Reduction in Dioxin Emissions by the Addition of Urea as Aqueous Solution to High-temperature Combustion Gas

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In order to study the effect of urea addition to the waste gas on the dioxin formation, a series of experiments is carried out using the fly ashes sampled from two different types of solid waste incinerators. A remarkable suppression effect is obtained for the dioxin formation, while no clear change is observed for the obtained organic chlorine. Considering these results, the method of urea addition to the water splayed into the cooling tower of waste gas is proposed as an effective measure to suppress the dioxin formation at the cooling stage of the combustion gases. A verification test is carried out using an actual solid waste incinerator. When the concentration of urea in the splayed water is set to 0.1%, the toxicity concentration of the dioxins in the waste gas is reduced to approximately half that in the case without the addition. Further, the addition of urea does not significantly affect the concentration of NOx in the waste gas.

KEY WORDS: suppression of dioxins; de novo synthesis; urea; waste gas; fly ash; organic chlorine; cooling tower.

1. Introduction

According to the recent inventory data of dioxin emissions in Japan (Table 1) compiled by the Ministry of Environment, the total emissions in 2005 have reduced to approximately 336 g TEQ (toxicity equivalent quantity). Surprisingly, this figure is less than 1/20th of the level obtained in 1997, i.e., approximately 7 910 g TEQ. The largest contribution to such a reduction was made by the waste incinerators and was attributed to the drastic change from small batch-type furnaces to large continuous-type facilities and also to the application of advanced waste gas treatment systems. In the waste incineration process, the rapid cooling of high-temperature gases to less than 200°C is recommended; this action will suppress the de novo synthesis reaction1) of dioxins during the cooling stage of waste gases. Additional measures such as activated carbon injection and catalytic decomposition process are often applied to waste gases. Remarkable reductions in the dioxin emissions have also been achieved in other "specified facilities" such as electric arc

| Emission source          | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 |
|--------------------------|------|------|------|------|------|------|------|------|------|
| Municipal W.I.           | 5000 | 1550 | 1350 | 1019 | 812  | 370  | 71   | 64   | 62   |
| Industrial W.I.          | 1500 | 1100 | 690  | 555  | 533  | 265  | 74   | 69   | 73   |
| Small-scale W.I.         | 927  | 927  | 683  | 310  | 398  | 124  | 86   | 88   | 85   |
| EAF for steelmaking      | 229  | 140  | 142  | 131  | 95   | 95   | 80   | 64   |
| Iron ore sintering       | 135  | 114  | 101  | 70   | 65   | 51   | 36   | 29   |
| Zinc recovery            | 47.4 | 25.4 | 21.8 | 26.5 | 9.2  | 14.7 | 5.5  | 8.1  |
| Aluminum alloy making    | 19.3 | 19.4 | 13.6 | 12.8 | 15.0 | 14.4 | 14.9 |
| Cement making            | 4.7  | 4.1  | 3.9  | 4.0  | 3.2  | 3.7  | 4.7  |
| Copper making            | 4.9  | 4.9  | 0.5  | 0.6  | 0.3  | 0.5  | 0.6  |
| Copper processing        | 3.2  | 3.2  | 1.2  | 1.3  | 1.3  | 1.3  | 1.4  |
| Power plant              | 1.6  | 1.6  | 1.6  | 1.6  | 1.6  | 1.9  | 2.0  |
| Crematories              | 2.1-4.6 | 2.2-4.8 | 2.2-4.9 | 2.2-4.6 | 2.2-4.9 | 2.3-5.1 | 2.3-5.1 | 2.4-5.3 | 2.4-5.3 |
| Automobile W.G.          | 1.4  | 1.4  | 1.4  | 1.4  | 1.4  | 1.4  | 1.3  |
| Industrial W.I.          | 5.3  | 5.3  | 5.3  | 2.5  | 1.5  | 0.86 | 0.60 | 0.65 |
| Caprolactam making       | 2.5  | 2.5  | 2.5  | 1.8  | 0.07 | 0.11 | 0.08 | 0.04 |
| Acetylene making         | 1.8  | 1.6  | 1.6  | 1.6  | 0.22 | 0.22 | 0.02 | 0.01 |
| Pulp bleaching           | 0.74 | 0.71 | 0.74 | 0.73 | 0.90 | 0.65 | 0.46 | 0.58 |
| Vinyl chloride making    | 0.54 | 0.53 | 0.55 | 0.20 | 0.58 | 0.16 | 0.10 |
| Sewage treatment         | 1.1  | 1.1  | 1.1  | 1.1  | 0.59 | 0.51 | 0.54 | 0.36 |
| Solid Waste landfill site| 0.09 | 0.09 | 0.09 | 0.09 | 0.056| 0.027| 0.021| 0.020|
| Total                    | 7910 | 3920 | 3040 | 2400 | 1960 | 957  | 386  | 352  | 336.8 |
furnaces (EAFs) for the steelmaking and sintering plants of iron ores. Waste gas treatment is important for such processes and also for an inflow control of the chlorine sources in the process. The operation of the bag filters at low temperatures and the application of the adsorption tower filled with activated coke are the main technologies for waste gas treatment of EAFs for the steelmaking and iron ore sintering processes, respectively. However, such systems generally lead to an increase in costs and render difficulties in heat recovery.

At the cooling stage of the waste gas, chlorinated organic compounds including dioxins are considered to be formed by the de novo synthesis reaction. Generally, this reaction is found to occur at a temperature between 200 and 500°C.2–6 It is apparently a direct formation reaction originating from carbonaceous materials such as soot, which is a macrostructural carbon that is usually formed through the condensation of unburnt carbon and/or hydrocarbon components in combustion gases. Soot particles formed during industrial processes usually have complex structures containing various metallic elements that at times promote the rate of the de novo synthesis reaction. In particular, the promotion effect of metallic chlorides is larger than the promotion effect of their oxides.7 The authors examined the effect of urea addition to the carbonaceous materials on the de novo synthesis reaction of dioxins and found a significant inhibitive effect.8 Considering this result, urea was added to the fly ash samples obtained from two different solid waste incinerators, and its effect on the dioxins and organic chlorine formations was experimentally studied by using a gas-flow-type reactor. Further, the effect of the urea addition to the water splayed into the cooling tower of waste gas on the dioxin concentration was verified by using an actual waste incinerator.

2. Experimental Procedure

2.1. Materials Used and Sample Preparation for de Novo Experiment

Two fly ash samples A and B were obtained from two different incinerators, i.e., fluidized-bed-type and stoker-type furnaces. The chemical and elemental compositions of these samples are listed in Table 2. The concentration of CaO is significantly higher in sample A, while those of SiO₂ and Al₂O₃ are higher in sample B. This is probably due to differences in the injection rate of slacked lime for the control of HCl emission with waste gas and the kind of the wastes treated by these incinerators. The chlorine levels in both the samples are the same. The concentration of Cu, whose chlorides are regarded as strong catalysts for the de novo synthesis reaction of dioxins, is higher in sample B. However, the concentrations of alkali components Na and K, which have strong affinity to chlorine, are also higher in sample B. Thus, by considering only the composition data of these samples, the assessment of the formation of dioxins appears to be difficult.

The amount of dioxins obtained from a laboratory-scale de novo experiment is usually not sufficient for quantitative analysis. Therefore, a certain amount of CuCl₂ was added to all the fly ash samples to enhance the reaction in the following manner: CuCl₂·2H₂O reagent was dissolved in aqueous solution containing various metallic elements that at times promote the rate of the de novo synthesis reaction. In particular, the promotion effect of metallic chlorides is larger than the promotion effect of their oxides.7 The authors examined the effect of urea addition to the carbonaceous materials on the de novo synthesis reaction of dioxins and found a significant inhibitive effect.8 Considering this result, urea was added to the fly ash samples obtained from two different solid waste incinerators, and its effect on the dioxins and organic chlorine formations was experimentally studied by using a gas-flow-type reactor. Further, the effect of the urea addition to the water splayed into the cooling tower of waste gas on the dioxin concentration was verified by using an actual waste incinerator.

Table 2. Chemical and elemental composition of fly ash samples.

| Sample A | Sample B |
|----------|----------|
| (Fluidized bed) | (Stoker) |
| SiO₂ | 13.5 | 20.5 |
| Al₂O₃ | 9.23 | 15.3 |
| CaO | 39.8 | 14.3 |
| Na₂O | 4.62 | 7.80 |
| K₂O | 3.83 | 7.99 |
| MgO | 2.32 | 4.26 |
| MnO | 0.39 | 0.11 |
| Fe₂O₃ | 0.21 | 0.70 |
| P₂O₅ | 2.31 | 1.02 |
| TiO₂ | 0.22 | 1.10 |
| Zn | 0.27 | 1.55 |
| Pb | 0.03 | 0.37 |
| Cu | 0.01 | 0.11 |
| T-C | 15.3 | 13.4 |
| T-S | 0.02 | 0.38 |
| Fixed C | 0.88 | 1.16 |

tone and the prepared solution was mixed well with the fly ash samples. The concentration of CuCl₂ in the samples was set to 0.5 mass% on a dry basis. In the case of urea addition, its aqueous solution was further mixed with the samples to obtain 20 mg of urea per gram of the sample on a dry basis. These samples were dried at 100°C for 2 h. Before the de novo experiment was conducted, the prepared sample was press-shaped as a disk tablet and then crushed into granules with sizes ranging between 1 and 2 mm.

2.2. Experimental Apparatus for de Novo Synthesis Reaction

The schematic drawing of the apparatus for the de novo experiment is shown in Fig. 1. Ten grams of the granulated fly ash sample was packed in the reaction tube made of heat-resistant glass with an inside diameter of 27 mm. The thickness of the sample bed was approximately 25 mm. After replacing the air inside the reaction tube with Ar–O₂ (10 mol%) gas mixture, it was inserted into an electric furnace at the target holding temperature. The time required to attain the target temperature, i.e., between 250 and 400°C, was approximately 15 min, and it was maintained at the same temperature for 120 min. During the experiment, the flow rate of Ar–O₂ (10 mol%) gas mixture was 2.0 L/min (S.T.P.).

2.3. Sampling and Analysis of Dioxins and Adsorbable Organic Chlorine (AOX)

The term “dioxins” generally refers to the following three groups of compounds: polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofuran (PCDFs), and coplanar poly-chlorinated biphenyls (PCBs or dioxin-like PCBs). However, in the de novo experiment, the concentration of PCDD and PCDF (PCDD/Fs) congeners combined with more than four chlorines, i.e., tetra- to octachlorinated PCDD/Fs, was analyzed. Since the contribution of co-PCBs to the toxic concentration in the combustion gases is usually small, i.e., less than 10% of the total values, tetra- to octa-chlorinated PCDD/Fs can represent the characteristics of the dioxin formation from fly ashes in terms of toxicity.9

For the sampling of PCDD/Fs contained in the outlet gas, the gas was passed through an ice-cooled gas trap that con-
tained five impingers and an XAD-II resinous column (see Fig. 1(a)). The first two impingers contained distilled water (100 cm³), the fourth one contained diethylene glycol (100 cm³), and the third and last ones were empty. After the experiment, the interiors of the impingers, gas tubes, and connectors were carefully washed with dichloromethane. Then, all the washing fluids were mixed with the sample solvents, i.e., water and diethylene glycol in the impingers, and subjected to PCDD/Fs analysis. PCDD/Fs present in the fly ash samples were also analyzed by the Soxhlet extraction method. The sampling of the outlet gas from the reactor and the clean-up and analysis of PCDD/Fs were carried out in accordance with the procedure of JIS K 0311.10)

The sampling of organic chlorine was carried out by introducing the outlet gas into ice-cooled columns of activated carbon (see Fig. 1(b)). The sampling column consisted of three beds, and each bed was packed with 1 g of activated carbon particles. After the experiment, the activated carbon was first rinsed with distilled water, followed by rinsing with an aqueous solution of potassium nitrate (0.8 mass% of KNO₃) in order to remove the inorganic chlorides. Subsequently, Ar gas was passed over the activated carbon particles to dry them. The amount of chlorine that remained on the activated carbon particles was determined using the “total organic chlorine halogen analyzer,” which employs the procedure of combustion/potentiometric redox titration. The obtained value corresponds to the amount of chlorine combined with organic compounds adsorbed on the surface of the activated carbon; therefore, it is referred as “adsorbable organic chlorine (AOX).”11)

2.4. Test Operation Using a Waste Incinerator

A verification test was carried out using a small solid waste incinerator. The outline of the incinerator is shown in Fig. 2. It consists of a fixed-bed-type furnace with a capacity of 400 kg/h, a heat exchanger, gas cooling tower with water splay, and bag filter. An aqueous solution of urea (10 or 20 mass%) was added to the water that was splayed into the cooling tower. The concentration of urea in the splayed water was set at three different levels, i.e., 0 (no addition), 0.1, and 0.2 mass%. The average splaying rate was approximately 2000 kg/h. However, in order to maintain the outlet gas temperature at the exit of the cooling tower to be less than 200°C, the splaying rate was occasionally changed depending upon the inlet gas temperature. Therefore, the concentration of urea in the splayed water varied slightly with time. In each case, urea addition was continued for 4.5 h, and the sampling of the dioxins in the waste gas at the stack was carried out for 4 h during the urea addition. Dioxin analysis was carried out in accordance with the procedure of JIS K 0311,10) although the dioxin concentration in the gas and dust samples was determined individually.

3. Results and Discussions

3.1. De Novo Experiment Using Dust Samples

Figure 3 shows the amount of PCDD/Fs discharged with the outlet gas during the de novo experiments using samples A and B. The values were compared on the basis of unit sample mass. In the case of a holding temperature of 300°C, the amount of PCDD/Fs discharged from sample A was halved by the addition of 20 mg of urea per gram of the sample. A further decrease was obtained when sample B was used. The results obtained at a higher holding temperature of 400°C, show a similar tendency as those obtained at 300°C. However, considerably less PCDD/Fs emissions were observed for all the cases; in particular, the samples
with urea addition yielded significantly small values.

The results of the AOX analysis of the outlet gas are shown in Fig. 4. For sample A, the amount of AOX increases with an increase in the temperature up to 350°C and subsequently decreases. Sample B shows a similar temperature dependence. Such a trend is also observed for the cases of urea addition to both the samples. It should be noted that the obtained amount of AOX decreases due to the urea addition; however, it is not significant as compared to that found for dioxins.

Certain suppression effects of nitrogen-containing compounds, e.g., urea, ammonia, monoethanolamine, triethanolamine, and EDTA (ethylenediaminetetraacetic acid) on the formation of dioxins have been reported. Some of them have attributed such an effect to the formation of the Cu–N bond or a complex composed of Cu and N because they may reduce the activity of Cu, which is regarded as the main catalytic material promoting the oxidation and chlorination reactions of carbonaceous materials. However, such mechanisms cannot explain the difference between the effect of the urea addition on dioxins (Fig. 3) and AOX (Fig. 4) emissions.

Figure 5 shows an image of the oxidation reaction of macrostructural carbon-like soot that coexists with copper chloride at approximately 300°C. Copper chloride acts as a supplier of chlorine and oxygen to the edge of the carbon surface through redox reactions. This facilitates the oxidation reaction of carbon even at a lower temperature such as 300°C. In this case, various organic compounds containing chlorine can be formed, for example, chloromethanes, chloroethanes, and chloroaldehydes, although the main products of the reactions are CO and CO₂. Further, cyclic hydrocarbons such as chlorophenols, chlorobenzenes, and dioxins are also formed. These reactions have often been called de novo synthesis. Figure 6 shows the possible reactions occurring in the case of the urea addition. On heating, urea (CO(NH₂)₂) changes to cyanuric acid (C₃N₃(OH)₃) or biuret (C₂H₅N₃O₂) by releasing ammonia (NH₃), as shown in Fig. 7. These compounds further change to other compounds such as cyanic acid (HOCN) along with the release of NH₃ and CN radicals. These radicals can react with the carbon atoms at the edge sites by replacing the functional groups. Further, some of them may aid the formation of pyridine-like structures at the carbon surface, wherein the carbon in the six-membered ring is replaced by nitrogen (pyridine nitrogen).

When macrostructural carbon is oxidized at relatively lower temperatures, various organic compounds will be formed. Further, there is a certain possibility that such compounds contain nitrogen when urea is added to the system. In fact, the formation of 2,2,2-trichloroacetamide, 4-chlorobenzonitril, 4-chloro-2-methyl-benzenamine, and 2,6-dichlorobenzonitrile was confirmed for certain concentrations. Further, the presence of pentachloropyridine was also detected. This supports the abovementioned formation of a pyridine-like structure on the carbon surface. With regard to the AOX analysis, the formation of the nitrogen-bearing organic compounds does not appear to substantially affect its concentration because chlorines combined with such compounds can be considered as AOX. A certain suppression effect of the urea addition on the AOX formation, as observed from Fig. 4, can be attributed to the reactions between the released nitrogen-containing compounds/radicals and reactive chlorines. For example, if NH₄Cl is formed by such reactions, the chlorination of organic compounds and formation of the C–Cl bond at the edge of the carbon surface will be prevented. However, in the case of
As shown in Fig. 8(a), there is a possibility of the formation of dibenzofurans (DFs) combined with both chlorine and CN and/or NH$_2$; however, such DFs are not considered as PCDFs. Besides, PCDFs are rarely formed from the pyridine-like structures formed on the carbon surface (Fig. 8(b)). This can explain the difference between the effects of the urea addition on the emissions in PCDD/Fs (Fig. 3) and AOX (Fig. 4).

3.2. Tests of Addition of Urea to the Splay Water of the Cooling Tower of Waste Incinerator

During the test operations using the waste incinerator, the concentration of urea in the splayed water of the cooling tower was checked every 30 min. Since the flow rate of the splayed water was varied with time as mentioned previously, the urea concentration changed within approximately 20% of the set value. Nevertheless, the average concentrations for the set values of 0.1% and 0.2% are 0.095% and 0.21%, respectively. Under the base condition (without urea addition), the concentration of urea in the splayed water was always less than the detection limit (<10 ppm).

The TEQ concentrations of the dioxins in waste gases are compared in Fig. 9. In this figure, the concentrations were normalized by the value obtained under the base condition. A remarkable decrease in the concentrations was observed due to the urea addition. However, a significant difference is not observed between the urea concentrations of 0.1 and 0.2 mass%. The toxic fractions of PCDDs, PCDFs, and co-PCBs in the waste gases are compared in Fig. 10. These fractions do not appear to be very clear; however, the
amount of PCDFs tends to increase and that of PCDDs decreases with urea addition.

Figure 11 shows the average concentration of NOx in the waste gas for each case. The concentration increases slightly with the urea addition. The NOx concentration in the splayed water is increased by 0.1%. Such an increase may be attributed to the oxidation of ammonia released from urea (refer to Fig. 7). Consider the case in which the gas flow rate at the cooling tower is 7300 Nm$^3$/h and the urea concentration in the splayed water is set to 0.1 mass%. If all the nitrogen atoms present in urea are converted to NOx, the concentration of NOx in the waste gas will increase by approximately 103 ppm; therefore, the conversion ratio of nitrogen in the urea to NOx is estimated to be less than 7%.

4. Conclusions

In order to elucidate the effect of the urea addition to waste gas during its cooling stage on the formation of dioxins through the de novo synthesis reaction, a series of experimental studies have been carried out using the fly ashes sampled from two different types of solid waste incinerators. The urea addition led to a remarkable decrease in the amount of dioxins formed from the fly ashes. The effect of the urea addition at a temperature of 400°C is greater than that at 300°C. However, there is no significant change in the amount of obtained organic chlorine. The suppression mechanism of the dioxin formation by the urea addition has been discussed from the viewpoint of the reactions in relation to the functional groups on the edge of the carbon surface.

Based on the abovementioned results, the method of urea addition to the water splayed into the gas cooling tower is proposed as an effective measure to suppress the dioxin formation at the cooling stage of the combustion gases. A verification test was carried out using a solid waste incinerator consisting of a fixed-bed-type furnace. When the urea concentration in the splayed water was set to 0.1 mass%, the toxicity concentration of the dioxins in the waste gas reduced to half that in the case without the addition. Further, the urea addition did not affect the concentration of NOx in the waste gas significantly.

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REFERENCES

1) L. Stiegitz and E. R. Altwicker: *Chemosphere*, 34 (1997), 1083.
2) L. Stiegitz, G. Zwick, J. Beck, W. Roth and H. Vogg: *Chemosphere*, 18 (1989), 1219.
3) M. S. Milligan and E. R. Altwicker: *Environ. Sci. Technol.*, 27 (1993), 1595.
4) L. Stiegitz, M. Eichberger, J. Schleiauf, G. Zwick and R. Will: *Chemosphere*, 27 (1993), 343.
5) R. Addink, F. Espouart and E. R. Altwicker: *Environ. Sci. Technol.*, 32 (1998), 3356.
6) V. Pekárek, R. Grabic, S. Marklund, M. Puncrochár and J. Ulrich: *Chemosphere*, 43 (2001), 777.
7) G. Mul, F. Kapteijn and J. A. Moulijn: *Appl. Catal. B: Environ.*, 12 (1997), 33.
8) S. Kuzuhara, H. Sato, N. Tsubouchi, Y. Ohtsuka and E. Kasai: *Environ. Sci. Technol.*, 39 (2005), 795.
9) M. Till, P. Behnisch, H. Hagenmaier, K. W. Bock and D. Schrenk: *Environ. Health Perspect.*, 105 (1997), 1326.
10) Method for determination of tetra- through octa-chlorodibenzo-p-dioxins, tetra- through octa-chlorodibenzofurans and coplanar polychlorobiphenyls in stationary source emissions (JIS K 0311), Japanese Standard Association, (1999).
11) H. Shintani, Y. Matsumoto and G. Meshitsuka: *J. Pulp Paper Sci.*, 22 (1996), 372.
12) P. Samaras, M. Blumenstock, D. Lenoir, K. W. Schramm and A. Kettrup: *Environ. Sci. Technol.*, 34 (2000), 5092.
13) P. Samaras, M. Blumenstock, D. Lenoir, K. W. Schramm and A. Kettrup: *Chemosphere*, 42 (2001), 737.
14) P. Ruokojarvi, M. Aattamila, K. Tuppuranen and J. Ruuskanen: *Chemosphere*, 43 (2001), 757.
15) P. Ruokojarvi, I. A. Halonen, K. Tuppuranen, J. Tarhanen and J. Ruuskanen: *Environ. Sci. Technol.*, 32 (1998), 3099.
16) C. Xhouet, C. Nadin and E. De Pauw: *Environ. Sci. Technol.*, 36 (2002), 2760.
17) R. Addink, R. H. Paulus and K. Olle: *Environ. Sci. Technol.*, 30 (1996), 2350.
18) T. Lippert, A. Wokaun and D. Lenoir: *Environ. Sci. Technol.*, 25 (1991), 1485.
19) K. Tuppuranen, M. Aattamila and P. Ruokojarvi: *Chemosphere*, 38 (1999), 2205.
20) A. Fullana, H. Nakka and S. Sidhu: *Organohalogen Compounds*, 63 (2003), 147.