Applications of Electron Beam to Environmental Conservation

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Abstract: The treatment of electron beam was tested for gaseous pollutants of volatile organic compounds (VOCs), dioxin, and inorganic oxides (NO_X and SO_X). The representative VOCs of xylene and toluene were oxidized completely with electron beams using prototype hybrid system equipped with electron accelerator and MnO_2 catalysts. More than 90% of dioxin in municipal solid waste incinerator gases was decomposed at a dose of 14 kGy. Nitrogen oxides and sulfur oxides in coal-fired flue gases were recovered as a fertilizer by the addition of NH_3 under electron-beam irradiation. Electron beam is expected to be a promising method for treating gaseous pollutants.

Keywords: *Electron Beam, Volatile Organic Compounds, Dioxin, NO_X, SO_X*

1. INTRODUCTION

Electron-beam technology is based on oxidation reactions with active species produced by the irradiation to air. When air containing gaseous pollutants is irradiated with electron beams, many active species such as OH, O, and N_2^+ are produced [1,2]. Among these species, OH plays an important role in the oxidation of the pollutants. In the present study, volatile organic compounds (VOCs), dioxin, and nitrogen and sulfur oxides (NOx and SOx) was irradiated with electron beams to test treatment performance for environmental conservation.

2. Experimental

2-1 Decomposition of VOCs in Gases

The emission of VOCs to the environment causes photochemical oxidant formation, stratospheric ozone depletion and tropospheric ozone formation. Laboratory-scale experiments on electron-beam treatment were carried out using the 20 VOCs of aromatics, aliphatics, alicyclics, and others. Experimental setup is shown in Figure 1. The sample gases containing the VOCs were irradiated with electron beams using an electron accelerator supplied on 170 kV with a current of 10 mA. The concentrations of the VOCs were measured with a gas chromatograph. Qualitative analyses of decomposition products were conducted with an FT-IR having a gas cell. Total flow rate was 5 L/min.

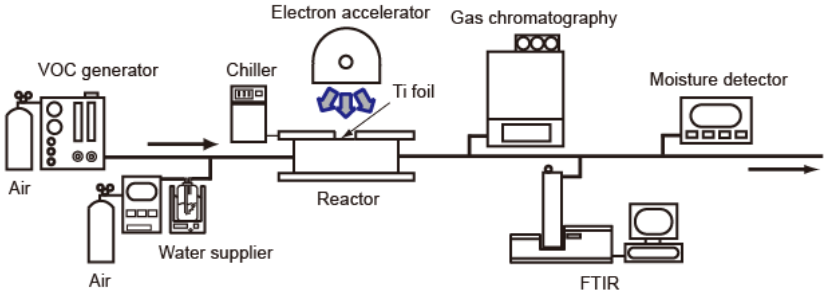

Figure 1. Experimental Setup for Electron-beam Treatment of VOCs.

2-2 Dioxin in Municipal Solid Waste Incinerator Gases

Approximately 80% of solid wastes have been incinerated in Japan. The incineration is the main source for the emission of dioxin. Dioxin can bind to a hormone receptor and cause a serious problem to the living organism. Dioxin involves polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzo-furans (PCDF), and polychlorinated biphenyls (PCBs). There are 75, 135, and 209 isomers of PCDDs, PCDFs, and PCBs, respectively. Because all the isomers don't show the same amount of risk, the toxic equivalent (TEQ) is used to evaluate their toxicity. The electron-beam treatment of dioxin from municipal solid waste incinerator was carried out at Takahama Clean Center in Japan. Figure 2 shows a schematic flow at the Takahama Center. An incinerator gas of 1000 m^3_N/h was diverted downstream of a dry electric precipitator and was irradiated with electron beams using an electron accelerator that supplied 300 kV with a maximum energy of 12 kW. The quantitative analyses of all the isomers were conducted with a HRGC/HRMS. It took about 7 days for the analyses.

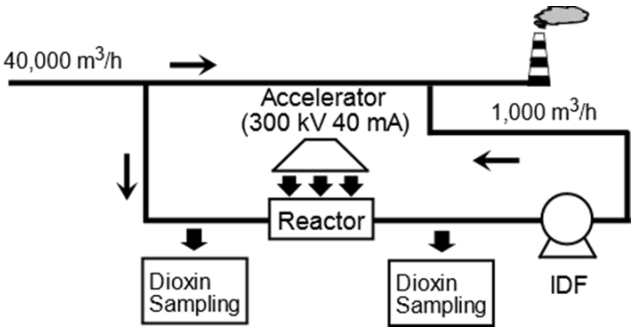

Figure 2. A Schematic Flow for Electron-beam Treatment of Dioxins.

2-3 NOx and SOx in Power Station Flue Gases

The emission of NOx and SOx) from coal-fired power stations causes photochemical smog and acid rain. Active species such as OH, O, and HO_2 produced under electron-beam irradiation oxidize the target chemicals of NOx and SOx in flue gases into nitric and sulfuric acids. Then, the acids react with ammonia added prior to the irradiation to produce ammonium sulfate and nitrate, which can be used as an agricultural fertilizer. A pilot plant was constructed at an actual thermal power station. A flue gas of 12,000 m^3/h was irradiated with electron beams using an electron accelerator suppled on 800 kV with current up to 135 mA as shown in Figure 3. Electron beam can simultaneously treat NOx and SOx in dry process.

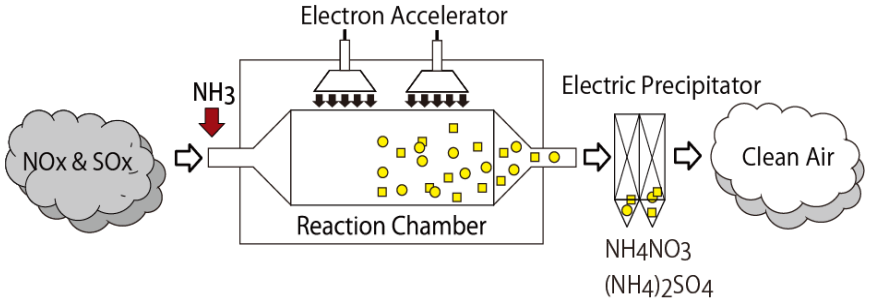

Figure 3. Pilot-plant Test for Electron-beam Treatment of NOx and SOx.

3. RESULTS & DISCUSSION

3-1 Decomposition of VOCs in Gases

The results of representative VOCs are shown in Figure 4. The concentrations of the VOCs decreased with a dose. More than 90% decomposition was obtained over 12 kGys. The G-values for the decomposition of the 20 VOCs were calculated from the initial slope of the decomposition profiles and plotted against logarithm of rate constant for reactions with OH. The straight lines in plots of $\log K_{OH}$ vs G were obtained from the results of aromatics, aliphatics, and alicyclics. This indicates that hydroxyl radicals are the predominant oxidants for the initial decomposition of the VOCs [3].

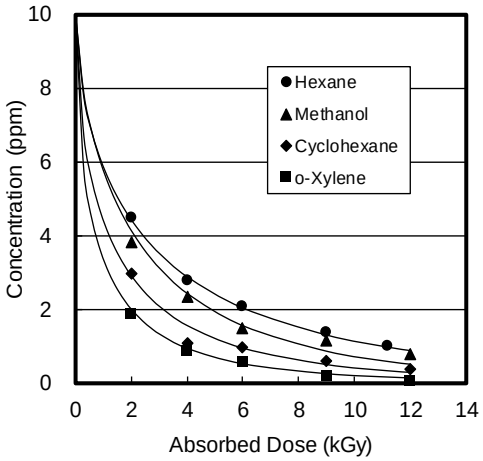

Figure 4. Concentration Change in Representative VOCs under Electron-beam Irradiation.

The oxidation through reactions with active species like OH radicals produces intermediates of gaseous and particle products. It's necessary to oxidize the intermediate completely because they still have an influence on the human body and the environment. Ozonolysis catalyst, MnO_2 is useful for further oxidation of the intermediates. Ozone produced by the irradiation of oxygen in gases is decomposed on the surface of MnO_2 to produce active oxygen. The intermediates can be oxidized completely into carbon dioxide by the active oxygen.

3-2 Decomposition of Dioxin in Municipal Solid Waste Incinerator Gases

Continuous 4-hour sampling of flue gases under the irradiation was required to obtain sufficient amount of dioxin for quantitative analyses. Although amount of PCDD/F in the flue gases depended on the contents of garbage and incineration condition, the concentrations of PCDD and PCDF were 0.22-0.88 and 0.35-1.24 ng-TEQ/m^3 respectively. The pilot-plant test showed that more than 90% of PCDD was decomposed at a dose of 12 kGy [4, 5], as shown in Figure 5. A dose of 16 kGy is required for 90% decomposition of PCDF. The data interpretation of the quantitative analyses showed that PCDD was mainly oxidized by the dissociation of ether and/or double bonds of PCDD after the addition of OH radicals. Dechlorination and dissociation occurred in the case of PCDF.

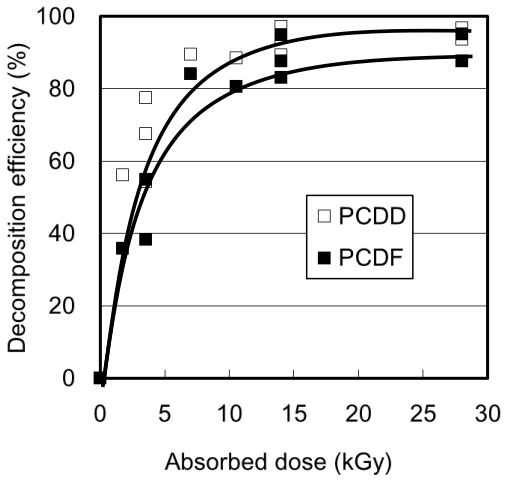

Figure 5. Decomposition of PCDD/FS in MSWI Gases with Electron Beams.

3-3 Removal of NOx and SOx in Power Station Flue Gases

Actual power station flue gases for the pilot-plant experiments contained 150-230 ppm NO_X and 650-950 ppm SO_2. Figure 6 shows removal efficiencies of NOx and SOx under the electron-beam irradiation. The removal of SOx increased by 15% when the temperature of the flue gas was lowered from 70 to 60℃. In the electron-beam treatment of NOx and SOx, SO_2 can directly react with NH_3 in the absence of the irradiation. This exothermic reaction improves removal efficiency of SOx at lower temperatures of flue gases. On the other hand, the change in NOx removal was within the error range at a temperature of 62-72℃ [6]. A dose energy of 11 kGy removed about 95% of SOx and 85% of NOx at a flue gas temperature of 70℃.

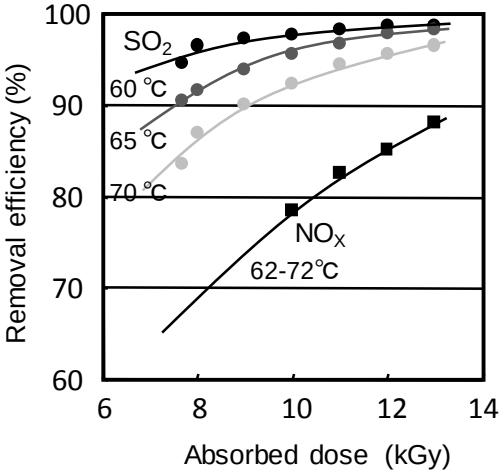

Figure 6. Removal of NOx and SOx in Flue Gases with Electron Beams.

4. CONCLUSION

The representative air pollutants of VOCs, dioxin, NOx, and SOx were treated with electron beams at laboratory and pilot-plant scale. The experiments demonstrated that electron beam can be a promising technology for the treatment of gaseous pollutants.

5. REFERENCES

1. H. Mätzing, in *Proceedings of an International Symposium on Applications of Isotopes and Radiation in Conservation of the Environment*, Karlsruche, Germany, IAEA-SM-325/186, 115-124 (1992).
2. C.Willis, A. W. Boyd, and M. J. Young, Radiolysis of air and nitrogen-oxygen mixtures with intense electron pulses: Determination of a mechanism by comparison of measured and computed yields. *Can. J. Chem.* ***48***, 1515-1525 (1970).
3. K. Hirota, H. Sakai, M. Washio, and T. Kojima, Application of electron beams for the treatment of VOC streams. *Ind. Eng. Chem. Res.* ***43***, 1185-1191 (2004).
4. K. Hirota, T. Hakoda, M. Taguchi, M. Takigami, H. Kim, and T. Kojima, Application of electron beam for the reduction of PCDD/F emission from municipal solid waste incinerators. *Environ. Sci. Technol.* ***37***, 3164-3170 (2003).
5. R. Atkinson, Estimation of OH radical reaction rate constants and atmospheric lifetimes for polychlorobiphenyls, dibenzo-*p*-dioxins, and dibenzofurans. *Environ. Sci. Technol.* ***21***, 305-307 (1987).
6. O. Tokunaga, Electron-beam technology for purification of flue gas. in *Environmental Application of Ionizing Radiation*, W. J. Cooper, R.D. Curry, and K.E. O'Shea, Eds. (Wiley, 1998) 99-112.