Destruction of dioxins and PCBs in solid wastes by supercritical fluid treatment

Takeshi Sako[1], Shin-ichiro Kawasaki[2], Hironori Noguchi[3], Takashi Kimura[4], Hiroaki Sato[5]

[1]Shizuoka University, Hamamatsu
[2]Organo Co., Tokyo
[3]Nagasaki Ryouden Technica Co.,Ltd., Nagasaki
[4]New Energy and Industrial Technology Development Organization, Kawasaki
[5]The Energy Conservation Center, Tokyo

Introduction

Most chlorinated aromatic compounds, such as dioxins and PCBs, are refractory and toxic chemical substances causing widely environmental problems. The technology of supercritical water oxidation (SCWO) has been developed for the decomposition of various hazardous materials including the above substances. As a national NEDO (New Energy and Industrial Technology Development Organization) project, we have been developing two processes for the destruction of dioxins and PCBs which cling to solid waste[1-8]. One is combined supercritical fluid process for the dioxins in fly ash, and the other is a hybrid SCWO process for solid wastes contaminated with PCBs. When SCWO is applied to municipal incinerator fly ash containing extremely small amount of dioxins, the concentration of dioxins is necessary for effective treatment. The former process uses supercritical carbon dioxide (sc-CO_2) with a large solvency capacity to extract dioxins in fly ash. Conventional SCWO has been limited to the decomposition of liquid PCB wastes rather than solid wastes such as holding lumbers, insulating papers and capacitor elements in the capacitor and/or transformer. The latter process can treat the PCB solid wastes as well as PCB liquid wastes.

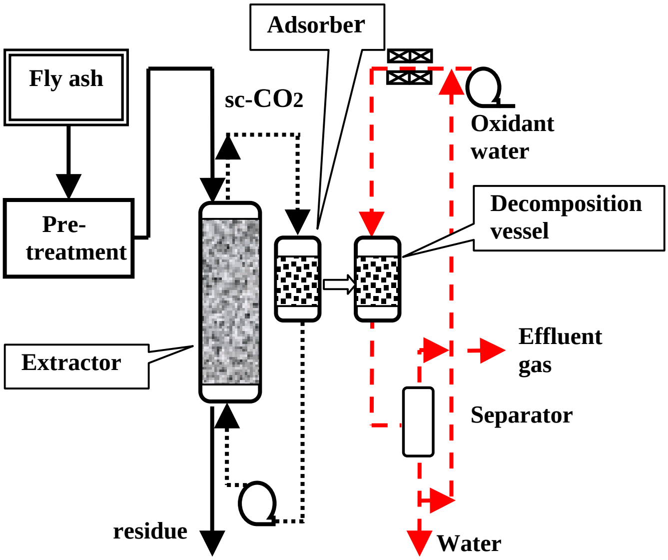

Figure 1. Combined process of sc-CO_2 extraction, adsorption, and SCWO for the treatment of fly ash.

Methods and Materials

Combined supercritical fluid process for the destruction of dioxins in fly ash

This process consists of extraction with sc-CO_2, concentration by adsorption, and destruction by SCWO. In the extraction-adsorption process, dioxins contained in fly ash can be transferred and concentrated into adsorbent (activated carbon). Then, the adsorbent containing dioxins is completely destructed by SCWO. The configuration of the process is shown in Figure 1. This process is suitable for the treatment by selective extraction of lower concentration substances such as dioxins in fly ash containing corrosive substances. In this work, we studied the effects of sc-CO_2 process of dioxins from fly ash by extraction –adsorption bench scale plant. The destruction of dioxins was also studied by SCWO bench scale plant.

Figure 2 shows the bench scale plant for the extraction and adsorption. The extraction experiment was conducted in semi-batch flow extractor where the samples were packed in the extractor vessel of 30L. The separated dioxins were adsorbed onto activated carbon in an adsorber of 2L.

Adsorber(2L) Extractor(30L)

Figure 2. Bench scale plant for extraction and adsorption of dioxins in fly ash.

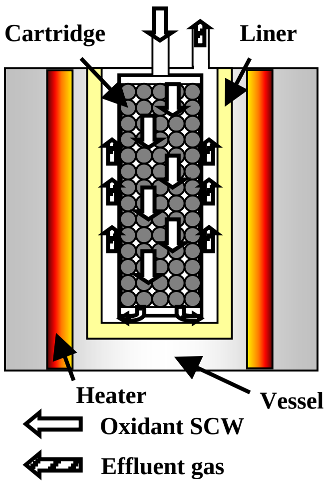

Figure 3. SCWO decomposition vessel.

The sample of fly ash was treated with hydrochloric acid to remove alkaline components that cover the surface of the fly ash particles, and dried for the pretreatment.

For the destruction of dioxins adsorbed on activated carbon, we carried out the SCWO of dioxins by decomposition bench scale plant. Dioxins and activated carbon were both decomposed at the same time as a whole treatment. The experiment was conducted in the decomposition vessel of 2L in volume. The structure of SCWO vessel is shown in Figure 3. The cartridge was charged with activated carbon adsorbing dioxins, and supplied with oxidant SCW. A typical experiment was carried out at conditions of 20MPa and 500^{o}C. The material of the inner wall of the decomposition vessel was Hastelloy.

Hybrid SCWO process for decomposition of solid wastes contaminated with PCBs

This hybrid process has two reactors: the first batch reactor (vessel type) and the second continuous flow reactor (tubular type). Figure 4 shows a configuration of the hybrid SCWO process and Figure 5 the chemical reaction formulae involved. This process is suitable for the treatment of relatively highly concentrated toxic substances such as PCBs in contaminated solid wastes (holding lumbers, insulating papers and capacitor elements in the capacitor and/or transformer). A high-pressure vessel and a reaction cartridge comprise the first reactor. A part of compressed air (balanced air) is supplied between the reaction cartridge and the high-pressure vessel, and this balanced air is discharged separately from the first reactor effluent. This balanced air contributes to reducing the pressure difference between inside and outside of the reaction cartridge. Therefore we can construct a thin reaction cartridge. The high-pressure vessel has a quick opener and closer system. Solid PCBs wastes are supplied into the reaction cartridge in large quantities without being converted into a slurry.

In the operation of the hybrid SCWO process, the reaction cartridge is heated to 270-300°C by heaters wound around it. The PCBs are dechlorinated and neutralized by subcritical water and KOH. In addition, organics are liquefied by subcritical water and KOH as shown in the first step inFigure 5. The effluent from the reaction cartridge is discharged to the second reactor by supplying subcritical water having the same temperature as the first reactor. During the heating of the first reactor, the second reactor that is supplied with SCW and air is maintained under the conditions of 600°C and 24MPa. Therefore the effluent from the first reactor is decomposed completely by SCWO in the second reactor. At last, the first reactor is reheated from 300 to 600°C, and the compressed air is finally supplied to decompose micro residues in the reaction cartridge, as shown in the second step of Figure 5.

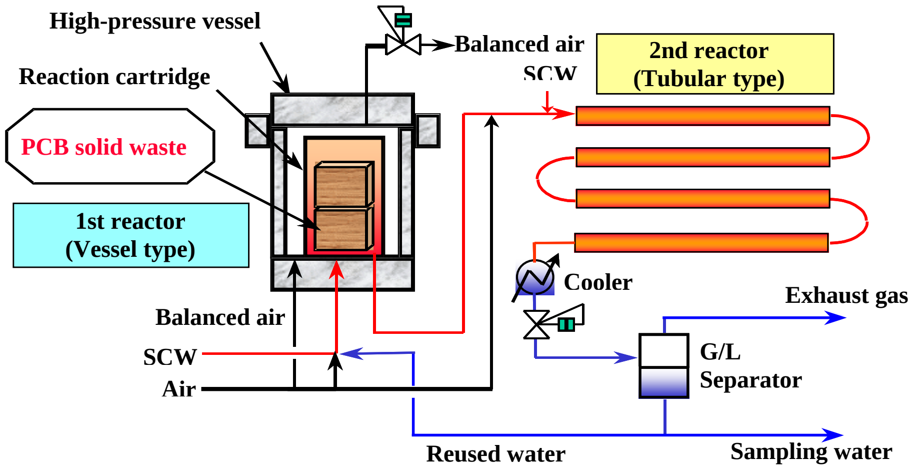

Figure 4. Configuration of hybrid SCWO process for treatment of PCB solid wastes.

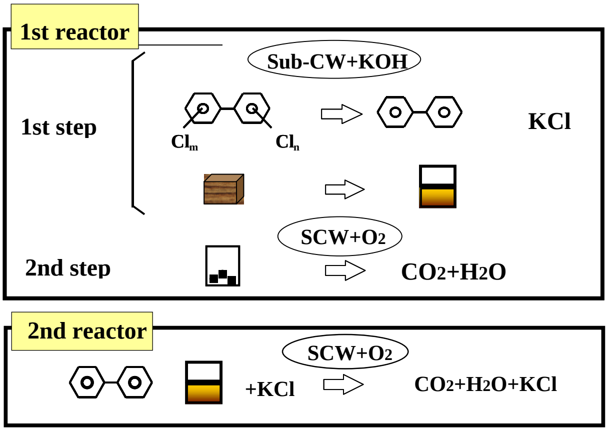

Figure 5. Chemical reaction formulae of hybrid SCWO for PCB solid wastes.

The advantages of the hybrid process are as follows: (1) large quantities of organics can be fed into the first batch reactor because of not supplying oxygen until the first reactor effluent is discharged, and (2) solid wastes can be fed without converting them into a slurry. Figure 6 shows the reactors of the pilot scale plant. The volumes of the high-pressure vessel and reaction cartridge of the first reactor of large type are 200L and 111L, and those of small type are 25L and 6.5L, respectively. The inner wall of the first and second reactors was made of Inconel-625.

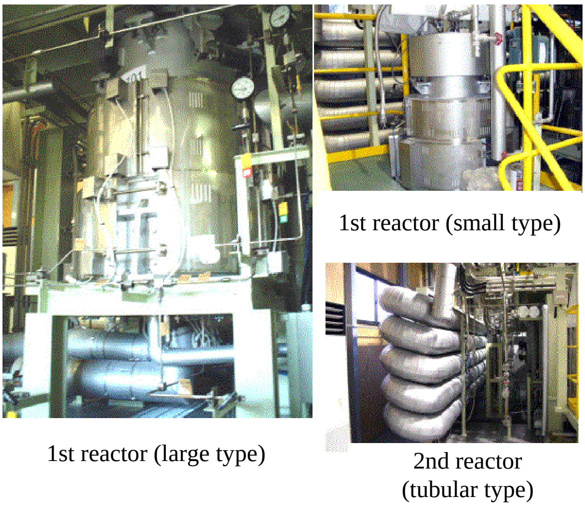

Figure 6. Reactors of the pilot scale plant.

Results and Discussion

Destruction of dioxins in fly ash

The investigations were made to search for the suitable conditions on promoting the extraction of dioxins in fly ash using sc-CO_2. As the results of the basic experiment are shown in Figure 7, the extraction efficiency for dioxins increased with the increase in pressure. The effect of pressure on the extraction was so dominant that at the pressure of 50MPa, the extraction efficiency attained 99.9 %. The experiment of the extraction bench scale plant was conducted at the conditions at 40^{o}C, 50MPa, solvent/feed=5, extraction time=1hr. These conditions were evaluated to be the most suitable. The results of bench plant experiment are shown in Table 1.

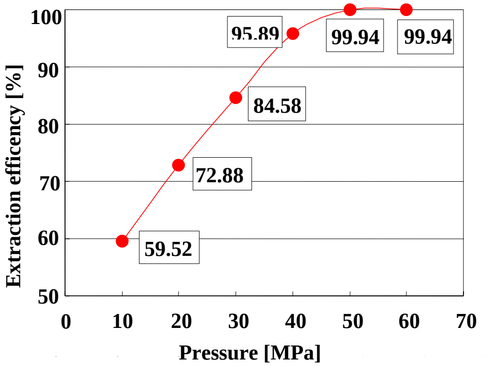

Figure 7. Effect of pressure on extraction efficiency (40^{o}C, 1hr, Solvent/Feed = 5).

For the destruction of dioxins adsorbed on activated carbon completely, we chose the treatment of both decomposition of dioxins and activated carbon. According to the basic experiment using the batch reactor, SCWO was effective. When the reaction temperature was higher than 500 ^{o}C, no dioxins were remained unreacted. A bench scale plant experiment was conducted on the destruction of dioxins adsorbed on activated carbon at conditions shown in Table 2. Complete decomposition of dioxins and activated carbon was confirmed from the results of chemical analysis of dioxins in residue and effluent water. The dioxin concentration was measured by CALUX bioassay.

Experiment	Dioxins content in residue [ng-TEQ/g]	Extraction efficiency [%]
RUN-1	0.014	**99.98**
RUN-2	0.013	**99.98**

Table 1. Sc-CO_2 extraction of dioxins in fly ash with bench scale plant

Table 2. Destruction condition of dioxins and activated carbon

Parameter	**Experimental conditions**	
Pressure	**20 MPa**	**20 MPa**
Temperature	**500 ^{o} C**	**500 ^{o} C**
Flow rate of hydrogen peroxide solution	**25 mL/min**	**100 mL/min**
Conc. of hydrogen peroxide	**5.0 %**	**7.5 %**
Weight of activated carbon	**100 g**	**500 g**
Dioxins content onto activated carbon	**2.25 mg/g**	**2.0 mg/g**
Reaction time	**80 min**	**250 min**
Excess oxygen ratio	**1.12**	**1.4**

Decomposition of solid wastes contaminated with PCBs

Some tests for the decomposition of PCB solid wastes were carried out based on fundamental experiments. Figure 8 shows before and after the treatment in the pilot scale plant (capacitor elements contaminated with PCBs). The materials were simply degreased by organic solvents for the purpose of the dilution of the PCB concentration. As a result, the PCB concentration decreased from 106,000mg/kg to 453mg/kg. The PCB concentration was measured by the official analytical method of special control wastes. That is, the PCB wastes were extracted by n-hexane in an ultrasonic washing machine. Then PCB was concentrated by an evaporator and measured by a GC/ECD. Capacitor elements were formed with polypropylene films and Al foils. The polypropylene films were decomposed to CO_2 and H_2O by SCWO. The Al foils were transformed to Al_2O_3 powder. Table 3 shows experimental results for the solid, effluent, and exhaust gas.

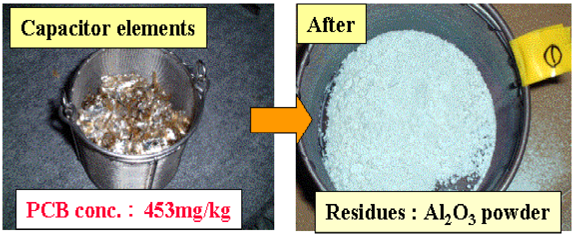

Figure 8. Experimental results of capacitor element.

Any organic residue was not detected in the reaction cartridge shown in Figure 8. TOC (Total Organic Carbons) concentration in the effluent was less than 1mg/L, and CO concentration in the exhaust gas was less than 1ppm during the operation. As shown in Table 3, PCB concentrations in the residue, effluent, and exhaust gas were very low. Dioxin concentrations in the residue, effluent, and exhaust gas fully satisfied the emission standards. PCBs and all organics were decomposed completely by the hybrid SCWO process.

Table 3. Treatment of capacitor elements contaminated with PCBs

Residue			
PCBs concentration	<0.01mg/kg	Dioxins concentration	<1.0ng-TEQ/g
Emission standard (residue)		Emission standard (residue)	
PCBs concentration	0.01mg/kg	Dioxins concentration	---
Effluent		Exhaust gas	
PCBs concentration	<0.0005mg/L	PCBs concentration	<0.0005mg/m^3
Dioxins concentration	<1pg-TEQ/L	Dioxins concentration	<0.0006ng-TEQ/m^3
Emission standard (effluent)		Emission standard (gas)	
PCBs	0.003mg/L	PCBs	0.15mg/m^3
Dioxins	10pg-TEQ/L	Dioxins	0.1ng-TEQ/m^3

Conclusion

On the complete destruction of dioxins from municipal incinerator fly ash, the applicability of the technique using sc-CO_2 extraction and SCWO was confirmed in a bench scale plant. The effect of extraction pressure was important on promoting the extraction efficiency. Dioxins and activated carbon (adsorbent) were both decomposed completely in SCWO.

An invention was made of a hybrid SCWO process consisting of a first batch reactor (vessel type) and a second continuous flow reactor (tubular type) for the treatment of solid wastes. A pilot scale plant based on this concept was built for tests on SCWO treatment of various hazardous solid wastes. Some materials (e.g. capacitor elements) contaminated with PCBs were decomposed completely. The extended SCWO processes are expected to find wide use for the treatment of hazardous solid wastes.

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References

1. Sako,T., Sugeta,T.,Otake,K., Sato,M., Tsugumi,M., J.Chem.Eng.Japan, **1997**, 30, 744.
2. Sako,T., Sugeta,T.,Otake,K., Kamizawa,,C., Okano,M., J.Chem.Eng.Japan, **1999**, 32, 830.
3. Goto, M., Kawajiri, S., Organohalogen Compounds, **2003**, 63, 232.
4. Kawajiri, S., Goto, M., Kodama, A., Hirose, T., High Pressure Chemical Engineering, **2001**, 1.
5. Kawajiri, S., Goto, M., Hirose, T., Organohalogen Compounds, **2000**, 45, 101.
6. Kawasaki, S., Fujii, T., Suzuki, A., Kimura, T., Sato, H., Proc. of 6th ISSF,**2003**, 1259.
7. Kawasaki, S., Iwamori, T., Anjoh, N., Suzuki, A., Proc. of 34 th Autumn Meeting, SCEJ, **2001**, G306 ,294.
8. Iwamori, T., Kawasaki, S., Anjoh, N., Suzuki, A., Proc. of 34 th Autumn Meeting, SCEJ , **2001**, G305 ,293.