

INFLUENCE OF WASTE INSULATING OIL CONTAINING PCBs FED INTO AN INCINERATOR ON PCDDs/Fs AND PCBs CONCENTRATIONS EMITTED FROM THE INCINERATORS

Song G-J^{1*}, Jung H-Y², Kim K-H², Seo Y-C³

¹Institute of Environmental and Energy Technology, POSTECH, Pohang, Kyungbuk, South Korea; ²National Institute of Environmental Research, Incheon, South Korea; ³Department of Environmental Engineering, Yonsei University, South Korea

Introduction

Since 1929, polychlorinated biphenyls (PCBs) have been produced in the United States, Germany, France, Russia and Japan and widely used in industrial and consumer applications in the world. In the 1970s, the commercial use of PCBs was prohibited and the capacitors and transformers containing PCBs were produced no longer. PCBs are among the twelve Persistent Organic Pollutants (POPs) addressed by the Stockholm Convention. Obligations under the Convention for Parties are to eliminate the use of PCBs in transformers and capacitors by 2025 and adopt environmentally sound management of PCBs-containing waste by 2028. Therefore, it is important to figure out adequate management and control methods to treat PCBs-containing waste. Recently, concern over the management or treatment for products and waste containing PCBs has risen all over the world. In Korea, waste containing PCBs of above 2 ppm can be incinerated in high temperature incinerators by Waste Management Law, but it has not been carried out until now because of public opposition and concerns. To solve the problem, many investigations have been carried out for years to find out other treatment methods, and washing and chemical treatment have been permitted by the POPs Management Law, since 2008. However, the capacity of washing and chemical treatment methods is not enough to treat waste insulating oil containing PCBs and PCBs contaminated transformers generated in Korea. Therefore, the co-incineration of hazardous wastes and waste insulating oil containing PCBs using the high-temperature incinerators for hazardous waste containing PCBs was investigated in Korea. In this study, the experiment was carried out in 3 test conditions using 2 different hazardous waste high temperature incinerators (HWIs) and PCDDs/Fs and PCBs concentrations of flue gases were measured in order to investigate the influence of waste insulating oil containing PCBs fed into the incinerators on concentrations of PCDDs/Fs and PCBs emitted from the incinerator.

Material and methods

(1) Type of incinerators and co-incinerated hazardous waste with waste insulating oil

The 2 high-temperature HWIs (noted as incinerator A and B) were used in this study. The incineration capacities were 1.27 ton/h (incinerator A) and 3.54 ton/h (incinerator B), and the type of the incinerators was rotary kiln + stoker. Their incineration temperatures were 1123-1231 °C and 1095-1132 °C for incinerators A and B, respectively. The flue gas temperatures after waste heat boiler (WHB) were 253-272 °C and 361-393 °C. Incinerator A had WHB, semi-dry reactor (SDR), dry reactor (DR), bag filter (BF) and incinerator B had WHB, cooling tower (CT), BF, wet scrubber (WS) (I) and WS (II) as air pollution control devices (APCDs), and also the incinerators had selective non catalytic reduction (SNCR). The types of co-incinerated hazardous waste with waste insulating oil containing PCBs were waste synthetic resin, waste polymer, waste paint, waste organic solvent and sludge. The co-incineration rate of hazardous waste and waste insulating oil containing PCBs was about 10-20 wt%. The hazardous waste fed into the incinerators was composed of mostly carbon and oxygen, and the waste insulating oil containing PCBs fed into the incinerators was composed of carbon and hydrogen. The carbon can form the graphitic layer on black carbon in the furnace, which can form the aromatic compounds in the post-combustion zone. In or after the post-combustion zone the aromatic compounds can react with oxygen and hydrogen into dioxin or furan. The low-heating value (LHV) of waste fed into incinerator A was 5276-5834 kcal/kg but the LHV of waste fed into incinerator B was 3451-3783 kcal/kg (solid waste) and 3051-4899 kcal/kg (liquid waste). The LHV and sort of hazardous waste fed into incinerator B was lower than that of waste fed into incinerator A. The LHV of waste insulating oil fed into the incinerators was 10331-10985 kcal/kg. The LHV of waste insulating oil was above 2 times more than that of hazardous waste. The heating value can affect incineration conditions.

(2) Test condition (TC) and PCBs concentration in waste insulating oil

Three different conditions were tested in this study. In the first condition only hazardous waste was incinerated, marked as TC0. In the second and third conditions hazardous waste was co-incinerated with waste insulating oil containing PCBs. The PCBs concentration of waste insulation oil fed into an incinerator were under 50 mg kg^{-1} (marked as TC1) and above 150 mg kg^{-1} (marked as TC2). In each test condition the PCDDs/Fs and PCBs concentrations of the flue gases emitted from incinerations were measured to investigate the influence of PCBs during incineration of waste insulating oil containing PCBs.

(3) Sampling and analysis methods

The flue gases were sampled and analyzed according to ES10905.1, ES10908.1 and ES10909.1 in the Korean Standard Testing Method (KSTM) for the POPs. The flue gases were taken three times in each point and analyzed separately. To analyze PCDDs/Fs, 2 ng of $^{13}\text{C}_{12}$ -PCDDs/Fs (15 kinds of $^{13}\text{C}_{12}$ -PCDDs/Fs) was added to the samples as internal standards prior to clean-up. The dichloromethane extract was cleaned up with sulfuric acid, followed by the multi-silica gel column (10-mm ID) cleanup eluting 150 ml of n-hexane, and the alumina column (10-mm ID) cleanup eluting 150 ml of n-hexane (this portion was discarded) and 150 ml of 50 % dichloromethane in n-hexane. The final eluate was concentrated to a volume of 1 ml, and after spiking of recovery standards (2 kinds of $^{13}\text{C}_{12}$ -PCDDs/Fs) further concentrated to about 25 μl . The concentrated eluate was separately analyzed by high-resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS) for PCDDs/Fs. The column equipped on HRGC was SP-2331, which has high polarity. To analyze PCBs, 2 ng of $^{13}\text{C}_{12}$ -PCBs as internal standards (27 kinds of $^{13}\text{C}_{12}$ -PCBs), was added to the samples prior to clean-up. The dichloromethane extract was cleaned up with sulfuric acid, followed by the multi-silica gel column (10-mm ID) cleanup eluting 150 ml of n-hexane. The final eluate was concentrated to a volume of 1 ml, and after spiking of recovery standards (5 kinds of $^{13}\text{C}_{12}$ -PCBs) further concentrated to about 25 μl . The concentrated eluate was also separately analyzed by HRGC/HRMS equipped with the non-polarity column, DB-5MS.

3. Results and Discussion

(1) PCDDs/Fs and PCBs concentrations of flue gases in tested incinerators

For incinerator A, PCDDs/Fs concentrations from post-combustion, WHB, SDR and the stack were 16.654-44.861, 182.297-508.811, 29.863-304.401 and 26.153-32.897 ng/Sm^3 , respectively, and PCBs concentrations from post-combustion, WHB, SDR and the stack were 76.301-88.231, 252.838-352.274, 49.964-301.751 and 6.799-13.208 ng/Sm^3 , respectively. Generally, it is known that PCDDs/Fs and PCBs are destroyed in furnace, but formed in the cooling system and removed in APCDs in a waste incinerator. PCDDs/Fs and PCBs in incinerator is thought to be formed mostly by re-synthesis (called *de novo* synthesis), known to occur in the temperature window between 250°C and 400°C on the surface of fly ash in the post-combustion or cooling zones. The temperature in WHB of this incinerator, which was under 641°C and above 255°C , was suitable to form PCDDs/Fs and PCBs. In post-combustion at the temperature of 617 - 641°C , black carbon and aromatic compounds (such as phenol, benzene and biphenyl) could be formed and react with oxygen and hydrogen into dioxin/furan and react with chlorine into PCDDs/Fs or PCBs. Although PCDDs/Fs and PCBs were removed by 86-95% and over 96%, respectively. PCDDs/Fs and PCBs concentrations from the stack were high, because large amounts of PCDDs/Fs and PCBs were formed in WHB, and also it can be estimated that the BF installed in this incinerator was not good enough to remove PCDDs/Fs and PCBs. **For incinerator B**, PCDDs/Fs concentrations from post-combustion, WHB, CT, BF and the stack were 2.527-3.776, 4.193-17.840, 5.447-7.382, 0.190-0.295 and 0.273-0.370 ng/Sm^3 , respectively, and PCBs concentrations from post-combustion, WHB, CT, BF and the stack were 41.707-148.421, 27.869-527.331, 6.957-24.417, 6.643-18.952 and 1.697-4.676 ng/Sm^3 , respectively. PCDDs/Fs and PCBs concentrations from post-combustion were lower than those from WHB or CT. After post-combustion, PCDDs/Fs and PCBs were formed in the cooling system such as WHB and CT. The temperature in WHB was a little high to form PCDDs/Fs and PCBs, and the temperature after CT was a little low to form PCDDs/Fs and PCBs. The suitable zone to form PCDDs/Fs and PCBs was after WHB and in CT. But the *de novo* synthesis could not occur easily in this zone, because the flue gas going into CT from WHB was rapidly cooled with spray water in CT and the fly ash, going into CT from WHB comes down rapidly with spray water in CT. PCDDs/Fs concentrations from the stack were higher than those from BF because of WSs installed after BF. Generally, it is known that PCDDs/Fs were enriched in WS owing to memory effect. However, PCBs

concentrations from the stack were lower than those from BF. It could be estimated that the memory effect in WSSs was more effective work in PCDDs/Fs than in PCBs.

(2) Influence of waste insulating oil containing PCBs fed into the incinerators on PCDDs/Fs and PCBs concentrations emitted from the incinerators

For incinerator A, the temperature of flue gases from post-combustion, WHB, SDR and the stack was not significantly changed according to the test conditions. However, PCDDs/Fs and PCBs concentrations of flue gases in TC0 were higher than those in TC1 or TC2. It could be guessed that the high heating value of waste insulating oil containing PCBs could make better combustion conditions to inhibit the factors (such as soot and aromatic compounds) that form PCDDs/Fs and PCBs in TC1 and TC2 than in TC0. The better combustion condition could form the incomplete combustion substances in furnace, which react with oxygen into dioxin/furan and react with chlorine into PCDDs/Fs or PCBs in post-combustion and WHB. Furthermore, the reduction of inhomogeneous hazardous waste fed into an incinerator could inhibit the factors that produce PCDDs/Fs and PCBs. Through the ignition loss of bottom ash the combustion condition in furnace could be evaluated. The ignition loss of bottom ashes were 3.19-4.67 (3.92_{avg}) w% in TC0, 2.31-3.10 (2.67_{avg}) w% in TC1 and 1.27-2.07 (1.67_{avg}) w% in TC2, respectively. Generally, it is known that if the waste is well combusted in the furnace, the ignition loss of bottom ash is lower. The ignition loss of bottom ashes in TC0 was higher than that in TC1 and TC2. It means that in TC1 and TC2 the combustion condition in furnace was better than at TC0. **For the incinerator B**, the temperature of flue gases from post-combustion, WHB, SDR and the stack was not significantly changed according to the test condition, like as incinerator A. PCDDs/Fs concentrations of flue gases did not show any trend according to the test conditions in this incinerator. PCDDs/Fs concentrations of flue gases from post-combustion, BF and the stack in TC1 were higher than those in TC0 or TC2. And PCDDs/Fs concentrations of flue gases from WHB and CT in TC0 were higher than that in TC1 or TC2. Like in incinerator A, the high heating value of waste insulating oil containing PCBs and the reduction of inhomogeneous hazardous waste fed into an incinerator could inhibit the factors that form PCDDs/Fs and PCBs. However, compared with incinerators A and B, those effects could not be more effective in incinerator B than in incinerator A, because the amount of waste insulating oil containing PCBs fed into the incinerator B was 50% of the amount of waste insulating oil containing PCBs fed into the incinerator A. Nevertheless, PCBs concentrations of flue gases in TC0 were higher than those in TC1 or TC2. It means that formation condition of PCDDs/Fs and PCBs should be a little different in this incinerator, unlike in incinerator A. Through the ignition loss of bottom ash the combustion condition in furnace could be estimated. The ignition loss of bottom ashes were 4.77-4.94 (4.85_{avg}) w% in TC0, 2.06-2.74 (2.47_{avg}) w% in TC1 and 3.04-3.79 (3.43_{avg}) w% in TC2, respectively. The ignition loss of bottom ashes at TC0 was higher than that in TC1 and TC2. It means that in TC1 and TC2 the combustion condition in furnace was better than in TC0.

From the results, it could be known that the PCBs concentration in waste insulating oil fed into an incinerator affects not PCDDs/Fs and PCBs concentrations of flue gases from an incinerator and the waste insulating oil fed into an incinerator affects the incinerated waste and incineration condition in furnace, which can form the factors that form PCDDs/Fs and PCBs in post-combustion and cooling system. Generally, the PCDDs/Fs and PCBs concentrations emitted from an incinerator can be dependent on types and amounts of incinerated waste, temperature conditions in the furnace and cooling system, and operating condition and configuration of APCDs. In this study, the PCDDs/Fs and PCBs concentration of flue gases formed in WHB were very different according to the tested conditions, but the removal efficiency of APCDs for PCDDs/Fs and PCBs of flue gases in each incinerator were similar at all test conditions.

Therefore, it was estimated that PCDDs/Fs and PCBs concentrations of the flue gases in an incinerator was dependent on the types and amounts of incinerated waste, and the types and amounts of incinerated waste could influence the incineration conditions of an incinerator, such as temperature conditions in the furnace and cooling system. Finally, the affected temperature conditions in furnace and cooling system could influence PCDDs/Fs and PCBs concentrations of flue gases in an incinerator.

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