APPLICATION OF A CONTINUOUS PYROLYSIS SYSTEM FOR REMEDIATION OF SOIL CONTAMINATED WITH PCDD/Fs, PCP AND MERCURY

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Introduction

PCP (Pentachlorophenol) is one of important precursors leading to PCDD/F (polychlorinated dibenzo-*p*-dioxin and polychlorinated furan) formation. A facility located in Southern Taiwan started to produce PCP and Sodium Pentachlorophenate (Na-PCP) in 1969. Extremely high OCDD and PCP concentration in soil was found in this site in 1994. Furthermore, relatively high mercury concentration was also found in soil of this site. Between 1946 and 1966, chlor-alkali industry was located at this site and mercury cell electrolysis process was used to generate hydrochloric acid and liquid chlorine.[1] Great amount of mercury accidentally contaminated the soil of facility. Field investigation of PCDD/F- and mercury-contaminated soil conducted by Taiwan EPA and some researchers have been published.[2,3,4] However, the literature on simultaneous removal of PCDD/Fs and mercury in contaminated soil is rare.

PCDD/Fs can be destroyed with high-temperature combustion/incineration, however, gas-phase elemental mercury is difficult to remove from flue gas and may be significantly emitted from the system. By the way, PCDD/F congeners may be formed with the improper operation of APCDs (air pollution control devices) while the contaminated soil is thermally remediated.

For treating PCDD/F-contaminated soil, a pilot-scale continuous pyrolysis system is developed and tested in this study. Operating the system at a relatively high temperature can effectively degrade organic compounds and desorb mercury from contaminated soil. Therefore, the pyrolysis system which can simultaneously remove organic compounds and mercury and remediation of contaminated soil is successfully developed.

Materials and methods

Figure 1 shows the scheme of the continuous pyrolysis and Hg recovery system. Contaminated soil is fed into the pyrolysis system from the stock container, and remediated soil is discharged and collected by remediated soil container. Nitrogen (N_2) as carrier gas is introduced into the system for achieving an oxygen-deficient condition. In this study, the continuous pyrolysis system is tested with the operating temperature of 600°C, 700°C and 760°C, respectively. After pyrolysis system, gas streams containing high concentrations of Hg and fine dust are generated. Therefore, the process of filtration, high performance quench system and multi-layer adsorption bed are put together as air pollution control devices (APCDs) to reduce the emission of toxic substances, including Hg, PCP and PCDD/Fs.

For better understand of the contaminant distribution in the whole system and removal efficiencies of contaminants achieved with APCDs, 6 sampling points are selected, i.e. at pyrolysis system outlet (Point A), filtration outlet (Point B), quench tower outlet (Point C) and each layer outlet of multi-layer adsorption bed with bead-shape activated carbon (Point D, E, F).

USEPA Method 23 is adopted for sampling andanalysis of PCDD/Fs via HRGC/HRMS (Thermo Trace GC / DFS, DB-5ms with 60 m * 0.25 mm * 0.25 μm). For PCP sampling and analysis, USEAP Method 8270C "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry" is applied in this study. Furthermore, USEPA Method 101A "Determination of Particulate and Gaseous Mercury Emission from Sewage Incinerators" is used for collection and analysis of mercury samples.

Results and discussion

The soil investigated in this study is contaminated by PCP, OCDD and mercury with the concentrations of 8,795 μg/kg (N=3), 86,715 ng-TEQ/kg (N=3) and 548 mg/kg (N=3), respectively. OCDD and mercury concentrations in contaminated soil are significantly higher than the regulatory limits of PCDD/Fs (1,000 ng-TEQ/kg) and mercury (20 mg/kg) in Taiwan. Table 1 shows PCP, PCDD/F and mercury concentrations in soil after pyrolysis treatment. The results indicate that operating the system at 3 temperatures adopted in this study can effectively remove contaminants from soil and PCDD/F and mercury concentrations in remediated soil are lower than the regulatory limits of soil. PCDD/F concentrations decreased with increasing operating temperature, while mercury concentrations in remediated soils vary differently with pyrolysis temperatures.

However, significantly high concentrations of PCDD/F and mercury are found in the outlet of pyrolysis system. Table 2 shows PCDD/F and mercury concentrations at different sampling points. At pyrolysis system outlet, PCDD/F concentrations of the gas streams are between 298 and 569 ng-TEQ/Nm^3. Interestingly, PCDD/F concentrations at sampling point A decreased with increasing operating temperature. It may be attributed to the fact that PCDD/Fs can be destroyed in pyrolysis system. However, effective pollutant removal is still needed since relatively high PCDD/F and Hg concentrations are found in gas streams after pyrolysis system.

Figures 2 and 3 show the removal efficiencies of PCDD/Fs and mercury achieved with different control devices. PCDD/F removal efficiencies achieved with filtration are between 57.2% and 62.1%. Particle concentration is effectively reduced from 484±27 mg/Nm^3 to less than 3 mg/Nm^3 via filtration. Although removal efficiency of particle is higher than 99%, relatively low PCDD/F removal efficiencies are achieved with filtration since most PCDD/Fs (higher than 63%) exist in gas phase. PCDD/F removal efficiencies achieved with the quench tower are between 35.2% and 47.4%. PCDD/F concentrations in gas stream of quench tower outlet (sampling point C) are between 65 and 158 ng-TEQ/Nm^3 and significantly higher than the emission standards (0.5 ng-TEQ/Nm^3 for stationary sources in Taiwan). Multi-layer adsorption bed with bead-shape activated carbon has been proved for effective PCDD/F removal.[5,6] A three-layer adsorption bed is applied in this study and PCDD/F removal efficiency achieved with each adsorption layer is between 87.4% and 97.6%. Total TEQ removal efficiency via multi-layer adsorption system is higher than 99.9% and PCDD/F emissions are effectively reduced to the level between 0.005 and 0.03 ng-TEQ/Nm^3.

As for mercury removal, low removal efficiencies (3.8% ~ 5.4%) are achieved with filtration since significantly higher gaseous mercury concentrations (1,216 ~ 1,283 mg/Nm^3) are measured compared with solid-phase mercury (51.4 ~ 70.9 mg/Nm^3) at sampling point A. The boiling point of the elemental mercury is 357^{o}C. For effectively recovering mercury, operating temperature of quench tower is set between 0 and 3^{o}C. Therefore, significant mercury recovery (higher than 91%) is achieved, but the mercury concentrations in gas stream of quench tower outlet are between 92.5 and 109 mg/Nm^3, which are significantly higher than the mercury emission standard (0.05 mg/Nm^3). Multi-layer adsorption bed is evaluated for its effectiveness in removing mercury. The results indicate that mercury adsorption efficiency achieved by each layer is higher than 82.7% and 99.9% of overall mercury removal efficiency is achieved with multi-layer adsorption system. The results indicate that mercury emission concentration can be decreased to lower than 0.05 mg/Nm^3 with the operation of a three-layer AC adsorption system.

Compared with PCDD/Fs, PCP destruction with high temperature is relatively easy and the removal efficiency of PCP in contaminated soil is higher than 99.9%. Although, PCP concentration at sampling point A is relatively high (2000 – 3680 ng/Nm^3), PCP emission concentration can be reduced to the level lower than 3 ng/Nm^3 with the proper operation of APCDs.

Based on the results of this study, PCDD/Fs (especially OCDD) and mercury in contaminated soil can be effectively removed via the continuous pyrolysis system developed. PCDD/F and mercury concentrations in remediated soil are lower than the regulatory limits of PCDD/Fs (1000 ng-TEQ/kg) and mercury (20 mg/kg). For gas streams, particulate matter, PCDD/F congeners and mercury can be effectively removed by the combination of filtration, quench tower and multi-layer adsorption beds. Hence, a total solution for remediation of the soil simultaneously contaminated with PCDD/Fs, PCP and mercury is successfully developed via the integration of a continuous pyrolysis system and effective APCDs.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the National Science Council (NSC95-2221-E-008-051-MY3 and NSC98-221-E-008-019-MY3) and Soil and Groundwater Pollution Remediation Fund Management Board of EPA in the Republic of China.

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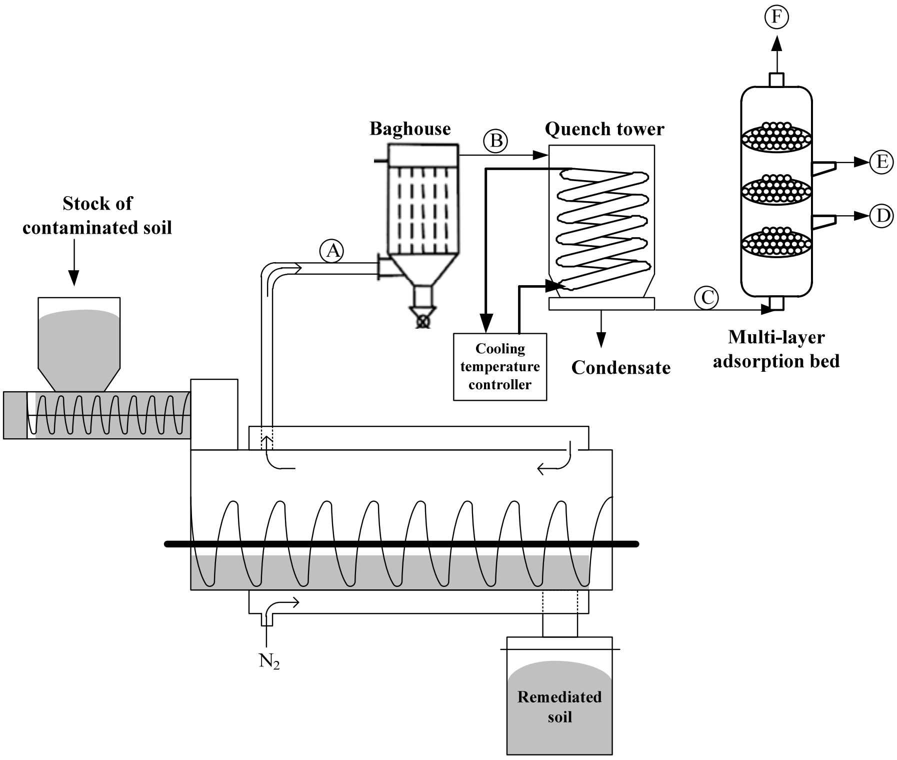

Figure 1. Schematic diagram of the continuous pyrolysis and mercury recovery system

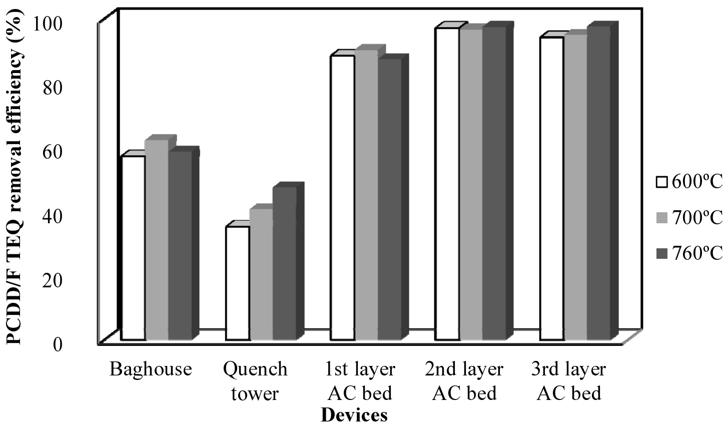

Figure 2. Removal efficiencies of PCDD/Fs achieved with different control devices at three operating temperatures

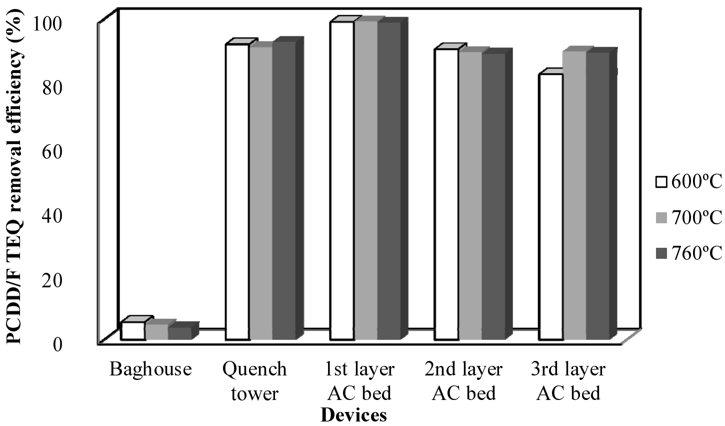

Figure 3. Recovery efficiencies of mercury achieved with different control devices at three operating temperatures

Table 1. PCP, PCDD/F and mercury in soil after pyrolysis

Operating temperature (°C)		PCP (µg/kg)	PCDD/Fs (ng-TEQ/kg)	Mercury (mg/kg)
Raw soil		8,800	86,700	548
Remediated soil	600	7.62	656	9.62
	700	0.84	542	11.2
	760	1.02	481	6.37
Regulatory limits of soil		-	1,000	20.0

Table 2. Pollutant concentrations in gas streams at different sampling points and operating temperatures

Operating temperature (°C)		PCDD/Fs (ng-TEQ/Nm^3)			Mercury (µg/Nm^3)		
		600	700	760	600	700	760
Sampling points	A	569	475	298	1.29×10^6	1.29×10^6	1.33×10^6
	B	244	180	124	1.22×10^6	1.23×10^6	1.28×10^6
	C	158	107	65.0	9.68×10^4	1.09×10^5	9.25×10^4
	D	18.2	10.4	8.21	953	921	1,070
	E	0.532	0.354	0.214	90.2	95.6	116
	F	0.0310	0.0180	0.00520	15.6	9.75	12.3