Novel Treatment of Hazardous Solid Wastes Using a Hybrid SCWO System

Report 1: Configuration of the Hybrid SCWO System and Results of Fundamental Experiments

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ABSTRACT

Supercritical water oxidation (SCWO) has been developed as a technology for decomposing hazardous wastes such as PCBs (Polychlorinated Biphenyls) and dioxins. Work on this technology has been limited to decomposition of liquid wastes rather than solid wastes.

The SCWO process may be carried out in two modes, that is, batchwise and continuous. Attempts have been made to decompose solid wastes in the batchwise mode of operation. But a batch system is not a commercially viable process for the decomposition of solid wastes owing to its limited treatment capacity.

If the SCWO process in the continuous mode of operation is adopted for the decomposition of solid wastes, these solid wastes are first converted into slurry. More specifically, solid wastes are broken, milled to little pieces and mixed with water before being pumped to the SCWO reactor. This kind of pretreatment requires a lot of energy and costs. What is worse, supplying slurry by a high-pressure pump is very difficult because of blockage in the pump head and pipes.

We have been working on overcoming those shortcomings to the conventional methods of practicing the SCWO process for the decomposition of solid wastes, and conceived a hybrid SCWO system that consists of two reactors. A pilot scale plant was constructed based on the hybrid SCWO system. In this paper, the hybrid SCWO system design is described in more detail and some of the important test results are given.

INTRODUCTION

It is known that PCBs and dioxins are typical EDCs (Endocrine-Disrupting Chemicals) as well as POPs (Persistent Organic Pollutants) causing widely environmental problems. The characteristics of PCBs oil are as follows. 1: High electric insulation, 2: High heat resistance, 3: High chemical stability. Therefore, PCBs were used in large amounts as insulating oil of high voltage capacitors and transformers and heat media. Fig.1 shows a high voltage capacitor filled with PCBs oil and its cut-away view. “Kanemi Oil Poisoning Incident (Kanemi Yusho Jiken)” by the rice oil contaminated with PCBs oil occurred in 1968. As a result, the Japanese government prohibited using and producing of PCBs in 1973. Existing PCBs oil and solid wastes contaminated with PCBs were designated the specially controlled wastes, and they have been stockpiled at various places throughout Japan for a long time. In 2001, the Japanese government enacted a special law which makes it compulsory to treat PCBs by 2016.

Some technologies for the treatment of PCBs wastes have been developed and PCBs disposal facilities have been proposed in some places in Japan. In the case of North America and EU, PCBs wastes have already been treated by high-temperature incineration or chemical dechlorination methods. In Japan, it is difficult to get public acceptance of the incineration.

Supercritical water oxidation (SCWO) has been developed for the decomposition of various hazardous wastes [(1)] and SCWO can decompose PCBs completely. We have already succeeded in establishing a continuous SCWO system for decomposition of PCBs oil[(2)]. We have selected some corrosion resistant materials suitable for the construction of SCWO reactors subject to high concentration HCl (10-20wt%)[(3)]. A bench scale plant and a pilot scale plant made of these materials were operated for an extended period of time without any troubles. However, work on this technology has been limited to decomposition of liquid wastes rather than solid wastes such as holding lumbers, insulating papers and capacitor elements in the capacitor and/or transformer. In this work was developed a hybrid SCWO system for decomposition of solid wastes contaminated with PCBs.

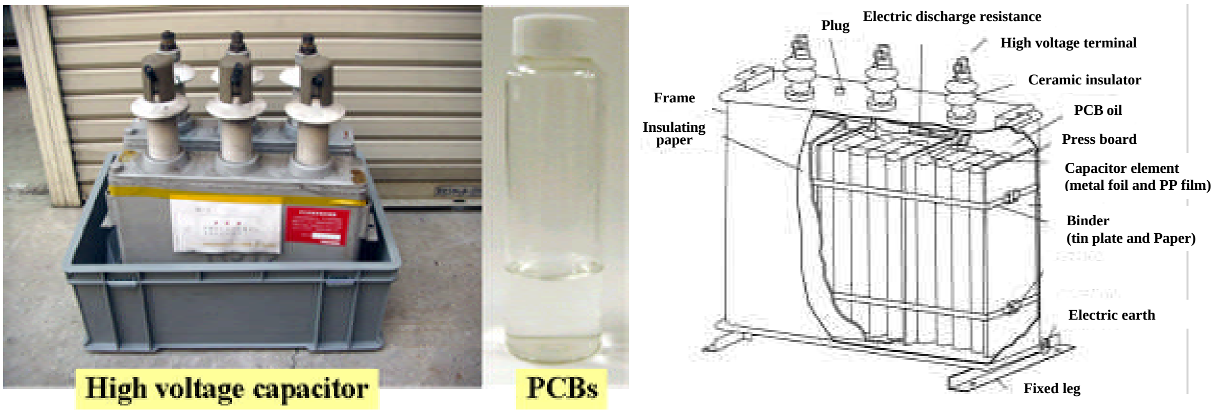

Fig.1 High voltage capacitor and PCBs oil

REACTION AND SYSTEM CONFIGURATION

The SCWO process for decomposition of PCBs has been operated successfully under the conditions of 600 degrees C and 24MPa in a few minutes. Fig.2 shows the fundamental reaction formulae of decomposition of PCBs by SCWO.

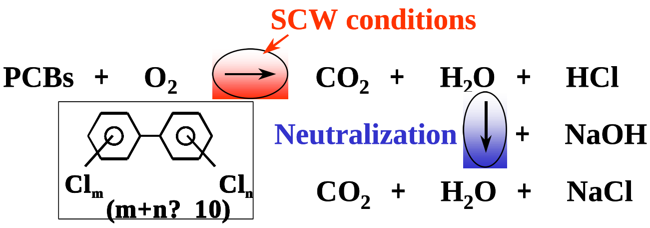

Fig.2 Fundamental reaction formulae of decomposition of PCBs by SCWO

The SCWO process for decomposition of solid wastes contaminated with PCBs may be carried out in two modes, that is, batchwise and continuous. Attempts have been made to decompose solid wastes in the batchwise mode of operation. However, in this mode, only a small amount of solid wastes can be treated in one batch operation because the heat of oxidation reaction of solid wastes is limited by overall heat balance. For example, the SCW density under the conditions of 600 degrees C and 24MPa is 0.07g/cc. In the case of a one-liter reactor, 70g of initial addition of water, a small amount of an oxidizing agent and only a few grams of organics can be fed into the reactor under these conditions. Hence, the batch system is not a commercially viable process for the decomposition of solid wastes.

If the SCWO process in the continuous mode of operation is adopted for the decomposition of solid wastes, these solid wastes are first converted into slurry. More specifically, solid wastes are broken, milled to little pieces and mixed with water before being pumped to the SCWO reactor. This kind of pretreatment requires a lot of energy and costs. The slurry loses its liquidity if its concentration exceeds a few weight percent. If the slurry concentration is decreased, a correspondingly larger process system is required. What is worse, supplying slurry by a high-pressure pump is very difficult because of frequent blockage in the pump head and pipes.

We have been working on overcoming these shortcomings to the conventional methods of practicing the SCWO process for the decomposition of solid wastes, and conceived a hybrid SCWO system that consists of two reactors.

Fig.3 shows a configuration of the hybrid SCWO system and Fig.4 the chemical formulae involved.

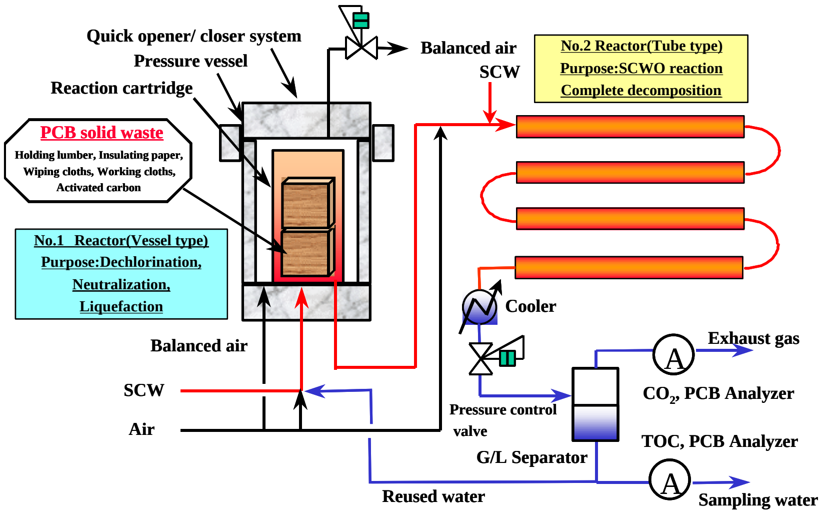

Fig.3 Configuration of the hybrid SCWO system

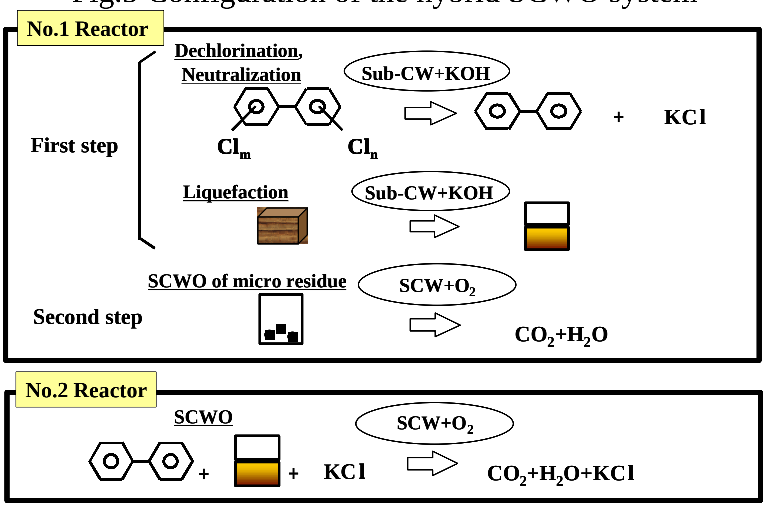

Fig.4 Reaction formulae of the hybrid SCWO system

The hybrid SCWO system 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 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.

In the operation of the hybrid SCWO system, the reaction cartridge is heated to 270-300 degrees C by some heaters wound around it. The PCBs are dechlorinated and neutralized by sub-critical water and KOH. In addition, organics are liquefied by sub-critical water and KOH as shown in the first step in Fig.4. The reasons why KOH is selected for the neutralizer in this system are given below.

Generally speaking, the solubility of inorganic salts decrease, if temperature exceeds that at the critical point of water (374 degrees C and 22MPa). The solubility of NaCl and KCl are approximately 100mg/L in supercritical water under conditions of 500 degrees C and 25MPa[4]. Fig.5 shows results of recovery rates of ions under the conditions of No.2 reactor (600 degrees C and 23.5MPa). These tests were carried out using a small tube reactor (5mm-id, 16m-length) simulating the No.2 reactor. In the case of NaCl solution (10,000mg/L), the recovery rates of Na ion and Cl ion decreased quickly, if reactor temperature increased. When the temperature increased to 550 degrees C, the pressure of the supplying pump increased to design pressure (30MPa) and the process shut down, because of NaCl plugging. On the other hand, the case of KCl solution (10,000mg/L), the recovery rates of K ion and Cl ion decreased at first, but the recovery rates were maintained at 90 to 100wt% during the operation. The recovery rates of these ions increased to 150wt% after the stopping of reactor heating. This behavior indicated that KCl could pass through the tube reactor better than NaCl under these conditions, although the solubility of KCl was the same as NaCl. And part of KCl adhered to the inner wall of tube reactor was easily re-dissolved, when the heating of the reactor was stopped. In addition, similar observations were made of the recovery rate of $KHCO_3$ and K_2CO_3. As a result of these passing through tests, It was determined that KOH should be used for the hybrid SCWO system in preference to NaOH.

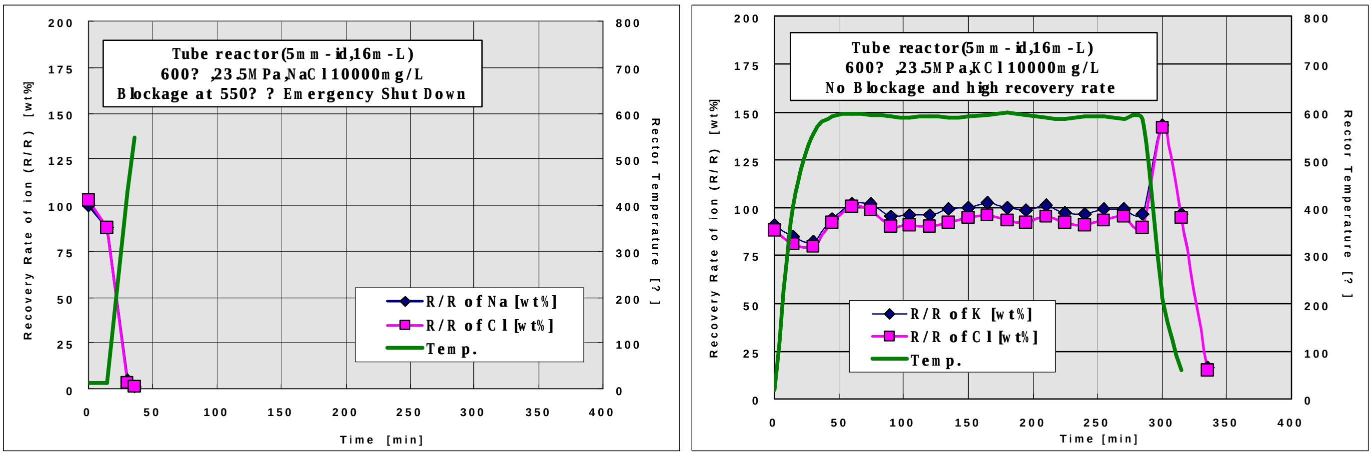

Fig.5 The recovery rate of ion under condition of 600 degrees C and 24MPa

Returning to Fig.4, the effluent from the reaction cartridge is discharged to No.2 reactor whole supplying sub-critical water having the same temperature as No.1 reactor, that 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 almost from No.1 reactor and decomposed by SCWO in the No.2 reactor.

At last, 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 of not supplying oxygen 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 reactors and single No.2 reactor for the purpose of establishing a simulated continuous system.

We constructed a pilot scale plant of the hybrid SCWO design in 2002. Fig.6 shows the reactors of the pilot scale plant. The treatment capacity of the pilot scale plant was 200kg/day based on solid waste. The small type of No.1 reactor was used for the fundamental experiments and No.2 reactor (tube type) was used common to each No.1 reactors.

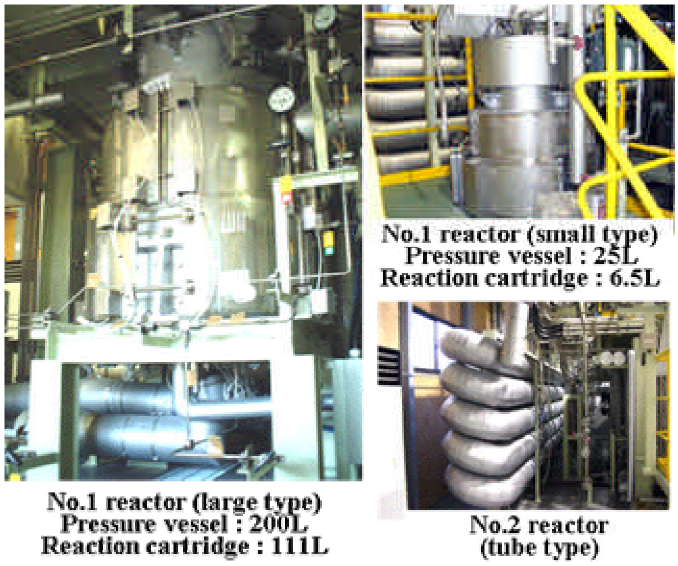

Fig.6 Reactors of the pilot scale plant

EXPERIMENTAL RESULTS AND DISCUSSION

For the purpose of studying the reaction behavior of the hybrid SCWO system, wood soaked in 1,2-Dichrolobenzane (DCB) was used as a model compound of PCBs solid waste. This wood contaminated with DCB was fed to the pilot scale plant (small type No.1 reactor). Table 1 shows the experimental conditions and Table 2 the results.

Table 1 Experimental conditions (wood contaminated with DCB)

DCB concentration in wood	50wt%	No.1, No.2 SCW flow rate	10kg/h, 15kg/h
DCB wood	126g	No.1 reactor temp. (First step)	360 degrees C
Cl concentration in No.1 reactor	7,500mg/L	No.1 reactor temp. (Second step)	580 degrees C
KOH concentration in No.1 reactor	18,000mg/L	No.2 reactor temp.	600 degrees C
Neutralization ratio in No.1 reactor	1.5	Process pressure	22MPa

Table 2 Experimental results (wood contaminated with DCB)

Effluent		Exhaust gas	
DCB concentration	<0.002mg/L	DCB concentration	0.045μ g/m^3
Dioxins concentration	0pg-TEQ/L	Dioxins concentration	0.0001ng-TEQ/m^3
Emission standard (effluent)		Emission standard (gas)	
Dioxins	10pg-TEQ/L	Dioxins	0.1ng-TEQ/m^3

Fig.7 shows the state of the wood contaminated with DCB before and after the treatment in the pilot scale plant (small type No.1 reactor).

Fig.7 Wood contaminated with DCB (before and after treatment)

Any organic residue was not detected in the reaction cartridge shown in Fig.7. TOC concentration (Total Organic Carbons) in the effluent was less than 1mg/L, CO concentration in the exhaust gas was less than 1ppm during the operation. DCB concentrations in the effluent and exhaust gas were very low. Dioxins concentration in the effluent and exhaust gas fully satisfied the emission standards. DCB and all organics were decomposed completely by the hybrid SCWO system.

CONCLUSION

An invention was made of a hybrid SCWO system consisting of No.1 batch reactor (vessel type) and No.2 continuous reactor (tube type) for treatment of solid wastes. A pilot scale plant based on this concept was built for tests on SCWO treatment of various hazardous solid wastes. Wood contaminated with Dichlorobenzene used as a model compound was decomposed completely. The hybrid SCWO system is expected to find wide use for the treatment of hazardous solid wastes.

ACKNOWLEDGEMENT

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REFERENCE

(1) Akira SUZUKI, Taro OE, Hiroshi SUZUGAKI, and Noriyuki ANJOH, 4th ISSF97, P.895, 1997.
(2) Shin-ichiro KAWASAKI, Tomoyuki IWAMORI, Noriyuki ANJOH, and Akira SUZUKI, 34th Autumn Annual Meeting, SCEJ, G306 (P.294), 2001.
(3) Tomoyuki IWAMORI, Shin-ichiro KAWASAKI, Noriyuki ANJOH, and Akira SUZUKI, 34th Autumn Annual Meeting, SCEJ, G305 (P.293), 2001.
(4) Jefferson W. Tester, H. Richard Holgate, Fred J. Armellini, Paul A. Webley, William R. Killilea, Glenn T. Hong, and Herbert E. Barner, ACS Symposium Series, ACE, P.35-76, 1993.