EXPERIMENTAL EVALUATION OF PCDD/DFs IN CEMENT SAMPLES FROM KILNS USING WASTE TIRES

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Introduction

Transportation using automobiles is increasingly prevalent in Taiwan. Appropriate disposal of vehicle tires is needed. An estimated amount of about 500,000 tons of waste tires from 1973 to 1989 are present in stockpiles. Currently approximately 60,000 tons of waste tires are discarded annually. Various disposal methods are available[1-4]. The use of waste tire as fuel substitutes in energy-processes such as cement kilns is an attractive option[4]. This is significant in Taiwan as local energy resources are very limited.

The utilization of waste tires as auxiliary fuel in cement production has been widely practiced. The impact of this reclamation method to the environment has been widely studied. However, most studies are focused on gaseous emissions, i.e., the speciation and quantification of emitted air pollutants[5-7]. Thermal reactions have been regarded as one of the four primary sources of PCDD/DFs and usually result in PCDD/DFs emissions into the air[8]. The influence of adding shredded tires to the cement kilns on the formation of hazardous materials, i.e., 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans (2,3,7,8-substituted PCDD/DFs) in the clinker is not clear. This information is critical to the acceptance of cement products by the public due to the epidemic fear of dioxin. This study is therefore focused on the analysis of PCDD/DFs in the raw materials, waste tire, clinker and fly ash from a cement kiln during trial burn. The aim is to investigate the quality of cement obtained by the incorporation of waste tires in a cement kiln for energy recovery.

Methods and Materials

A total of 6 samples were collected from the cement kiln. They are raw materials (mill consisting of limestone, clay, silica, iron dregs, gypsum and coal), waste tire, clinker-1 (produced using raw materials only), clinker-2 (produced using raw materials with 25% of the coal replaced by shredded tires), fly ash-1 (collected when producing clinker-1) and fly ash-2 (collected when producing clinker-2), abbreviated as RM, WT, C1, C2, F1 and F2, respectively, hereafter. The fly ash samples were collected from the electrostatic precipitator. All samples were grounded and sieved with a 60-mesh. Approximate 20-g of RM, 2.5-g of WT, 10-g of C1 and C2, 18-g of F1 and F2 were analyzed using USEPA method 1613B. The spiked concentrates were analyzed using a HP-5890GC/Fisson Ultima HRMS equipped with a J&W DB-5ms column (60 m x 0.25 mm i.d. x 0.25 μm film). The recoveries of the internal standards are all within the quality control limits. The detection limits are from 0.01 pg/g to 0.05 pg/g. The toxic equivalents (TEQ) were calculated using the I-TEF/89 system[9] while the concentrations of the not detected congeners are calculated with zeros.

Results and Discussions

The TEQ (pg/g) from the 17 2,3,7,8-substituted PCDD/DFs are listed in Table 1. A wide range of concentration levels was observed. The TEQ ranges from 0.0026 pg/g in sample F2 to 8.91 pg/g in WT. The TEQ value of the system blank sample is 0.0021pg/g, indicating that the analytical system and method perform well. The 6 samples could be categorized into three sets, the feed-in set of RM and WT, the clinker set of C1 and C2, and the fly ash set of F1 and F2. The TEQ level detected in the feed-in set (4.62 pg/g average TEQ) is about an order of magnitude higher than that detected in the clinker set (0.447 pg/g average TEQ), indicating that native PCDD/DFs in the feed-in were destroyed under the combustion conditions in the cement kiln, namely between 900~1450 °C for 2~4 hours. The correlation of the TEQ levels in the clinker to those in the feed-in, i.e., the higher the TEQ in the feed-in (namely WT) the higher the TEQ in the clinker (namely the C2), indicating that the formation of PCDD/DFs in the clinker might still be influenced by the feed-in materials. The average TEQ level in the fly ash is 0.0068 pg/g, which is much lower than the TEQ levels found in fly ashes from other kinds of incinerators[10]. This might be attributed to the high combustion temperature and long resident time (2~5 s) in the cement kiln. The TEQ levels in all cement samples are far below the level of concern, i.e., the 1 ng-TEQ/g in resident soil recommended by the Center for Disease Control[11]. This level is based on health risk assessments of ingesting soil daily over a lifetime period. Hence, it is fair to conclude that the quality of the cement obtained by the incorporation of waste tires in a cement kiln for energy recovery meets the environmental standards.

Table 1 TEQ (pg/g) of 2,3,7,8-substituted PCDD/DFs in cement samples

Analyte	Sample					
	RM	WT	C1	C2	F1	F2
PCDDs	0.0090	2.74	0.0069	0.13	0.0019	0.0016
PCDFs	0.36	6.17	0.087	0.67	0.0088	0.00098
PCDDs+PCDFs	0.37	8.91	0.094	0.80	0.011	0.0026
PCDDs/PCDFs	0.025	0.44	0.079	0.20	0.21	1.60

The ratios of the PCDDs' TEQ to PCDFs' TEQ listed in Table 1 for RM and C1 are smaller than 0.1. Similar TEQ ratios for WT and C2 are between 0.2 and 0.6, which are similar to fly ashes collected form other kinds of incinerators[10]. The characteristic profiles of 17 2,3,7,8-substituted PCDD/DFs of WT and C2 shown in Fig. 1 are also similar to fly ashes collected form other kinds of incinerators[10], again implying the correlation of formation of PCDD/DFs between the feed-in and the products. This observation warrants further investigation. In summary, the dioxin content in the cement became higher when using waste tires as auxiliary fuel in a cement kiln. However, the dioxin content still meets the environmental standards.

Acknowledgements

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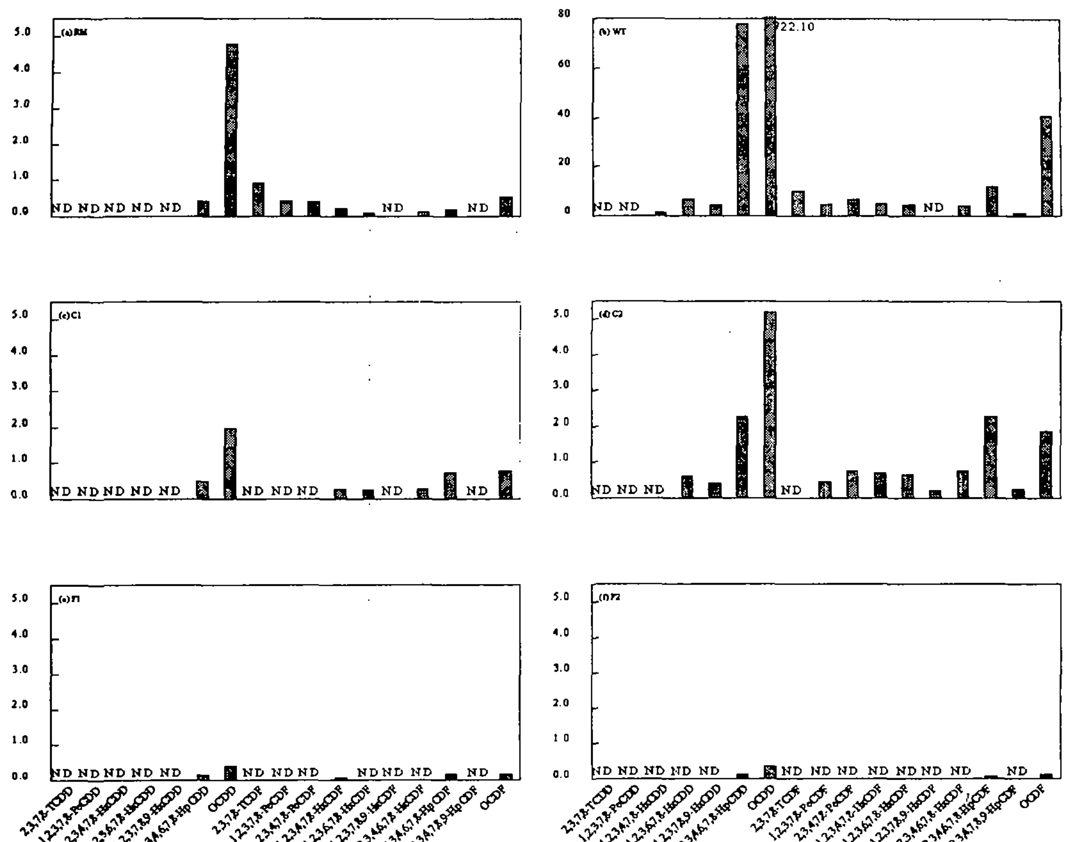

Fig.1 Characteristic profiles of 2,3,7,8-substituted PCDD/DF congeners in cement samples. The unit in the *y*-axis is pg/g.

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