REMOVAL OF DIOXINS FROM FLY ASH BY A COMBINED PROCESS OF SUPERCRITICAL CO_2 EXTRACTION AND SUPERCRITICAL WATER OXIDATION

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Introduction

Removal of toxic substances such as dioxins and PCBs in the environmental matrices such as fly ash and soil is becoming important. The extraction of these toxic substances has been achieved conventionally by using organic solvent. In the analytical process, dioxins are leached from solid samples by toluene in a Soxhlet extractor. Supercritical fluid technology may be suitable for environmental application because of environmentally friendly solvent such as carbon dioxide or water. Supercritical water was applied as an extraction solvent or reaction media for oxidative decomposition. When supercritical water oxidation is applied directly to environmental samples, huge amount of solid materials must be supplied to high pressure and high temperature reactor. Thus the process could not be economically feasible.

We have been developing combined process of extraction with supercritical carbon dioxide, concentration by adsorption, and then destruction by supercritical water oxidation (SCWO). In the extraction – adsorption process, dioxins contained in solid samples can be transferred and concentrated into adsorbent. Then, the adsorbent containing dioxins is completely destructed by supercritical water oxidation. The process outline is shown in Figure 1. As a national project (NEDO/Energy Conservation Center) we have been developing the process for the treatment of fly ash or soil containing dioxins[1-3].

In this work, we studied the effects of pressure, temperature, time, and CO_2 flow rate in the sc-CO_2 extraction process of dioxins from fly ash. The destruction of dioxins in fly ash by supercritical water oxidation is also studied.

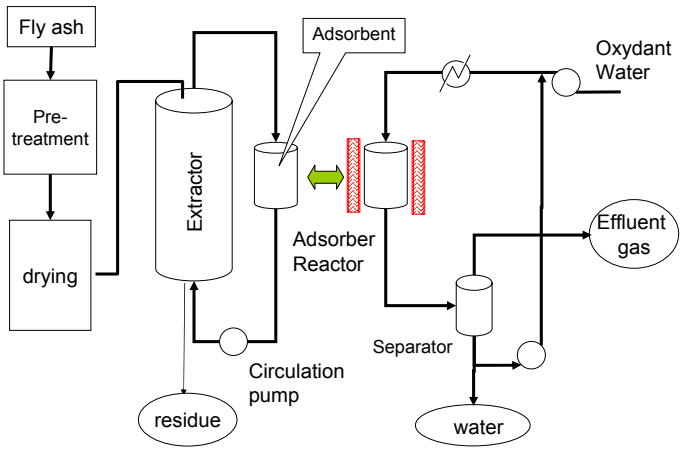

Figure 1. Combined process of sc-CO_2 extraction, adsorption, and SCWO for the treatment of fly ash.

Experiments

Fly ash samples were collected at the bottom of electric precipitator of municipal incinerator. The measured characteristic properties of fly ash samples are; solid density: 2.29g/cm^3, average particle size: 21.18x10^{-6}m, surface area: 8.36m^2/g, dioxins content: 3.00ng-TEQ/g. PCDD toxicity equivalent in the sample fly ash was shown in Figure 2.

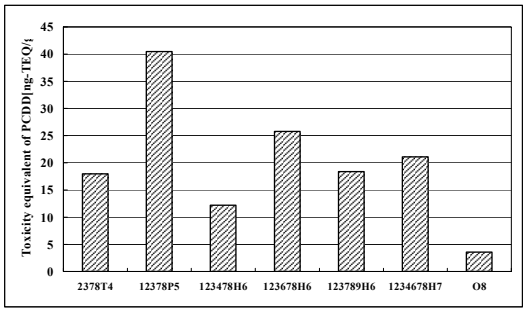

Figure 2. Toxicity of PCDD isomers in the sample fly ash.

The sample was treated in 2N-hydrochloric acids in order to remove alkaline component that covers the surface of the fly ash particle. After the washing, it was separated into solid and liquid in filtration with aspirator. Fly ash was dried overnight in an electric oven at 303K. As a result of acid treatment, the specific surface area increased about 10 times. Dioxins in fly ash were concentrated in the solid phase, and dioxins were not eluted into the liquid phase.

The apparatus for the extraction experiment is shown in Figure 3. Semi-batch flow extractor where samples were packed in the extractor vessel of 500 ml was used. The extracted dioxins were adsorbed onto activated carbon in an adsorber vessel.

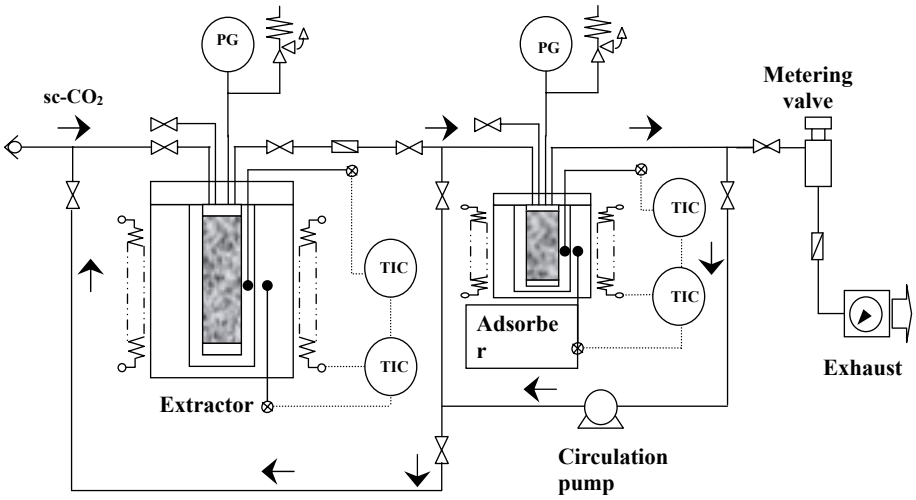

Figure 3. Experimental setup for $scCO_2$ extraction from fly ash.

For the destruction of dioxins adsorbed in activated carbon, we preliminary carried out the SCWO of dioxins in the fly ash. The experiment was carried out with a batch reactor of 9 ml in volume. The reactor charged with fly ash, water, and hydrogen peroxide was heated for a certain period of time and the product was analyzed.

Quantitative analysis of the extracted PCDDs and PCDFs was carried out at Sumika Chemical Analysis Service.

Results and Discussion

The extraction pressure was changed from 10 to 60 MPa. As shown in Figure 4, the extraction efficiency for PCDD isomers remarkably increased with the increase in pressure. At the pressure of 60 MPa, the extraction efficiency attained 99.8 %. Similar results were obtained for PCDFs and co-PCBs. The extraction efficiency for these isomers also reached over 99 %.

The average extraction efficiency based on TEQ reached over 90% when the pressure was higher than 40 MPa as shown in Figure 5. The efficiency attained over 99 % at the pressure of 60 MPa.

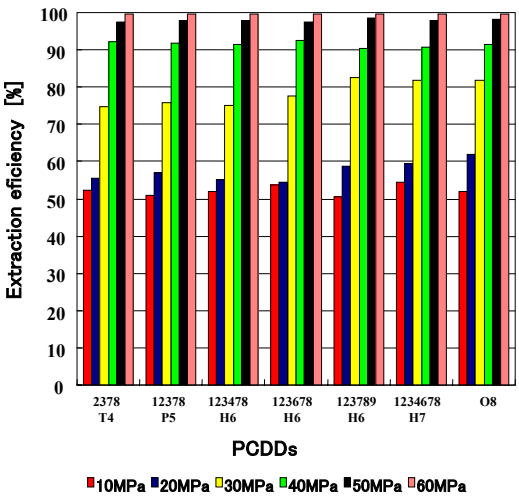

Figure 4. Effect of pressure on the extraction efficiency. (323 K (313K), time: 1-2 hr)

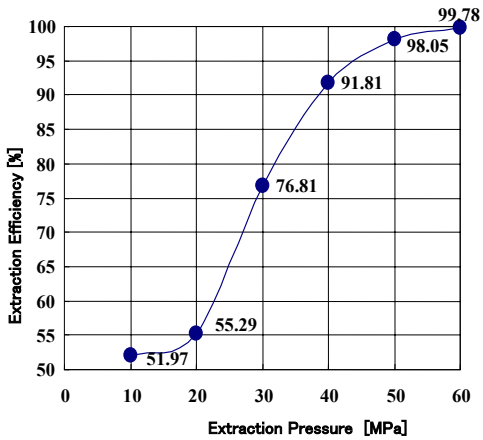

Figure 5. Effect of pressure on the extraction efficiency based on TEQ %.

The sc-SC_2 extraction was compared with Soxhlet extraction with toluene as a solvent. As shown in Figure 6, the extraction efficiency increased gradually with extraction time in case of the Soxhlet extraction. The extraction for 8 hr was required to attain the extraction efficiency over 95 %. On the other hand, the extraction efficiency of sc-CO_2 was independent of the extraction time when the extraction was carried out over 1 hr. The efficiency significantly depended on the extraction pressure. Then the pressure was 30 MPa, the efficiency did not improved more than 85 % even after 16 hr extraction. Therefore, sc-CO_2 extraction was relatively fast and the extraction efficiency reached certain value depending on the pressure.

To investigate the effect of entrainer, 10 % of methanol was added to CO_2. As shown in Figure 7, the entrainer improved the efficiency at lower pressure. When the pressure was 30 MPa, the efficiency considerably increased from 76.8 % to 88.9 %. However, there is no improvement at the pressure of 50 MPa.

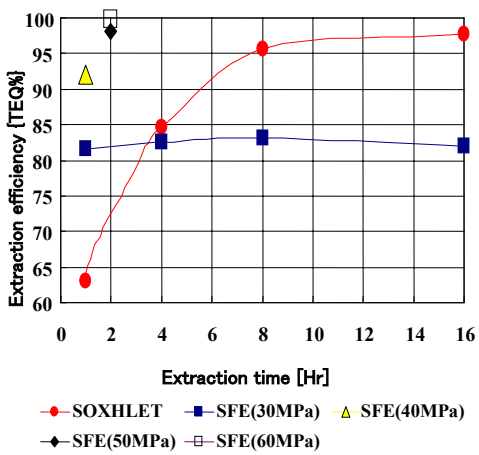

Figure 6. Comparison between sc-CO2 extraction and soxhlet extraction with toluene. (presssure: 30-60 MPa, temperature: 323, 313 K, Solvent flow rate: 5.0 ml/min)

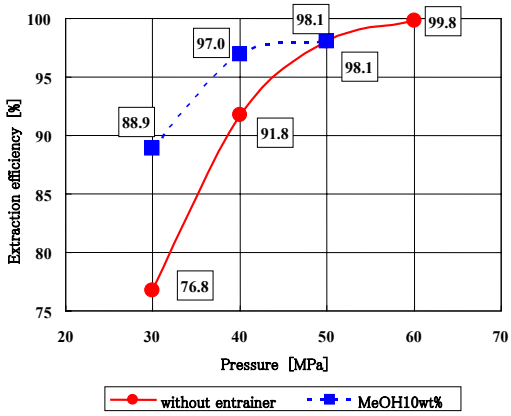

Figure 7. Effect of entrainer on the extraction efficiency.

Figure 8 shows the comparison of the extraction efficiency between sample without acid treatment and with acid treatment. When the fly ash was not treated by acid to remove surface alkaline compounds, the extraction efficiency was less than 40 % even at the pressure of 50 MPa. Since the acid treatment reduced the volume of fly ash one tenth to one twentieth of the original sample, the size of the extraction vessel can be reduced significantly. Therefore, the acid treatment is essential for the fly ash used in this work.

For the destruction of dioxins in fly ash, the effect of reaction temperature in SCWO was studied. At lower temperature, 400 C, dioxin isomers with low chlorine content which has higher TEQ coefficient remained after the reaction. Thus, the remaining amount based on TEQ is larger than those at 500 and 600 C. However, even at 400 C, the remaining amount was about 0.8 ng-TEQ/g, which is lower than low regulation (1 ng-TEQ/g). When the reaction temperature was higher than 500 C, almost no dioxins were remained unreacted.

Figure 9 shows the temperature dependence of destruction efficiency of dioxins in fly ash at 25 MPa. The destruction efficiency of dioxins was about 99 % at 400 C and over 99.99 % at the temperature higher than 500 C.

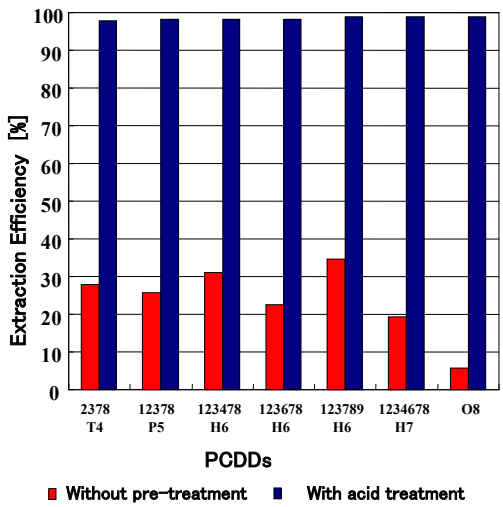

Figure 8. Effect of acid treatment on the extraction. (50MPa, 1-2 hr, 5.0ml/min, MeOH10%)

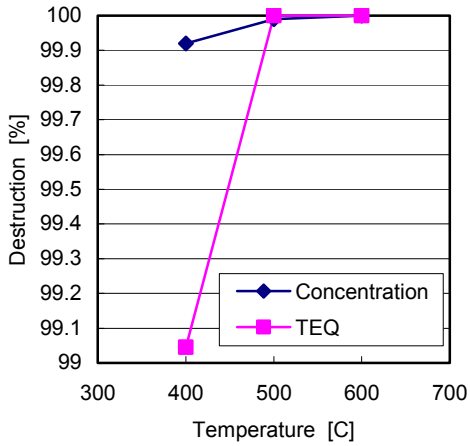

Figure 9. Destruction of dioxins in fly ash by SCWO.

Conclusion

For the extraction of dioxins from municipal incinerator fly ash using the sc-CO_2, the effect of each parameter was examined. With the increase in the extraction pressure, the extraction efficiency was remarkably improved. The extraction time was not influencial for sc-CO_2, whereas the extraction efficiency for Soxhlet extraction increased with time. This indicates that the extraction with sc-CO_2 is completed in less than 1 hr. Dioxins in fly ash or soil were almost completely destructed in SCWO.

Acknowledgemen

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References

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2. Kawajiri, S., Goto, M., and Hirose, T., Extraction of Dioxins from Municipal Incinerator Fly Ash with Supercritical CO2 in Comparison with Soxhlet Extraction, *Organohalogen Compounds*, **2000**, 45, 101-104
3. Kawajiri, S., Goto, M. and Hirose, T., Extraction of the Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Municipal Incinerator Fly Ash with Supercritical Carbon Dioxide, *Organohalogen Compounds*, **1999**, 40, 153-155