the test data, the committee believes that availability goals can be met with grade 2 titanium thermowells of appropriate wall thickness.

Recommendation 2-3. The corrosion issue with thermowells should not be resolved by attempting to qualify another material. Grade 2 titanium should be used as planned. Other potential strategies for extending thermowell life (i.e., coatings, alternative geometries, reduced operating temperature, and hardened titanium alloys) need not be explored since simply increasing the wall thickness of the thermowells will extend their operational life and thus reactor uptime.

Elemental Sulfur Additive

It was originally planned to add sulfuric acid to blended GB/energetic hydrolysate before SCWO processing. The sulfuric acid would perform two functions. First, along with hydrochloric acid, it would neutralize the basic hydroxide used in the hydrolysis reaction. Second, it would provide sufficient sulfate to form the sodium sulfate/phosphate eutectic system upon SCWO processing of the neutralized hydrolysate.[8] When sulfuric acid was used with GB hydrolysate, however, the resulting pH was low enough to cause concerns about the possible reformation of GB. This concern led to the testing of elemental sulfur as a replacement for the sulfuric acid in an attempt to raise the pH of the GB hydrolysate. Elemental sulfur would eliminate the pH concern associated with sulfuric acid while still forming the desired eutectic system. The oxygen in the SCWO environment acts on the sulfur to form SO_3^-, which hydrates to form sulfuric acid. This sulfuric acid is neutralized by the caustic feeds. This is the source of the sulfate that forms and maintains the eutectic. Four items were investigated when testing the elemental sulfur additive:

1. Does the elemental sulfur additive perform equivalently to sulfuric acid during systemization by similarly creating a eutectic salt concentration in the SCWO reactor that allows for simplified salt handling (i.e., less reactor rinsing?)
2. Can the replacement of the sulfuric acid with elemental sulfur avoid unnecessarily low pH conditions?
3. Does the solid elemental sulfur remain suspended and dispersed so that the feed has uniform composition, as would the solute sulfuric acid?

[8] A eutectic system is a chemical mixture that has a freezing/melting point lower than any of the chemicals in the mixture would normally have. The effect in this application is to keep the salts molten and flowing through the SCWO reactor.

4. Would addition of elemental sulfur change any corrosion parameters?

To avoid unnecessarily low pH, testing was carried out with the sulfuric acid replaced by elemental sulfur, avoiding formation of strongly acidic hydrolysate. The minimum acceptable pH to prevent GB reformation was determined to be 5. An initial target pH of 6 was chosen to provide a safety margin (BPBGT, 2012). The elemental sulfur was added in the form of sublimated flowers of sulfur with a 200 mesh particle size (BPBGT, 2013). When 83 percent of the sulfuric acid was replaced with 0.2 wt-% elemental sulfur, the neutralized hydrolysate simulant had a pH of 6. When all the sulfuric acid was replaced with elemental sulfur, the pH of the neutralized hydrolysate simulant was approximately 7.5. The simulants containing elemental sulfur showed process equivalency to simulants with sulfuric acid. The simulants with elemental sulfur were processed in an equivalent manner with similarly complete oxidation of the organics in the FOAK testing. This addresses the first two concerns (BPBGT, 2013).

The third concern above pertains to uniform distribution of the sulfur in the blended hydrolysate. The solubility of nonpolar sulfur in water is low (2×10^{-8} mol S_8/L H_2O, or about 5 µg/L) and likely to be slightly lower in the hydrolysate salt solution (Boulegue, 1978). As sulfur does not dissolve in aqueous solutions, agitation is needed to keep it in suspension so that compositionally it behaves equivalently to a solution during SCWO processing. Consistent values for SCWO effluent pH and the lack of salt buildup during GB surrogate processing confirm sufficient uniformity of the blended surrogate feed.[9]

The draft FOAK report provided a description of the heating and mixing systems to keep the elemental sulfur dispersed. The initial FOAK test heaters caused sulfur agglomeration due to melting of sulfur (sulfur begins to melt at about 240°F). Agglomeration of the sulfur could lead to inhomogeneous composition within the batch, clogging of the hydrolysate feed apparatus, and, potentially, a noneutectic salt mixture (off-spec sulfate/phosphate ratio) within the SCWO. To keep this from happening, the original FOAK heaters were replaced with lower wattage elements, which resulted in lower temperatures and eliminated the problem of agglomeration.

Any variation in the testing caused by the use of elemental sulfur did not disrupt the SCWO processing. As no salt buildup was present in the SCWO reactor, any minor compositional changes which may have occurred during the SCWO processing did not affect the ability of the reactor to efficiently move salts through the reactor.

Regarding the fourth concern listed above, the potential for the sulfur to change the corrosion parameters of the blended GB hydrolysate feed, several sets of tests were conducted. In one set of tests the sulfuric acid was replaced by enough elemental sulfur to reach the target pH of 6. This resulted in a maximum average corrosion rate for the liner of 1.6 mil/hr and 1.9 mil/hr for the thermowells. When the sulfuric acid was completely replaced with elemental sulfur in a second set of tests, the maximum average corrosion rate for the liner was 1.8 mil/hr and the maximum average corrosion rate for the thermowells dropped to 1.6 mil/hr. In a subsequent set of tests, the amount of sulfur in the feed stream was varied by ±2 percent. These variations produced no change in the maximum average corrosion rate for the liners (1.0 mil/hr). During the −2 percent sulfur test, the maximum average thermowell corrosion rate was 1.7 mil/hr, and it was 1.5 mil/hr during the +2 percent sulfur test. In the final 100-hr test with simulated blended GB and energetics hydrolysate, the maximum average corrosion rate for the liner was 1.1 mil/hr and for the thermowells was 1.5 mil/hr (BPBGT, 2013). These corrosion data are summarized above in Table 2-4.

It is also useful to look at this in the context of the simulated H blended hydrolysate recipe from Table 2-11 in BPBGT, 2013. The 0.43 wt-% solid sulfur addition amounts to less net sulfur than is present in the simulated blended H hydrolysate. The corrosion rates in the SCWO testing of blended H simulant (which had the highest sulfur concentrations of all the simulants) were the lowest of the three feedstocks (simulated blended VX, GB, or H hydrolysate simulants). Therefore, sulfur does not significantly add to the SCWO corrosion rates (BPBGT, 2013).

Finding 2-8. The elemental sulfur additive did not have any adverse impact on FOAK testing and successfully resolved the issues it was intended to.

Recommendation 2-4. Elemental sulfur additive should be used instead of sulfuric acid additive.

Variations in Feed Composition

There is a direct relationship between any additions to the SCWO feed streams and the chemistry within the SCWO. The potential effects of any variability in SCWO feed composition could be a concern and should be evaluated as the process parameters were evaluated for a specific simulant composition. For example, some variations in feed composition did result in changes in corrosion, as summarized in Table 2-4. Variations in any of the compositions or concentrations within the hydrolysate feed beyond those tested during FOAK testing could yield SCWO conditions different from

[9]Kevin Downey, advanced process system manager, General Atomics, "SCWO FOAK Test Status," presentation to the committee on February 4, 2013.

those evaluated in the FOAK tests. As part of FOAK testing, variations in the SCWO feed composition and flow rate for a limited set of parameters were tested as follows:[10]

- Elemental sulfur (for GB hydrolysate simulant): 0.20 wt-% and 0.26 wt-%, and ±2 percent from the amount planned to be used at BGCAPP.
- HCl: ±2 percent from the amount planned to be used at BGCAPP.
- Hydrolysate flow into the SCWO: 1,000±200 lb/hr.

The sulfur concentration varies from low (hydrolysate feed at pH = 6) to high (hydrolysate feed at pH = 7.5). As an example of how significant the impact of feed variations can be, the apparently minor difference of 0.06 wt-% between the low and high sulfur additive concentrations represents a change of 1.5 pH units, or a factor of approximately 32 in acid concentration. The final FOAK tests were completed at nominal 1,000 lb/hr simulant feed rates. The variations in SCWO feed that were tested did not have any negative impacts on the SCWO process itself.

Upon systemization, the hydrolysate storage area will hold the contents from multiple 750-gal energetics neutralization batches. The combined energetics hydrolysate batches will be diluted, neutralized, filtered to remove aluminum salts, and then blended with agent hydrolysate to create the SCWO feed. The agent hydrolysate will itself be a mixture of multiple hydrolysis batches and the additives to those batches. All of this will serve to homogenize any minor variations in the feedstock that might come from initial variations in the munition agent fills or energetics. Additionally, neutralization to a specific pH also dampens any fluctuations caused by variations in the original feedstocks.

Finding 2-9. The limited feed variations tested during FOAK testing did not result in any negative impacts to the SCWO process. Variations other than those tested during FOAK testing could be a concern and are addressed in Chapter 3.

Functionality During FOAK Testing

This section of the report discusses specific pieces of SCWO process equipment. Not every piece of equipment or process is discussed here. Only those pieces and circumstances that stood out to the committee are discussed here.

High-Pressure Air Compressor

The SCWO system needs high-pressure air to provide the oxygen for the SCWO process. The air is provided by a modified commercial compressor. The high-pressure air compressor, manifold, and feed systems worked as designed and were able to feed the liner purge, reactor feed, and thermowell/blowdown line purges as long as the compressor remained operational. That said, the compressor had numerous failures throughout the testing period. Events such as a high-pressure cooling loop failure, expansion tank bladder failures, and a low oil level/demister failure repeatedly interrupted the test cycles. Makeshift measures such as wiring dummy transducers, warrantied repairs, and other workarounds enabled target availability to be met, but operations were not as smooth as desired. Additionally, all the failures occurred in new equipment.

Another concern related to the high-pressure air compressors is the oil-water separator (OWS). While four air compressors are planned for use at BGCAPP (three operational, one spare), only one OWS is planned for use with all three of the operational air compressors. There were several instances where workarounds in the OWS system or in the lubrication system were necessary for the system contractor to be successful in keeping the system operational and achieving the operational goals of the test (BPBGT, 2013). The committee's concern is that if there are problems with the OWS during systemization and BGCAPP operations, the entire SCWO process could be shut down because all three air compressors would have to be shut down. There could also be a risk of sympathy shutdowns, where perturbations in one system could ripple across the other systems, causing shutdowns. This seems to present a risk for a significant single-point failure.

Finding 2-10. There was a much higher failure rate for the high-pressure air compressor than would be expected from a mature system. These failures repeatedly interrupted FOAK testing. The multiple issues with the air compressor, which is a single, critical component of the SCWO system, are of concern to the committee.

Recommendation 2-5. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should review the maintenance and start-up plan for the air compressors so that they are maintained to industry standards. The project staff should use the time between compressor delivery and systemization to run the compressors, to discover any problems similar to those which occurred during FOAK testing, with the goal of obtaining reliability comparable to that of the supercritical water oxidation reactors.

Finding 2-11. The oil-water separator appears to present the risk of a critical single-point failure that could shut the entire SCWO process down.

Recommendation 2-6. In addition to the action recommended in Recommendation 2-5, the Blue Grass Chemical Agent Destruction Pilot Plant project staff should consider mitigation strategies such as having an additional oil-water

[10] Kevin Downey, advanced process system manager, General Atomics, "Status of SCWO FOAK Testing," briefing to the Committee on Chemical Demilitarization on December 4, 2012.

separator (OWS) in parallel that could run should the main OWS require maintenance. Additionally, a spare OWS could be kept on hand.

High-Pressure Quench Water

In SCWO systems in general, salts are always a potential issue in the supercritical portions of the reactor, yet they mostly dissolve in the subcritical portions of the reactor. If salts are not handled properly, they can lead to excessive downtime due to frequent rinsing or clogging of the SCWO reactor. In the SCWO system to be used at BGCAPP, salts move through the reactor and dissolve in the warm subcritical solution as the effluent leaves the SCWO reactor. High-pressure quench water will be injected into the end of the SCWO reactor to facilitate salt removal. The test results indicated that no rinse was needed to remove residual salts from the SCWO reactor. The consistent conductivity of the effluent reveals a well-controlled system. The fact that a reactor rinse is not necessary directly addresses the original test objective, to determine the rinsing requirements.

Despite the fact that reactor rinses were not necessary the concentration of sodium hydroxide in the H blended simulant was reduced by 8 percent to "reduce build up of salts in the reactor" (BPBGT, 2013, p. 87). Additionally, the temperature of the H processing was raised to 1275°F from the original target of 1200°F.

Finding 2-12. The processing of the modified blended H hydrolysate simulant recipe at 1275°F proceeded smoothly with little corrosion and complete oxidation.

Recommendation 2-7. The Blue Grass Chemical Agent Destruction Pilot Plant supercritical water oxidation system test plan should ensure that the recipe for the blended H hydrolysate is the same as the recipe used in the FOAK tests.

High-Pressure Hydrolysate Feed

The hydrolysate flows through check valves as it is pressurized for delivery to the SCWO unit. Particulates in the blended hydrolysate simulant, which was not filtered, caused the check valves to stick, reducing the efficiency of the pressurization operation. In preliminary lessons learned, system contractor personnel recommend that Hastelloy check valves be replaced by a more wear-resistant alloy such as Stellite, because the pump must handle solids inherent to the SCWO process such as iron oxide and sulfur (BPBGT, 2013).

The final function of the high-pressure hydrolysate feed pump is to flush the piping/reactor. The flush conditions are mild compared to the hydrolysate feed conditions during operation of the SCWO, 109°F for more than 10 min. No issues are anticipated with the flushing operations.

Minor adjustments to control set points were made and some equipment modifications were performed. All of the actions and troubleshooting activities were expected and normal for FOAK testing. No issues are anticipated with this equipment.

Finding 2-13. Particulates in the blended hydrolysate simulant, which was not filtered, caused the check valves to stick during testing.

Gas and Liquid Sampling and Analyses

The FOAK test process was monitored by gas analyzers measuring O_2, CO, CO_2, and total hydrocarbons as well as by liquid analyzers measuring TOC and pH. These monitors are planned for use at BGCAPP as part of systemization and operations. The gas sampling is used to confirm that sufficient O_2 is present for the oxidation process (the O_2 analyzer) and that complete oxidation is occurring (the CO analyzer) and to monitor the effluent concentration of oxidized organics (the CO_2 analyzer) and the concentration of residual hydrocarbons (the total hydrocarbon analyzer). The liquid effluent is analyzed to confirm destruction of the target organics in the hydrolysate and destruction of the isopropanol (the TOC analyzer) to a target of less than 10 ppm organic carbon in the effluent. The pH of the effluent is measured as a simple check on processing consistency (the pH analyzer). All these measurements delivered relatively consistent results. Some scatter and occasional outlier points were observed, but the general and specific trends of the gas concentrations were clear.

The TOC measurement takes several minutes and is an important indicator of SCWO reaction completion. Regardless of minor, normally expected process variations, if the TOC value is low then the organics have been destroyed. During different FOAK tests, the TOC analyzer inlets became plugged. A backup TOC analyzer was then used to obtain the TOC measurement.

Temperature and Pressure Letdown and Effluent Heat Exchanger

The gas-rich effluent salt solution in the SCWO reactor must be cooled from the SCWO operating temperature to a warm temperature and the pressure reduced to levels appropriate for post-SCWO operations in a controlled manner. The quench water flow at the bottom of the SCWO reactor reduces the temperature of the SCWO effluent from supercritical to subcritical values and dissolves the entrained salts. Subsequent heat exchangers, pressure letdown valves, gas-liquid separators, and two-stage gas pressure letdown valves take the liquid to its final effluent state. Preliminary indications are that the high-temperature, high-pressure reactor effluent is cooled, reduced in pressure, and stripped of its excess gas in an efficient manner. The target temperature is 140°F at the outlet of the heat exchanger, which was achieved during testing (BPBGT, 2012).

High-Pressure Water Feed, Preheater

The high-pressure water feed and the preheater bring the reactor and its contents to supercritical condition. When the isopropanol is added as the reactor warms (at 700-801°F), it reacts with the feed air and is oxidized. The preheater is then allowed to cool. The air and isopropanol flows are increased until the reactor reaches 1099-1150°F, when temperature is then controlled by monitoring O_2 in the effluent and adjusting the effluent O_2 to 5 percent by varying the compressed air feed.[11] The reactor comes to rough thermal equilibrium as the heat of reaction becomes sufficient to maintain the temperature and pressure conditions necessary for efficient SCWO. Then, hydrolysate is added to start the destruction of the organics it contains. During the testing, the preheater/high-pressure water pump was able to reliably initiate oxidation in the SCWO reactor. The various high-pressure air compressor failures gave the operators additional practice in shutting the reactor down and bringing the reactor up to operational (steady-state) conditions.

Isopropyl Alcohol Fuel Issues

There were problems during FOAK testing with accurate SCWO fuel composition. The contractor did not provide adequate specifications for the fuel, and the incorrect fuel was delivered and used during FOAK testing (70 percent isopropyl alcohol by weight instead of 70 percent by volume). This error and attempts to correct for the error resulted in some problems in achieving SCWO conditions. The committee includes this as an example of the simple things that could create problems during SCWO systemization and operation if they are not watched.

Maintainability

Thirty-two system shutdowns and start-ups were included in part of the FOAK test plan resulting from the simulation of a wide variety of system errors. Simulated errors included low and high levels in various pieces of process equipment, high temperatures beyond what is safe, and low and high flow levels for various feeds and effluents (BPBGT, 2012). There were also unplanned shutdowns due to real system errors, such as the failure of a thermowell, discussed above. During these shutdowns seven maintenance activities were demonstrated during FOAK testing:

1. Reactor liner change-out (reactor liners were removed, inspected, and/or replaced 17 times);
2. Reactor thermowell change-out;
3. Reactor feed nozzle removal and replacement;
4. Effluent heat exchanger inspection;
5. High-pressure gas-liquid separator solids cleanout;
6. Preheater thermocouple replacement; and
7. Liquid pressure letdown valve inspection.

All of the maintenance activities were performed in the expected manner. The titanium liners were replaced and the reactor returned to fully operational status within 12 hr. The thermowells were replaced and the reactor returned to fully operational status within 7 hours. Numerous adjustments were made to equipment and to control set points. These adjustments are a normal result from learning to efficiently operate FOAK equipment. Other maintenance activities were routine industrial tasks and were accomplished using standard industrial procedures/practices.

Finding 2-14. The overall first-of-a-kind testing objectives for the supercritical water oxidation system to be used at the Blue Grass Chemical Agent Destruction Pilot Plant were met. The processes and subsystems, inclusive of maintenance activities, performed individually and collectively to meet test objectives and exceed the target of 76 percent availability.

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BPBGT. 2013. Test Report for Supercritical Water Oxidation (SCWO) First-of-a-Kind (FOAK) Test, April, Preliminary Draft. Richmond, Ky.: Blue Grass Chemical Agent Destruction Pilot Plant Program Office.

[11]Kevin Downey, advanced process system manager, General Atomics, "SCWO FOAK Test Status," presentation to the committee on February 4, 2013.

3

Implementation of Supercritical Water Oxidation at Blue Grass

The supercritical water oxidation (SCWO) process at the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) will process the agent and energetics hydrolysate streams resulting from agent and munition destruction. Three SCWO units have been designed and constructed for use at BGCAPP. One of these was used for first-of-a-kind (FOAK) testing. All of the units will be shipped to BGCAPP site sometime in mid-2013 but are not scheduled to begin processing stimulant hydrolysate until at least 2017 (BPBGT, 2012).[1]

The SCWO systemization process is intended to demonstrate that the plant, procedures, and personnel are ready for operating the SCWO system. Systemization is planned to proceed through seven sequential subphases. These are (BPBGT, 2012) the following:

1. Presystemization—planning and document preparation;
2. Construction support—review of the actual plant against plant design documents;
3. Precommissioning—input/output testing for major equipment (e.g., electrical and mechanical systems checks for each piece of equipment);
4. Commissioning—instrument calibration, logic controller interface verification, alarm operation verification, etc.;
5. System start-up—attention shifts to the system level and integration of the subsystem components, interlock checks, standard operating procedure validation and revision as necessary, and safety checks;
6. System demonstration—functional demonstration of system capabilities including start-up, normal operation in automatic and manual modes, processing simulant where applicable; and
7. Optimization—integrated plant operations, as if actual chemical agent were being processed, conducted before start of agent operations.

At this writing, the systemization process has not yet begun. Also, at this writing, precommissioning activities are scheduled to begin in March 2015, with the system demonstration to conclude June 2020.[2,3]

Procedures are in place to hand off elements of the overall BGCAPP system from construction to commissioning/start-up. This process is organized by dividing portions of the overall BGCAPP system into quality data packages (QDPs), and the BGCAPP project has a schedule and process for this hand-off for all of the different QDPs. Some of these QDPs are scheduled for turnover in 2014, others not until 2016. The final optimization stage includes 20 weeks for training and preparing the plant workforce. The same personnel involved in systemization will be used in plant operations to take advantage of the accumulated system knowledge and experience. After all the subsystems have been systemized into the overall BGCAPP system, a final operational readiness review will be performed to verify that the people, paperwork, and plant equipment are ready to support agent operations (BPBGT, 2012).

Figure 3-1 shows a SCWO block flow diagram. The fuel, isopropanol, and hydrolysate flows are continuous and operate until the unit is shut down. A complete operating schedule is still under development.

The hydrolysate storage tanks hold the output streams from the neutralization of agent and energetics. These tanks can hold about one third of the total output expected from the neutralization reactors. This total output is roughly 50

[1]The BGCAPP schedule has undergone continuous modification, including during the course of this study. The committee has given the best dates available to it at the time of this report. The findings and recommendations in this report do not depend on the exact dates quoted.

[2]Ron Hawley, plant general manager, URS Corporation, "Systemization Overview," presentation to the committee on February 4, 2013.

[3]Joe Novad, deputy program executive officer, Assembled Chemical Weapons Alternatives (ACWA), "Program Executive Office Assembled Chemical Weapons Alternatives Update," presentation to the Committee on Chemical Demilitarization on April 9, 2013.

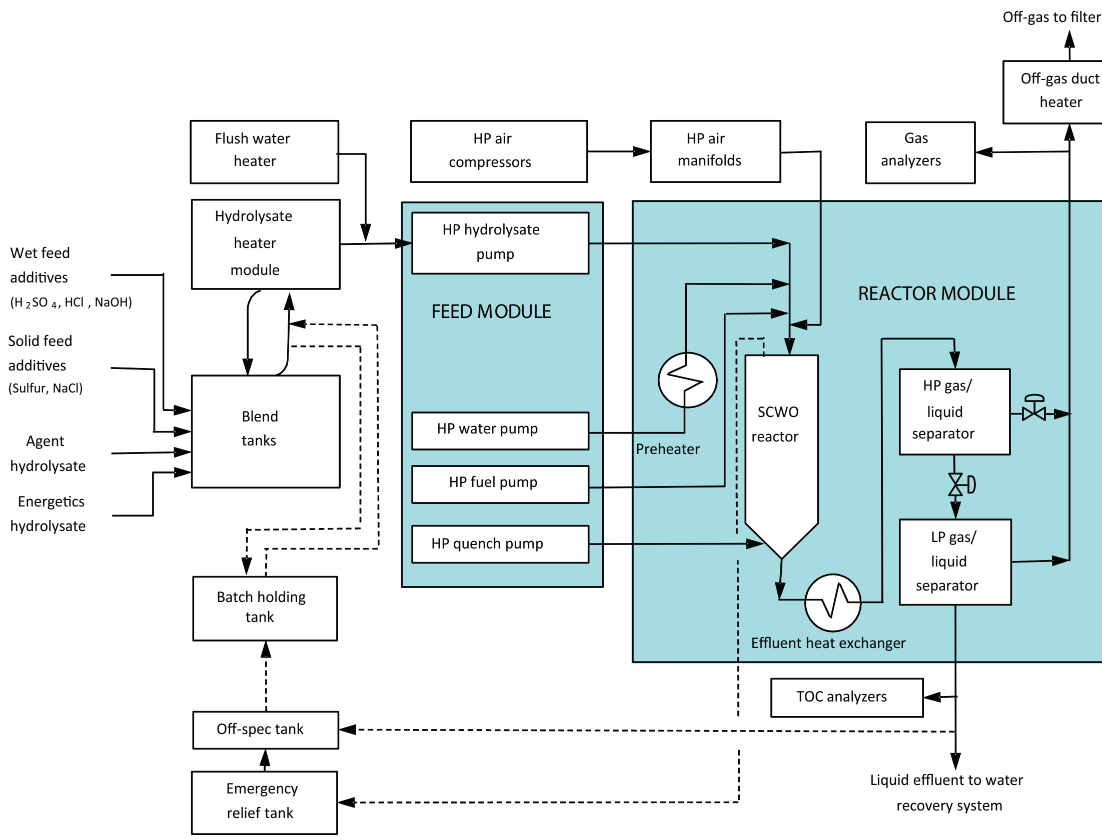

FIGURE 3-1 SCWO block flow diagram showing only the SCWO system. SOURCE: Program Executive Officer, ACWA, Presentation to the Supercritical Water Oxidation Technical Review on April 22, 2013.

million lb.[4] If each of the three SCWO units processes 760 lb/hr of material (1,000 lb/hr nominal rate, in operation at the defined 76 percent availability) on a continuous basis (365 days/yr, 24 hr/day), then 2.5 years would be required for SCWO treatment of all of the hydrolysate. If only two SCWO units operate at one time, then 3.8 years would be required to treat all of the hydrolysate.

SCWO FEED COMPOSITION

The effectiveness of the SCWO system depends on the composition and flow rate of the feed stream, which makes a thorough understanding of the feed composition and its potential variability essential for ensuring that the SCWO system attains the destruction efficiencies required by permit. To date, however, there are no data on the potential variability in the SCWO feed composition coming from the blend tank. There is also no indication of what constitutes an off-spec feed. As is discussed in Chapter 2, however, the mixing of multiple batches of both energetics and agent hydrolysate and the neutralization of hydrolysate to a specific pH will homogenize any minor variations in the SCWO feed that might have arisen as batch-to-batch differences. Also as discussed in Chapter 2, the FOAK testing showed satisfactory SCWO unit performance when several parameters (elemental sulfur, HCl, hydrolysate flow rate) were varied individually within the small ranges anticipated during operation.

Although these tests provided useful information, varying each parameter individually may not have been sufficient to reveal the limitations of the SCWO system. Variations in more than one feed component at a time might have resulted in a more challenging environment. System contractor personnel reported that they could not afford to test all possible combinations, and the committee concurs. Computer simulation, however, might allow estimating the combined effects of these variables based on their individual effect (see the final section of this chapter, "Overall System Operations and Computer Model," for a more detailed discussion).

As noted in Chapter 2, there were problems of sulfur melting and agglomeration with the original heaters used during FOAK testing. These were successfully addressed by using a lower wattage electric heater (BPBGT, 2013). However, steam heat will be used at BGCAPP, and the committee is unsure how this will affect the potential for

[4]John Barton, chief scientist, Bechtel Parsons Blue Grass Team (BPBGT), "BGCAPP Process Overview," presentation to the committee on January 7, 2013.

sulfur melting and agglomeration. Also, the elemental sulfur additive will likely be less soluble in the hydrolysate than in water (Boulegue, 1978). The results of FOAK testing confirmed that the issue of sulfur insolubility was adequately addressed.[5] From a systemization standpoint, because of differences between the FOAK and operational settings, BGCAPP staff need to check that the sulfur will be sufficiently agitated so that it behaves chemically in the same manner as a solution with sulfuric acid.

Finding 3-1. Compositional variations within the energetics and agent feedstocks are dampened by the blending of multiple batches and post-hydrolysis neutralization to a common pH range. It is unclear, however, how the SCWO system would respond if it received a feed with a composition outside the range tested during FOAK testing.

Recommendation 3-1. The range of acceptable feed compositions for the SCWO unit, which must be achieved in the hydrolysate blend tank, should be clearly specified. These compositional parameters should be based on the range of compositions actually used and verified during testing of the SCWO unit.

Finding 3-2. There is uncertainty as to whether the agitation and heating methodologies used during FOAK testing accurately represent the conditions that will be present in the full-scale hydrolysate storage tanks.

Recommendation 3-2. The full-scale agitation/circulation system at the Blue Grass Chemical Agent Destruction Pilot Plant should be evaluated upon systemization. Care should be taken to avoid conditions where sulfur can melt on the heater surfaces, and vigorous agitation should be applied near the bottom of the tank. The blended sarin (GB) hydrolysate should be sampled to confirm that the agitation and heating conditions are sufficient to maintain uniform feed composition.

SAFETY

In the course of its work, the committee encountered two things that raised safety concerns. The first involves plans to have personnel in the SCWO bay performing maintenance while adjacent SCWO systems are operating. The second involves the venting of SCWO process exhaust into the SCWO process building.

Maintenance

According to committee discussions with BGCAPP staff, the current operating plan is to have two SCWO units operating at a time, with the third as a spare. It is, however, conceivable that all three units could be operating at once if unforeseen downtime requires makeup SCWO operation.

The system contractor developed safety protocols for the operation of SCWO units during FOAK testing. While there were exceptions during FOAK testing, the general operating philosophy was that personnel were not supposed to be in the SCWO bay while the SCWO unit was operating. There has, however, been only limited discussion of the safety issues associated with operating three SCWO units in parallel at BGCAPP during systemization, conducting system maintenance between systemization and plant operations, and conducting maintenance while SCWO units are operating.

The committee is specifically concerned about plans to perform maintenance on one SCWO unit while the adjacent unit is operating. The unexpected release of steam due to failure of an operating unit, for example, might pose a safety hazard to a worker doing maintenance on an adjacent unit. Based on information provided to the committee, such maintenance activity would be inconsistent with the safety practices used during FOAK testing. Nevertheless, the presence of plant personnel performing maintenance in the SCWO bays during SCWO operations is anticipated to be normal practice at BGCAPP. The committee does not believe that ensuring the safety of these workers is adequately considered in the existing safety planning.

The system contractor believes that the design of the SCWO units makes performing maintenance while an adjacent SCWO unit is operating safe. The contractor that will operate the SCWO units at BGCAPP has stated that no significant safety analyses have been conducted to date, but are planned.[6] There are Lexan panels mounted on the SCWO process equipment skids. The system contractor states that these panels will be capable of containing emissions from minor leaks and even a major pipe failure, protecting personnel. There are also blow-off panels on the tops of the equipment skids to direct the force from any catastrophic failures upwards, away from personnel (though there are questions about the debris environment and how dangerous that might be to personnel in the area).[7] Even so, the system contractor did state that personnel access to the SCWO bay should be restricted during operations, and that there should not be any long-term presence of personnel, such as foot traffic between

[5] Kevin Downey, advanced process system manager, General Atomics, "SCWO FOAK Test Status," presentation to the committee on February 4, 2013.

[6] Personal communication between Steven Mantooth, Blue Grass Chemical Agent Destruction Pilot Plant program office, and James Myska, NRC study director, on February 7, 2013.

[7] Dan Jensen, advanced process system program manager, General Atomics, "SCWO System Testing and Lessons Learned," presentation to the Committee on Chemical Demilitarization on April 10, 2013.

SCWO units.[8] This still leaves the committee concerned about personnel performing maintenance activities adjacent to an operating SCWO unit.

If BGCAPP does carry through on plans to have workers perform maintenance activities in close proximity to operating SCWO reactors, supplemental safety steps could improve worker safety. Additional barriers could be placed between the workers and an operating SCWO reactor. Such barriers could also capture debris. Barrier materials and their placement must be tailored to the characteristics of the debris threat.

Finding 3-3. There is uncertainty regarding which parts of the SCWO system may have to shut down during parts (e.g., liner or thermowell) replacement. There are also concerns about worker safety since at least two SCWO units will be running simultaneously and they are located close to each other in the process building.

Finding 3-4. Current plans permit maintenance personnel to be in the SCWO bay while adjacent SCWO units are operating. The committee is concerned that existing safety planning and procedures may be inadequate for this situation. If current plans are implemented, the committee believes additional worker protection would be warranted.

Recommendation 3-3. The safety protocols used during first-of-a-kind testing need to be adapted and applied to operation and maintenance of the three parallel units at the Blue Grass Chemical Agent Destruction Pilot Plant. This includes not conducting maintenance adjacent to operating supercritical water oxidation reactors.

Recommendation 3-4. If the safety protocols used during first-of-a-kind testing are not adopted for SCWO operations and maintenance, the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) project staff should conduct detailed operational risk and safety analyses before allowing personnel to conduct maintenance activities in close proximity to operating SCWO reactors. BGCAPP staff should also investigate additional worker protection, such as supplemental barriers between workers and operating SCWO reactors, which could also capture debris.

While the committee was not in a position to address safety in any real depth, it does want to call the reader's attention to the NRC report *Assessment of Approaches for Using Process Safety Metrics at the Blue Grass and Pueblo Chemical Agent Destruction Pilot Plants* (NRC, 2011). The committee that wrote the 2011 report conducted a review of process safety incidents that had occurred at other chemical agent disposal facilities and identified primary causal factors that led to the incidents. It then went on to discuss the identification and use of process safety metrics as leading indicators to prevent safety incidents. The committee also wrote about process safety metrics that are used in the chemical industry. The present committee believes the 2011 report would be a useful resource in addressing safety concerns raised by the SCWO system.

[8] Kevin Downey, advanced process system manager, General Atomics, "SCWO System Testing and Lessons Learned," presentation to the Committee on Chemical Demilitarization on April 10, 2013.

Process Exhaust

During FOAK testing, gas effluents from the single SCWO train operated were vented to a holding tank outside the process building. Process design descriptions outlined in the FOAK testing report indicate that for the BGCAPP facility the gas effluents from the SCWO units will be discharged into the emergency relief tank room. After release to the airspace in that room, the gas effluents from the SCWO units are to be drawn through the carbon filters of the SCWO process building ventilation system for eventual release to the atmosphere (BPBGT, 2013). It thus appears to the committee that SCWO process gas effluents are to be released into the general SCWO processing building atmosphere via the emergency relief tank room, where they could impact any personnel in the area. The committee is concerned that, depending on the volume of SCWO gas effluent, the general SCWO processing building atmosphere might be either high in carbon monoxide and/or low in oxygen.

Finding 3-5. The discharge of process gas effluents into the general atmosphere of a building is not a good design practice. Such discharge can pose any number of safety risks to personnel depending on the composition and volume of the gas effluent.

Recommendation 3-5. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should evaluate the SCWO process building design to ensure that the quality of the air inside the emergency relief tank room is safe for personnel. Remedial action could include the discharge of SCWO gas effluent through the appropriate offgas treatment system rather than to the atmosphere inside the building, air quality monitoring inside the emergency relief room with appropriate alarm settings, or other approaches that would ensure the room and building air quality is safe for personnel.

Recommendation 3-6. If process exhaust is to be not vented through the appropriate offgas treatment system, an operational risk and safety evaluation should be conducted on the venting of process exhaust into the SCWO process building.

PERSONNEL ISSUES AND KNOWLEDGE TRANSFER AND RETENTION

This section discusses the training of the BCGAPP staff who will operate and maintain the SCWO system, the transfer of knowledge and expertise from the system contractor SCWO operators to the BGCAPP SCWO operators, and the retention of that knowledge at BGCAPP during the several years between SCWO unit delivery to BGCAPP and SCWO operation to treat hydrolysate. While BGCAPP personnel shadowed the system contractor SCWO operators during FOAK testing, the BGCAPP personnel were not permitted to conduct any hands-on work.[9] Expertise is built by actually doing a job. The system contractor operators will not move to BGCAPP to operate the SCWO units there. Thus, there is a risk that the accumulated expertise of the system contractor operators will be lost. Given the long duration of systemization and number of years that will pass from when the SCWO units are delivered to BGCAPP and when they begin to process hydrolysate, there is a very real chance that knowledge, know-how, and key process metrics could be lost. A SCWO process operation manual designed specifically for use during the interim between SCWO unit delivery to BGCAPP and SCWO system operation with hydrolysate could be a valuable way to ensure preservation of knowledge.

Training is another area of concern. It will be critical to train operators who will not have had experience in running SCWO units. The committee visited the FOAK test site during its first meeting and observed the control systems and spoke with the operators. The discussions and observations indicated to the committee that training people in the basic operation of the SCWO units will not be particularly challenging.[10] A detailed high-level framework and approach has been proposed to train SCWO operators and, based on the accumulated chemical industrial expertise of the committee, seems to be well thought out. The details of implementing this high-level plan have not yet been worked out. The approach and framework include knowledge training (classroom instruction) and skills training (training lab, process control simulator, and on-the-job-training) along with demonstration of knowledge retention (written and oral exams) and demonstration of skills (measuring job performance). Operators will be trained on all aspects of the SCWO system, including start-up, normal operation, manual system operation, response to alarms, shutdown, and emergency shutdown. Similarly, SCWO process maintenance workers will be trained, including hands-on learning using a mockup SCWO vessel. [11] Another contractor, different from the SCWO system contractor, is responsible for training the BGCAPP staff. The committee was told that staff members from the training contractor have never been to the SCWO system contractor site to observe the SCWO system much less to observe actual operation.[12] This would have been an opportunity to attempt to capture operational experience for the purposes of training the BGCAPP staff.

It should be noted that SCWO technology in general is fairly mature and the system contractor supplying the SCWO to BGCAPP has been in the business of selling systems for some time. The SCWO units designed and built for this application are based on a significant amount of prior experience and testing, and debugging efforts have been conducted on the actual units that will be installed and operated at BGCAPP. Additionally, the workforce at the plant is composed in part of personnel who have worked at other chemical demilitarization facilities. While the technologies they managed were different, they bring with them a great deal of experience in the disposal of chemical munitions and a strong safety culture. The combination of these factors provides a path that should allow the operators to be trained appropriately and the units to be operated safely. The committee's concerns are not that it will be difficult to train the operators but that much of the operational expertise, the art, of running the SCWO system smoothly will be lost in the transition from system contractor staff to BGCAPP staff.

Finding 3-6. The committee is concerned about how the know-how, knowledge, and experience obtained by the system contractor SCWO system operators and engineers, and by the Blue Grass Chemical Agent Destruction Pilot Plant staff who shadowed the system contractor operators, will be preserved during the multiyear hiatus between equipment delivery and systemization.

Recommendation 3-7. Plans should be made for periodically providing refresher training opportunities for SCWO plant operators and personnel during downtime and systemization activities. This training should include actual system operations to the extent possible. A manual should be developed for SCWO system operations and used routinely as part of training and maintaining the readiness of the plant personnel and the process equipment and systems throughout systemization. Such a manual is described more fully in a later section in Chapter 3.

EFFECTS OF AGING AND STORAGE ON COMPONENT OPERABILITY

The committee's biggest maintenance concern is the long downtime between equipment delivery and installation and the eventual operation of the system in a (semi)continuous mode. Preliminary schedules shared with the committee showed potential years-long delays between delivery of

[9] Discussions between the committee and BGCAPP and General Atomics staff during the first meeting on January 7-9, 2013.

[10] Ibid.

[11] Doug Plummer, BPBGT training manager, GP Strategies Corporation, "SCWO Training Plan," presentation to the committee on February 4, 2013.

[12] Discussions between the committee and BGCAPP and General Atomics staff during the first meeting, January 7-9, 2013.

equipment and installation and operation of that equipment. For simple equipment, like a stainless steel tank, the delay is not a concern. For complex mechanical equipment with electronics, such as an air compressor, these delays are a concern. Electronics can become damaged, components can corrode, and other age-related failures can occur. The committee believes there is significant schedule risk if complex equipment sits for years exposed to changes in temperature and humidity before installation and operation. Both the operation of long-idle equipment and knowledge preservation of the operators are concerns.

Finding 3-7. Systemization will use equipment that is to be acquired years before its operation.

Recommendation 3-8. A detailed maintenance schedule should be created that leaves ample time to test and evaluate all subsystems of the SCWO system. The schedule should include ample training time for operators to familiarize themselves with the equipment.

The most critical issue in the SCWO systemization plan is the 6 yr or more delay between receipt of the SCWO units at BGCAPP and when the units will be expected to handle the hydrolysate under operational conditions. This delay is a serious issue and, to the best of the committee's knowledge, one never before encountered in the start-up and operation of any commercial chemical processing unit. A detailed procedure has been proposed to deal with both personnel and equipment issues associated with this delay. This procedure, which is part of the systemization plan, includes testing the mechanical and electrical operability of each subsystem, testing and calibrating all instruments, validating standard operating procedures, demonstrating that individual system components operate as an interdependent whole, and operating the entire plant with simulated hydrolysate to ensure that everything is in working order.[13] Because this delay is unprecedented, at least in the experience of the committee, the committee cannot judge the procedure's likely effectiveness. It was also unclear to the committee whether the equipment-related activities associated with systemization (i.e., those items outlined above) would be done just once or whether they would be performed periodically. If they are done just once, then there remains the possibility that process equipment will sit idle, conceivably for years, prior to, during, and after the systemization phase.

Finding 3-8. SCWO system process equipment (e.g., reactor and peripherals, compressor, and pumps) will be shipped to the Blue Grass Chemical Agent Destruction Pilot Plant and remain in storage for several years prior to start-up of the SCWO process for systemization and eventually for operations. Additional extended periods of idleness are likely. The committee has concerns about whether the equipment, either as a working system or as individual components, will perform as designed and expected after sitting idle for such a long time.

Recommendation 3-9. In addition to planned systemization activities, plans should be made for regularly testing or operating the various SCWO and water recovery system components. These plans should be included in the interim SCWO operations manual for the interim period between delivery and operations, described in the next section.

SCWO OPERATIONS MANUAL FOR INTERIM PERIOD

Operations procedures and operation manuals have been provided by the system contractor for the SCWO system when it is in full operation. However, to the committee's best knowledge, such procedures have not been codified for system monitoring and maintenance during the period between equipment delivery and systemization, during systemization, and between systemization and full plant operation. Also, to the committee's best knowledge, there are no integrated operating procedures for the combined SCWO and water recovery system (WRS).

In particular, for the interim period between systemization and operation, the committee has concerns about personnel training, safety, equipment resilience and reliability, prevention of corrosion and other system degradation possibilities such as that of the reverse osmosis (RO) membrane (see Chapter 4), and compressor maintenance (see Chapter 2). These concerns include the need for continual personnel training; cycling and rinsing the system to prevent corrosion, the potential for solutions freezing in system lines, and precipitation in the lines; maintenance of the high-pressure compressors; and treating the RO membranes to prevent degradation during this period. Many of these challenges may differ from what the operations manual provided by the system contractor says about full plant operation of the SCWO.

The methods for individually handling each of these factors have been discussed and in most cases have been satisfactorily resolved. However, no comprehensive schedule or manual has been prepared as a guide to implementing these procedures for the interim period between systemization testing and plant operation.

A manual for the periods between equipment delivery and systemization, during systemization, between systemization and operations, and for the integrated SCWO and WRS could forestall extended downtimes. Such a manual would include a defined schedule for performing all of the identified interim training and maintenance tasks on the SCWO and WRS. It would include standard operating procedures for the various system components, safety procedures to be used during operation and during maintenance, maintenance

[13] Ron Hawley, plant general manager, URS Corporation, "Systemization Overview," presentation to the committee on February 4, 2013.

intervals, steps for corrosion prevention, steps for maintaining RO membrane integrity, diagnostics and monitoring of potential system degradation, equipment testing intervals, and protocols to be used throughout the time period prior to processing hydrolysate. It could include process metrics such as the acceptable range of SCWO feed concentrations for key components and the target performance values for the SCWO units (e.g., total organic carbon and total hydrocarbons in the SCWO effluent). Creating the manual in electronic format would make all this information available to operators in a searchable framework. It could also be made accessible on tablet computers, enabling portability and increasing utility. Electronic manuals are the industry standard. In addition to assisting in the maintenance of equipment operability, the manual could address the challenges of knowledge and experience transfer and retention during the time preceding SCWO systemization, throughout the SCWO systemization time period, and during the time following SCWO systemization, prior to the processing of hydrolysate.

Finding 3-9. A manual is needed that addresses the concerns discussed above for the periods between equipment delivery and systemization, during systemization, and between systemization and operations, and including integrated SCWO and water recovery system operation. Creating the manual in electronic form would allow for maximum visibility across a wide range of information in a searchable framework on portable platforms such as tablet computers.

Recommendation 3-10. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should prepare a manual specifically to be used in the interim period preceding SCWO systemization, throughout the SCWO systemization time period, and during the time following SCWO systemization, prior to plant operation. This manual should also address integrated SCWO and water recovery system maintenance and operation during these periods and should address all the concerns discussed above. The manual should be prepared in electronic form.

CYANIDE

Certain of the munitions types in the Blue Grass stockpile contain energetic materials in the form of either propellant or burster charges. These materials include composition B4, tetrytol, and M28 propellant. The energetic materials will be treated with hot caustic (NaOH), and the resulting hydrolysate will be strongly basic. Cyanide (CN^-) is a minor side product of hydrolysis of the energetics. The presence of cyanide or hydrogen cyanide (HCN) could pose contact and inhalation hazards should a worker touch the hydrolysate or breathe any vapors that might be above the liquid in the hydrolysate storage tanks. This would be limited to maintenance activities as no worker should be in contact with hydrolysate or the vapor space in the hydrolysate storage tanks during operations. A formal risk analysis would be needed to quantify the extent of the actual risks.

A recent white paper (BPBGT, 2011) analyzes the results of earlier hydrolysis studies and calculates the expected concentrations of HCN/CN^- resulting from the hydrolysis of energetics in the Blue Grass stockpile. Cyanide concentrations in the aqueous phase were measured for the hydrolysates of all the various types of energetics and all had positive detects. The hydrolysates showed concentrations ranging from 1.7 to 705 mg/L (ppm). The level regarded as safe is <0.2 mg/L. Gaseous hydrogen cyanide (HCNg) concentrations were measured above the hydrolysis solution with values ranging from nondetect to 0.08 mg/m^3. The measured HCNg concentrations in the off-gas were all well below established exposure limits (5 mg/m^3).[14]

Aluminum will also be present in the hydrolysate since the rocket warhead bodies will be hydrolyzed. The aluminum must be removed before SCWO processing. Accordingly, the basic hydrolysate will be neutralized with acid in the aluminum precipitation reactor to precipitate aluminum salts. Upon neutralization, CN^- is converted to HCN in solution and released into the gas phase above the solution. The specific CN^-/HCN equilibrium in solution depends on the pH of the solution. HCN has an acid strength (pKa) of ~9, so 99 percent of the cyanide in solution at neutral pH (7) will be in the form of HCN. The concentration of HCN in solution versus the gas phase in the hydrolysate storage tanks (i.e., the distribution of HCN between the liquid and the gas over the surface of the liquid) depends on pH, salt concentrations, the presence of a liquid/gas interface, mixing, and temperature.

In addition to the measurements cited above, the white paper calculated the estimated HCN concentrations in the gas phase above the hydrolysate at 77°F and 140°F for pH ranging from 6 to 10. The results ranged from 8 to 3,200 mg/m^3 (gas) above the solutions, depending on the combination of temperature and pH of the hydrolysate. The level of HCN that is immediately dangerous to life and health (IDLH) is 25 mg/m^3.[15]

After neutralization of the hydrolysate to precipitate the aluminum salts, the gas over the hydrolysate/salt slurry in the aluminum precipitation reactor will be vented to carbon-containing canisters in the SCWO processing building. This is a closed system and limits opportunities for worker exposure. The venting is through activated carbon filters. In the worst case calculated, a filter change-out every two weeks or so would be required (BPBGT, 2011).

The neutralized solution, including any HCN/CN^- present in the solution, will next be sent to the aluminum filtration system, in the SCWO processing building, where

[14]This is a Short-Term Exposure Limit (STEL) assigned by the National Institute for Occupational Safety and Health (NIOSH). It is a 15-minute time-weighted average (BPBGT, 2011).

[15]The IDLH is defined by NIOSH as the level of a chemical that is "likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment" (NIOSH, 2004).

it will be filtered to remove precipitated aluminum salts. The aluminum filtration system is vented to the atmosphere, so any HCN gas released from the liquid during the filtration operation will be vented to the atmosphere.[16] The solution will then be pumped to the SCWO feed system tank, where it will be combined with agent hydrolysates and stored as the blended feed for the SCWO.

HCN is soluble in aqueous solutions, therefore, the HCN/CN^- remaining in the hydrolysates will be transported in solution to the SCWO reactor from the blended hydrolysate tank and destroyed by hydrolysis and oxidation. Earlier experiments showed that the SCWO process destroys cyanide to below detection levels (<10 µg/L in aqueous solution; <4 µg/m^3 in gas). The process involves either oxidation to isocyanate and then hydrolysis to CO_2, or hydrolysis to formate then oxidation to CO_2.

The BGCAPP project staff are investigating a variety of mitigation strategies. These include oxidation strategies, other chemical treatment strategies, physical separation strategies, and the reengineering of hazard controls. This work is under way as of this writing and is not ready to be evaluated by the committee. Whatever strategy is eventually selected will have to be evaluated for impacts on the SCWO process.

Finding 3-10. Cyanide will be present in the energetics and blended hydrolysate streams. This must be managed to protect worker safety. The testing done to date shows that the SCWO process will destroy any HCN or CN^- present in the liquid hydrolysate feed to undetectable levels. A formal risk analysis would be needed to quantify the actual risks to workers.

Recommendation 3-11. If cyanide cannot be removed from the hydrolysate, affected personnel should be informed that if exposure to hydrolysate occurs in an off-normal situation, the hydrolysate could have contained up to approximately 7 ppm, or 300 µM, cyanide. Information about the possible presence of cyanide should also be included in emergency response manuals or other documentation so that first responders are aware of the potential risk. Workers should be trained in how to recognize exposure to cyanide and what should be done while awaiting first responders.

Recommendation 3-12. The Blue Grass Chemical Agent Destruction Pilot Plant project management should quantify the amount of HCN gas that vents from the aluminum filtration system and install an appropriate mitigation to avoid worker/public exposure if the concentrations are above the local air quality release limits. If cyanide cannot be removed from the hydrolysate, project management should conduct a risk and safety analysis to identify the risks and mitigation strategies.

Finding 3-11. Which methodology will be used to manage the cyanide problem has not yet been determined. Whatever methodology is used will change the chemistry of the SCWO system feed and could impact the performance of the system.

Recommendation 3-13. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should identify an effective cyanide management system that does not negatively impact the performance of the SCWO unit.

OVERALL SYSTEM OPERATIONS AND COMPUTER MODEL

To prepare for system operations, BGCAPP will take various steps to simulate the actual operations. They have designed full-size indoor simulators for thermowell and liner replacement to acquaint workers with actual operations and safety processes. Process control simulators are also being developed. One of the simulators will replicate the SCWO control room human–machine interface and allow control room operator trainees to manipulate simulated controls and experience subsequent system responses— for example, the expected responses to opening a valve, initiating feed flow, and the like. This simulation will not, however, allow the exploration of unexpected operational conditions and their impact on the system. There is no computer simulation model of the SCWO and the integrated SCWO/WRS system, nor is one currently planned.[17]

A computer simulation model imitates the operation of a real-world process or system over time. It is a tool to investigate virtually the behavior of the system under study. Computer simulation is critical to understanding how a system will perform when in operation by allowing operators to vary system parameters in the simulation model to see how the system would react. This capability is invaluable for planning operations, testing alternative system settings, understanding system interdependencies, training personnel, understanding risks, and improving safety and emergency response readiness.

In the context of this study, a computer simulation model would represent the operation of the SCWO unit and the entire SCWO/WRS over time. By changing variables in such a simulation model, predictions could be made about system behavior in various operational circumstances and conditions. This could serve to familiarize operators with potential bottlenecks in operations and to identify safety concerns. A computer model also offers a mechanism for examining ways to mitigate those concerns by simulating changes in opera-

[16] John Barton, chief scientist, Bechtel Parsons Blue Grass Team, "BGCAPP Process Overview," presentation to the committee on January 7, 2013.

[17] Personal communication between Steven Mantooth, Blue Grass Chemical Agent Destruction Pilot Plant program office, and James Myska, NRC study director, on February 7, 2013.

tions, processes, feed composition, maintenance and replacement intervals, and the like before operations commence. BGCAPP could use such a computer simulation model to optimize maintenance schedules, to forecast performance for long-term operations, and to uncover and prepare for otherwise unexpected events. The results of these simulation scenarios could differ sharply from the 100-hr factory acceptance tests that were conducted using simulant and can prepare the operators for actual SCWO/WRS operations at BGCAPP.

In addition to understanding the operations of the entire SCWO/WRS system, the computer simulation model could be designed to study the interaction of multiple SCWO units so that intersystem dependencies (physical as well as operational) on schedules and maintenance and related safety and risk issues could be understood and assessed.

Critical input parameters for a computer simulation model would come from the FOAK test results and later systemization of the SCWO units. The computer model could then simulate the long-term operations of the SCWO/WRS system. A few potential benefits of a computer simulation model are these:

- A wealth of process data have been obtained through numerous simulant tests of the SCWO unit and ancillary systems. The data reside in many different and often lengthy reports, which makes it difficult to access them, even if one knows that some desired datum resides within a given report. A computer simulation model would allow the compilation of this information from diverse sources into a single comprehensive depository that would then be easily accessible to all.
- There has been concern about knowledge retention, especially considering the long time and change in personnel between the time of SCWO FOAK testing and BGCAPP operation with hydrolysate. The compilation of the existing knowledge and data into a computer simulation model would be a way to retain that knowledge.
- Safety protocols for workers performing routine maintenance on one SCWO system while a second system is operating in an adjacent space have not yet been developed. The computer simulation model would allow analysis of what-if scenarios, so that engineers could probe potential failure modes and design safety protocols to protect workers.
- A computer simulation model could aid in optimizing the operation of the SCWO system. The committee recognizes that this is a unique, short-term project and not an ongoing industrial operation that would span many years or decades. Still, optimizing the SCWO process to a reasonable degree could aid in achieving the project schedule by making operations more efficient, helping with maintenance scheduling, and avoiding unscheduled shutdowns of the SCWO reactors.

The development of a computer simulation model could provide benefits for understanding and optimizing the combined SCWO/WRS system. On the other hand, chemical plants routinely operate processes with complexity similar to SCWO without the benefit of computer simulation models. The SCWO at BGCAPP will process only a few, highly characterized streams and has been shown through extensive testing to successfully treat these streams. Also, the SCWO at BGCAPP will only operate for a few years and then be shut down and disposed of. Clearly, the effort to create a computer simulation model would need to be considered in the context of the benefit it would provide.

Finding 3-12. There is no computer simulation model that describes the integrated system operations, over time, of all SCWO system processes or of the entire SCWO/WRS. A model tailored for the SCWO and the integrated SCWO/WRS systems would permit system performance to be optimized.

Recommendation 3-14. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should consider investing in a simulation-optimization study where external experts can help develop a computerized simulation-optimization model that describes the operations, over time, for the entire combined supercritical water oxidation and water recovery system.

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4

Systemization of the Supercritical Water Oxidation System with the Water Recovery System

In 2011 and 2012, the Committee to Review the Water Recovery System for the Blue Grass Chemical Agent Destruction Pilot Plant (WRS committee) reviewed the WRS planned for use at the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP). The WRS committee's statement of task focused on corrosion and materials of construction. In its work, the WRS committee also commented on the adequacy of the pretreatment system and the fact that the reverse osmosis (RO) membranes will be sitting for several years before the WRS is systemized. Its report is titled *The Blue Grass Chemical Agent Destruction Pilot Plant's Water Recovery System* (NRC, 2012).

This chapter discusses systemization of the WRS in consideration of the findings and recommendations of the WRS committee. To do this, the chapter first describes the WRS and provides a summary of the WRS committee's concerns, which were reflected in its findings and recommendation. Next, actions taken by BGCAPP in response to the 2012 WRS report are considered and findings are made about those actions. This committee then uses the basis of the WRS committee's findings and BGCAPP's responses, together with the results of first-of-a-kind (FOAK) testing of the supercritical water oxidation (SCWO) system, to discuss systemization of the WRS and the integrated SCWO and WRS systems.

OVERVIEW OF THE WATER RECOVERY SYSTEM

The BGCAPP WRS will treat and recover water from a combined feed stream comprising SCWO effluents, cooling tower blowdown, and steam boiler blowdown. Recovered water will be reused as quench water in the SCWO process. The system was designed to operate at 70 percent product water recovery as permeate and a maximum of 500 mg/L total dissolved solids (TDS) in the product water and to ensure that one full day of SCWO quench water requirements is stored (to permit continuous SCWO operation in case the WRS is nonoperational). The WRS includes the following system components:

- Three SCWO effluent storage tanks where the effluent will be analyzed to ensure that the total organic carbon (TOC) concentration is less than 10 ppm (BPBGT, 2013);
- A conventional pretreatment system consisting of coagulant and antiscalant addition (dual pumps on each unit), media filtration (six units), and canister filters (three) prior to the RO units;
- Three spiral wound RO units (two operational, one spare); and
- Storage tanks used to hold RO permeate for use in periodically cleaning the RO membranes.

Figure 4-1 shows the flow of material from the agent and energetic hydrolysis processes, through the SCWO process, up to the pretreatment step in the WRS. It also indicates where the cooling tower and steam blowdown is blended with the SCWO effluent. The dashed arrows indicate changes recommended by the WRS committee (discussed in more detail below): namely, two additional RO bypasses, one to redirect blowdown water directly to the tanks holding blowdown water or to the RO reject tank if the water softener fails, and the other to divert softened water directly to RO permeate if water quality allows.

Figure 4-2 shows the flow of material through the WRS. The following process performance indicators of the WRS operation will be continuously monitored by the facility:

- Temperature indication for the feed to the RO units,
- Flow indication for the feed to and discharge from the RO units,
- TDS concentration (through conductivity monitoring) of RO permeate,
- Differential pressure across the RO unit (feed versus reject),

- Differential pressure across the multimedia filters and canister filters, and
- Proportional flow ratio and total flow rate indication for the caustic injection system (BPBGT, 2009).

2012 NRC REPORT ON THE BGCAPP WATER RECOVERY SYSTEM

Key Concerns

The findings and recommendations of the WRS committee raised several concerns in three main areas: pretreatment, the RO membranes, and the materials of construction. Rather than merely list the WRS committee's findings and recommendations, this committee summarizes their intent in this report.

Pretreatment

The WRS committee's concerns focused largely on the pretreatment system design and operation. There was, first of all, some uncertainty about the solids loading that would arrive at the pretreatment system—mainly the media filters—from the SCWO effluent, especially considering the elimination of the originally planned clarifier. The WRS committee's specific concern was that the media filtration system would be rapidly overloaded with incoming solids, particularly in the case of H hydrolysates, which are expected to have very high iron particle content in SCWO effluents. Any overload and shutdown of the pretreatment system would have a catastrophic effect on the RO membranes and could ultimately shut down the WRS system for more than a day.

Secondarily, the WRS committee was concerned about

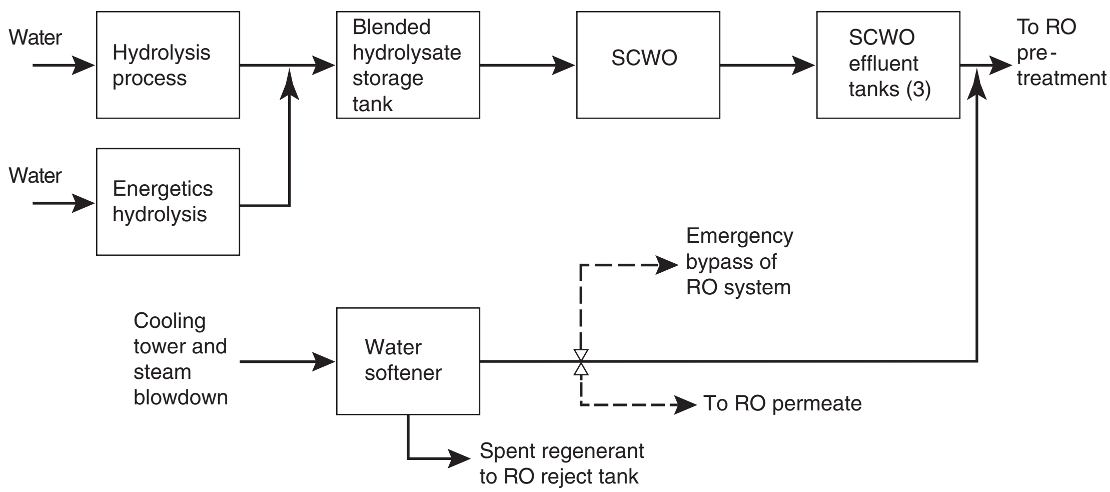

FIGURE 4-1 Flow of material from hydrolysis, through SCWO, up until the pretreatment step in the WRS. The dashed lines show changes recommended by the WRS committee, as discussed in this report. SOURCE: Adapted from NRC, 2012.

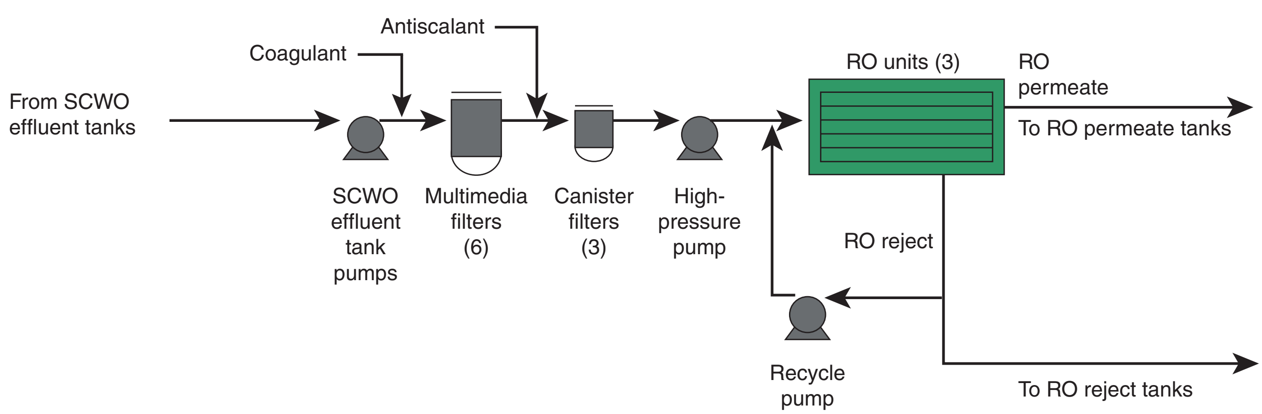

FIGURE 4-2 Process flow diagram for the BGCAPP WRS, including the pretreatment and RO system. SOURCE: NRC, 2012.

the choice of coagulant and whether it would perform adequately. Accordingly, the WRS committee discussed risk mitigation options for the media filtration system, as well as the option of replacing media filtration with membrane filtration, which would completely clarify WRS feed water without the use of coagulants and with a smaller footprint.

The WRS committee concluded that membrane fouling would not be a significant problem if the pretreatment steps are effective in removing suspended solids from the effluents to be passed through the RO membranes and also that, given other feed water quality indicators, the product water recovery could exceed the target of 70 percent.

RO Membranes

The WRS committee's main concern with the RO system was the length of time the membranes would be stored in place, 3 years. The WRS committee recommended taking late delivery of the membranes to alleviate this concern. It also discussed membrane chemical cleaning considerations, as some fouling over time would be inevitable.

Materials of Construction

The WRS committee noted that the materials of construction would not be tested for use in the WRS influent water stream, which was expected to be highly corrosive. The WRS committee recommended that candidate materials of construction be tested and discussed some tests that could be performed to give better insight into the suitability of the selected materials of construction. The WRS committee recognized that the opportunity for representative testing might be limited prior to the start of operations, so it also recommended the possible use of a duplex alloy, such as 2205, in the WRS as a conservative approach.

BGCAPP Response to the 2012 NRC Report

Pretreatment

BGCAPP conducted additional analyses and confirmed that the design of the SCWO effluent tank would serve as a clarifier. Hence, the WRS committee's concerns about the pretreatment system design and operation were appropriately addressed. Given the anticipated residence times for the SCWO effluent in the SCWO effluent storage tanks, the majority of particles should settle out of the effluent before the water is fed into the media filters. Given the settlement of particles ahead of the filters, concerns about the choice of coagulant may be moot; however, BGCAPP also had the equipment supplier research the best available chemical coagulants for use in the WRS as a safeguard.

Finding 4-1. Although stable, fouling-free performance cannot be guaranteed ahead of time, the Blue Grass Chemical Agent Destruction Pilot Plant project staff appear to have taken appropriate engineering design measures to safeguard the reverse osmosis membranes from excessive fouling conditions.

RO Membranes

In response to the WRS committee's concerns, BGCAPP has indicated that the RO membranes will be stored according to manufacturer recommendations and that adequate replacement membranes will be stored on-site at all times. They have also arranged for the appropriate membrane chemical cleaning agents to be provided by the equipment supplier.

Finding 4-2. The WRS committee's concerns about the storage of the RO membranes between delivery and systemization and their chemical cleaning appear to have been adequately addressed.

Materials of Construction

In response to the WRS committee's concerns, BGCAPP conducted an array of additional corrosion tests at various salinities and temperatures. The tests were U-bend weld tests, oxidation reduction potential tests, and cyclic polarization tests. The U-bend weld tests were to evaluate materials for stress corrosion cracking. The oxidation reduction potential tests characterized the test solutions. The cyclic polarization tests investigated general and pitting corrosion. The materials tested were 316L, 904L, and 2205.[1] Based on the test results, BGCAPP has concluded that as far as could be simulated with surrogate waters and conditions, 316L stainless steel will resist corrosion over the working life of the WRS system for the anticipated operating environment.

Finding 4-3. The materials of construction planned for use in the WRS now appear to have been adequately tested in representative environments. It is now possible to have confidence that the planned materials will perform adequately for the amount of time that the water recovery system will operate and in the anticipated environments.

SYSTEMIZATION OF THE WRS

RO Membrane Storage After Systemization

During systemization, the combined SCWO and WRS system will be tested using simulated blended hydrolysate. Following systemization, the combined system will be flushed with fresh water. Following flushing at the end of systemization, the components will sit idle until plant

[1] Surajit Amrit, mechanical process lead, BGCAPP, "Water Recovery System Update," presentation to the committee on January 7, 2013.

start-up. This period may last many months. As noted, the previous NRC study of the WRS stated concerns about long-term storage of the RO membranes prior to systemization (NRC, 2012). BGCAPP engineers responded by contacting the membrane vendor, which suggested dry storage of the membranes after delivery for long-term preservation.[2] This may not be possible after systemization testing because the membranes will have been used during this testing.

Finding 4-4. There is the potential for membrane degradation between systemization and full plant operation unless care is taken to preserve the membrane.

Recommendation 4-1. Blue Grass Chemical Agent Destruction Pilot Plant operators should obtain, review, and follow manufacturer recommendations for membrane preservation between systemization and start-up of plant operations.

Development of Water Balance

A portion of the permeate from the WRS will be recycled for use as quench water in the SCWO system. It is shown that each RO system will produce 61 gal/min (gpm) of permeate when all three SCWO units are operating (BPBGT, 2007). According to the SCWO process flow diagram, approximately 21.5 gpm of permeate will be required for use as SCWO quench water in each SCWO unit. Process water included elsewhere in the system leads to roughly 24.5 gpm from each SCWO unit into the RO (stream 670 in BPBGT, 2008), suggesting that the greatest contribution to the water effluent is from the quench water (BPBGT, 2008). It appears to the committee that the water balance for the integrated SCWO/WRS system has not yet been addressed and optimized. Whether there will be an excess of permeate relative to the required quench water or, possibly, a small deficit is hard to say based on the sources provided to the committee. FOAK testing would have provided an excellent opportunity to investigate optimization of the combined SCWO and WRS. It appears that this was not possible, however, because the two systems are being provided by separate vendors whose delivery schedules are not coordinated.

Finding 4-5. The operation of the WRS has not been optimized for use with the SCWO system.

Recommendation 4-2. Blue Grass Chemical Agent Destruction Pilot Plant staff should optimize permeate generation to match supercritical water oxidation system quench demand.

Impact of Water Recycling on the SCWO System

Site tap water was used for all testing of the high-pressure quench flow. During systemization and operations, RO-purified recycle water will be used as the quenching water. The committee explored the impact of switching these input streams when moving from FOAK testing to systemization. The RO system reduces the salt concentration by a factor of approximately 20-60, yielding 70 percent net volume of recovered water containing no more than 500 mg/L TDS (NRC, 2012). Though the committee could not locate data describing the specific values for dissolved solids in the process water used during FOAK testing, the 500 mg/L target for dissolved solids should not represent a significant perturbation to the SCWO system. Also, because the prequench concentration of salt and TDS in the effluent is expected to be 10,000-20,000 mg/L, the anticipated level of TDS in the WRS effluent should not have a dramatic impact on the performance of the SCWO quench system. Thus, the committee believes that the use of RO permeate in the quench water flow instead of the tap water used during testing does not significantly change the process, though "normal" levels of effluent conductivity may need to be reestablished upon systemization using RO permeate.

The continued recycling of water through the SCWO quench and the RO system will not continually concentrate the salts in the recovered water because the RO system delivers water with a specified, constant maximum total dissolved solids concentration. Incidental solids such as titanium and iron oxides do not accumulate in the recycled water as solids are filtered from the SCWO effluent prior to RO processing to preserve RO membrane integrity.

Finding 4-6. The committee foresees no problems with using the water recovered via reverse osmosis in the SCWO system other than slight changes that may need to be made to the monitoring parameters.

Recommendation 4-3. The Blue Grass Chemical Agent Destruction Pilot Plant project staff should characterize the reverse osmosis effluent for each agent campaign. They should then reestablish normal operating conductivities when reverse osmosis permeate is injected (recycled) at the bottom of the SCWO reactor.

INTEGRATED SCWO AND WRS OPERATIONS

The committee noted that SCWO rinse water during FOAK testing of the SCWO unit was provided by plant water at the contractor's site on an as-needed basis. The use of a storage tank for RO permeate effectively replaces city water during SCWO/WRS operations. The committee sees no problems in using RO permeate for SCWO quench.

Earlier in this chapter, it was reported that the contents of the SCWO effluent tank would be monitored to ensure

[2] Surajit Amrit, mechanical process lead, BGCAPP, "Water Recovery System Update," presentation to the committee on January 7, 2013.

that TOC is below 10 ppm. The previous NRC report on the BGCAPP WRS (NRC, 2012) assumes a TOC level in the SCWO effluent tank of <2 ppm, based on the System Design Description for the Water Recovery System (BPBGT, 2009). This was based on the best information available at the time of that report. FOAK testing of the SCWO system now assumes that a monitored TOC level of less than 10 ppm will exist in the SCWO discharge. This level may be reduced somewhat in the SCWO effluent tanks because cooling tower and steam blowdown effluent may also be added to the tanks. However, the FOAK test report also states as follows:

> The actual set point for effluent diversion to off-spec effluent tank will be determined by finalized permit levels based on allowable effluent TOC for the effluent disposal path chosen. (BPBGT, 2013, p. 73)

This seems to indicate that the SCWO effluent tanks and WRS feed may contain up to 10 ppm TOC, or even more if permitting allows. These are significantly higher levels than considered in the WRS report and could cause more rapid degradation of RO membranes than envisioned in the WRS report.

Finding 4-7. Since the final effluent total organic carbon (TOC) level will be based on permit levels, the WRS feed may have a considerably higher level of TOC than envisioned in previous reports, and this could lead to more rapid and severe fouling of the reverse osmosis membrane than originally envisioned in the WRS design. The main concern is the need for more frequent and extensive cleaning (ideally between campaigns), which could lead to rapid membrane degradation and call for premature replacement.

Recommendation 4-4. Blue Grass Chemical Agent Destruction Pilot Plant operators should monitor the reverse osmosis membranes and system during systemization testing to determine if there is any evidence of premature membrane degradation. If this is observed, then the membranes would need to be replaced sooner. This is a minor operational issue that can be handled by keeping a spare set of membranes on-site at all times.

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Appendixes

Appendix A

Committee Activities

FIRST COMMITTEE MEETING
JANUARY 7-9, 2013
SAN DIEGO, CALIFORNIA

Objective: To introduce required administrative procedures set forth by the National Research Council; conduct the composition and balance discussion; read the committee statement of task and background review with committee sponsor; receive briefings on the demilitarization process at the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP), the supercritical water oxidation (SCWO) system, changes to the water recovery system (WRS), and factory acceptance testing of the SCWO; review preliminary report outline and report writing process; turn the report outline into a concept draft; confirm committee writing assignments; and discuss next steps and future meeting dates.

BGCAPP Process Overview, John Barton, chief scientist, Bechtel Parsons Blue Grass Team (BPBGT)

Cyanide—Its Presence and Potential Impacts, Dan Jensen, advanced process system program manager, General Atomics

SCWO Factory Acceptance Testing, Kevin Downey, advanced process system manager, General Atomics

SCWO System Equipment and Layout, Dan Jensen, advanced process system program manager, General Atomics

Water Recovery System Update, Surajit Amrit, mechanical process lead, BGCAPP

SECOND COMMITTEE MEETING
FEBRUARY 4-6, 2013
LEXINGTON AND RICHMOND, KENTUCKY

Objective: Complete bias discussion with remaining members; receive briefings and engage in discussion with BGCAPP staff; BGCAPP site walk-through; discuss adequacy of data gathering to date; formulate plan to complete any necessary data gathering; conduct committee deliberations; discuss report status; conduct report drafting; make work assignments; and discuss timing of third meeting.

SCWO FOAK Test Status, Kevin Downey, advanced process system manager, General Atomics.

SCWO Training Plan, Doug Plummer, BPBGT training manager, GP Strategies Corporation

Systemization Overview, Ron Hawley, plant general manager, URS Corporation

THIRD COMMITTEE MEETING
APRIL 29-30, 2013
WASHINGTON, D.C.

Objective: Conduct committee deliberations, discuss report, decide and agree on findings and recommendations, conduct report drafting to achieve at least a preconcurrence draft, and make any necessary work assignments.

VIRTUAL MEETINGS
MAY 21 AND 22, 2013

Objective: Discuss and develop the report draft.

Appendix B

Biographical Sketches of Committee Members

John R. Howell (NAE) is the Ernest Cockrell, Jr., Memorial Chair Emeritus at the Cockrell School of Engineering in the Department of Mechanical Engineering at the University of Texas at Austin. Before joining the University of Texas in 1978 he was a heat transfer researcher at the NASA Lewis (now Glenn) Research Center and taught at the University of Houston. In 1994 and 1995, he served as director of the Thermal Transport and Thermal Processing Program with the National Science Foundation (NSF). He has received a number of awards for his work in radiative transfer, including the American Society of Mechanical Engineers (ASME) Heat Transfer Memorial Award, the American Institute of Aeronautics and Astronautics (AIAA) Thermophysics Award, and the Max Jakob Award. In June 2013, he received the Poynting Award for his contributions to radiative transfer. He is a life fellow of ASME and a fellow of the AIAA, was elected a foreign member of the Russian Academy of Science in 1999, and became a member of the National Academy of Engineering (NAE) in 2005. He has coauthored 4 books and published over 300 articles, papers, and reports. Dr. Howell also served on the National Research Council's (NRC's) Panel on Benchmarking the Research Competitiveness of the US in Mechanical Engineering and the Panel on Review of NASA's Exploration Technology Development Program. Dr. Howell received his B.S. and M.S. in chemical engineering and his Ph.D. in engineering from the Case Institute of Technology.

Martin A. Abraham, P.E., received a B.S. in chemical engineering from Rensselaer Polytechnic Institute and a Ph.D. from the University of Delaware. Dr. Abraham joined Youngstown State University as professor of chemical engineering and founding dean of the College of Science, Technology, Engineering and Mathematics in July 2007, after serving as professor and dean of the College of Graduate Studies at the University of Toledo. In addition to his duties as dean, Dr. Abraham maintains an active research program in reaction engineering and catalysis, with recent work on carbon capture, supported through a decade-long research and development relationship with a small business that focuses on applying ceramic coatings to metal foils. The primary research focus area has been green engineering and sustainability, with an emphasis on issues of sustainable energy. He has over 70 refereed publications and over 30 additional publications, has authored or edited nine books, has participated in three patent applications, and has given over 100 technical presentations.

He serves as editor for the American Institute of Chemical Engineer's quarterly *Environmental Progress and Sustainable Energy*, is past chair of AIChE's Sustainable Engineering Forum, and is counselor and a former chair for the ACS Industrial and Engineering Chemistry Division. He was selected as the 2012 Business Advocate of the Year by the Youngstown/Warren Regional Chamber of Commerce and serves on the Board of the TechBelt Energy Innovation Center and the executive committee of the TechBelt Initiative, and is also a member of the board for the Youngstown Business Incubator and the Children's Center for Science and Technology of the Mahoning Valley. Dr. Abraham received the 2006 Dion D. Raftapoulous/Sigma Xi Outstanding Research Award, a Lucent Technologies Fellowship in Industrial Ecology in 1998, and was recognized in 1989 with the Ralph R. Teetor Educational Award of the SAE. He is a fellow of the American Chemical Society and the AIChE.

David J. Duquette is the John Tod Horton Professor of Engineering at the Rensselaer Polytechnic Institute in Troy, New York. Professor Duquette began his career as a commissioned officer in the U.S. Coast Guard from 1961 through 1965. He then earned a doctoral degree at the Massachusetts Institute of Technology, where he also served as a research assistant for the Department of Metallurgy and Materials Science. Upon graduation, he spent 2 years at Pratt & Whitney Aircraft, as a senior research associate in the Advanced Materials Research & Development Laboratory. In 1973, he spent 6 months at the Imperial College of Science, Technology and Medicine, University of London, as a visiting professor of metallurgy. Following that assignment, he served as a visiting senior scientist at the Max Planck Institut fuer Eisenforschung in Dusseldorf, Germany. He joined Rensselaer in 1970 and was named a full professor 6 years later. Dr. Duquette has earned numerous awards, including the Alcoa Foundation Award for Outstanding Research Achievement from 1978 to 1979; Case Centennial Scholar, Case-Western Reserve University in 1980; and the Humboldt Prize from the Alexander von Humboldt Foundation in 1983. He is a fellow of both the American Society for Metals (ASM) and the National Association of Corrosion Engineers (NACE).

He served as the chairman of the Gordon Research Conference on Corrosion in 1988 and as president of Alpha Sigma Mu from 1987 to 1988; the organization named him an honorary member in 1988. He earned the Acta Metallurgica Outstanding Paper Award in 1987 and the Willis Rodney Whitney Award from NACE in 1990. He also presented the Alpha Sigma Mu Distinguished Lectureship in 1991.

Professor Duquette received his B.S. from the U.S. Coast Guard Academy in 1961 and a Ph.D. in metallurgy and materials science from MIT in 1968.

Eric M.V. Hoek is a professor in the Department Civil & Environmental Engineering at the University of California, Los Angeles (UCLA). Dr. Hoek is also a faculty member at the California NanoSystems Institute and the UCLA Water Technology Research Center. Dr. Hoek's research explores the union of nanomaterials and membrane technologies and their application to water purification, energy production, and environmental protection—all keys to a more sustainable future.

In the past decade, Dr. Hoek and his students have published more than 60 peer-reviewed articles in journals such as *Nature Materials*, *Nano Letters*, *Environmental Science & Technology*, *Energy & Environmental Science*, *Langmuir*, *Journal of Membrane Science*, and *Desalination*. Dr. Hoek also has nine patents awarded or pending, which have led to several start-up water technology companies, including NanoH_2O Inc. Dr. Hoek received the 2011 American Society of Civil Engineers' Walter L. Huber Award for Achievements in Civil Engineering Research for his pioneering work on thin-film nanocomposite, reverse osmosis membranes.

Dr. Hoek received a B.S. in civil and environmental engineering from the Pennsylvania State University; an M.S. in civil and environmental engineering from UCLA; and an M.S. and a Ph.D. in chemical engineering from Yale University.

Eva K. Lee is a professor in the H. Milton Stewart School of Industrial and Systems Engineering and is director of the Center for Operations Research in Medicine and HealthCare at the Georgia Institute of Technology. The center has been established with funds from the NSF and the Whitaker Foundation. It focuses on biomedicine, public health, and defense, advancing domains from basic science to translational medical research; intelligent, quality, and cost-effective delivery; and medical preparedness and protection of critical infrastructures. She is also the codirector of the Center for Health Organization Transformation, an NSF Industry/University Cooperative Research Center. Dr. Lee partners with hospital leaders to develop novel transformational strategies in delivery, quality, safety, operations efficiency, information management, change management, and organizational learning.

Professor Lee received her B.S. in mathematics and computer science from Hong Kong Baptist University, and an M.A. and Ph.D. in computational and applied mathematics from Rice University in Houston, Tex.

Murray Glenn Lord is associate environmental health and safety (EH&S) director in the EH&S Operations Technology Center at Dow Chemical Company. He is responsible for the research program for technology development for Global Environmental Operations, which includes projects in process optimization, technology development, and capital project execution. Mr. Lord has experience in project areas across multiple business and technology areas. He is also accountable for EH&S performance, budget performance, project development, and personnel leadership of research group from four locations, and he leads the Environmental Technology Leadership Group, accountable for environmental technology development for Dow.

Previously, Mr. Lord was a technical leader of propylene oxide process research and was responsible for research in support of technology development of the propylene oxide process. He was also responsible for development and coordination of research studies at laboratory, pilot plant, and full commercial scale.

Julius Rebek, Jr. (NAS) is the director of the Skaggs Institute for Chemical Biology and professor of chemistry at the Scripps Research Institute in La Jolla, California. He received a Ph.D. degree in chemistry from MIT (1970) for studies in peptide synthesis. He has held positions at the University of California, Los Angeles (1970-1976), where he devised the three-phase test for reactive intermediates; the University of Pittsburgh (1976-1989), where he developed cleftlike structures for studies in molecular recognition; and at MIT (1989-1996), where he was the Camille Dreyfus Professor of Chemistry and devised synthetic, self-replicating molecules. He is a member of the Hungarian Academy of Sciences, the European Academy of Science, a fellow of the Royal Society of Chemistry and a fellow of the American Academy of Arts and Sciences. He is the author of more than 500 publications, and his current research interests include self-assembling systems, molecular behavior in small spaces, uranium recovery, and the detection and destruction of chemical warfare agents.

T.W. Fraser Russell (NAE) is currently the Allan P. Colburn Professor Emeritus of Chemical and Biomolecular Engineering. He worked as a research engineer at the Research Council of Alberta, as a design engineer with Union Carbide Canada, and as a consultant with a number of industrial organizations, including a 30-year consultation with the DuPont engineering department. He served from 2000 until 2005 on the board of directors of Ascent Solar Technologies Inc., a firm producing thin-film flexible photovoltaic modules. His administrative contributions to the University of Delaware include as chair of the Chemical Engineering Department, associate dean and dean of the College of Engineering, and 16 years as director of the Institute of Energy Conversion, a laboratory at the University of Delaware devoted to thin-film photovoltaic research and a Department of Energy University Center of Excellence. He most recently served for 5 years as the vice provost for research.

Professor Russell's research areas include semiconductor reaction and reactor engineering and fundamental studies of multiphase fluid motions. He has successfully applied these basic studies to the design and operation of commercial-scale equipment for both the photovoltaic and chemical process industries. He has served as a consultant to a number of companies including DuPont, Union Carbide (10 years), Pfizer (5 years), and Ethyl (2 years) He holds 6 patents and has published over 90 technical publications and coauthored 3 texts used in chemical engineering undergraduate programs.

Professor Russell is a fellow of the AIChE and a registered professional engineer (P.E.) in the State of Delaware. He has received many other national and local honors.

Professor Russell received a B.Sc. and M.Sc. from the University of Alberta and a Ph.D. from the University of Delaware, all in chemical engineering.

Phillip E. Savage is the Arthur F. Thurnau Professor of Chemical Engineering in the Department of Chemical Engineering at the University of Michigan, and he has been on the University faculty since 1986. He earned a B.S. from Penn State and M.Ch.E. and Ph.D. degrees from the University of Delaware. All of his degrees are in chemical engineering. Supercritical water oxidation is one of the many technologies his lab has examined.

His research and teaching focus on the rates, mechanisms, and engineering of chemical reactions that move us toward a more environmentally sustainable society. His current research projects deal with reactions that can be used for hydrogen production from biomass and for liquid transportation fuel production from algae. His research group uses experiments, modeling, and simulation to explore different reaction systems. His teaching focuses on chemical reaction engineering and environmental sustainability.

Dr. Savage has served as an associate editor for the *AIChE Journal* and is on the editorial boards of the *Journal of Supercritical Fluids, Energy & Fuels,* and *Environmental Progress & Sustainable Energy.* He has served as chair of the Catalysis and Reaction Engineering division of AIChE and the Industrial and Engineering Chemistry division of the American Chemical Society.

Dr. Savage has a long record of service to the College and University of Michigan. At the University level, he serves on the advisory board on intercollegiate athletics and has served on the Rackham Executive Board, SACUA, the Senate Assembly, the CRLT Advisory Board, and the Provost's Honor Council in addition to other committees. At the college level, Dr. Savage has served on the Rules Committee, Curriculum Committee, and Nominating Committee, and he has previous experience on the College Executive Committee.

Dr. Savage is a fellow of the AIChE. He received the 2009 Michigan Governor's Award for Green Chemistry and the 2001 National Catalyst Award from the American Chemistry Council in recognition of his outstanding teaching and contributions to chemical education. He was also selected as a Thurnau Professor in 1997 and was named a Rackham Distinguished Graduate Mentor in 2006. He has received both Research Excellence and Education Excellence awards from the College of Engineering.

Tim J. Shepodd is deputy director, Security Systems and Reliability, Sandia National Laboratories, Livermore, California. He manages approximately 75 scientists and engineers in five groups and with a budget of $25 million. The work in his groups spans basic research to system studies to the design/reliability of nuclear weapon components. Previously, Dr. Shepodd was the manager of the Materials Chemistry Department, where he managed a group of about 20 scientists who researched fundamental materials (organics) issues for the nuclear stockpile, chemical weapon demilitarization, solar energy materials, explosives chemistry, corrosion in extreme environments, and other topics. He also managed an aggressive hiring program and ran multiple ES&H-intensive facilities (electrodeposition, organics processing, explosives chemistry, composites fabrication, chemical synthesis/characterization) and pushed the inclusion of science-based decisions into nuclear weapons research projects and component design. From 1994 to 2004, Dr. Shepodd was the coinventor and lead chemist for the Explosives Destruction System, Sandia's mobile destruction system used to batch-neutralize explosively configured chemical munitions. He developed procedures, recipes, and analytical protocols with the host sites to destroy mustard, phosgene, sarin, phosphorous, and smokes. He also tested a prototype reactor for the batch SCWO of explosively configured chemical munitions and designed and qualified air filters for the waste drums.

Dr. Shepodd received a B.S. in chemistry from the University of California, Los Angeles, and a Ph.D. in organic chemistry from the California Institute of Technology.