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Supercritical water oxidation of transformer oil contaminated with PCBs—A road to commercial plant from bench-scale facility

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ABSTRACT

Polychlorinated biphenyls (PCBs) are one of the eradication compound lists of Stockholm convention. Korea started to analyze the PCBs concentration in high-voltage transformers in June 2004 and is developing PCBs disposing technology. As most of the transformers in Korea were contaminated at very low level of less than 5 ppm, it was decided that SCWO (supercritical water oxidation) process is suitable to treat them.

The destroying parameters of SCWO process including optimum process temperature, pressure, residence time, and amount of oxidant were studied with a bench-scale facility. Based on these results and simulation, a pilot plant was designed and built to confirm the suggested condition. Recently detail design of a commercial plant was completed based on these results. In this paper, the procedures to scale up the design from a bench-scale facility to a commercial plant and major check points in each stage are introduced.

1. Introduction

Polychlorinated biphenyls (PCBs), one of the persistent organic pollutants (POPs) which can damage the environment and human health for a long period of time due to their strong toxic, persistence, long distance migration, and bio-accumulation, are one of the eradication compound lists of Stockholm convention. The convention effectuated in May 2004 made it mandatory to ban the use of products containing PCBs by 2025 and to eco-friendly dispose of PCBs containing wastes by 2028. Hence Korea is developing PCBs disposing technology with the time limit of 2015 [1].

Korea started to analyze the PCBs concentration in high-voltage transformers of power plants in June 2004. Through social agreement, it was decided that wastes containing more than 2 ppm of PCBs are classified as 'designated wastes' and wastes containing more than 50 ppm will be exported for disposal. Some of the high-voltage transformers have already been exported for disposal. In Korea, it is legal to treat PCBs contaminated wastes by incineration or molten metal technology according to the environmental law. However, due to NIMBY syndrome more practical alternative technologies are needed and being developed.

The treatment of wastes contaminated PCBs with supercritical water oxidation (SCWO) process was initially studied by Mitsubishi Heavy Industries, Hitachi Heavy Industries, and Organo Corporation in Japan. Their researches were focused on using SCWO process for destroying extracts produced by supercritical fluid extraction (SFE, mainly using carbon dioxide) of waste water produced from the treatment of PCBs contaminated soil or disassembling power transformers, and chemical weapons. On the other hand the organic alkaline metal decomposition method (*t*-BuOK method) co-developed by Kansai Electric Power Co. Inc. and its subsidiary company separates chlorine in the PCBs by adding small amount of potassium *tert*-butoxide (*t*-BuOK) and destroys them to non toxic potassium chloride (KCl) and substances not containing chlorine to detoxicate transformer oil contaminated with PCBs. Kinetrics, a Canadian company, announced that the transformer oil contaminated with PCBs can be treated by a transportable treatment unit using sodium dispersion process [2–4].

The data, collected between 2004 and 2005, of PCBs concentration in transformer oil of high-voltage transformers (>154 kV) from 6 power subsidiary companies of KEPCO (Korea Electric Power Corporation) are presented in Table 1. From the table, PCBs were not detected in transformer oil of 782 units, about 53% of total examined units of 1484. It is made up of about 80% of total units when 28% of units where PCBs concentration was lower than Korean designated waste concentration of 2 ppm were included. Only 38 units were analyzed to have more than 50 ppm. The analyses performed later on transformers for power transmission and distribution also

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Table 1
Classification of transformers (about 1500 units) by concentration of PCBs.

Concentration of PCBs (ppm)	ND	0.01–1.99	2.00–4.99	5.00–49.00	>50.00
No. of transformer (unit)	782	410	142	112	38

ND: non-detectable (detection limit: 0.05 ppm).

showed that about 15–20% were contaminated with PCBs and most of the units were contaminated at very low level of less than 5 ppm.

In consideration of low concentration of PCBs in transformer oil in Korea, it was decided that SCWO process is suitable to treat them [5]. The destroying parameters of SCWO process including optimum process temperature, pressure, residence time, and amount of oxidant were studied for the treatment of transformer oil contaminated with PCBs with a bench-scale facility. Then, a bench-scale facility with a tubular reactor and a vessel reactor was built separately and tested to determine the optimum flow rate of reactor. Based on these results and simulation, a pilot plant was designed and built to confirm the suggested condition. Recently detail design of a commercial plant was completed based on these results.

In this paper, the procedures to scale up the design from a bench-scale facility to a commercial plant and major check points in each stage are introduced [2,6,7]. For the details of determination of optimum reaction condition for the bench-scale facility, the corrosion test of reactor and the analysis of surrounding environment, refer to our published works [1,8–10].

2. Experiment

2.1. Sample preparation

The waste transformer oil used in this study was taken from discarded transformers and kept for study. The concentration of PCBs was 1541.86 mg/L. To adjust the concentration of PCBs to the desired value of 50 ppm, the waste transformer oil was mixed with fresh transformer oil of the same kind. From this 50 ppm oil samples, the model transformer oil sample (named after this as "sample") containing 3 wt% of the oil were prepared by dispersing the oil in the water to form emulsion. As mentioned in our previous work, to prepare the sample in the form of emulsion containing 3 wt% of PCBs from waste oil with 50 ppm PCBs, 0.2 wt% of PEG 1000, PEG 2000, LEA-3 mixture (1:1:1 weight ration) was added to the waste water sample [1,8,10].

2.2. Total organic carbon (TOC) analysis

To quantify the amount of destruction of the sample, TOC concentration was utilized as a destruction index. TOC measuring system with an auto-sampler (Shimadzu, TOC VCPH) was used. Identical analysis was repeated several times on each sample for accurate analysis. The sample prepared above was analyzed to have TOC of 18,200 ppm.

2.3. Measurement of heat of combustion

The transformer oil to be treated was a mineral oil contaminated with 50 ppm of PCBs used in high-voltage transformers. Its main components are alkane compounds having the structure of C_nH_{2n+2}. The heat of oxidation (or combustion) was measured using fresh transformer oil. The heat of combustion according to KS E 3707:2001 procedure was 45,380 J/g, which was significantly higher than those of other organic wastes. Since the heat of combustion was high, it was decided that the content of transformer oil in the supercritical reaction medium should be kept small.

2.4. Analysis of effects on the environment

After SCWO process, the samples were passed through depressurizing and cooling processes and then separated to liquid and gas phases in liquid–gas separator as shown in Fig. 1. The liquid and gas effluents were analyzed for dioxin and PCBs concentrations. The analysis was in compliance with EPA-1613. HRGC/HRMS (high resolution gas chromatograph/high resolution mass spectrometer, JMS 700D, Jeol) was used at resolution over 10,000 and in SIM (selected ion monitoring) mode [11,12]. Refer to our published works for details about the analysis of gas effluents in the adsorbent tube, sampling and nitrogen oxides analysis of air around the pilot plant [9].

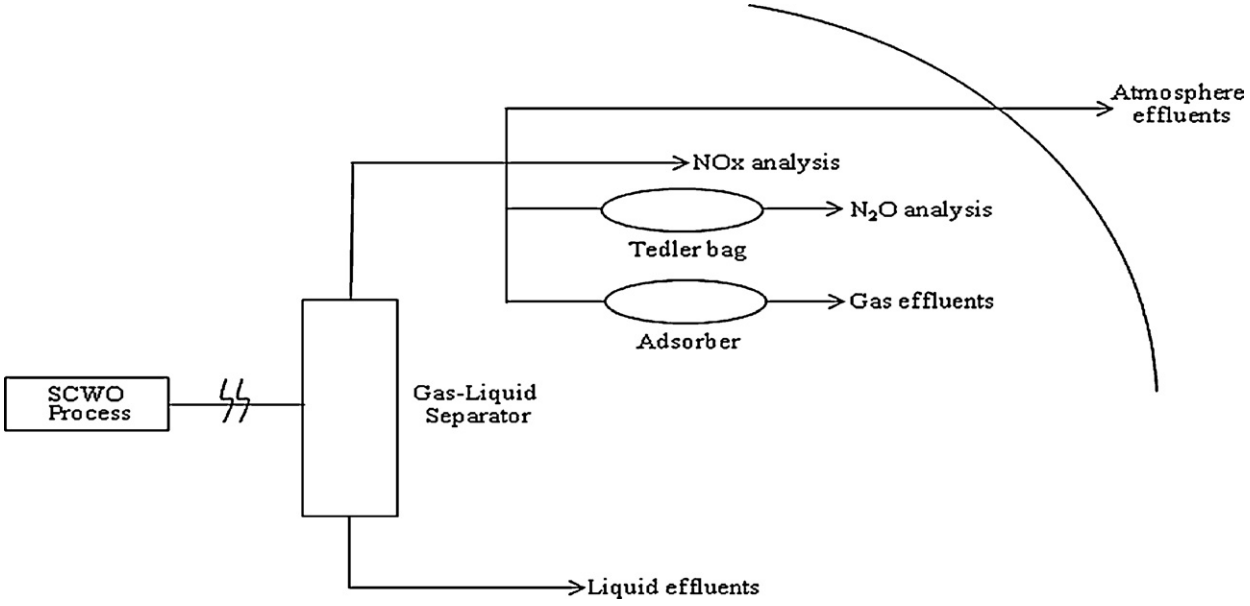

Fig. 1. Sampling positions.