Name of Process: Supercritical Water Oxidation (SCWO) **Applicable POPs wastes:** BHC, Chlordane, PCB, mixtures of tetra- and octachlorinated dibenzo-p-dioxins and tetra- and octachlorinated dibenzofurans, Kelthane, permithrin and mixtures of 2,4 D and 2,4,5 T	**Status:** Commercial SCWO systems are operated in Japan, the US, the UK, Korea, and France. At present in Japan, 3 companies are working with SCWO systems. A joint-venture of 2 companies is using the basic technology of a US company for the further development of the SCWO technology. In Japan, a plant is currently operating processing university laboratory wastewater. In the US, one company is continuing to develop the SCWO technology for Government and Commercial markets. Since 1992, this company has built approximately 20 SCWO units for various Government and Commercial programs. As of Summer 2007, 3 additional SCWO units are under fabrication. Another SCWO plant consisting of 3 individual SCWO units will be fabricated at the Blue Grass Army Depot as part of the ACWA Program for the destruction of chemical warfare agents. This plant will have a total capacity of ~12000 T/y. In Korea, one SCWO unit is processing dinitrotoluene (DNT) production wastewater at a capacity of 1800 kg/hr. In France, one company is processing food industry wastewater at a rate of ~100 kg/hr. Also PCB destruction has been tested successfully.

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Technology description:

Supercritical water oxidation (SCWO) is the destruction technology for organic compounds and toxic wastes that makes use of the unique properties of water exhibited under supercritical conditions, that is, temperatures above 374°C and pressures above 22 MPa. Typical SCWO reactor operating temperatures and pressures are 600-650°C and 23.5 MPa, respectively. The oxidant is typically high-pressure air, but pure oxygen, nitric acid, and other oxidizing agents can also be used. In supercritical water, organic materials are quickly destroyed to yield carbon dioxide and water. Heteroatoms such as chlorine, fluorine, and sulphur, are converted to inorganic acids or to salts if sufficient cations such as sodium or potassium are present. If present, metals such as iron and nickel will produce the metal oxides.

Supercritical water (SCW) is one of the states of water which has higher temperatures and pressures than those at critical point. At this state, water is not condensed under any high pressure and SCW has intermediate properties between liquid and vapor. When SCW is used for the decomposition of organics, the organics and oxidant are miscible with SCW, creating a good condition for oxidation with no mass transport limitations. SCW has good fluidity and there is no diffusion rate-determining step in reactions involving SCW. Therefore, SCWO is a high-rate reaction which has high-decomposition efficiency.

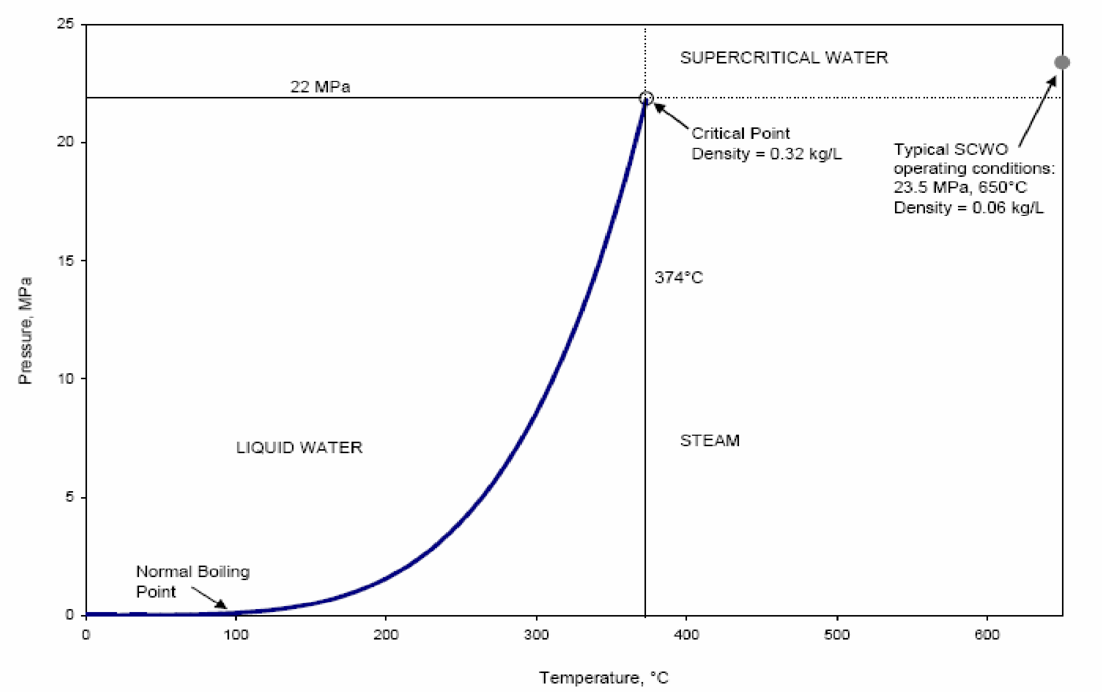

Figure 1: what is supercritical water (SCW)

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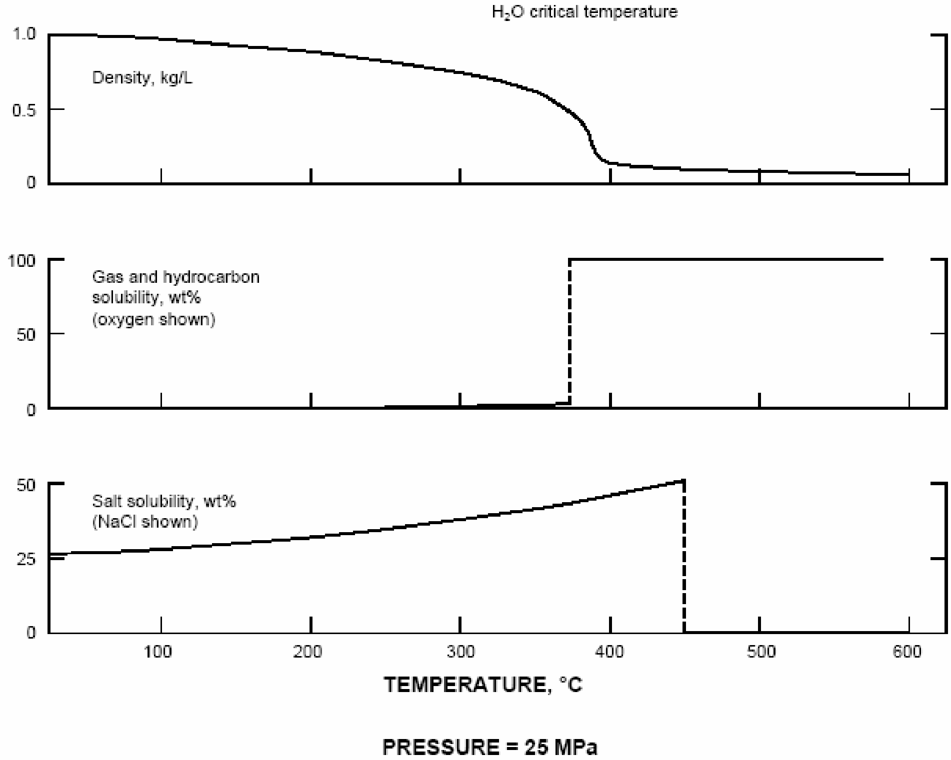

Figure 2: Temperature in relation to 1) Density 2) gas and hydrocarbon solubility, 3) salt solubility
(Downey, Wheatley)

SCWO reactions are generally considered as follows:

Organic Compounds($C_xH_yN_zO_p$) + pO_2
→ $rCH_3COOH + sNH_3 + tO_2$
→ $uH_2O + vCO_2\uparrow + wN_2\uparrow$
ex. $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+$
$NH_4^+ + NO_2^- \rightarrow N_2\uparrow + 2H_2O$

Inorganic Materials
→ Acids + Salts + Oxides
ex. $HCl + NaOH \rightarrow NaCl\downarrow$
$S + 2O_2 \rightarrow SO_4^{2-}(aq)$

Unlike incineration, SCWO does not produce NOx or SOx as exhaust gases, and neither NO_2^- , NO_3^- (both are consumed) and SO_4^{2-} remains as H_2SO_4 if cations are not present) or salt (if cations are present) in the water after the oxidation reactions. Therefore, there is no need to treat gas and liquid which are produced by SCWO, and that is a reason why SCWO has received public acceptance easily.

The SCWO process is typically operated under temperatures of 600-650 °C and pressures of 22-25MPa. There are two issues that have to be dealt with for POPs treatment:

1. Material corrosion problem caused by high concentration HCl which is generated by the SCWO reaction.
2. Salt deposition by neutralization in the supercritical water resin.

Corrosion is typically dealt with through selection of proper reactor liner materials. Salt deposition has been successfully addressed through a variety of methods, including the use of internal reactor salt scrapers by the US and Japan or the use of proprietary feed additives in the US. General Atomics has used salt feed additives to continuously process organic wastes containing up to 20 wt% salts

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Process diagram:
Process

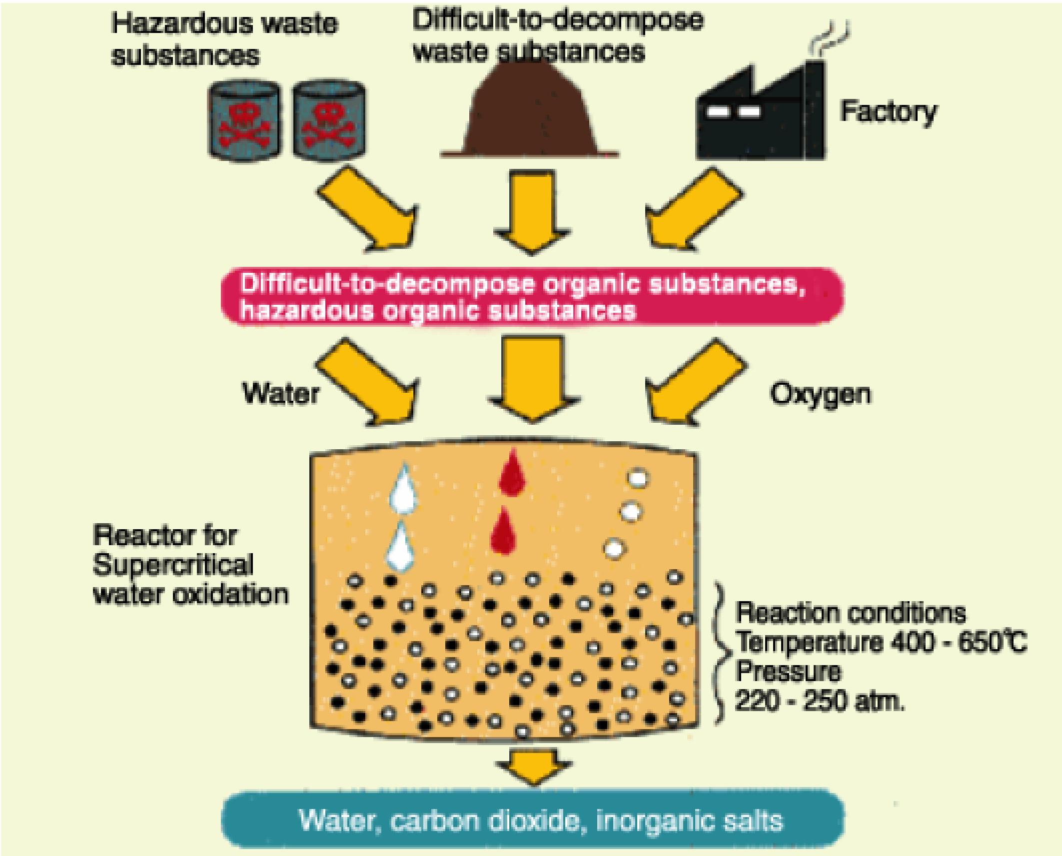

Figure 3: Process Principle

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Description of Flow sheet: example Japan

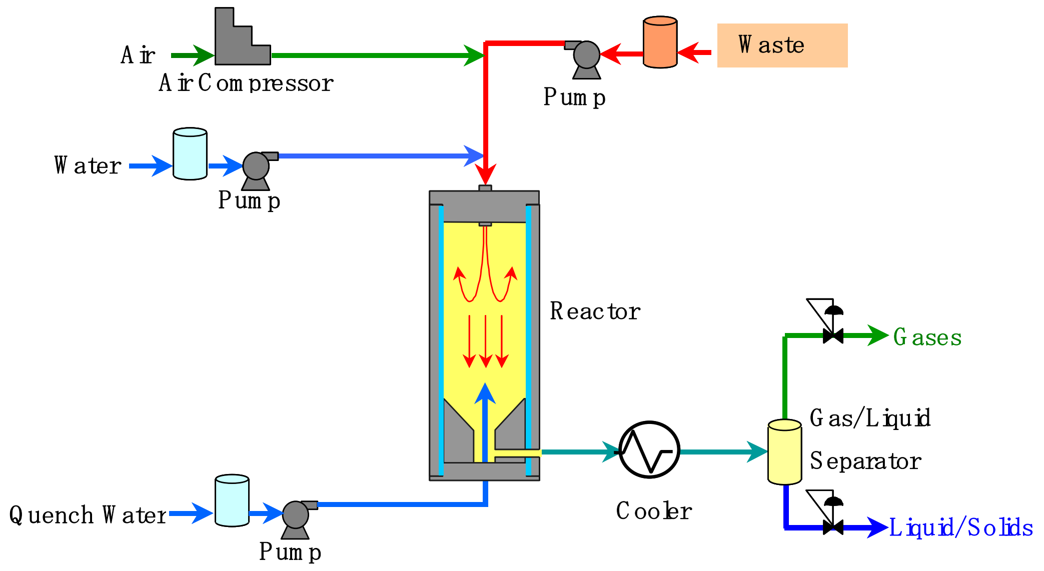

Figure 4: Flow of one of the systems used in Japan (Noma)

The reactor of this SCWO system is a vertically oriented cylindrical vessel with a feed injection nozzle at upper end, an effluent outlet at bottom and an anticorrosion liner on the wall.

The treatment starts by feeding the waste, water and air into the reactor that is under supercritical condition using starter fuel, air and water. The feed substances are injected continuously through the nozzle without preheating, and the feeds are quickly heated to be oxidized in the reactor. The reaction temperature and pressure in case of the treatment of BHC and Chlordane treatments is set at 670 degree C and 23.4 MPa. Air is used as the oxidant for this SCWO system.

The after-reaction fluid is cooled and neutralized at the bottom of the reactor by quench water including neutralizer such as sodium hydroxide. The effluent out from reactor is cooled by cooler and lead to the gas/liquid separator. The effluent gas and liquid are depressurized and discharged.

The reaction temperature is controlled by continuously adjusting the waste or water feed rates. The reaction pressure is generated by air compressor and high pressure pumps and is controlled by pressure let down valves. These controls are performed by the automatic operation control system (Nomi, 2004).

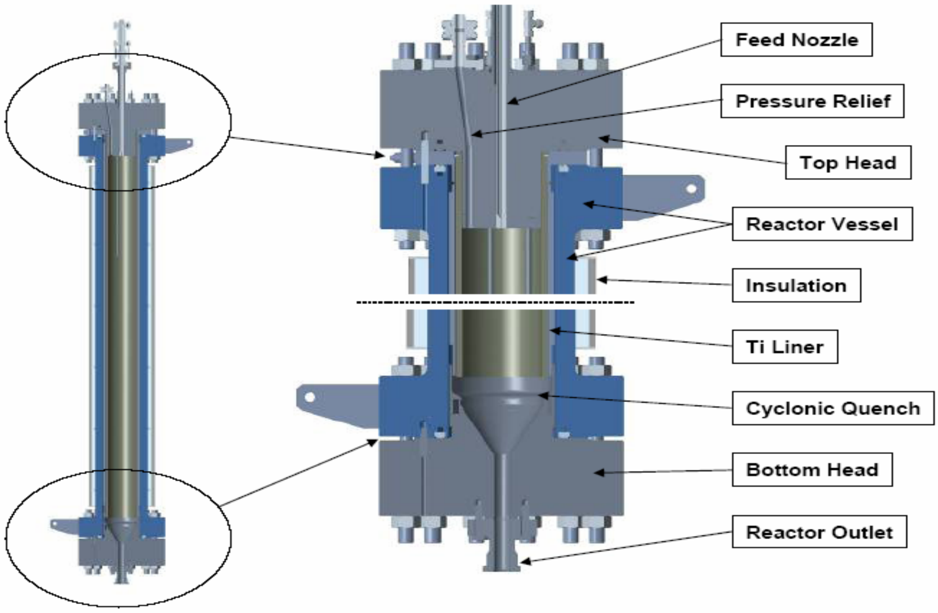

Figure 5: Blue Grass Chemical Agent-Destruction Pilot Plant SCWO Reactor Assembly
(Downey, Wheatley)

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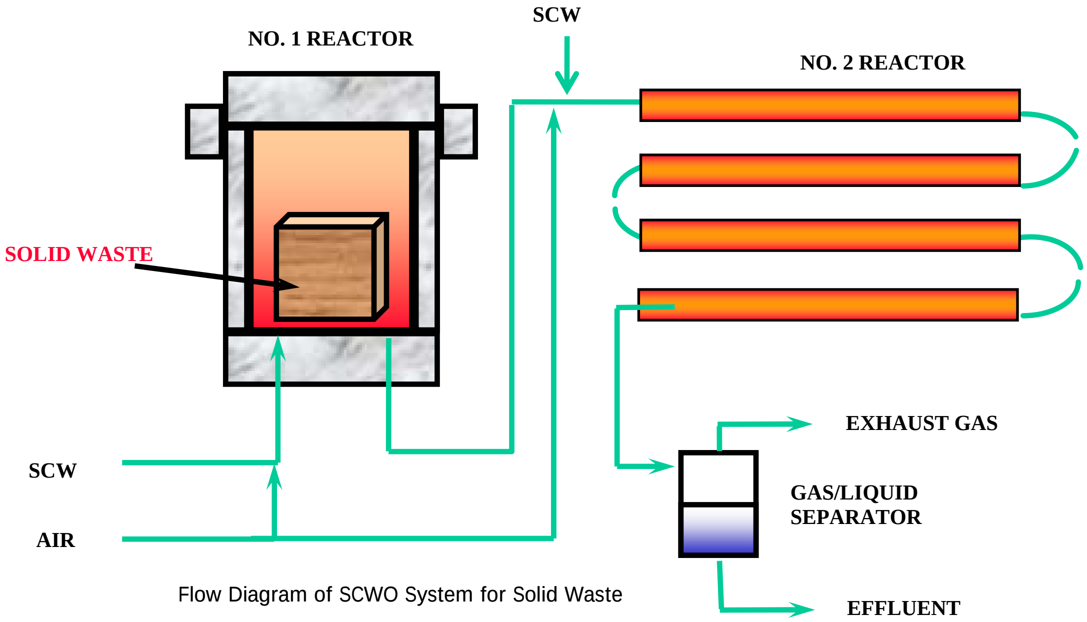
PART I: Criteria on the Adaptation of the Technology to the Country

A. Performance:

1. Minimum pre-treatment:
In principal the technology can be applied for liquid or slurry wastes with an organic content of less than 20% (ref 1) and a particle size less than 200 Um. However, the organic content can be much greater. Diluent water is simply required to control reactor temperature if the heat value is above ~2000 Btu/lb.
But special pre-treatment devices can be made. For example, at the Blue Grass Army Depot, which is at present under construction, for the destruction of slurried double-base propellant, RDX, and TNT, the 12 000 t/y SCWO unit will be fitted with a slurry-grinding feed preparation module for propellant size-reduction. The propellant is slurried in water at a concentration of approximately 20 wt% for direct feed to the iSCWO unit.

So far there only in Japan a test with a batch system with capacity of 50kg/day for solid waste contaminated with PCBs has been performed. The concentration of POPs was here limited below 1000 mg/kg For that test a hybrid SCWO system has been used consisting of 2 reactors. No.1 batch reactor as vessel and No 2 being a continuous reactor as a tube. It is stated that in case of a commercial facility, the system will have parallel the No-.1 reactor and single No.2 reactor for the purpose of establishing a simulated continuous system.



Flow Diagram of SCWO System for Solid Waste

2. Destruction efficiency (DE):
In this chapter various opinions are represented on possible dioxin formation, based on conclusions by Weber in 2006:

A study on the PCB destruction by Super Critical Water Oxidation (SCWO) by Weber, 2006 concludes the following:
"High concentrations of PCDFs can be generated during destruction of PCBs under sub- and supercritical water conditions. The increase in total TEQ even when achieving PCB destruction efficiencies of 99.8% (resulting in total TEQ increase of ca. 50%; 450°C, 5 min) or 98.7% (total TEQ increase of ca. 1000%; 425°C, 15 min) demonstrate that destruction efficiencies of PCB/POPs destruction technologies have to be based on total TEQ (toxicological considerations) and not only on destruction efficiencies of total PCBs/POPs. This implicates that PCDD/PCDF monitoring is mandatory in the assessment of a PCB/POPs destruction technology and also essential for the supervision of pilot and full-scale destruction process operation. The present study further reveals that a technology listed in the highest rank of non-combustion technologies from UNEP and UNIDO has the potential to form high concentrations of PCDFs even at conditions of possible application (the temperature of practical application can not be considerable higher than 450°C due to material limitations). This shows the necessity of a more rigorous assessment of non-combustion technologies with respect to their PCDD/PCDF formation potential16) and their actual applicability for PCB/POPs destruction." Weber mentioned also that: "for example, Hatakeda et al. found insufficient PCB degradation rates in SCW with oxygen at 400°C. On the other hand, Anitescu and Tavlarides7) found high destruction efficiency in the temperature range between 450 and 550°C within seconds. Lower destruction rates were found in the present experiments when comparing with the results of Anitescu and Tavlarides." (See Weber).

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Kevin Downey representing the US developer stated (14 Sept 2007):
Several years ago, we performed PCB destruction testing in our SCWO pilot plant on a contaminated sludge containing a mixture of Aroclors, primarily Aroclor 1016 and 1254. Testing was performed under continuous-flow conditions representative of normal SCWO operations.

The testing was conducted at a reactor temperature and pressure of ~650C and 3400 psi, respectively. Liquid and gas samples were collected during the test per approved EPA methodology and then analyzed to determine the PCB, dioxin, and furan content. In the liquid samples, no PCBs, dioxins, or furans were detected.

In the gas samples, 17 separate dioxins/furans were evaluated (2,3,7,8-TCDD; 1,2,3,7,8-PnCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,6,7,8-HpCDD; OCDD; 2,3,7,8-TCDF; 1,2,3,7,8-PnCDF; 2,3,4,7,8-PnCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; and OCDF). Fourteen of the 17 were below detection limits.
The remaining three (OCDD, HpCDF, and OCDF) were detected at extremely low concentrations.

Taking into consideration the Toxic Equivalency Factor for these species, the concentration of dioxins/furans in the SCWO gaseous effluent is estimated to be approximately 2 orders of magnitude below the MACT standard of 0.2 ng/dry std cubic meter on a Toxicity Equivalent Quotient basis.

Downey commented on Webers paper (see references):
The subject paper does not represent the state of the art of the SCWO technology, either today or in 2004 when the paper was published. Operating conditions typical for industrial SCWO applications, e.g., reactor temperature, feed/oxidant mixing, and residence time, differ significantly from those used in the subject testing. The tests results therefore, at least in my opinion, are not relevant to the evaluation of the SCWO technology for PCB destruction. Specific comments are summarized below.

- The highest SCWO operating temperature investigated in the subject paper was 450C. This temperature is well below our normal operating temperature of ~650C. It is therefore not surprising that poor destruction of PCBs would be observed as well as formation of undesirable compounds such as PCDDs and PCDFs.
- The results of batch-mode testing such as those described in the paper should be considered qualitative at best since they do not accurately represent the continuous-flow operations normal for most SCWO applications. It has been our experience that batch testing often yields spurious results, so we prefer to do as few of them as possible and instead perform more-representative continuous flow tests.
- The author states that for SCWO "the temperature of practical application cannot be considerably higher than 450C due to material limitations". However, SCWO does not have the stated temperature limitation now, nor did it in 2004. We have been using a variety of materials since 1994 that exhibit very low corrosion rates, even for feeds with high chloride concentrations.

Taro Oe representing the Japanese developer comments (12 Sept. 2007) on Webers paper are as follows:
If the reaction condition is not adequate, it remains possible that the dioxins are created. Especially, we believe the temperature and the air ratio (AR) are important factor. Most of our decomposition conditions on PCB are that the temperature is around 600C, AR is greater than 1.2. Weber said SCWO created PCDFs below 450C, and SCWO is limited under 450C due to material. Because we have not tested below 450C, we cannot report the results below 450C. We believe 450C is too low to decompose PCB including PCDFs without catalysts. We have tested around 600C using our SCWO process which is made of Ti-alloy and Ta. Furthermore, it was said SCWO typical condition is 600C and 25MPa (ref 1). So I cannot fully agree Weber's opinion. (See also Marrone, Hodes, Smith, Tester)
As reference, I attached the PDF file on PCB and Dioxins decomposition and material selection.
In Japan, "Mitsubishi Heavy Industries, Ltd." has developed a SCWO process for PCB decomposition, too.
It is said that MHI condition is around 400C. They are doing well in PCB decomposition using catalysts.

They have made contracted with JESCO, and constructed the commercial plant (2t-PCB/day) in Tokyo.
Their plant has treated PCB since 2005. JESCO (Japan Environmental Safety Corporation) is a special company wholly owned by the government.

http://www.mhi.co.jp/nsmw/htmle/pcb.html

http://www.jesconet.co.jp/eg/index.html

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3. Toxic by-products:
None for normal POPs. If chromium is present, some Cr+6 may be present in the liquid effluent. If present, ion exchange can be used to remove the chromium.

4. Uncontrolled releases:
None with standard incorporation of pressure relief vessel.

5. Capacity to treat all POPs:
Proven in pilot studies at General Atomics and elsewhere.

6. Throughput:
1000-5000 lb/hr of 2000 Btu/lb equivalent feed per SCWO unit. (Note that the 1000 lb/hr SCWO unit size is equivalent to the current Blue Grass SCWO unit size for chemical agent hydrolysate destruction, while the 5000 lb/hr SCWO unit size is the same as a unit currently under construction for the Blue Grass Army Depot for processing of conventional munition energetics.)

6.1 Quantity [tons/day, L/day]
In Japan, one plant is operating with a capacity of 10 m^3/d.
In the US a unit at Blue Grass Army Depot project with a capacity of 12 000 tons/year is under construction**.** On industrial scale, iSCWO units in the US are under construction with a throughput of approx. 4000 t/y.

6.2 POPs throughput : [POPs waste/total waste in %]
1000-5000 lb/hr of 2000 Btu/lb equivalent feed per SCWO unit.

7. Wastes/Residuals:

For the Japanese tests on BHC, chlordane and PCB it is stated that the treatment Effluent contains harmless salt, such as NaCl, $NaHCO_3$. Exhaust gas is mainly composed of CO_2, N_2, O_2. Unlike incineration, SCWO does not produce NO_X or SO_X as exhaust gases, and neither NO_2^- , NO_3^- or SO_4^{2-} remains in the water after the oxidation reactions. Therefore, there is no need to treat gas and liquid which are produced by SCWO. The same applies for the tests of PCB at the American company.

For example at the Blue Grass Army Depot for the destruction of slurried double-base propellant, RDX, and TNT, the unit has also been fitted with a post-treatment module for removal of heavy metals such as lead.

7.1 Secondary waste stream volumes:

7.2 Off gas treatment:

7.3 Complete elimination:

Detailed information and treatment examples:
Table 1: Technology overview technology – Summary-Technical Details
Table 2- Part 1: Overview project experience per technology suppliers in Japan
Table 2 – Part 2: Overview project experience per technology suppliers in US
Table 3: Overview detailed project information per project in US and Japan– Project name (from Table 2)

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PART II: Criteria on the Adaptation of the Country to the Technology

Note: This part has to be filled in every time the "suitability" of the technology has to be examined for a certain country situation!!

A. Resource needs:

Note that the following is for a current iSCWO project, with a basis of 3 gpm feed of a 2000 Btu/lb feed

1. Power requirements :

Electrical supply: 550 HP (410 kw) for high-pressure air compressor and 40 HP (30 kw) for remaining components (Note that a diesel-powered air compressor can be used if desired to reduce the site electrical requirements, depending on site capabilities)

2. Water requirements:

Feed Water: up to 9.8 kg/min, little or none for low-heat value feeds

Quench Water: Up to 21.3 kg/min, depending on feed composition

3. Fuel volumes:

Diesel Fuel: 1.3 kg/min (less for higher heat value feeds, and not required for feeds with heat content in excess of 2000 Btu/lb)

Natural gas: 42 scfm (Startup only, i.e., <1 hour per week)

4. Reagents volumes:

NaOH: generally low but dependent on feed composition

5. Weather tight buildings

For most locations, overhead cover desirable for rain and snow load protection.

6. Hazardous waste personnel requirement:

See personnel requirements cited below.

7. Sampling requirements/facilities:

None specific; driven by site/permitting requirements

8. Peer sampling:
The requirements from the US authorities are monthly

9. Laboratory requirements:
HPLC and normal standard laboratory equipment.
On site requirements:

HPLC method able to measure very low concentration of PCBs.

Requirements in country:

10. Communication systems:

Mobile network:

None

Fixed network:

Standard telecommunication facilities.

11. Number of personnel required: Average of 1 Full-time equivalent (FTE) (designed for remote operation with minimal supervision)

11.1 Number of Technicians required (skilled labour):
0.5 on average for feed preparation (feed dependent)

11.2 Number of Labourers required (unskilled labour):
0.5 on average for feed preparation (feed dependent)

B. Costs:

Capital costs: $1.2-1.5M
Operating Costs: Site dependent, but can be estimated from above utility and personnel requirements.

1. Installation and commissioning costs [US Dollars]:

2. Site preparation costs [US Dollars]:

3. Energy & Telecom installation costs:

4. Monitoring costs:

5. Complying costs:

6. Reporting costs:

7. Running costs with no waste:

8. running costs with waste:

9. Decommissioning costs:

10. Landfill costs:

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11. Transport costs of residues:

C. Impact:

1. Discharges to air:
Approximately 50 kg/min.
Exhaust gas is mainly composed of N_2, CO_2, O_2, and water vapor. Unlike incineration, SCWO does not produce NOx, SOx, or particulates in the exhaust gases, and there is no need to further treat the product gas.

2. Discharges to water:
Approximately 12 kg/min.
Product is a brine solution, with the salt concentration dependent on the feed composition. Neither NO_2^- nor NO_3^- remains in the water after the oxidation reactions. Therefore, as long as there are no significant heavy metals in the feed, there is no need to further treat the SCWO effluent.

3. Discharges to land:

Discharge contains harmless salt, such as NaCl, $NaHCO_3$. Final salt concentration is dependent on the feed composition. The salts can typically be land-filled.

4. Soil impact (noise etc):

D. Risks

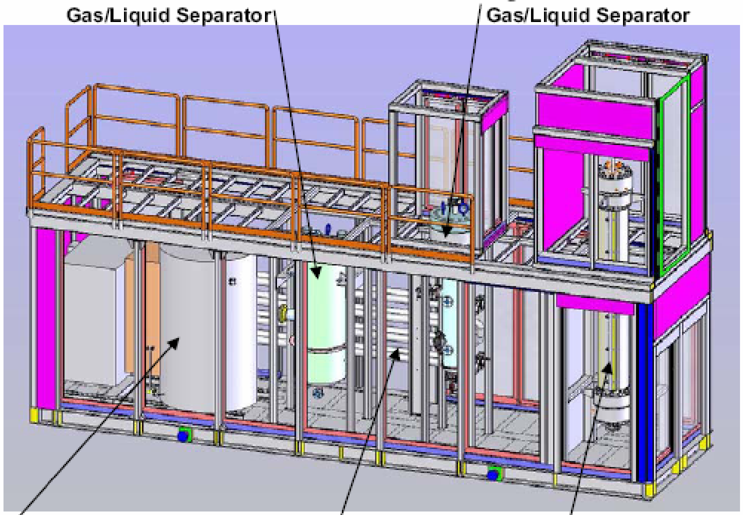
1. Risks of reagents applied:

2. Risks of technology:

Standard industrial safety practices for diesel-type fuels.

3. Operational risks:

E. Constructability:



Blue Grass Chemical Agent-Destruction Pilot Plant (BGCAPP) SCWO Reactor Skid

1. Ease of installation/construction of plant:
In the US for the chemical agent hydrolysate feeds, a SCWO unit consists primarily of a feed skid containing the high-pressure feed pumps and a reactor skid containing all high-pressure/high-temperature equipment items. See figure of Blue Grass Chemical Agent-Destruction Pilot Plant with reactor skid. Plant includes 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. For typical industrial applications where an iSCWO unit is used (e.g., for PCB destruction applications), a SCWO unit consists of a single skid housing the SCWO equipment, supplemented by a compressor skid. Feed and effluent tankage are also required, depending on the specific feed and existing site infrastructure.

2. Ease of shipping/transit:
All materials easily transportable in standard size containers.

3. Ease of operation:
i-SCWO system is designed to require minimal training of personnel.

4. Ease of processing :
i-SCWO system is designed to require minimal training of personnel.

F. Output/generation waste:

1. Generated waste (% of input waste)

2. Deposited waste at landfill (% of input waste)

3. Waste quality properties (pH, TCLP)

Analyses performed to date have passed TCLP

**Note: This Technology Specification and Data Sheet (TSDS) 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 companies or other sources, which have been made available to the author and refers the reader to original documents for further evaluation. Without the efforts below listed technology suppliers it would not have been possible to set up this TSDS. Date: 09.06 2008*

Technology suppliers that have contributed to this TSDS: :

Kevin Downey, General Atomics

Kurita Water Industries

Komatsu Limited

Dr. Yukio Noma, National Institute for Environmental Studies, Japan

Taro Oe, Organo Cooperation

Roland Weber, POPs Environmental Consulting

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