

Name of Process: Sub-critical water oxidation	Status: MHI has introduced SRI technology from the US, has conducted verification testing in a pilot plant at a PCB treatment rate of 0.5kg/hr, and has succeeded in the practical application of sub-critical water oxidation.
Vendor: Mitsubishi Heavy Industries, Ltd. Web site: http://mhi.co.jp	
Applicable Pesticides and related POPs wastes: BHC(benzene hexachloride) aldrin dieldrin chlordane PCB(polychlorinated biphenyl) dioxin	A PCB processing plant with total capacity of 2t/day is currently under construction in Japan, with plans to begin operations from November 2005.
Technology description: Principle <ul style="list-style-type: none"> Organic chlorine compounds are rendered harmless by means of dechlorination and simultaneous oxidation decomposition treatment in sub-critical water at 370°C and 26.7MPa. $C_p H_q Cl_r + \frac{r}{2} Na_2CO_3 + \left(p + \frac{q}{4} + \frac{r}{4} \right) O_2 \rightarrow \left(p + \frac{r}{2} \right) CO_2 + \frac{q}{2} H_2O + rNaCl$ $(2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O)$ Characteristics <ul style="list-style-type: none"> Decomposed substances consist of harmless carbon dioxide (CO₂), water (H₂O), and salt (NaCl). Highly corrosive hydrochloric acid is not formed, enabling superior equipment endurance. Large-scale processing can be conducted in a continuous processing plant. Verification background <ul style="list-style-type: none"> PCB treatment verification testing was initiated in a pilot plant in 1998, confirming that PCBs and PCB-contaminated organic substances can be decomposed. PCB decomposition rate: Over 99.9999% Organic C decomposition rate: Over 99.9% Decomposition testing performed in a pilot plant in Japan under consignment by the Institute of Environmental Toxicology during 2001~2003 with respect to BHC (benzene hexachloride), aldrin, dieldrin, and chlordane. It was confirmed that pesticides containing organic chlorine can be decomposed. Pesticide decomposition rate: Over 99.9999% 	
Process diagram: The flow diagram for MHI's hydrothermal decomposition process is shown below. <ol style="list-style-type: none"> At the start of operations, oil and oxygen react in the reaction tower, rising to the specified temperature and pressure (370°C, 26.7MPa), while the carbon dioxide generated by the oxidation of the oil is reacted with sodium hydroxide to produce sodium carbonate. When the specified conditions are reached inside the reaction tower, the oil is replaced by the substance to be treated, and decomposition processing is conducted. Processed liquid (that has completed decomposition processing) is cooled in a cooling unit, and after 	

depressurization by means of the pressure adjustment valve, separation occurs in the liquid/gas separation tank.

4. Processed liquid is placed in a holding tank, and is released after analysis to confirm that the substance in question has been decomposed. As a precaution, exhaust gas is passed through active carbon before being released.

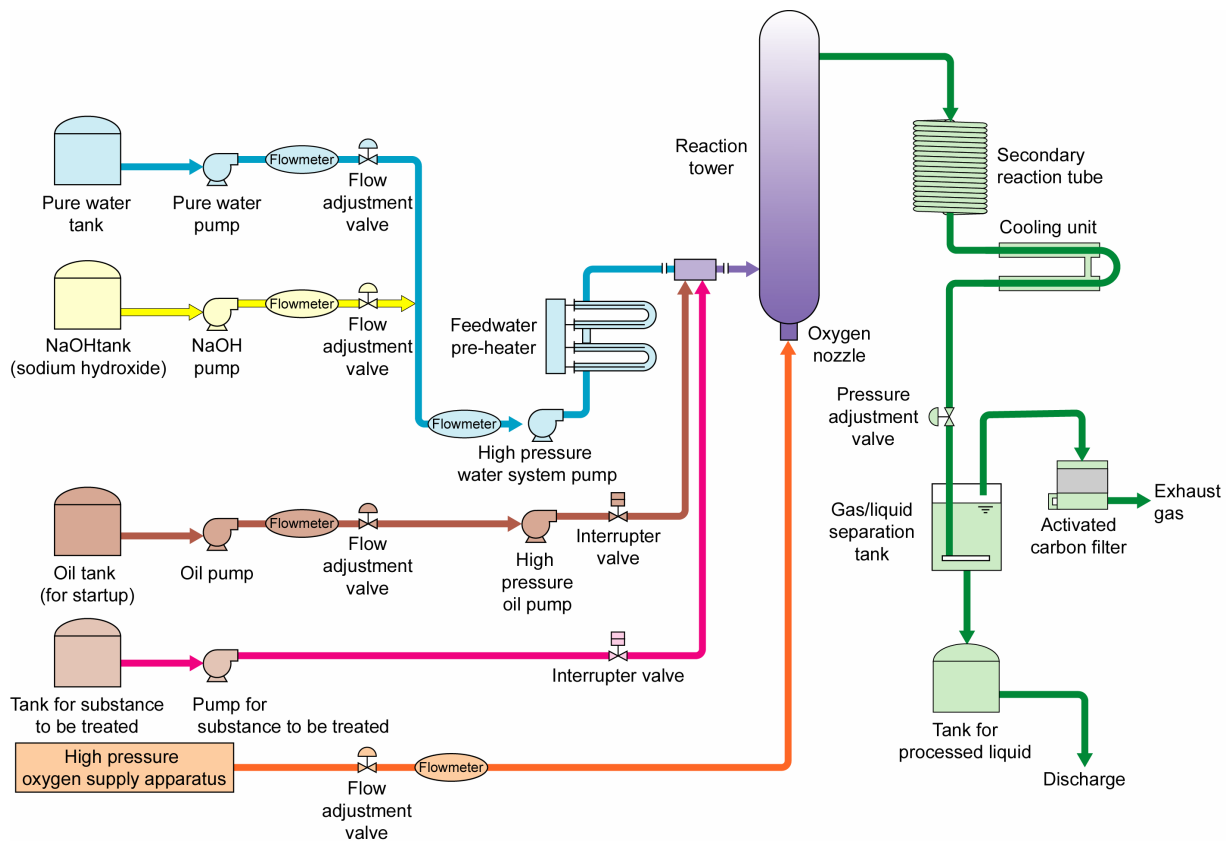


Figure MHI Sub-critical Water Oxidation Continuous Process Flow Diagram

Performance:

Treatment efficiency:

Table Description of demonstration experiment (Concentration, DEs and DREs)

NO.	Input POPs		Exhaust gas	Effluents	DEs	DREs (Effluents)
		wt%	$\mu\text{ g/m}^3\text{N}$	$\mu\text{ g/L}$	%	%
Test 1	Chlordane	20	0.0070	0.00036	> 99.9999934	> 99.9999951
	BHC	10	0.0015	0.013	> 99.9999868	> 99.9999868
Test 2	BHC	4.0	0.0025	0.0044	> 99.99999297	> 99.99999304
	Aldrin	0.20	< 0.00005	0.000012	> 99.99999926	> 99.99999933

<p>Throughput:</p> <p>○PCBs Pilot plant: 12kg-100% PCBs/day PCB processing facility (operation scheduled to begin Nov. 2005): 670kg-100% PCBs/day x 3 units</p> <p>○Pesticides Pilot plant: 28.8kg- acetone extract liquid/day (Pesticides adsorbed onto bentonite are extracted into acetone, with the extract liquid subjected to verification testing.)</p>
<p>Wastes/Residuals:</p> <p>Waste water contents sodium chloride (NaCl), sodium carbonate (Na₂CO₃) and sodium hydrogen carbonate (NaHCO₃).</p> <p>Exhaust gas contents carbon dioxide gas and excessive oxygen gas.</p>
<p>Reliability:</p> <p>The MHI Sub-critical Water Oxidation Process pilot plant has been processing PCBs for over 3500 hours without encountering difficulties.</p>
<p>Limitations:</p> <p>In cases where there are substantial amounts of inorganic substances coexist, pre-treatment such as by extraction using an organic solvent is required.</p>
<p>Transportability:</p> <p>The pilot plant and 670kg/day PCB processing plant are intended for fixed locations, but transportable apparatus can be designed.</p>
<p>Detailed information:</p> <p>NO Annex</p>
<p>Conclusion:</p> <p>Pre-treatment of pesticides using the extraction method has been conducted, with verification testing performed on continuously supplied extract liquid. Results were obtained as follows.</p> <ol style="list-style-type: none"> 1) BHC, aldrin, and dieldrin were detected in effluent and exhaust gas samples, but the amounts were extremely slight (BHC = 4400pg/L, 2.48ng/m³, aldrin + dieldrin = 21.1pg/L, 0.07ng/m³). These values were well within pesticide environmental control guidelines. 2) Results in effluent were under 1.0mg/L for n-hexane extract, 2.1mg/L for COD, and 1.6mg/L for TOC. Organic substance decomposition was thus satisfactory. 3) Results in effluent were under 0.005mg/L for organic chlorine, and 600mg/L for chlorine ions. This means that nearly all of the input organic chlorine remained as inorganic chlorine in effluent. 4) Results for dioxin were 3.3pg-TEQ/L in effluent and 0.057pg-TEQm³ in exhaust gas. Both of these values are below the regulatory standard values.

Full Scale Treatment examples:

A PCB processing plant with total capacity of 2t/day (670kg/day x 3 units) is currently under construction in Japan, with plans to begin operations from November 2005.

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Patents:

Japan Patent No.3495616
Japan Patent No.3546136

References:

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