

SUPERCRITICAL WATER OXIDATION (SCWO) OF CHEMICAL AGENT HYDROLYSATES AND ENERGETICS HYDROLYSATE

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Abstract

Supercritical Water Oxidation (SCWO) is an advanced hazardous waste treatment technology that makes use of the unique properties of water at conditions above its thermodynamic critical point of 705°F (374°C) and 3,206 psia (22.1 MPa). At these supercritical conditions, most organic materials, oxidation reactants, and oxidation products are miscible in water, thus allowing complete oxidation reactions to take place in relatively compact equipment and without significant mass transport limitations. The products of SCWO processing include CO₂, H₂O, and salts, with NO_x, SO_x, and particulate concentrations at or below detection limits, all without any post-treatment.

General Atomics (GA) has been developing the SCWO technology since 1992 and is currently providing SCWO units for the destruction of a variety of military wastes. GA is nearing completion of the final design for supply of three 1000-lb/hr SCWO units for destruction of the hydrolysis products resulting from the caustic neutralization of GB, VX, and H munitions at the Blue Grass Chemical Agent-Destruction Pilot Plant (BGCAPP). These units will process a mixture of agent and energetics hydrolysates based on a design that has been validated through extensive testing with actual hydrolysates and surrogates. GA is also building two SCWO units for the treatment of conventional munition wastes. A 1500-lb/hr unit is under construction for the Tooele Army Depot for the treatment of the caustic neutralization products of Cartridge Actuated Device (CAD) and Propellant Actuated Device (PAD) processing. GA is under contract to design and build a 5000-lb/hr unit for the Blue Grass Army Depot for the destruction of double-base propellant, RDX, and TNT. The 5000-lb/hr SCWO unit will be fitted with a slurry-grinding feed preparation module for propellant size-reduction and a liquid product post-treatment module for removal of heavy metals.

1. Introduction to SCWO

The SCWO process makes use of the unique properties of water at conditions above its thermodynamic critical point of 705°F (374°C) and 3,206 psia (22.1 MPa). Under ambient conditions, water is a polar solvent in which salts are highly soluble, and typical organic compounds are essentially insoluble. Under supercritical conditions, however, the properties of water change dramatically, and it behaves more like a non-polar solvent in which salts are insoluble, and most organic materials and combustion gases are miscible. Salts, if present, will therefore precipitate, and a strategy for ensuring continuous salts transport through the reactor is required. The elevated pressure for SCWO operations significantly increases the mixture density in the reactor. The high density combined with the solubility of organics and combustion gases allows complete oxidation of organic compounds to be accomplished in relatively compact equipment and without significant mass transport limitations. Total organic carbon concentrations in the liquid effluent are typically less than 1 ppm. Relative to incineration, the reactor operating temperatures are low, so NO_x formation is not favored. The gaseous products of SCWO can typically be directly vented to atmosphere without any

post-treatment since NO_x, SO_x, CO, and particulate concentrations are all near or below detection limits.

A simplified SCWO Process Flow Diagram is shown in Fig. 1. The waste feed, water, and oxidant (typically air) are pressurized to ~3400 psi (23.4 MPa) and fed to the reactor. Oxidation of the organic content of the waste provides heat to maintain the desired reaction temperature of ~1200°F (650°C). If the heat content of the feed is less than ~2000 Btu/lb, (1109 kcal/kg), auxiliary fuel and/or feed preheat may be required. At reactor operating conditions, the destruction kinetics for even the most refractory compounds are sufficiently fast such that complete destruction is accomplished in less than 15 sec. The reactor effluent, consisting of water, CO₂, N₂, O₂, and mineral salts or acids depending on the specific feed, is cooled to 100-140°F (38-66°C) in a heat exchanger. Gases are then separated from the cooled reactor effluent and vented to atmosphere, and the solids/liquids are recovered, recycled, or shipped off-site for disposal. For feeds containing high salt concentrations, quench water is injected at the bottom of the reactor to dissolve the salts and ensure reliable salts transport through downstream piping.

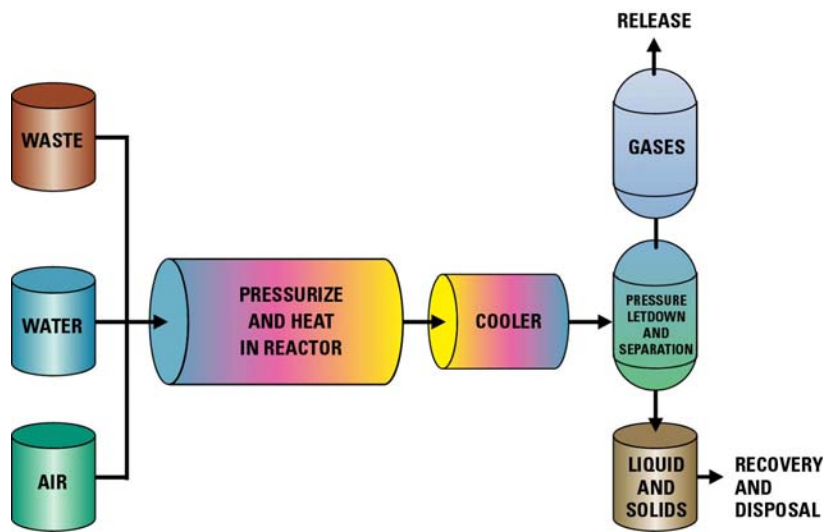


Fig. 1 – Simplified SCWO Process Flow Diagram

The GA SCWO process uses down-flow, solid-wall reactors fitted with removable/replaceable liners to provide corrosion and thermal protection for the reactor vessel wall (see Fig. 2). A variety of liner materials can be used for corrosion protection, including titanium and high-nickel alloys.

2. SCWO Units for the Blue Grass Chemical Agent-Destruction Pilot Plant

GA is a member of the Bechtel Parsons Blue Grass Team that is under contract to the Program Manager for Assembled Chemical Weapons Alternatives (PMACWA) to design, build, operate, and close a facility for destruction of the chemical munitions stored at the Blue Grass Chemical Activity (BGCA). BGCA stores GB rockets, VX rockets, and H projectiles. The BGCAPP will use neutralization-SCWO as the agent and energetics destruction process. Following separation from the munitions, the agents and energetics are separately hydrolyzed in caustic to yield hydrolysate solutions that are then destroyed via SCWO. The GB and VX hydrolysates are corrosive, while the H hydrolysate and energetics hydrolysate are not. Therefore, for the BGCAPP, the agent and energetics hydrolysates are

combined to yield more uniform, less corrosive feeds. Proprietary salts transport additives are also used to ensure reliable and continuous transport of salts through the reactor and downstream equipment.

Using both actual hydrolysates and surrogates, greater than 8,000 hr of chemical agent hydrolysate and energetics hydrolysate testing has been conducted by GA in support of a variety of Government programs. Specifically in support of the BGCAPP SCWO system design, GA conducted both pilot-scale and near-full-scale testing using surrogate feeds. The surrogate feeds contained the same elemental species and concentrations as the actual agent hydrolysate/energetics hydrolysate blended feeds. Testing was initially performed in a pilot-scale reactor (3.1-in. inner diameter (ID), compared to a full-scale reactor ID of 7.625 in.) and then in a near-full-scale reactor (6.1-in. ID) to validate the benefits of processing blended feeds as opposed to separate processing of agent hydrolysates and energetics hydrolysates. Short-duration tests were initially performed, with testing culminating in 100-hr tests for each of the three blended feed campaigns: GB blended feed, VX blended feed, and H blended feed. Testing showed continuous and reliable salts transport throughout the tests, with no need for reactor flushing. The effluent analyses (see Table 1) confirmed excellent organic destruction for all testing performed.

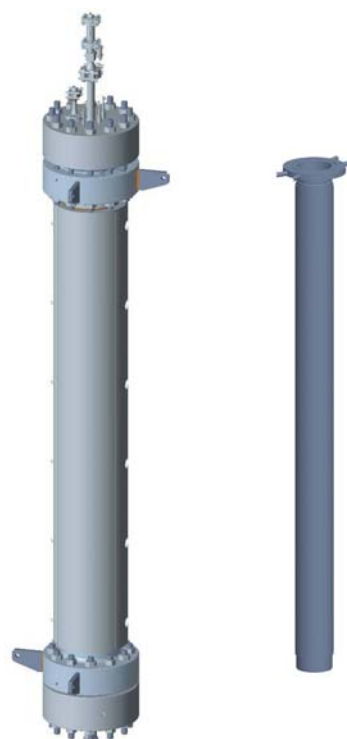


Fig. 2 – GA Down-Flow, Solid-Wall Reactor and Removable Liner Assembly

**Table 1
Summary Effluent Results for BGCAPP Blended Feed Testing**

Description	GB	H	VX
TOC (liquid) ppm	<2	<2	<1
Chromium (liquid) ppm (TCLP limit 0.6 ppm)	<0.3 ppm	<0.3 ppm	<0.02
Nickel (liquid) ppm (TCLP limit 11 ppm)	<0.3 ppm	<0.4 ppm	<0.09
CO (gas) ppm	<4 ppm	<1 ppm	<1 ppm

GA is nearing completion of the final design for three 1000-lb/hr SCWO units for use at BGCAPP. Each SCWO unit includes a feed skid containing the high-pressure feed pumps and a reactor skid containing all high-pressure/high-temperature equipment items. A 3-dimensional model view of the reactor skid is provided in Fig. 3. Also included in GA's BGCAPP scope of supply are supporting feed and effluent collection tanks, high-pressure air compressors and air feed control equipment, and a relief tank to be used in the event of an unplanned reactor depressurization. Following completion of design, work will begin on fabrication of the first SCWO unit to be used for extended "First Article" testing. Following completion of testing, work will begin on fabrication of SCWO units 2 and 3.

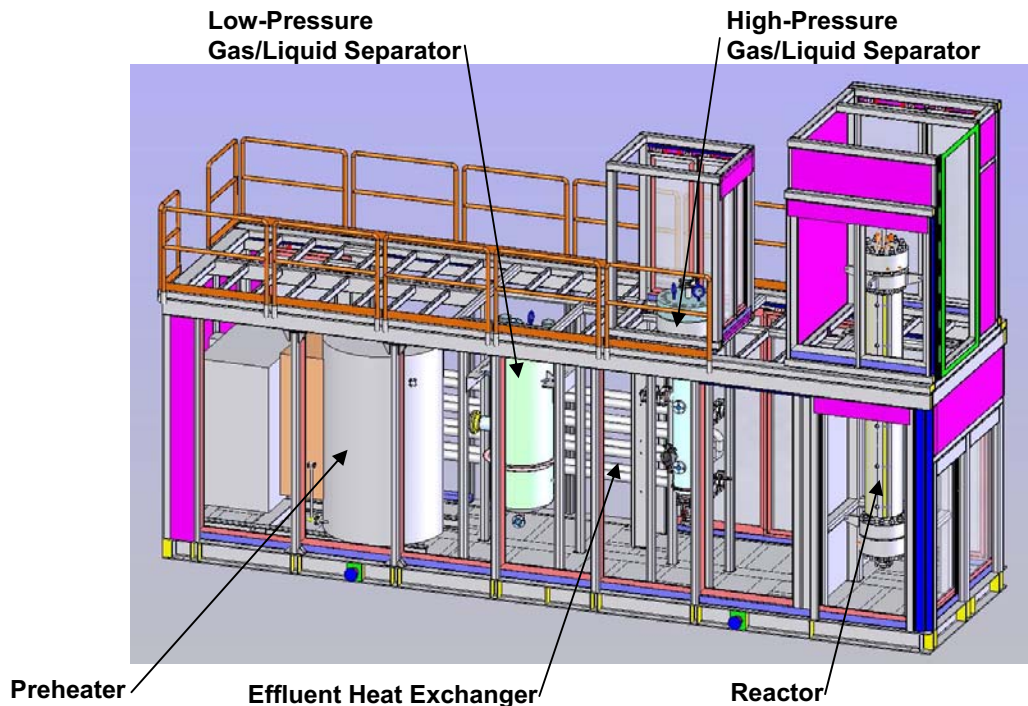


Fig. 3 – BGCAPP SCWO Reactor Skid

3. Industrial SCWO for Energetics and Waste Processing

Processes designed for chemical demilitarization sites typically require elaborate monitoring and control systems and component redundancy. These requirements arise primarily from three issues: (1) the very strict design requirements associated with chemical demilitarization plants; (2) significant interfaces with other systems, facilities, and control systems; and (3) the compositions of chemical agents and their resulting hydrolysis products being varied, complex, and corrosive. Significantly simpler, less-expensive SCWO systems can be used for non-agent military applications and commercial hazardous waste processing.

GA has been developing Industrial SCWO (iSCWO) systems since 2003 for the processing of simpler, less-corrosive feeds such as hydrolyzed or slurried energetics. The design of these systems makes use of the extensive existing SCWO data base for chemical demilitarization projects. The Air Force Research Laboratory (AFRL) at Tyndall Air Force Base has funded several programs to develop iSCWO technology into a state-of-the-art, environmentally-friendly, and economically-viable process for a wide variety of Air Force, Department of Defense (DOD), and industrial waste streams. GA has developed and tested a low-cost iSCWO system that retains the primary operational advantages of traditional GA SCWO systems, but at a significantly reduced cost. The first iSCWO system (see Fig. 4), built and tested in 2005 at the GA test facility in San Diego, California, demonstrated that the technology is highly effective for the destruction of typical organic feeds. This first system demonstrated the efficacy of the iSCWO design and is being used to gather data for future systems.



Fig. 4 – GA iSCWO Skid

A 1500-lb/hr iSCWO unit is currently under construction for the Tooele Army Depot for the treatment of the caustic neutralization products of CADs and PADs. CADs and PADs are typically small, 0.75-in. ID X 3-in. long (~2 cm X 7.5 cm), aluminum-bodied devices containing double-based propellants, TNT, and HMX. They are used in numerous aeronautical applications, including aircraft ejection seat systems for canopy disengagement and separation and in the aircraft exterior for payload separation. The caustic solution both dissolves the aluminum containment body to gain access to the energetics and hydrolyzes the energetics to yield an inert hydrolysate.

GA is also under contract to design and build a 5000-lb/hr iSCWO unit for the Blue Grass Army Depot for the destruction of slurried double-base propellant, RDX, and TNT that is in storage and currently slated for demilitarization. The 5000-lb/hr SCWO unit will be fitted with a slurry-grinding feed preparation module for propellant size-reduction. The propellant will be slurried in water at a concentration of approximately 20 wt% for direct feed to the iSCWO unit. The unit will also be fitted with a post-treatment module for removal of heavy metals such as lead.

4. Conclusions

Through greater than 8,000 hr of chemical agent hydrolysate and energetics hydrolysate testing, using both actual hydrolysates and surrogates, GA SCWO systems have consistently been proven to be extremely efficient at organic destruction. The SCWO system design for BGCAPP is nearing completion and has been validated through extensive testing and engineering review. Fabrication of the first BGCAPP SCWO unit is scheduled to begin later this year. For simpler, non-chemical agent-related applications, this extensive data base has given rise to the GA iSCWO process that can provide broad waste disposal options at a significantly reduced cost.

About the Authors

Kevin Downey has a MS degree in Chemical Engineering and has been working for General Atomics for 21 years, primarily focusing on chemical demilitarization technologies. He has been developing the SCWO technology for the past 15 years for the disposal of chemical agents, energetics, and general hazardous wastes. Kevin has been the lead engineer for numerous SCWO programs and is the SCWO Lead for the Blue Grass Chemical Agent-Destruction Pilot Plant.

Noel Wheatley has a BS degree in Mechanical Engineering and has been working for General Atomics for 7 years focusing on chemical demilitarization technologies, with 20 years previous experience in consulting engineering and power plant construction. He has been extensively involved with the design of systems for hydrolyzing energetics and is the Project Engineer for the Energetics Batch Hydrolyzer (EBH) and SCWO systems for the Blue Grass Chemical Agent-Destruction Pilot Plant.