Supercritical water oxidation (SCWO)

Name of Process:
Supercritical water oxidation (SCWO) Process – Oxidation of aqueous organic wastes at conditions above the critical point (22.1 MPa, 374 deg C) of water

Vendor(s):
Forster Wheeler
Website: http://www.fwc.com/
General Atomics
Web site:
http://www.ga.com/atg/aps/scwo.html

pplicable Pesticides and related POPs wastes:
chlordane, kelthane, permithrin and mixtures of 2,4-D and 2,4,5-T

Status:
Considerable progress and practical experiences have been made in the last years within ACWA Assembled Chemical Weapons Assessment in the US:
1. General Atomics 0.5 gpm Pilot Unit where Agent, Explosive, Dunnage Hydrolysates have successfully been destroyed. General Atomics has now more then 12000 processing hours gained on destruction of POPs related and warfare agents. A commercial scale 2 gpm General Atomics demonstration system is operating in Japan under a joint development agreement with Japanese companies.

2. Foster Wheeler, under an Army contract conducted demonstration tests on the transpiring wall SCWO system at Army's Dugway Proving Ground in Utah. A pilot system has operated for over 2000 hours at up to 500 lb/hr (1 gpm) with halogenated wastes that result from chemical agent neutralization. Based on test results, neutralization followed by SCWO was recently announced by the US DOD as the "agency preferred alternative" to incineration for destruction of assembled chemical weapons at a facility in the USA.

Technology description:
Supercritical water oxidation (SCWO) is a high temperature and pressure technology that uses the properties of supercritical water in the destruction of organic compounds and toxic wastes. Under supercritical conditions, carbon is converted to carbon dioxide; hydrogen to water; chlorine atoms derived from chlorinated organic compounds to chloride ions; nitro-compounds to nitrates; sulfur to sulfates; and phosphorus to phosphate [1].

The unique properties of super critical water are the key to the operation of this process. Gases including oxygen and organic substances are completely soluble in super critical water, whereas inorganic salts exhibit greatly reduced solubility under process conditions. Organic substances dissolve in the super critical water, and oxygen and the organic substances are brought into intimate single phase contact at temperatures and molecular densities that allow the conventional oxidation reactions to proceed rapidly to completion.
Process residues are contained and consist of water, gas and solids if the waste contains inorganic salts or organics with halogens, sulfur or phosphorous. The effluent gases contain no oxides of nitrogen or acid gases such as hydrogen chloride or sulfur oxide. The process generates no particulates and less than 10 ppm carbon monoxide has been measured [1].

Designs and methods that enable reasonable operating costs, increase plant reliability and alleviate the corrosion and plugging that plagued earlier SCWO systems are progressing. There are 2 major systems being applied:

1. Foster Wheeler has implemented the Aerojet GenCorp transpiring platelet technology in a transpiring wall SCWO reactor. This design utilizes a pressure housing with an internal transpiring wall liner. As shown in Figure 1, the platelet liner flows a uniform water film that protects the liner from salt deposition and corrosion while providing a thermal and corrosion barrier for the pressure housing. This allows for higher reaction zone operating temperatures and shorter residence times. The reactor pressure vessel is exposed to low-temperature deionized water, resulting in a safer design. Platelet cooling technology has been mature for decades and has been implemented by Aerojet Corp in commercial, military and aerospace applications [10].
2. General Atomics has another liner system that utilizes a simple replaceable cylinder inside the reactor vessel to contain the reaction process. The cylinder is insulated from the pressure vessel, allowing higher reaction process temperatures. Pretreatment of solid wastes by grinding to a fine slurry has been demonstrated and feeds with up to 25% solids have been successfully pumped and processed. Resolution of salts and corrosion problems has allowed current research into partial oxidation and production of selected compounds using supercritical water.

The National Research Council (NRC 1993) has pointed out that this system must be constructed of materials capable of resisting corrosion caused by halogen ions. They also note that the precipitation of salts may cause plugging problems in the system [2]. The NRC recently stated that the General Atomics system "has reached a level of maturity where construction and testing of a full scale [Blue Grass facility] reactor to treat agent hydrolysate is the next logical step" (NRC 2002)

DREs of greater than 99% have been reported for the treatment of numerous hazardous organic compounds using SCWO. For example, bench scale tests have shown DREs of 99.999% or higher for chlorinated solvents, PCBs and pesticides, and >99.99994% for dioxin contaminated MEK.157 No data have yet been found that allow the destruction efficiencies of this technology to be determined. i.e., the concentrations of undestroyed chemicals in process residues have not been reported for process residues other than gaseous emissions. Similarly, no data were presented describing the concentrations in all process residues of dioxins and other POPs potentially generated [3].

John Vijgen, International HCH and Pesticides Association, Fellowship report: "New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils." NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)"

In the last years there have been major developments within the ACWA in the US:

Foster Wheeler has conducted pilot plant studies by on widely varying feedstocks [4], including shipboard excess hazardous materials [5,6] and obsolete munitions such as smokes and dyes [7]. Under an Army contract, Foster Wheeler conducted demonstration tests on the transpiring wall SCWO system at Army's Dugway Proving Ground in Utah. The Army required performance of transpiring wall SCWO tests with feed materials derived from caustic hydrolysis of chemical agents VX, GB and HD and energetic materials such as TNT and Comp B. In some cases, simulants of hydrolysates were used. A total of 231 hours of validation testing was performed between July and September 2000. The demonstration testing validated destruction of Schedule 2 compounds to acceptable levels [8].

Process diagram:

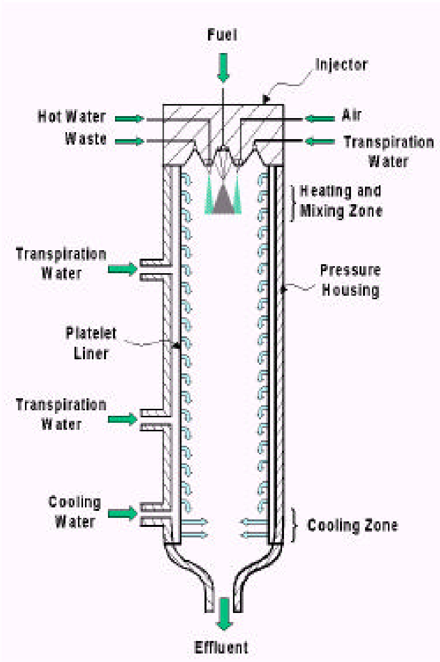

Figure 1: Transpiring Wall Reactor Foster Wheeler/ GenCorp Aerojet

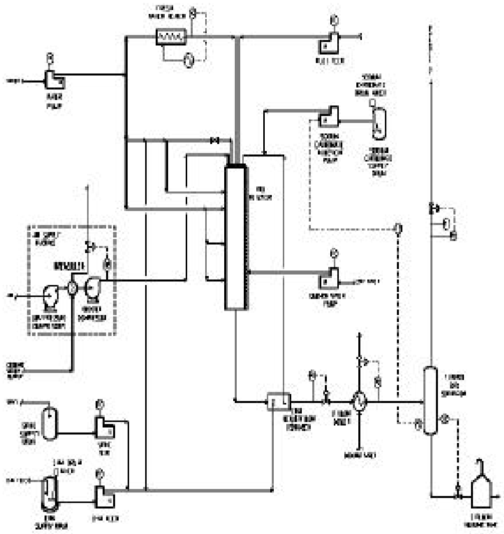

Figure 2: ACWA SCWO Process Flow Diagram (Foster Wheeler)

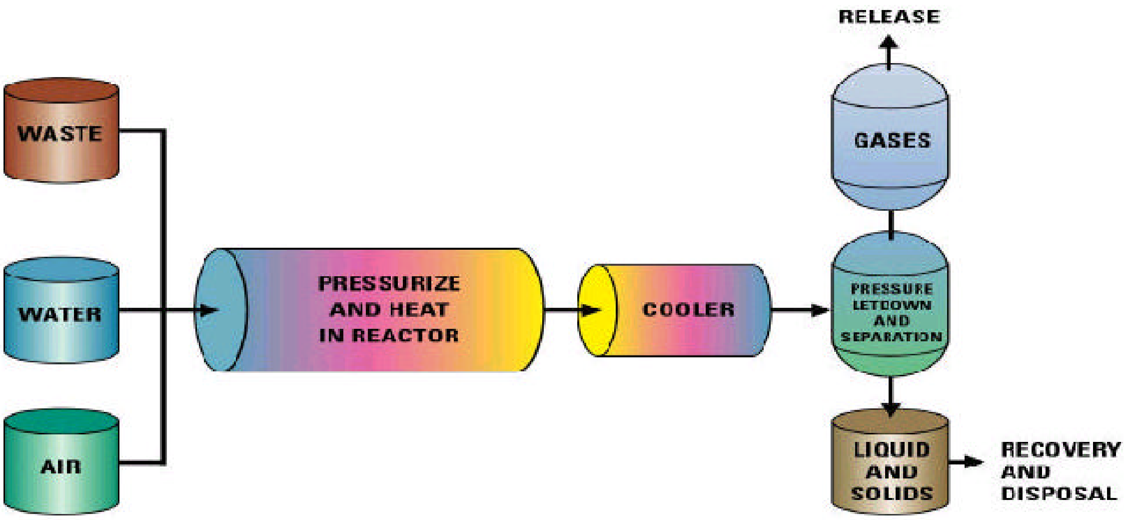

Figure 3: Flow Schedule General Atomics

At the General Atomics 0.5 gpm Pilot Unit Agent, Explosive, Dunnage Hydrolysates have successfully been destroyed. General Atomics has now more than 12000 processing hours gained on destruction of POPs related and warfare agents.

John Vijgen, International HCH and Pesticides Association, Fellowship report: "New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils." NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)"

Performance:

Treatment efficiency:

General Atomics' experience with Test-, Demo- and Pilot-units is summarized in the following Table [9]:

General Atomics SCW Experience			
PROGRAM	**EQUIPMENT**	**WASTE TYPES TESTED**	**PROCESSING HOURS**
DoD/DARPA	0.03 gpm Test Unit	Chemical Agents	<100
DoD/DARPA	1.0 gpm Pilot Unit	Chemical Agent Simulants Salts & Solids Stability Limits Shipboard Wastes Other Hazwastes	>500
Air Force	0.03 gpm Test Unit	Solid Rocket Propellant	>40
Air Force	0.5 gpm Pilot Unit	Solid Rocket Propellant	>150
Air Force	0.1 gpm Test Unit	Aircraft Film Forming Foam	<100
Navy/DARPA	2.0 gpm Demo Unit	Shipboard Wastes	>850
Army ATA	1.0 gpm Pilot Unit	Hydrolysate from VX Agent	>300
Private	1.0 gpm Pilot Unit	Municipal and Industrial Sludges	<100
DOE	1.0 gpm Pilot Unit	Hydrogen Production from Waste	<100
DOE	0.35 gpm Pilot Unit	Organic Wastes	900
Various	0.35 gpm Pilot Unit	Contaminated Trimsol Halogenated Wastes Solvents, Biological Wastes PCB Contaminated Sludges	2200
NASA	0.03 gpm Test Unit	Biomass	<100
Private	0.03 gpm Test Unit	Organic Wastes	40
Army ACWA	0.5 gpm Pilot Unit	Agent, Explosive, Dunnage Hydrolysates	>5788
Army EST	0.5 gpm Pilot Unit	Agent Hydrolysate. Simulants	>600
Private (Japan)	2.0 gpm Demo Unit	Sludges, Pharmaceutical Wastes	>1000
AF/DOE	0.5 gpm SCW Test Unit	Energetics, Biomass, Wood, Cornstarch	>175
Total			>13,000

SCWO has been applied to a broad range of materials, e.g., aqueous waste streams, sludges, contaminated soils, industrial organic chemicals, plastics, synthetics, paints and allied products, industrial organics, agricultural chemicals, explosives, petroleum and coal products, and rubber and plastic products. It is applicable to the treatment of a range of contaminants including acrylonitrile wastewater, cyanide wastewater, pesticide wastewater, PCBs, halogenated aliphatics and aromatics, aromatic hydrocarbons, MEK and organic nitrogen compounds [3].

Between October 2001 and April 2002, Foster Wheeler completed engineering design (EDS) testswith feed materials derived from caustic hydrolysis of chemical agents GB, VX and H and energetic materials such as TNT and Comp B by, at the US Army's Dugway Proving Ground in Utah. In some cases, simulants of hydrolysates were used. The tests were performed to support the design and procurement of a full-scale chemical weapons destruction facility. Over 2000 hours of testing was performed. Table III lists the tests completed during EDS testing.

Table III Feed Parameters:

Test	Feed Material	Feed Rate (kg/hr)	Actual Duration (hours)
1	GB/Comp B/Aluminum Hydrolysate	227	500
2	VX/Comp B/Aluminum Hydrolysate	159	500
3	H/Tetrytol/Aluminum Hydrolysate	95	500

Foster Wheeler [8] quotes:

The tests demonstrated transpiring wall SCWO can effectively manage salt plugging with chemical agent hydrolysate feeds. During testing the liner differential pressures remained within the design range without any indication that the liner or reactor was plugging. Post-test visual inspections revealed no salt plugs that would limit long-term operations in a full-scale facility. Corrosion was evaluated based on visual inspections of the reactor after each test. The transpiring wall reactor provided corrosion protection from the salts and acids formed during hydrolysate oxidation. Some corrosion was observed during post-test inspections, but it will not have any major impact on the full-scale facility design or operations.

John Vijgen, International HCH and Pesticides Association, Fellowship report: "New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils." NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)"

Another important result of the testing was the ability to maintain pressure control while processing materials with high concentrations of aluminum oxides. The pressure control valve was utilized for all feeds including the combined hydrolysate containing high concentrations of aluminum hydroxide. The aluminum hydroxide forms oxides of aluminum during oxidation. The aluminum oxides can erode components such as a valve where high velocities are encountered. The valve was able to withstand the aluminum oxides and maintain pressure control during testing.

Most importantly testing also demonstrated the ability of SCWO to destroy the byproducts of chemical agent and energetics neutralization. Analytical test results indicate that Schedule 2 compounds (agent neutralization byproducts) were destroyed to acceptable levels during each of the tests. Total organic carbon in the process effluent was measured in the single digit range.

Conclusion (for the Foster Wheeler tests) [8]:

The transpiring wall SCWO testing conducted with hydrolysates of chemical agent and energetics demonstrated the technology's capability as an alternative destruction technique. Long duration steady-state operating periods while processing chemical weapon agent and energetic hydrolysates were achieved. Destruction of Schedule 2 compounds was demonstrated. The ability of the transpiring wall design to greatly reduce salt plugging and corrosion while simultaneously feeding agent, energetics and aluminium hydrolysates was demonstrated. Satisfactory demonstration of salt and corrosion management with a transpiring wall design indicates safe, practical and cost effective SCWO designs and operations can be anticipated at the full-scale size." Recently the US DOD announced that neutralization followed by SCWO is the "agency preferred alternative" to incineration for destruction of assembled chemical weapons that are currently stored at a facility in Kentucky, USA.

General Atomics testing for the ACWA program is summarized in the following table. All results met the requirements of the ACWA program.

ACWA GA SCWO Test Summary

Test	Feed Material	Test Duration hrs	TOC ppm	CO ppm	NOx ppm	SOx ppm
1	HD hydrolysate or simulant	500	<1.3	<10	<1	<1
2	Tetrytol hydrolysate/dunnage	537	<1	<10	<1	<1
3	Propellant hydrolysate /cyclotol hydrolysate/dunnage	523	<1.9	<10	<1	<1
4	GB hydrolysate or simulant	543	<2.6	<10	5.2	0.2
5	VX hydrolysate or simulant	513	<1.4	<10	0.5	0.3
Total		2616				

Throughput:
Pilot tests up to 227 kg/hr. Full-scale Blue Grass design is 2700 kg/hr. General Atomics commercial demonstration system throughput is 500 kg/hr.

Wastes/Residuals:
Environment Australia (1997) notes that end products such as ash and brine require disposal. The Agency also finds that the technology is limited to the treatment of waste that is liquid or has a particle size less than 200 µm, and it is most applicable to wastes with an organic content of less than 20% [1]. General Atomics SCWO effluent from VX hydrolysate feed was de-listed in 1999 based on pilot scale test results.

Reliability:
Availability of the Foster Wheeler SCWO system was greater than 90% during ACWA engineering design testing. Availability of the General Atomics SCWO system was greater than 80% during over 2600 hours ACWA testing.

Limitations:
Foster Wheeler **-** Dissolved aluminum up to 500 ppm.

Transportability:
SCWO systems are highly transportable.

Detailed information:
No Annex

Full Scale Treatment examples:
Commercial demonstration of the General Atomics system is in progress in Japan.

Conclusion:
SCWO has been gaining a lot of experience especially in the ACWA program on war far agents. With the General Atomics 0.5 gpm Pilot Unit Agent, Explosive, Dunnage Hydrolysates have successfully been destroyed.
General Atomics has now more than 12000 processing hours gained on destruction of POPs related and warfare agents. Pilot tests up to 227 kg/hr. Full-scale Blue Grass design is 2700 kg/hr. General Atomics commercial demonstration system throughput is 500 kg/hr. Also Foster Wheeler's pilot system has operated for over 2000 hours at up to 500 lb/hr (1 gpm).

On the basis of data provided, SCWO has been proven at pilot demonstration phase. Throughputs for the ACWA programme up to 227 kg/hr. Full-scale Blue Grass design is 2700 kg/hr. General Atomics commercial demonstration system throughput is 500 kg/hr.

Translated to commercial application this would mean only 1 t/day respectively 4 t /day. General Atomics has a commercial scale General Atomics demonstration system, which is operating in Japan under a joint development agreement with Kurita Water Industries, Ltd and Komatsu, Ltd [12]. The system has operated more than 1000 hours and at commercial scale at 1 ton/hour (8 t/day).

The Blue Grass application would give a maximum production of 23.6 tons/day. If Blue Grass Design and Demonstration will be put into practise a further jncrease in scale would be possible.

On the basis of available information one can conclude that SCWO has passed the barrier of pilot-scale and is now full-scale operationable.

Vendor Contact details:

Foster Wheeler Development Corporation
K.S. (Al) Ahluwalia
12 Peach Tree Hill Road
Livingston, NJ 07039
United States
Ph: +1 973-535-2246
Fax: +1 973-535-2242
Email: al_ahluwalia@fwc.com

General Atomics
Michael Spritzer
3550 General Atomics Court
San Diego, CA 92121-1194
USA
Ph: +1 858 455 2337
Fax: +1 858 455 4111
Email: Michael.spritzer@gat.com

**Note: This NATO/CCMS fellowship report does not certify any particular technology, but tries to summarise the state of the art of the concerned technology on the basis of data delivered by the company or other source, which have been made available to the author and refers the reader to original documents for further evaluation. Without the efforts of the Technology supplier it would not have been possible to set up this fact sheet.*
*** Note:The text for this report is verified by th e Technology suppliers. By Forster Wheeler on 1. December and by General Atomics on 11 and 20 December 2002*

References:

1. Environment Australia, 1997
2. The National Research Council (1993)
3. Technical Criteria for The Destruction of Stockpiled Persistent Organic Pollutants, Pat Costner, Greenpeace International Science Unit, Darryl Luscombe, Greenpeace Australia, and Morag Simpson, Greenpeace Canada, Third Meeting of the Intersessional Group at Intergovernmental Forum on Chemical Safety, Yokohama, Japan, 1 - 4 December 1998
4. E. F. Gloyna and L. Li, "Progress in Supercritical Water Oxidation: Research and Development," Fifth Intl. Chem. Oxidation Symposium and Principles and Practices Workshop, Nashville, TN, 1995.
5. M. Soto and A. Lardis, "Hydrothermal Oxidation (SCWO) For Destruction of Shipboard Wastes," IT3 Conference, Salt Lake City, UT, 1998.
6. P.J. Crooker, et. al., "Final Results of Shipboard Hydrothermal Oxidation with a Transpiring Wall Reactor," IT3 Conference, Portland, OR, 2000.
7. M. C. Stoddard, et al., "Supercritical Water Oxidation for Colored Smokes and Dyes," IT3 Conference, Salt Lake City, UT, 1998.
8. Use of Supercritical Water Oxidation Technology for Demilitarization of Assembled Chemical Weapons, K. S. Ahluwalia, Paul J. Crooker, Foster Wheeler Development Corporation, Gregory M. Meagher, GenCorp Aerojet
9. General Atomics SCWO Experience, dated 5. August 2002, supplied by General Atomics to the author.
10. L. Schoenman, M. Young, and K.S. Ahluwalia, "Use of Transpiring Wall Platelet Reactor in Hydrothermal Oxidation of Organic Materials," IT3 Conference, San Francisco, CA, 1997.
11. The National Research Council (2002)
12. Press Release: New Agreement will accelerate commercializiation of supercritical water oxidation systems, December 20, 2002, supplied by General Atomics to author

John Vijgen, International HCH and Pesticides Association, Fellowship report: "New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils." NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)"