Name of Process:

Supercritical Water Oxidation

Vendor:

Organo Corporation
Web site: http:// www.organo.co.jp/

Applicable Pesticides and related POPs wastes:

PCB
BHC
Chlordane

Status:

Organo had operated SCWO test plant based on MODAR technology since 1995.
35 ton / day SCWO facility for the semi-conductor manufacturing wastes which consist of tetramethylammonium hydroxide, NH3 and isopropyl alcohol had been constructed in 1998.
250kg-PCBs oil /day plant using a continuous system and 50kg/day plant for solid waste contaminated with PCBs using a batch system had been operated.
Thickened sewage sludge had been treated by the test plant had a capacity of 10 ton / day.

Technology description:

Supercritical water (over 374 ℃ and 22MPa) has so high solubility for organic and oxygen that there substances form a homogeneous phase in supercritical water, which makes it easy to oxidize organic matter easily. Furthermore, hydrolysis and pyrolysis occur in supercritical water. Therefore, SCWO (supercritical water oxidation) process has high decomposition ability for organic compounds.

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 mix well with oxidant, creating a good condition for oxidation. 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.

SCWO reactions are generally considered as follows:

Organic Compounds($C_xH_yN_zO_p$) + pO_2

$\rightarrow$ $rCH_3COOH + sNH_3 + tO_2$

$\rightarrow$ $uH_2O + vCO_2\uparrow + wN_2\uparrow$

ex. $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+$

$NH_4^+ + NO_2^- \rightarrow N_2\uparrow + 2H_2O$

Inorganic Materials

$\rightarrow$ 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^- 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, and that is a reason why SCWO has received public acceptance easily.

The SCWO process is typically operated under temperatures of 600-650℃ and pressures of 22-25MPa. There are two hurdles that have to be overcome if SCWO is to be used commercially for POPs treatment. One is material corrosion problem caused by high concentration HCl which is generated by the SCWO reaction. The other is salt deposition by neutralization in the supercritical water resion. The continuous plant for PCBs oil decomposition was constructed of corrosion resistance materials. The capacitor’s PCBs oil was decomposed completely for 1000h of operation time. PCBs and dioxins was not discharged in the exhaust gas and effluent.

Process diagram:

A schematic diagram of SCWO system plant for PCBs oil is shown in Fig.1. The reactor is shown in Fig.2. The reaction region was designed to have a uniform temperature profile for the purpose of decomposing of PCBs waste completely under the SCWO environment. Therefore high concentration HCl (10～20wt%) wasn't neutralized in the reaction region because salts didn't dissolve in supercritical water. The HCl was neutralized in the quenching section located closely to downstream of reaction cartridge. The SCWO effluent was quenched from a reaction temperature of 630℃ to 300℃ and neutralized by a NaOH solution rapidly without depositing salts.

The materials of the reaction cartridge and quenching section were selected on the basis of the results of corrosion tests using autoclaves. These results established that a titanium alloy can be used at temperature higher than 390℃ and tantalum can be used at temperature lower than 450℃. We selected the titanium alloy for reaction cartridge material. The quenching section was a double layer structure of titanium alloy and tantalum. Inside of double layer was the titanium alloy and outside was tantalum. If inside titanium alloy had been corroded, outside tantalum would have resisted corrosion. The reactor was assembled by a reaction cartridge and a pressure vessel (pressure balanced reactor). A part of compressed air as oxidant was supplied between the reaction cartridge and pressure vessel to decrease pressure difference. Therefore we could construct a thin titanium reaction cartridge.

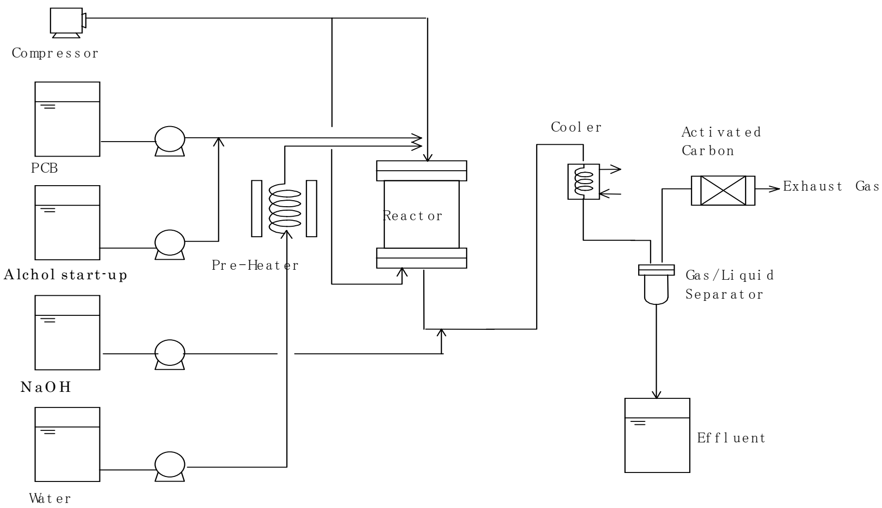

Fig.1 Flow Diagram of SCWO System for PCBs oil

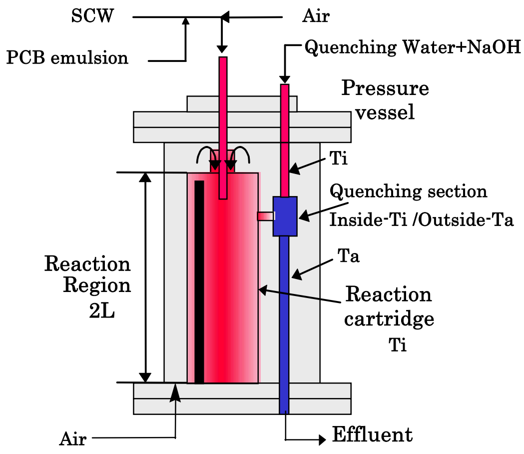

Fig.2 Reactor for PCBs oil

As shown in Fig.3, the hybrid SCWO system for solid waste has two reactors, No.1 batch reactor (vessel type) and No.2 continuous reactor (tube type). A pressure vessel and a reaction cartridge that are separated comprise the No.1 reactor. A part of compressed air (balanced air) is supplied between the reaction cartridge and pressure vessel, and this balanced air is discharged separately from No.1 reactor effluent. This balanced air contributes to reducing pressure difference between inside and outside of the reaction cartridge. Therefore we can construct a thin reaction cartridge. The pressure vessel has a quick opener and closer system. Solid PCBs wastes are supplied into the reaction cartridge in large quantities without converting into slurry.

The effluent from the reaction cartridge is discharged to No.2 reactor whole supplying sub-critical water that have the same temperature as No.1 reactor, which is 270-300 degrees C. During the heating of No.1 reactor, No.2 reactor that is supplied with SCW and air is maintained under the conditions of 600 degrees C and 24MPa. Therefore the effluent from No.1 reactor is completely decomposed by SCWO in the No.2 reactor. If CO_2 concentration in exhaust gas decreases from No.2 reactor, it indicates that organics are discharged from No.1 reactor and decomposed by SCWO in the No.2 reactor.

No.1 reactor is reheated from 300 to 600 degrees C by the heaters and SCW, and compressed air is finally supplied to decompose micro residues in the reaction cartridge (second step of Fig.4). The merits of the hybrid system are as follows, 1: Large quantities of organics can be fed into the No.1 batch reactor because no oxygen is supplied until No.1 reactor effluent is discharged, 2: Solid wastes can be fed without converting into slurry, 3: High-pressure pump isn't necessary to supply slurry.

In the case of commercial facility, this system will have parallel No.1 reactor and single No.2 reactor for the purpose of establishing a simulated continuous system.

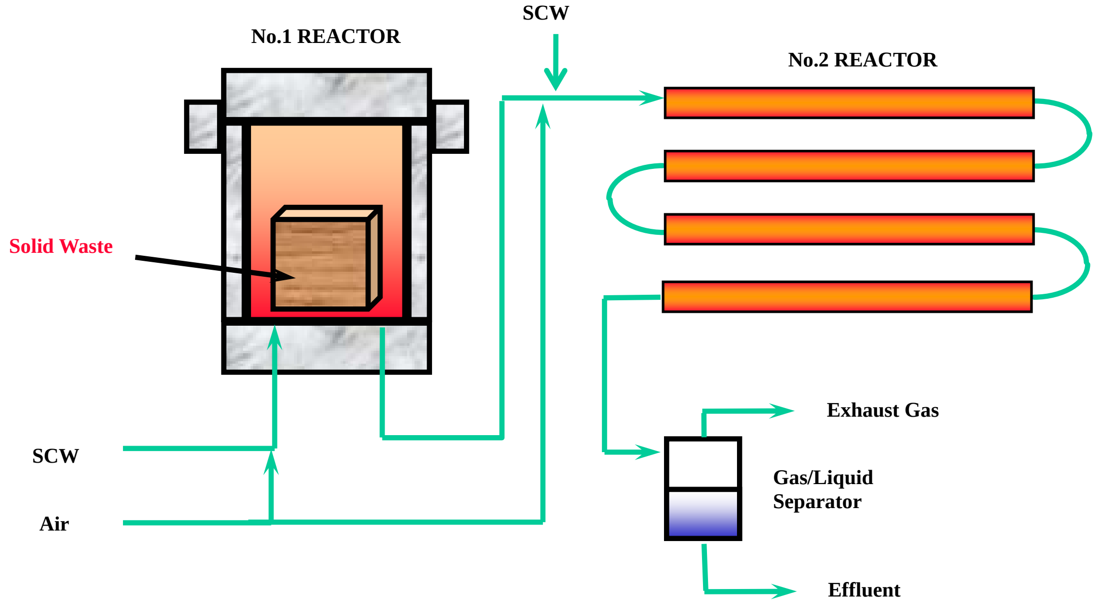

Fig.3 Flow Diagram of SCWO System for Solid Waste

The flow diagram for test plant for BHC and Chlordane using continuous system is shown in Fig.4. Flow rate of POPs emulsion was 0.75L/h. 25% hydrogen peroxide was used as a oxidizing reagent.

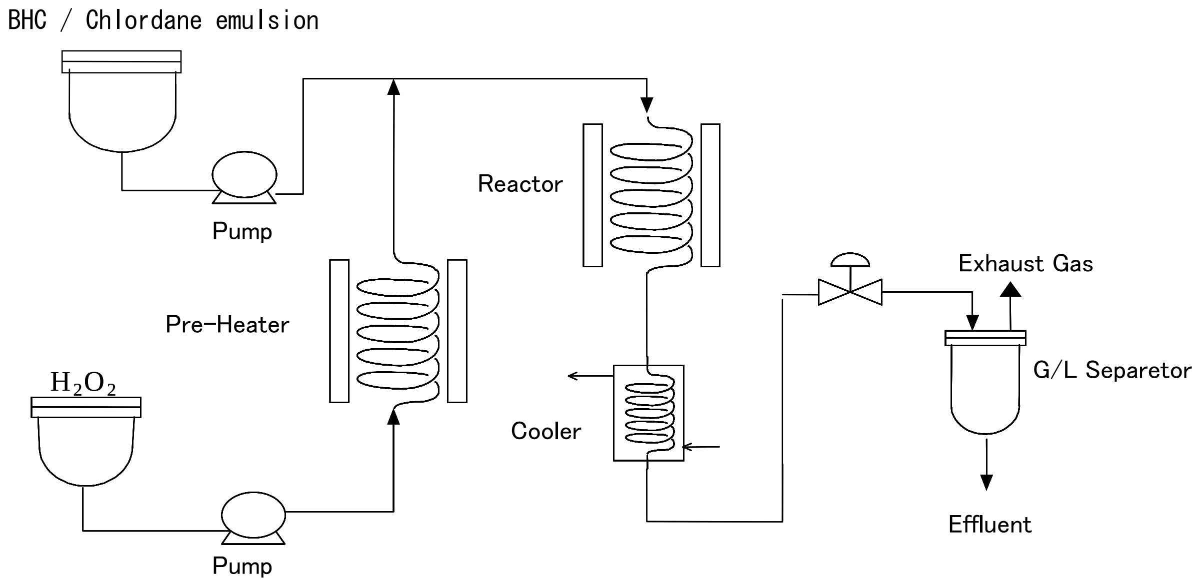

Fig.4 Flow Diagram of test plant for BHC/ Chlordane

Performance:

Treatment efficiency:

Result of BHC/Chlordane decomposition is summarized in the following Table;

POPs emulsion concentraition		Temperature	Pressure	Exhaust gas	Effluents	DREs(Gas) DREs(Effluent)	DEs
%		℃	MPa	μg/m3N	μg/L	%	%
BHC	0.00646	640	24	0.046	0.014	＞99.99996 ＞99.99975	＞99.99971
Chlordane	0.00067	640	24	0.014	0.007	＞99.99984 ＞99.99862	＞99.99846

Dioxins in reaction products is summarized in the following Table;

	Exhaust gas	Effluents
	ng-TEQ/m3N	ng-TEQ/L
BHC	0.0018	0.04
Chlordane	0.00015	0.0075

Throughput:

PCB oil : 250kg/d
Solid Waste contaminated with PCB : 50kg/d

Wastes/Residuals:

Effluent contains harmless salt, such as NaCl, NaHCO3. Exhaust gas is mainly composed of CO2, N2, O2. Unlike incineration , SCWO does not produce NOx or SOx 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.

Reliability:

SCWO system for PCB oil had been operated for 1000hours as a integrated operation time.

Limitations:

For the continuous SCWO system, feed material is limited to liquid or slurry.
For the batch SCWO system, POPs concentration of solid waste is limited to below 1000 mg/kg.

Transportability:

SCWO systems are transportable.

Detailed information:

No Annex

Conclusion:

250kg-PCBs oil /day plant using a continuous system and 50kg/day plant for solid waste contaminated with PCBs using a batch system had been operated.　The test of decomposition BHC and chlordane using continuous system was performed at 0.75L/h of POPs emulsion flow rate.

Full Scale Treatment examples:

Organo had decomposed 213 kg PCBs oil in 2003.

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Patents:

Organo have owned about 100 of Japanese Patent for SCWO system

References:

1. Taro Oe, et. al., “Commercialization of the First Supercritical Water Oxidation Facility for Semiconductor Manufacturing Wastes”, Semiconductor Pure Water and Chemicals Conference, (1998)
2. Shin-ichiro Kawasaki, et. al., “Complete decomposition of capacitor’s PCBs waste by supercritical water oxidation”, 34^{th} Autumn Annual Meeting, SCEJ, G306,P294,(2001)
3. Shin-ichiro Kawasaki, et. al., “Novel Treatment of Hazardous Solid Wastes Using a Hybrid SCWO System”, 6^{th} international symposium on supercritical fluids, Versailles, France, (2003)