

Removal of PCDD/Fs and PCBs from sediment by oxygen free pyrolysis

HU Zhan-bo^{1,3}, Saman Wijesekara R.G.², Ronald R. Navarro², WU De-yi¹, ZHANG Da-lei¹, Masatoshi Matsumura², KONG Hai-nan^{1,*}

(1. School of Environmental Science and Engineering, Shanghai Jiaotong University, Shanghai 200240, China. E-mail: hnkong@sjtu.edu.cn; 2. Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba-shi 305-8572, Japan; 3. Guangxi University, Nanning 530004, China)

Abstract: Few studies have dealt on the evaluation of volatilization and decomposition reactions of dioxins from sediment by oxygen free pyrolysis. In this study, the performance of pyrolysis on the removal of dioxins from sediment was investigated. Dioxin concentrations of the raw sediment and the solid residues after pyrolysis were analyzed at different conditions. Results showed a removal efficiency of 99.9999% for total dioxins at 800°C and retention time of 30 min. All the polychlorinated dibenzo-furans (PCDFs) have been removed and were not formed in the solid residues at the retention time range of 30–90 min at 800°C. Close to 100% removal of polychlorinated dibenzo-*p*-dioxins (PCDDs) was also achieved. Only trace PCDDs were detected in the solid yields at a retention time of 60 min. The highest removal efficiency of polychlorinated biphenyls (PCBs) was more than 99.9994% at a retention time of 30 min. During cooling period following pyrolysis, however, the concentration of total dioxins in solid residues increased 130 times as compared to that of the raw sediment under air atmosphere. This confirmed that some complex reactions do occur to form PCDD/Fs and PCBs from 800 to 400°C in the presence of oxygen. Oxygen-free atmosphere therefore can prevent formation of dioxin during thermal process thus generating clean solid residues.

Keywords: dioxins; pyrolysis; oxygen free; sediment; PCBs

Introduction

Large quantities of dioxin-contaminated sediments have been found in many rivers, harbours and estuaries in China and around the world and these has remained a significant problem (Sun *et al.*, 2005; Okumura *et al.*, 2004; Paul *et al.*, 2005). These contaminated sediments pose direct toxic effects on aquatic life as well as contribute indirect risk to humans through the bioaccumulation of toxic contaminants in the food chain (Rausa *et al.*, 1999; Neigh *et al.*, 2006). In order to reduce the amount of sediment wastes as well as convert these into recyclable materials, the toxic substances of the sediment should be removed or made more chemically stable. A great deal of work has been undertaken by researchers to develop treatment systems for polychlorinated dibenzo-*p*-dioxins (PCDDs) or polychlorinated dibenzo-furans (PCDFs) and polychlorinated biphenyls (PCBs) from sediments. These methods include mechanical, physical, biological, chemical and thermal processes (Kenna *et al.*, 1996; Rausa *et al.*, 1999).

Thermal technologies such as incineration and pyrolysis (Malkow, 2004; Calaminus *et al.*, 1997), which volatilize or destroy the organic contaminants, are the preferred methods for municipal solid waste (MSW) treatment and disposal. Among these, incineration is the most common method applied to deal with the increasing production of MSW throughout the world (Ferreira *et al.*, 2003). In conventional incineration, partial decomposition or complete destruction of the pollutants in the presence

of oxygen are achieved at a temperature range of 650 to 1200°C (Tetra Tech, 1994). However, in the presence of C, H, O and Cl, incineration can yield some PCDD/Fs under suitable conditions of time and temperature (Altwicker, 1991; Altwicker *et al.*, 1994). The biggest challenge for incineration remains on the transfer of pollution from the waste to the air, which result in more serious environmental problems. Although in the oxygen atmosphere, the PCDD/Fs content is decreased when temperature is increased (Kakuta *et al.*, 2005), however, regeneration of PCDD/Fs has also been found in oxygen-containing atmosphere during treatment of MSW fly ash by combustion (Chang and Huang, 2000; Benfenati *et al.*, 1991). Incinerations can also emit harmful pollutants (SO_x, HCl, HF, NO_x, etc.) and toxic volatile organic compounds (VOCs) especially polyaromatic hydrocarbons (PAHs), PCBs and PCDD/Fs. VOCs in particular have gained more attention due to the fact that some are carcinogenic (Malkow, 2004; Ferreira *et al.*, 2003; Benfenati *et al.*, 1991; Griffin, 1986; Morselli *et al.*, 1992). As the legislation for dioxins emissions from MSW is now becoming strict in many countries, the development of new environmentally sound technology for treatment of dioxin-contaminated sediments is necessary.

In recent years, pyrolysis had been considered as an alternative to the existing waste incineration technology for disposing and recycling waste (Yoshiyuki and Yutaka, 2003; Zhou and Yang, 2004). However, the competitiveness of pyrolysis with waste incineration has to be proven (Weber and Sakurai, 2001). MSW pyrolysis is different from incineration

due to the absence of O₂ (Khiari *et al.*, 2004). Hence, it is very effective in preventing PCDD/Fs formation (Malkow, 2004; Calaminus *et al.*, 1997; Ferreira *et al.*, 2003).

Despite the great deal of research and investigation about the occurrence of dioxins in incineration of MSW, less information is available regarding the dioxins formation during pyrolysis processes. Especially, there is limited literature concerning the behavior of dioxins during cooling down period of pyrolysis treatment for contaminated dredged sediment. Now we have developed a pilot scale system of oxygen free pyrolyzer for treating the dioxins contaminated sediment. This paper presents the results of preliminary studies on a lab scale pyrolysis of sediments. The main objective of the paper was to obtain detailed information on the fate of dioxins during such thermal treatment and to find significant information that can be applied in the large scale operation of a pilot scale pyrolyzer.

1 Materials and methods

1.1 Sediment samples and pyrolysis process

Dioxin-contaminated sediment was obtained from Tagonoura Harbor, Japan. All the samples were air dried and then pulverized to achieve homogenized size distribution prior to use.

A special horizontal lab-scale pyrolyzer was designed and used for pyrolysis experiments (Fig.1). The pyrolysis chamber is made up of quartz tube (i.d. internal diameter = 15 cm, length = 50 cm). The quartz tube was housed within a three-zone electrically heated furnace with a programmable temperature controller. Temperature profiles were obtained using a thermocouple positioned at the center of reactor.

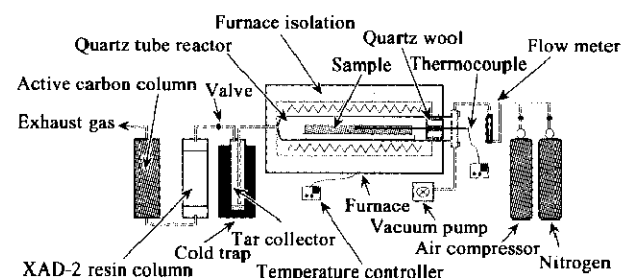


Fig.1 Schematic diagram of the pyrolysis system

Nitrogen gas was allowed to flow into the furnace tube to maintain non-oxidative conditions during the entire pyrolysis process. The flow rate of nitrogen gas was fixed at 1000 ml/min. This flow rate was considered sufficient to prevent the accumulation of pyrolysis gas generated in the tube furnace and at the same time not to affect the temperature of the surface of sediment sample. The gases generated by the pyrolysis reaction were allowed to pass through a cold trap to collect tar condensates. The uncondensed gases

were then passed through a XAD-2 resin column where the dioxin compounds were absorbed. A final column containing activated carbon was installed for the cleanup of remaining exit gas prior to its release to the atmosphere.

The quartz tube reactor was heated at a constant heating rate of 10°C/min to a desired pyrolysis temperature and maintained at this temperature for various retention times of 30, 60 and 90 min. Thermocouple readings showed that the sample reached a desired temperature according to the programmed value. After each run, the furnace was turned off and the reactor was allowed to cool down at N₂ gas or air atmosphere to room temperature. The cooled samples were collected, weighed and subjected to chemical analysis.

1.2 Thermal analysis

Thermal analysis (TG-DTG) experiments were performed with a TG/DTA-6300 analyzer (Seiko Instruments Inc., USA). Approximately 20 mg of sample was placed in an open platinum holder. Each TG-DTG run was carried out up to 900°C at a heating rate of 10°C/min in inert atmosphere (400 ml/min of Ar). The thermogravimetric weight loss curve (TG, wt %) and the weight loss derivative curve (Derivative Thermo-Gravimetry (DTG), µg/min) were recorded as a function of temperature.

1.3 Dioxin analysis methods

Quantitative analysis of PCDD/Fs and PCBs were performed for solid residues at each run. Reference standards, which were ¹³C₁₂-2,3,7,8-TCDD-OCDD, ¹³C₁₂-2,3,7,8-TCDF-OCDF, ¹³C₁₂-TCB-HCB, ¹³C₁₂-2,3,4,5-TeCB, ¹³C₁₂-1,2,7,8-TeCDF and ¹³C₁₂-1,2,3,4,6,8,9-HpCDF congener standards solution, were obtained from Wellington Laboratories (Ontario, Canada).

Analysis of PCDD/Fs and PCBs were performed using an HRGC (TRACE GC 2000, ThermoQuest Co., USA)/HRMS (Finnigan MAT 95XL, Thermo Quest Co., USA) with selected ion monitoring (SIM) mode. HRMS was operated in electron impact ionization mode at a resolution of $R \geq 10000$ (10% valley).

A gas chromatograph equipped with a capillary column RH-12ms (60 m × 0.25 mm, Inventx Co., USA) and a mass spectrometric detector was used. The conditions were as follows: injector temperature at 280°C, interface temperature at 280°C, injection volume: 1 µl. Helium at a column head pressure of 175 kPa was used as the carrier gas. The temperature program for the GC oven was as follows:

For analysis of PCDD/Fs containing 4–8 chlorine: initial oven temperature at 130°C for 1.0 min, heating to 210°C at 15°C/min, then to 310°C at 3°C/min, then to 320°C at 5°C/min with a final holding time of 3 min.

For analysis of 2, 3, 4, 7, 8-PeCDF, 2, 3, 4, 6, 7, 8-HxCDF, 1, 2, 3, 7, 8, 9-HxCDF and PeCDFs: injector temperature at 280°C, interface temperature at 280°C, initial oven temperature at 130°C for 1.0 min, heating to 210°C at 15°C/min, then to 310°C at 3°C/min, then to 320°C at 5°C/min with a final holding time of 12 min.

For analysis coplanar-PCB: initial oven temperature at 130°C for 1.0 min, heating to 210°C at 15°C/min, then to 310°C at 3°C/min.

The mass spectrometric detector conditions were as follows: ion source: EI, positive; resolution: $R \geq 10000$ (10% valley); ion source temperature : 260°C.

2 Results and discussion

2.1 TG-DTG analysis of sediments

To evaluate the temperature suitable for sediment pyrolysis, thermo-gravimetry (TG) and derivative thermo-gravimetry (DTG) experiments were initially conducted. Data from TG analysis is essential in evaluating mass reductions at a wide range of temperature so that optimum temperature for maximum removal of sediment components may be established.

TG-DTG curves for Tagonoura Harbor sediment are shown in Fig.2. Main and minor peaks in the DTG curve (reaction rates) were observed at around 250–600°C and 750–780°C, respectively. Such peaks, which are related to mass reductions, may indicate volatilization as well as decomposition reactions of inorganic and organic compounds presented in the sediment. Also, from a previous study on the thermal treatment for contaminated soil, temperatures ranging from 500–600°C were found sufficient to obtain removal efficiencies of more than 99% for organic contaminants (Rienks, 1998). Although the Tagonoura Harbor sediment also displayed more or less similar temperature range for maximum mass reductions, subsequent pyrolysis experiments were conducted at a temperature of 800°C to assure the complete removal of all the organics.

2.2 Fate of dioxins in sediment before and after oxygen free pyrolysis

The removal efficiencies of PCDDs, PCDFs and dioxin-like PCBs in oxygen-free pyrolysis experiments were compared over the retention time range of 30, 60 and 90 min at 800°C (Table 1). Results showed that almost all PCDFs molecules were removed at all applied temperatures and retention times. Specifically, the toxic equivalents (TEQ) concentration of PCDFs decreased from 4.805 pg-TEQ/g to zero values during pyrolysis. The removal of PCDDs also reached 100% at the retention times of 30 and 90 min, respectively. More than 99.9990% of PCDDs was removed at a retention time of 60 min, with only trace amounts of OCDD (0.0005 pg-TEQ/g) of PCDDs detected in the

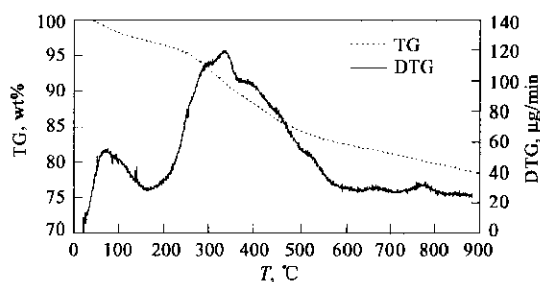


Fig.2 TG-DTG curves of Tagonoura Harbor sediment in Ar gas at 10°C/min

solid products.

For total PCDDs and PCDFs, therefore, almost complete removal has been achieved. Only at the 60 min retention time where some PCDDs were detected yet these TEQ concentration were very low.

For the dioxin-like PCBs, the highest removal efficiency of 99.9994% has been obtained at the shortest retention time of 30 min. At this condition, the lowest TEQ concentrations of 0.000085 pg-TEQ/g was achieved. The content of PCBs in solid residues increased to 0.0005 pg-TEQ/g and 0.0066 pg-TEQ/g when the retention time was extended to 60 and 90 min, respectively. This result demonstrated that trace amount PCBs could possibly be formed at longer retention times at 800°C during oxygen free pyrolysis. This might be due to the fact that the formation of PCBs molecules does not require oxygen (Fig.3). Further experiments are needed to understand the possible mechanism for formation of PCBs in this respect.

To summarize, the above data showed that a retention time of 30 min was already sufficient to achieve maximum removal of all dioxins and dioxin-like PCBs. Furthermore, removal efficiencies slightly decreased when the retention time is increased to 60 and 90 min due mainly to some remaining PCBs. At a retention time of 30 min some PCBs particularly 2, 3, 4, 4, 5-PeCB (#123) was also detected but its concentration was almost negligible at 0.000085 pg-TEQ/g. Therefore, from the view of economics point of reducing energy requirements, the lowest retention time of 30 min at 800°C may be sufficient for actual pyrolysis operations.

2.3 Mechanism of removal dioxins during oxygen free pyrolysis process

In any thermal treatment systems, the resulting dioxins concentration in the solid product may be related to the mass balance of formation and thermal destruction reactions. Complex organic materials can be degraded by thermal treatment in an inert atmosphere, causing organic material to change into three phases (liquid, gas and carbon) (Khiari *et al.*, 2004). Previous pyrolysis tests on PCDD/Fs suggested that they could be totally destroyed at temperatures

Table 1 TEQ concentrations of PCDD/Fs and PCBs in Tagonoura Harbor sediment before and after pyrolysis*

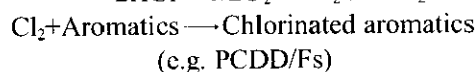
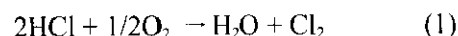
Congener	Raw sediment, pg-TEQ/g dw	Solid residues at 800°C and different retention time, pg-TEQ/g dw		
		30 min	60 min	90 min
PCDFs				
2,3,7,8-TeCDF	1.1	0	0	0
1,2,3,7,8-PeCDF	0.09	0	0	0
2,3,4,7,8-PeCDF	1.65	0	0	0
1,2,3,4,7,8-HxCDF	0.59	0	0	0
1,2,3,6,7,8-HxCDF	0.39	0	0	0
1,2,3,7,8,9-HxCDF	0	0	0	0
2,3,4,6,7,8-HxCDF	0.5	0	0	0
1,2,3,4,6,7,8-HpCDF	0.41	0	0	0
1,2,3,4,7,8,9-HpCDF	0.061	0	0	0
OCDF	0.014	0	0	0
Total PCDFs	4.805	0	0	0
Removal of PCDFs, %		100	100	100
PCDDs				
2,3,7,8-TeCDD	30	0	0	0
1,2,3,7,8-PeCDD	3.1	0	0	0
1,2,3,4,7,8-HxCDD	0.87	0	0	0
1,2,3,6,7,8-HxCDD	3.8	0	0	0
1,2,3,7,8,9-HxCDD	1.9	0	0	0
1,2,3,4,6,7,8-HpCDD	12	0	0	0
OCDD	0.77	0	0.0005	0
Total PCDDs	52.44	0	0.0005	0
Removal of PCDDs, %		100	99.9990	100
PCBs				
3,4,4',5'-TeCB(#81)	0.016	0	0	0
3,3',4,4'-TeCB(#77)	0.37	0	0.00024	0.0022
3,3',4,4',5'-PeCB(#126)	12	0	0	0
3,3',4,4',5,5'-HxCB (#169)	0.047	0	0	0
2',3,4,4',5'-PeCB(#123)	0.023	0.000085	0	0
2,3',4,4',5'-PeCB(#118)	0.63	0	0.00026	0.00421
2,3,3',4,4'-PeCB(#105)	0.16	0	0	0.00021
2,3,4,4',5'-PeCB(#114)	0.085	0	0	0
2,3',4,4',5,5'-HxCB (#167)	0.0056	0	0	0.00012
2,3,3',4,4',5'-HxCB (#156)	0.55	0	0	0
2,3,3',4,4',5'-HxCB (#157)	0.13	0	0	0
2,3,3',4,4',5,5'-HpCB (#189)	0.022	0	0	0
Total PCBs	14.0386	0.000085	0.0005	0.006622
Removal of PCBs, %		99.9994	99.9964	99.9528
Total dioxins**	71	0.000085	0.001	0.0066
Removal of total dioxins, %		99.9999	99.9986	99.9907

Notes: *The TEQ value is calculated using the toxicity equivalent factor (TEF) according to the World Health Organization (WHO) (1998); the limit of determination (LOD): for PCDD/Fs: 0.1 pg/g dw; for PCBs: 0.2 pg/g dw; in the calculations of TEQ, results below the LOD were considered zero; ** total dioxins: PCDFs+PCDDs+PCBs

above 700°C (Hatanaka *et al.*, 2001). Furthermore, the previous works have also reported that the volatilization behavior of dioxin from fly ash was shown at 400°C (Shiomitsu *et al.*, 2001). Now, to determine the mechanism of dioxins removal, that is, to evaluate the extent of volatilization and decomposition (if any) reactions, the dioxins composition of the off-gas during pyrolysis at 30 min retention time was also monitored. For this purpose, dioxins in the tar of cold trap as well as in the gas adsorbent (XAD-2 resin) were analyzed.

Mass balance data showed that almost equal amounts of total dioxins were present in the raw material as well as in the gas phase (Fig.4). Specifically, around 99.45% of the total dioxins that was originally present in the raw sediment were detected in the gas phase, which is distributed in the tar condensate and gas adsorbent. The individual contents of total dioxins in tar condensate and gas adsorbent were 53.72% and 45.73%, respectively. From these results, it appeared that volatilization is the main mechanism for its removal from sediment under experimental conditions. The dioxins had been escaped prior to their destruction at higher temperature of 800°C.

Extensive research has been done to study the formation of PCDD/Fs in thermal processes, the precise mechanisms have not been clarified yet for the complexity of the processes (Dickson *et al.*, 1992; Stanmore, 2004). In general, two mechanisms have been put forward primarily to explain for dioxin synthesis — the precursor mechanism and the De Novo synthesis (Lundin and Marklund, 2005; Chang and Huang, 2000; Dickson *et al.*, 1992). In the precursor mechanism, chloroaromatic precursors are necessary for dioxin formation. In most cases, these compounds might be already present in the fuel, but they could also be formed at higher temperature by multistep reaction, including aromatization of aliphatic compounds and chlorination. Aromatic rings are chlorinated by Cl₂ from HCl with O₂ via the Deacon reaction (Eq.(1); Vogg *et al.*, 1987; Griffin, 1986; Gullett *et al.*, 1990; Dickson *et al.*, 1992), and formation of dual ring structures by metal-catalyzed reaction (Eq.(2); Gullett *et al.*, 1992). In the formation of PCDD/Fs via De Novo synthesis, on the other hand, carbon can be oxidized to form CO or CO₂ by oxygen, Eq. (3) (Addink *et al.*, 1995) and Eq. (4) (Tuppurainen *et al.*, 1998). Gaseous oxygen also plays a crucial role for the De Novo theory (Huang and Buekens, 1995, 2001; Stanmore, 2004).



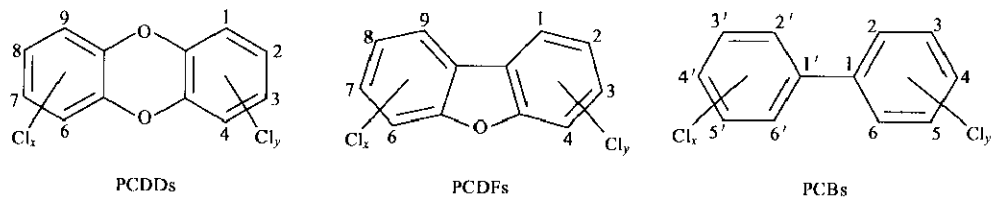


Fig.3 Structural formulate of PCDDs, PCDFs and PCBs

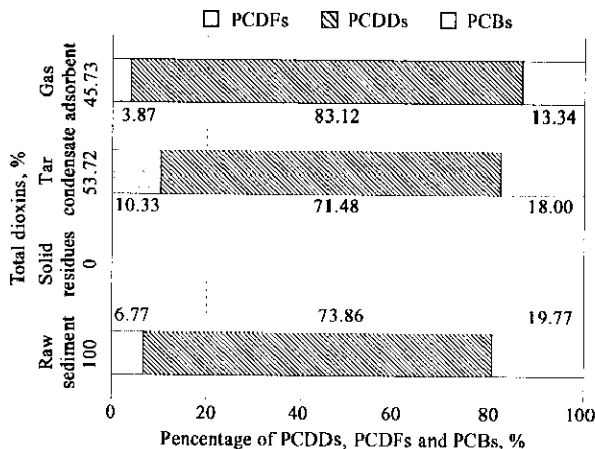


Fig.4 Fate of dioxins in the raw sediment, solid residues and volatile phase during pyrolysis

For both mechanisms mentioned above, the formation of dioxins is much dependent on the concentration of oxygen so that even at oxygen concentrations as low as 1%, increases in PCDD/Fs are observed (Addink and Olie, 1995). This was also confirmed in this work where the role of oxygen for formation of dioxins was evaluated during the cooling stage (Table 2). In these runs, pyrolysis was initially allowed to occur at 800°C and 30 min retention time. However, during the cooling period, air was allowed

to enter the system. As a result, dioxin concentrations in solid residues dramatically increased to 130.99 times that of its original content in the raw sediment. Following the same process, the concentrations of total dioxins in solid residues were also increased by 197.18 and 154.93 times at 600°C and 500°C at retention time of 60 min, respectively. It can be concluded that the formation of dioxins was remarkably enhanced by the presence of oxygen even during the cooling period. Furthermore, there was increasing of 1732.30 to 2455.15 times in the TEQ concentration of PCDFs. Nevertheless, for PCDDs and PCBs, the TEQ increase was range from 11.09 to 81.18 times only. The above results demonstrated that PCDFs, can be synthesized more easily than PCDDs and PCBs under these conditions. Finally, it has been mentioned that dioxins can form at the temperature window of 200–450°C (Vogg *et al.*, 1987). In one experiment when the nitrogen atmosphere was continuously supplied for cooling down the system from 800°C to 400°C prior to the entry of air below 400°C until room temperature is reached, very few dioxins were generated and none of the PCDDs was detected. These data further indicate that the range of temperature for dioxins formation particularly for this pyrolysis sediment system may be higher than 400°C.

Table 2 Increasing times of dioxin concentration in solid residues under different atmosphere during cooling down period

Pyrolysis temp., °C	Retention time, min	Cooling atmosphere	Increasing times of dioxin concentration*			
			PCDFs	PCDDs	PCBs	Total dioxins
800	30	N ₂	0	0	0	0
800	30	Air	1732.30	11.09	29.02	130.99
800	60	N ₂ (air)**	0.0239	0	0.0149	0.0046
600	60	Air	2455.15	25.39	81.18	197.18
500	60	Air	1926.78	22.79	38.19	154.93

Notes: * TEQ concentration of dioxin in solid residues / TEQ concentration of dioxin in raw sediment; ** 800–400°C: N₂ atmosphere, 400°C—room temperature: air atmosphere

Going back to the pyrolysis result, the non-formation of dioxins in the solid residues may be clearly attributed to the absence of oxygen in the system. If any increase in the concentration of a certain dioxin species or any new species has been detected in the gas phase, these can only be attributed to transformation reactions since no oxygen is present to initiate formation of new species. Although the formation of dioxin-like PCBs may occur since its reaction does not require oxygen, experiments revealed that this occurrence was rather minimal.

With these information, it can be stated that the full scale pyrolysis must be conducted at an oxygen free atmosphere during the entire operation to prevent further dioxin formation. Concerning the dioxins that are initially present in the sediment, since the main mechanism for their removal is volatilization rather than decomposition reaction, off-gases from the pyrolyzer must be directed to a secondary burner, which operates at higher temperatures (> 1000°C) to accomplish their complete destruction. These are important steps that must be undertaken in the design

and operation of a large pyrolysis process.

3 Conclusions

Removal efficiency of 99.9999% has been achieved for total dioxins during oxygen free pyrolysis of contaminated sediment. PCDFs were not formed in the solid products over the retention time range of 30–90 min at 800°C. The removal of PCDDs also reached 100% at a retention time of 30 and 90 min, respectively. Only trace amounts of PCDDs were detected in the solid products at the retention time of 60 min. The highest efficiency of PCBs was around 99.9994% at retention of 30 min. However, the PCBs contents increased with increasing the retention time. The results demonstrate the potential of oxygen free pyrolysis as an alternative technology to either prevent formation of PCDD/Fs or minimize the release of these compounds into the environment.

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