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Emission Characteristics of PCDDs/PCDFs from Power Station using COG, BFG and LDCG as a Fuel

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The emission pattern of PCDDs/PCDFs from power station using blast furnace gas (BFG), coke oven gas (COG) and Linz-Donawitz converter gas (LDCG) in the iron-and-steel foundries could be summarized as follows. PCDDs/PCDFs emission levels were in the range of 0.017 to 0.023 ng-TEQ/Sm^3, and averaged 0.02 1ng-TEQ/Sm3. PCDFs showed an approximately four times higher concentration than PCDDs, showing that the ratio of PCDDs to PCDFs averaged approximately 19:81. The main contributor to total TEQs was 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 40.5% and 9.5% of total TEQs, respectively. Carbon monoxide concentrations in emission gases showed a considerable difference by power station: one was 2 ppm, the other was 876 ppm on average.

Key words : Emission Pattern, PCDDs/PCDFs, Power station, BFG, COG

1. Introduction

Coke is used as a major fuel and reducing agent in iron-and-steel manufacturing. Coke is the carbonized material produced by pyrolysis of certain coals or bituminous coals at a high temperature: flue gas temperature is normally 1,150~1,350°C, indirectly heating the coal up to 1,000~1,100°C. The coke making process can be subdivided into: 1) coal preparation, 2) battery operation, 3) coke handling and preparation, 4) collection and treatment of coke-oven gas with recovery of by-products[1)].

First, coal preparation comprises bed blending, bunker blending and crushing, and recycled substances such as tar can be added at this blending stage. Coke-oven battery operations include coal charging, heating of chambers, coking, coke pushing and quenching. In coal charging, pulverized coal (70~85% is below 3 mm) is charged into coke ovens, which are approximately 12 m long, 4 m high and 0.5 m wide, equipped with doors on both side. Each oven in the battery can hold up to 30 tons of coal. The single coke ovens are separated by heating walls, in which inside temperatures are usually set between 1,150 and 1,300°C. Cleaned coke-oven gas is used as a fuel, and other gases like blast-furnace gas can be used as well. Charged coal is coked at a temperature of 1,000~1,100°C for 16~17 hours, producing the coke-oven gas of which composition depends on coking time and coal composition. For each ton of coke produced, approximately 3 kg of NH_3 and 2.5 kg of H_2S are generated[1,2)]. In some cases, light oil that contains some aromatics such as benzene, toluene and xylene is recovered from the raw coke-oven gas as valuable by-product. Up to 15 kg of light oil can be recovered per ton of coke produced. For gas cooling, the hot pyrolyzed coal gas, coming from the coke ovens, enters the ascension pipes at a temperature of approximately 800°C, then it is directly cooled in the goose neck by ammonia-liquor spry to a temperature of about 80°C.

After cooling, coke-oven gas is collected to reservoirs as a fuel for power generation because it contains a lot

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of combustibles such as hydrogen (55.9%), methane (27.4%), carbon monoxide (7.3%) and hydrocarbons (3.1%)[1,2], thus having a calorific value of approximately 4,450 kcal/Sm^3. Coke is removed from the ovens by pushing car, and further treated to improve blast-furnace productivity.

Blast-furnace gas and oxygen-converter gas are used as fuels for power generation in the iron-and-steel foundries as well. Major components of blast-furnace gas are carbon monoxide (20.0~23.5%) and hydrogen (1.6~6.0%)[1,2], having a calorific value of 680~830 kcal/Sm^3. Unlike the blast gas, oxygen-converter gas contains mainly carbon monoxide at a high concentration of above 60%, and its calorific value is approximately 2,000 kcal/Sm3. In comparison to coke-oven gas, since blast-furnace gas and oxygen-converter gas have relatively low calorific values, generally these three gases are properly mixed at certain ratios when they are used as fuels. In particular, these gases from coking, melting and converting processes may contain a small portion of chlorine compounds due to the inherent chlorine contents of coals and iron ores. Thus, it can be thought that chlorine compounds may provide the formation condition of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) when they are burned. More recently, some papers reported PCDDs/PCDFs emissions from coke oven[3] and oxygen converter[4].

This sturdy, therefore, was performed to investigate how much PCDDs/PCDFs are produced at the power station, where the coke-oven gas mixed with blast gas and converter is used as a fuel, and to take a proper countermeasure for reducing the emission amounts of pollutants.

2. Material and Methods

Two power stations, which use coke-oven gas (COG), blast-furnace gas (BFG) and Linz-Donawitz converter gas (LDCG) as fuels, were selected from two iron-and-steel manufacturing factories (Fig. 1). PCDDs/PCDFs were sampled two times at the stacks of each furnace by using a sampling train: which consisted, in order, of a probe, a cylindrical filter assembly (silica fiber thimble, 90 mm in length and 25 mm outside diameter, Whatman) three impingers (two of which were filled with 150 ml of distilled water, and one of which was empty), a sorbent (XAD-2) module, and two impingers (one of which was filled with 150 ml of ethylene glycol, and the other was empty). After spiking 2 ng of 37Cl4-2,3,7,8-TCDD to the sorbent, two traverse-point sampling over the respective cross-sections was iso-kinetically done at the stack for about 4 hours. During the sampling, the cylindrical filter was kept below 120 °C with cooling water, and sorbent trap was kept below 30°C by chilling the impingers with ice water.

After sampling, the PCDDs/PCDFs samples were divided into two portions: one is solid portion (cylindrical filter and sorbent) and aqueous portion (impinger water, ethylene glycol, probe-rinsed solvent). An internal standard cocktail, 2 ng of $^{13}C_{12}$-PCDDs/PCDFs was added to each portion of samples as internal standards prior to extraction. Then, each portion of samples was separately extracted with toluene: Soxhlet extraction for solid portion and liquid extraction for aqueous portion. Toluene extracts were combined into one and cleaned up by 5 ml of concentrated sulfuric acid 4 or 5 times, followed by silica gel column cleanup eluting 150 ml of n-hexane, and basic alumina column cleanup eluting 100 ml of 2% dichloromethane in n-hexane (this portion was discarded) and then 150 ml of 50% dichloromethane in n-hexane. Final eluate was concentrated to a volume of 1 ml, and further concentrated to about 50 μl after spiking 2 ng of recovery standards.

Concentrated eluates of the samples were analyzed by high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). The HRGC/HRMS setup consisted of a Agillant 6890 GC coupled with Autospec Ultima (Micromass Co.) with OPUS quantification programme. Selected ion monitoring with electron impact of 36 eV was performed above a resolution of 10,000 with an SP-2331 column of 60 m × 0.32 mm ID × 0.25 μm [120°C (3 min) → 10°C · min-1 to 200°C (3 min) → 3°C · min-1 to 265°C (15 min)]. The eluates were introduced in splitless mode with a

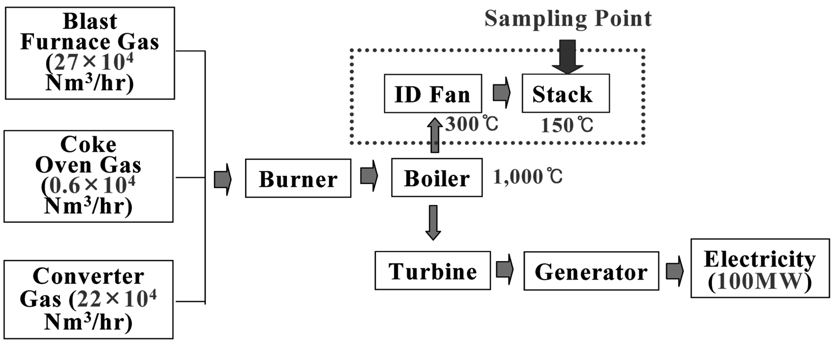

Fig. 1. Schematic diagram of power station in iron-and-steel manufacturing investigated.

flow rate of 2.5 ml·min^{-1} helium, and temperatures of injector and ion source were 260°C and 270°C, respectively.

Toxic equivalents (TEQs), expressed as 2,3,7,8-TeCDD values, were calculated without correction of oxygen concentration in flue-gas stream by using the international toxicity equivalency factor (I-TEF) and OPUS quantification programme. All processes mentioned above, including sampling, sample preparation, and HRGC/HRMS analysis, were performed according to the Korean Standard Testing Method (KSTM) for Dioxins and Furans (Ministry of Environment Republic of Korea, 1996)$^{5)}$.

3. Results and Discussions

As shown in Table 1, emission volumes of off-gases averaged about 6,180 Sm3/min (371×10^3 Sm^3/hr), which amounts to approximately 10 times off-gas volumes of 200 ton/day municipal solid waste (MSW) incinerator (37,800 Sm^3/hr)$^{6)}$, and oxygen concentrations in off gases averaged approximately 4.8%, ranging from 4.1% to 5.6%. Carbon monoxide concentrations in emission gases showed a considerable difference by power station: one was 2 ppm, the other was 876 ppm on average. This difference of emission concentration in carbon monoxide can be explained by the compositional difference of fuels used for power generation in iron-and-steel foundries. That is, the mixed off-gas that consisted of BFG, COG and LDCG is used as a fuel gas for electric power generation by properly mixing those off-gases at certain ratios. But, as shown in Table 2, they contains considerably different concentrations of carbon monoxide, showing that LDCG (above 60%) has much higher concentration than BFG (5%) and COG (5%). Thus, if the proportion of LDCG in a fuel gas predominated those of BFG and COG, and air supply for fuel combustion was insufficient, carbon monoxide could be released into the atmosphere as a high level.

Meanwhile, as shown in Table 3, PCDDs/PCDFs emissions were in the range of 0.017 to 0.023 ng-TEQ/Sm3, and averaged 0.021 ng-TEQ/Sm3 from four measurements. Off-gases contained four times more PCDFs than PCDDs, showing that the ratio of PCDDs

Table 1. PCDDs/PCDFs emission from power station in iron-and-steel manufacturing

Power Station	Emission Process	APCD	Emission Gas		E. Gas / Coke. (Sm^3/ton)	E. Gas Temp. (°C)	CO (ppm)	PCDDs/PCDFs (ng-TEQ/Sm^3)	
			(Sm^3/min)	(Sm^3/hr)				1st	2nd
A1	Boiler	-	5,053	303×10^3	1,136	156	2*	0.020	0.017
A2	Boiler	-	7,307	438×10^3	1,353	161	876**	0.023	0.017
	Average		6,180	371×10^3	1,245	159	439	0.019	

* : 1st= 2 (0 ~24), 2nd= 2 (0 ~33), **: 1st= 1,504 (0~4,863), 2nd= 248 (0~1,619)
Note: APCD: Air Pollution Control Device, E. Gas/Coke : Emission Gas/Coke.

Table 2. Major components in fuel gases used for power generation

Fuel Gas	Korea (2002)[7]	EU[1]
COG	H_2: 56.4%, CH_4: 26.6%, CO: 8.4%, HCs: 2.9%, H_2S: 1.5 kg/ton-coke, NH_3: 1.7 kg/ton-cake, Calorific Value: 4,400 kcal/Sm^3	H_2: 55.9%, CH_4: 27.4%, CO: 7.3%, HCs: 3.1% H_2S: 2.5 kg/ton-coke, NH_3: 3 kg/ton-cake, Calorific Value: 4,450 kcal/Sm^3
BFG	H_2: 3.2%, CO: 22.0%, Calorific Value: 750 kcal/Sm^3	H_2: 1.6~6.0%, CO: 20.0~23.5%, Calorific Value: 680~830 kcal/Sm^3
LDCG	CO: 64.2%, Calorific Value: 2,000 kcal/Sm^3	CO: >60%, Calorific Value: 2,000 kcal/Sm^3

to PCDFs was 19:81 on average. The most abundant 2,3,7,8-congener was 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD (Fig. 2), and their TEQ values constituted 40.5% and 9.5% of total TEQs, respectively. The most toxic 2,3,7,8-TCDD was detected at a level of 6% of total TEQs. In particular, emission pattern of 2,3,7,8-PCDDs/PCDFs was very similar to that of ferrous metal melting furnaces such as sintering and electric furnaces[8,9] and MSW incinerator[10-12] in a fact that three major 2,3,7,8-congeners were 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD and 1,2,3,6,7,8-HxCDF, and their compositional percentile was about 60% to total TEQs.

4. Conclusions

The emission pattern of PCDDs/PCDFs was investigated from two power stations in iron-and-steel foundries, each of which produced 100 MW electricity using BFG, COG and LDCG as fuels. From four

Table 3. PCDDs/PCDFs emissions of power station using COG, BFG and LDCG as fuels in the iron-and-steel foundries (Unit: ng TEQ/Sm3)

2,3,7,8-PCDDs/PCDFs	Power Station 1		Power Station 2		Mean (n=4)	
	1st	2nd	1st	2nd		
2,3,7,8-TCDD	0.001	0.001	0.001	0.002	0.001	5.95
1,2,3,7,8-PeCDD	0.002	0.002	0.002	0.002	0.002	9.52
1,2,3,4,7,8-HxCDD	0.000	0.000	0.000	0.000	0.000	0.00
1,2,3,6,7,8-HxCDD	0.001	0.000	0.001	0.000	0.001	2.38
1,2,3,7,8,9-HxCDD	0.000	0.000	0.001	0.000	0.000	1.19
1,2,3,4,6,7,8-HpCDD	0.000	0.000	0.000	0.000	0.000	0.00
OCDD	0.000	0.000	0.000	0.000	0.000	0.00
PCDDs	**0.004**	**0.003**	**0.005**	**0.004**	**0.004**	**19.05**
2,3,7,8-TCDF	0.001	0.001	0.002	0.002	0.002	7.14
1,2,3,7,8-PeCDF	0.001	0.001	0.001	0.001	0.001	4.76
2,3,4,7,8-PeCDF	0.009	0.008	0.010	0.007	0.009	40.48
1,2,3,4,7,8-HxCDF	0.001	0.001	0.001	0.001	0.001	4.76
1,2,3,6,7,8-HxCDF	0.002	0.002	0.002	0.001	0.002	8.33
2,3,4,6,7,8-HxCDF	0.002	0.001	0.002	0.001	0.002	7.14
1,2,3,7,8,9-HxCDF	0.000	0.000	0.000	0.000	0.000	0.00
1,2,3,4,6,7,8-HpCDF	0.000	0.000	0.000	0.000	0.000	0.00
1,2,3,4,7,8,9-HpCDF	0.000	0.000	0.000	0.000	0.000	0.00
OCDF	0.000	0.000	0.000	0.000	0.000	0.00
PCDFs	**0.016**	**0.014**	**0.018**	**0.013**	**0.017**	**80.95**
PCDDs+PCDFs	**0.020**	**0.017**	**0.023**	**0.017**	**0.021**	**100.00**

Note: The figures in shaded areas represent the compositional percentiles of each 2,3,7,8-congeners to total TEQs.

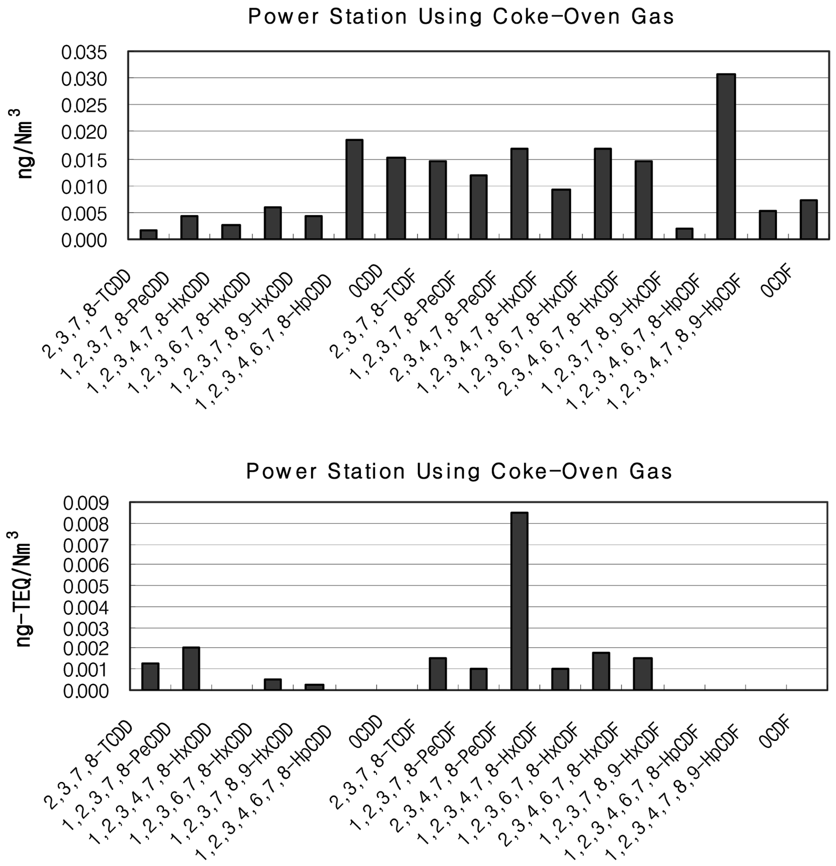

Fig. 2. 2,3,7,8-congener profiles in power station using COG, BFG and LDCG as fuels.

summarized as follows:

1) Emission volumes of off-gases averaged about 371×10^3 Sm^3/hr, which amounts to approximately 7 times off-gas volumes of 200 ton/day MSW incinerator. and carbon monoxide concentrations in emission gases showed a considerable difference by power station: one was 2 ppm, the other was 876 ppm on average.

2) PCDDs/PCDFs emission levels were in the range of 0.017 to 0.023 ng-TEQ/Sm^3, and averaged 0.021 ng-TEQ/Sm^3.

3) PCDFs showed approximately four times higher concentrations than PCDDs, showing that the ratio of PCDDs to PCDFs averaged approximately 19:81.

4) The main contributor to total TEQs was 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 40.5% and 9.5% of total TEQs, respectively.

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