



Title	Mechanism of Dioxins/Furans Fromation at High Temperature in Combustion Processes
Author(s)	Kawabata, Hitoshi; Usui, Tateo; Marukawa, Katsukiyo et al.
Citation	ISIJ International. 2003, 43(3), p. 461-467
Version Type	VoR
URL	https://hdl.handle.net/11094/26411
rights	© 2003 ISIJ
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Mechanism of Dioxins/Furans Formation at High Temperature in Combustion Processes

Hirotoishi KAWABATA, Tateo USUI, Katsukiyo MARUKAWA,¹⁾ Shigeta HARA, Toshihiro TANAKA and Hideki ONO-NAKAZATO

Department of Materials Science and Processing, Graduate School of Engineering, Osaka University, Japan.

1) Collaborative Research Center for Advanced Science and Technology, Osaka University, Japan.

(Received on October 7, 2002; accepted in final form on November 6, 2002)

To understand the mechanism of toxic dioxins/furans (Dioxins) formation in incineration processes, the combustion experiments were carried out with an electric furnace in laboratory scale at 1 073 K using mainly the powder of reagent grade polyvinyl chloride (PVC powder) as a combustion material under a complete and an incomplete combustion conditions. In addition, the thermodynamic evaluations have been done on the formation and decomposition of Dioxins.

Dioxins are formed even at the combustion temperature of 1 073 K under the conditions in which the fly carbonaceous matters exist. It is supposed that Dioxins are mainly formed on the surface of the fly carbonaceous matters where high CO/CO₂ ratio is established. Dioxins' concentration is correlated with the number of the fly carbonaceous matters in an exhaust gas. The formation/suppression of Dioxins is dependent upon the amount of the fly carbonaceous matters remained in the exhaust gas from the combustion furnaces.

KEY WORDS: dioxins/furans; fly carbonaceous matters; formation at high temperature; incineration; CO/CO₂

1. Introduction

It is well known that dioxins/furans (Dioxins) are highly toxic and unintentionally formed in combustion processes such as municipal and industrial waste incinerations. Many studies^{1–10)} have been done to suppress the formation of Dioxins and their emission in combustion processes. It is said that Dioxins virtually decompose at high temperatures over 873 K⁴⁾ or 973 K.¹¹⁾ Most of the studies focus on a *de novo* synthesis of Dioxins at nearly 573 K in cooling processes (in the present study, the formation of Dioxins in cooling processes is called the *de novo* synthesis), and the mechanisms of Dioxins formation and decomposition are mainly discussed with the combination of catalytic reactions. Some other studies^{12–14)} have been carried out on the formation of Dioxins in the combustion process at high temperature.

The experimental studies on the *de novo* synthesis indicate that Dioxins are mainly formed at nearly 573 K within fly ash under O₂ surplus conditions,^{5,6)} and the concentration of Dioxins increases with an increase in the amount of fly ash and fly carbonaceous matters.^{15,16)} On the other hand, thermodynamic evaluations¹⁷⁾ for the formation of Dioxins represent that (1) Dioxins are never formed in the case of O₂ surplus under the complete combustion conditions, and (2) Dioxins are not formed under the conditions coexisting solid carbon, *i.e.* when carbon deposition is considered. The discrepancies between Dioxins formation obtained from the thermodynamic evaluations¹⁷⁾ and those of the experimental studies described above^{5,6,15,16)} may come from the reason that Dioxins are formed under the non-

equilibrium or non-uniform site near the fly ash coexisted and any kinetic factors are not taken into account.

It is very difficult to accomplish the thermodynamic equilibrium in the combustion experiments¹⁸⁾ and in the actual incineration processes. For example, fly ashes included small amounts of unburned carbon and some carbonaceous matters are observed in many incineration processes although they should be burned out at high temperature. In other words, they are formed microscopically in an incomplete combustion which is not an equilibrium state, even if they are macroscopically under the complete combustion conditions, namely O₂ surplus conditions. Consequently it is considered that the reactions of many incineration processes under the complete combustion conditions occur under non-equilibrium conditions from the microscopic view, *i.e.* apparently incomplete combustion states.

The purpose of the present study is to elucidate the reasons for the discrepancy between the thermodynamic evaluations and the experimental results on the Dioxins formation at high temperature, and to understand the mechanism of the Dioxins formation at high temperature in the incineration processes. In the present work, the combustion experiments were done with an electric furnace in laboratory scale at 1 073 K under apparently complete and incomplete combustion conditions. The powder of reagent grade polyvinyl chloride (PVC powder) with high possibility of the formation of Dioxins was mainly used as the combustion materials. In addition, the thermodynamic evaluations of Dioxins at high temperature have been carried out using the thermodynamic software, MALT 2.¹⁹⁾

2. Experimental

Figure 1 shows a schematic layout of the combustion furnace. The combustion furnace is composed of an electric furnace with three-divided heating parts to obtain a long isothermal zone by controlling the temperature separately. A combustion tube is made of SUS 316 with 157 mm inside diameter. The temperature in the combustion tube was controlled at 1073 K. The isothermal zone at 1073 ± 10 K, in which a part of an exhaust pipe is included, is 250 mm long as shown in Fig. 1. The feed rate of combustion materials, mostly PVC powder having a size of $200 \mu\text{m}$, was set to be 0.1 g/min by using a fixed quantity feeder which was installed in the upper part of the combustion tube. A combustion zone is composed of the primary combustion part and the secondary combustion part. This primary combustion part is for the preheating, the gasification and the combustion of the combustion materials, and the secondary combustion part is within a bed packed with mixtures of alumina balls having two sizes of $\phi 10$ and 15 mm, where gas and unburned materials are well mixed and combusted with a heat exchange. Total flow rate of the supplied gas mixtures of O_2 and N_2 was set to be 2 l/min (s.t.p.) by controlling each gas flow rate with the mass flow controllers. The PVC powder, a fine powder of carbon (C powder) or the mixtures of their powders (PVC and C) was fed together with gas mixtures from the top of the combustion tube. Reynolds number Re based on the inside diameter of the combustion tube is about 8 at 1073 K and residence time of the gas in the isothermal zone at 1073 K within the combustion tube is about 22 s in the present experimental conditions, when gas stream is assumed to be a plug flow.

Water cooling tube was installed in the top of the combustion tube (see Fig. 1) to shorten the temperature region below 1073 K. In order to avoid the *de novo* synthesis of Dioxins in the gas cooling process as much as possible, an exhaust gas must be rapidly cooled. Therefore the gas was injected directly into the two impingers filled with distilled water keeping at 278 K (a gas sampling system for Dioxins). The time needed to cool the exhaust gas from 773 to 278 K in the gas sampling system was evaluated about 0.5 s. To monitor the combustion conditions, the main compositions of the exhaust gas were continuously measured by using a gas-mass analyzer.

In the present experiments, the feed rates of combustion materials were 0.1 and 0.04 g/min in the case of PVC and C powder, respectively. These feed rates were determined for the reason that the combustion materials could be burned out with the amount of 5 vol% O_2 in the supplied gas of 2 l/min (s.t.p.). Two kinds of the gas compositions were selected as follows:

- 1) 40vol% O_2 –60vol% N_2 , 2) 5vol% O_2 –95vol% N_2

Even under the combustion conditions with the gas composition of 40vol% O_2 –60vol% N_2 and the residence time of 22 s at 1073 K, an extremely small amount of the fly carbonaceous matters in the exhaust gas was detected in the present experiments. Therefore it is considered that the microscopically non-uniform site is retained in the exhaust gas even under the complete combustion conditions. In the present study, the combustion experiments in the case of

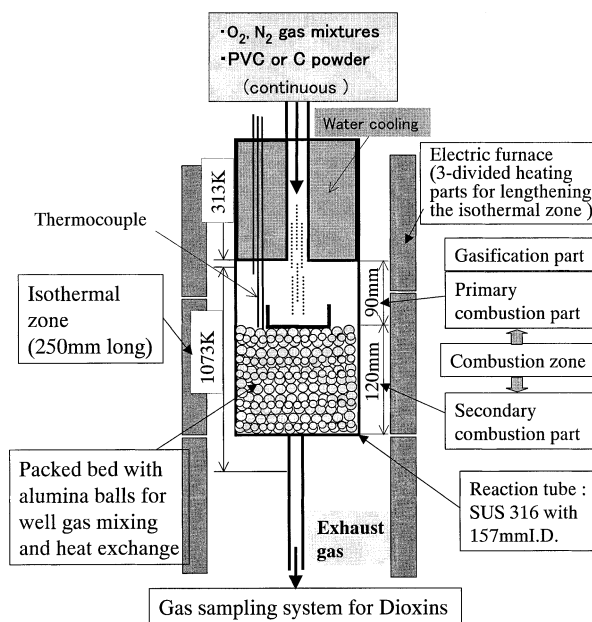


Fig. 1. Schematic layout of the combustion furnace.

Table 1. Experimental conditions and Dioxins' concentrations in the exhaust gas under the complete combustion conditions (40vol% O_2 –60vol% N_2 , 1073 K).

Run No.	Combustion materials (mass%)	PVC, C feed rate (g/min)	Dioxins' concentration (ng/m ³)(s.t.p.)		O_2 , CO in exhaust gas (vol %)	Conditions of packed bed
			Total	TEQ		
1	100%PVC	0.1	230	8.8	35, 0	Alumina balls
2	100%PVC	0.1	110	3.5	35, 0	Alumina balls + Ceramic fiber blankets
3	5%PVC + 95%C	0.05	7.1	0.13	35, 0	Alumina balls

40vol% O_2 –60vol% N_2 are called “the complete combustion condition”.

Although it is assumed that the combustion materials were burned out in the thermodynamic equilibrium conditions with the gas composition of 5vol% O_2 –95vol% N_2 , the large amount of the fly carbonaceous matters was observed in the present experiments. Therefore these combustion conditions are called “the incomplete combustion condition” in the present study.

3. Experimental Results and Discussions

3.1. Formation of Dioxins under the Complete Combustion Conditions at 1073 K

(a) Combustion of 100 mass% PVC (Run No. 1)

Table 1 summarizes the experimental conditions and Dioxins' concentrations in the exhaust gas under the complete combustion conditions. The feed rate of the PVC powder is 0.1 g/min. Under this condition, O_2 concentration of the exhaust gas was about 35 vol% and CO could not be detected, but the extremely small amount of the fly carbonaceous matters was found in the exhaust gas by a capturing equipment with fiber papers made of silica. The fly carbonaceous matters observed by an optical microscope and a scanning electron microscope (SEM) were extremely fine

particles from about 0.5 to 40 μm (shown in Figs. 5, 6 later). Since the fly carbonaceous matters which seem to be formed from the unburned materials in microscopically incomplete combustion are detected, it can be considered that the microscopically non-uniform site is retained in the exhaust gas even under the complete combustion conditions.

As shown in Table 1, the total TEQ (Toxic Equivalent Quantity) and the total Dioxins' concentrations of the exhaust gas of Run No. 1 including the fly carbonaceous matters were 8.8 ng-TEQ/m³ (s.t.p.) and 230 ng/m³ (s.t.p.), respectively.

Although the cooling time of the exhaust gas from 773 to 278 K is about 0.5 s in the present gas sampling system mentioned above, Dioxins' concentration in the present experiments has a little influence of the *de novo* synthesis in the cooling process.^{20,21)} To investigate the influence for the *de novo* synthesis of Dioxins in the present experiments, the exhaust gas was more rapidly cooled by injection of N₂ gas at room temperature with 8 l/min (s.t.p.) into the exhaust gas at temperature zone of 773 K. Dioxins' concentration of the exhaust gas by the above rapid gas cooling was almost the same as that of Run No. 1. Therefore Dioxins in the present experiments can be regarded to be mainly formed in the combustion process at high temperature.

(b) Influence of Decrease of the Fly Carbonaceous Matters (Run No. 2)

It is important to investigate whether Dioxins' concentration decreases or not when the fly carbonaceous matters can be decreased in the combustion process at high temperatures. In order to capture the fly carbonaceous matters temporarily and to promote their combustion in the combustion tube, four ceramic fiber blankets made of silica were put between alumina ball beds in the combustion tube shown in Fig. 2. Ceramic fiber blanket has the fiber diameter from 2

to 5 μm , the void from 20 to 100 μm and the thickness of 15 mm. Then, zigzag flow of combustion gas is formed in blankets with voids of various sizes, gas mixing and heat exchange are promoted.

Dioxins' concentration in the exhaust gas of Run No. 2 with 100 mass% PVC decreases from 8.8 to 3.5 ng-TEQ/m³ (s.t.p.) by installing ceramic fiber blankets under the same complete combustion conditions as that of Run No. 1 (Table 1). The decrease of Dioxins' concentration is considered to be due to the decrease of the amount of the fly carbonaceous matters in the combustion process at high temperature. The promotion of the combustion of the fly carbonaceous matters has an effect on Dioxins' concentration by the enhancement of gas mixing and heat exchange at the high temperature.

(c) Influence of Chlorine Concentration (Run No. 3)

An influence of a chlorine concentration on the formation of Dioxins was investigated by using the mixtures of PVC powder of 5 mass% and C powder of 95 mass%. The chlorine concentration is 1/40 in comparison to the case of 100 mass% PVC (Run No. 1), because the feed rate of the mixtures was set to be half (0.05 g/min) of that for Run No. 1. O₂ concentration of the exhaust gas was about 35 vol% and CO could not be detected. Dioxins' concentration in the exhaust gas of Run No. 3 is as low as 0.13 ng-TEQ/m³ (s.t.p.) and total 7.1 ng/m³ (s.t.p.) as shown in Table 1. The Dioxins' concentration is approximately proportional to the chlorine concentration of the combustion materials, because the total Dioxins' concentration is about 1/30 in comparison to the case of 100 mass% PVC (Run No. 1).

3.2. Formation of Dioxins under the Incomplete Combustion Conditions at 1073 K

(a) Combustion of 100 mass% PVC (Run No. 4)

Table 2 summarizes the experimental conditions and Dioxins' concentrations in the exhaust gas under the incomplete combustion conditions. CO, CO₂ and O₂ concentrations in the exhaust gas of Run No. 4 were about 0.2, 3 and 1.5%, respectively. Since large amount of the fly carbonaceous matters was observed, this combustion condition should be actually regarded as the incomplete combustion.

Dioxins' concentration of Run No. 4, in which many fly carbonaceous matters are included in the exhaust gas, is as high as 170 ng-TEQ/m³ (s.t.p.) and total 15 000 ng/m³ (s.t.p.). This total value is about 70 times larger than that under the complete combustion conditions using 100 mass% PVC (Run No.1) described above.

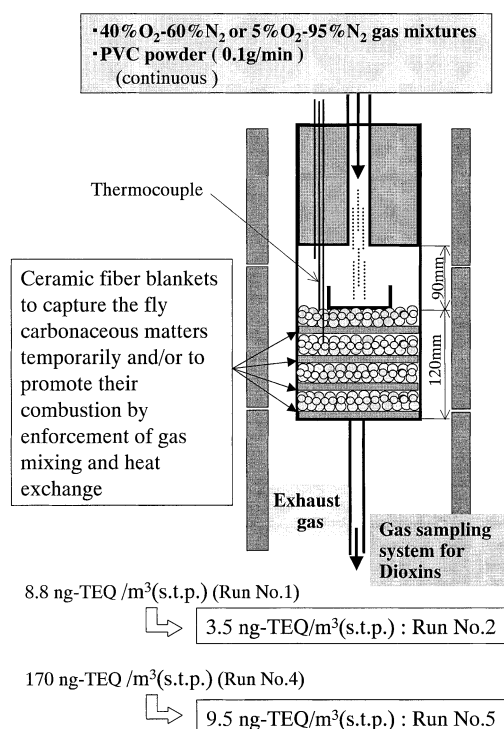


Fig. 2. Effect of the decrease in the fly carbonaceous matters at high temperature on Dioxins' concentration.

Table 2. Experimental conditions and Dioxins' concentrations in the exhaust gas under the incomplete combustion conditions (5vol%O₂-95vol%N₂, 1073 K).

Run No.	Combustion materials (mass%)	PVC, C feed rate (g/min)	Dioxins' concentration (ng/m ³)(s.t.p.)		O ₂ , CO in exhaust gas (vol %)	Conditions of packed bed
			Total	TEQ		
4	100%PVC	0.1	15,000	170	1.5, 0.2	Alumina balls
5	100%PVC	0.1	340	9.5	0.1, 2.5	Alumina balls + Ceramic fiber blankets
6	H ₂ + Cl ₂ and C powder	0.04	44	1.3	0.7, 0.1	Alumina balls

(b) Influence of Decrease of the Fly Carbonaceous Matters (Run No. 5)

Run No. 5 with 100 mass% PVC shown in Table 2 and Fig. 2 was carried out by using four ceramic fiber blankets to decrease the fly carbonaceous matters in the combustion tube under the same incomplete combustion conditions as that of Run No. 4. In the experiment of Run No. 5, O₂ concentration in the exhaust gas decreased from 1.5 to 0.1 vol% and CO concentration increased from 0.2 to 2.5 vol%. Dioxins' concentration in the exhaust gas decreases from 170 to 9.5 ng-TEQ/m³ (s.t.p.). The decrease of Dioxins' concentration comes from the reason that the amount of the fly carbonaceous matters decreased in the combustion process at high temperature. The promotion of the combustion of the fly carbonaceous matters by the enhancement of gas mixing and heat exchange at high temperature has great effect on Dioxins' concentration.

Several examples of the fingerprints of Dioxins in the case of 100 mass% PVC as the combustion materials are summarized in Figs. 3(a), 3(b), which are obtained under the complete combustion conditions. The fingerprints in Fig. 3(a) shows that the higher chlorinated dioxins for dioxin congeners (PCDDs) have higher concentration, while the trend of furans for furan congeners (PCDFs) shows similar

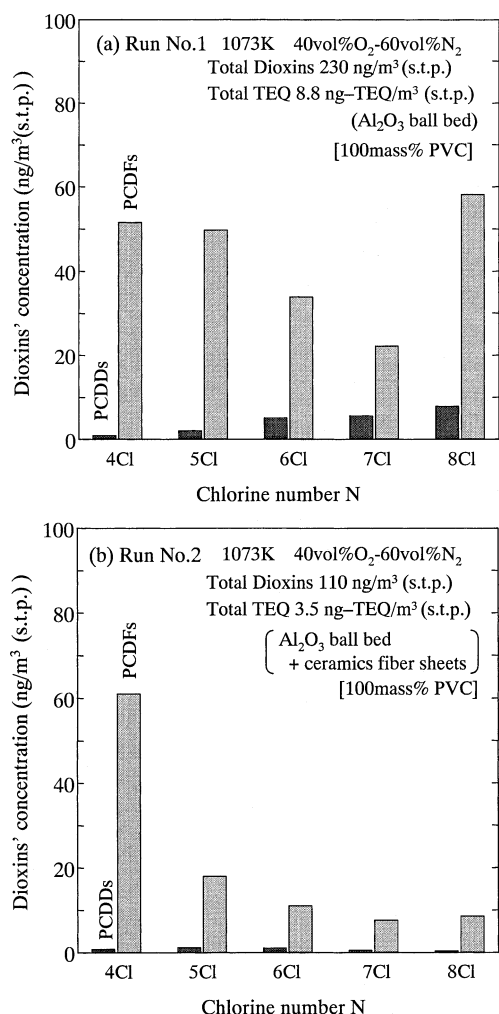


Fig. 3. Effect of the enhancement of combustion on the fingerprints of Dioxins under the complete combustion conditions. (a) The bed packed with only Al₂O₃ balls. (b) Four ceramic fiber blankets put between Al₂O₃ ball bed.

concentrations except H₂CDFs (Run No. 1). On the other hand, Run No. 2 using the ceramics fiber blankets for enhancement of the combustion of the fly carbonaceous matters represents the completely reverse trend that the concentrations for both furans and dioxins increase as the chlorinated numbers decrease (Fig. 3(b)). Comparison between the trends of Run No. 1 and 2 indicates that Dioxins (Run No. 1) formed at high temperatures decompose to the lower chlorinated Dioxins (Run No. 2) by the enhancement of the combustion. This tendency is also recognized in the fingerprints of Run Nos. 4 and 5 under the incomplete combustion conditions with 100 mass% PVC. Therefore, it is suggested that the trend of fingerprints has been changed in the combustion conditions at high temperature.

(c) Combustion of Fine C Powder in H₂, Cl₂, O₂ Gas Mixtures (Run No. 6)

Although the experimental results using PVC powder have been described above, it is important to investigate whether Dioxins are formed or not in the combustion condition without an organic compound. Then, the combustion experiment without PVC powder was carried out using H₂, Cl₂, O₂ gasses and C powder with the size of 60 μm at 1 073 K. The supplied mol ratios of H, Cl and C were the same as those of 100 mass% PVC and the other combustion conditions were identical to the incomplete combustion conditions (Run No. 4). The experimental result (Run No. 6) is shown in Table 2. Although the Dioxins' concentration is 1.3 ng-TEQ/m³ (s.t.p.) and total 44 ng/m³ (s.t.p.), Dioxins are actually formed in the condition even without organic compounds.

3.3. Relation between Dioxins' Concentration and the Number of Fly Carbonaceous Matters

The number of fly carbonaceous matters captured with the filter papers made of silica from the exhaust gas was counted by using an optical microscope. The number of those fly carbonaceous matters in the cases of 100 mass% PVC (Run No. 1), 5 mass% PVC (Run No. 3) under the complete combustion conditions and 100 mass% PVC (Run No. 4) under the incomplete combustion conditions are 980, 270 and 12 000 pieces/l, respectively. Figure 4 shows

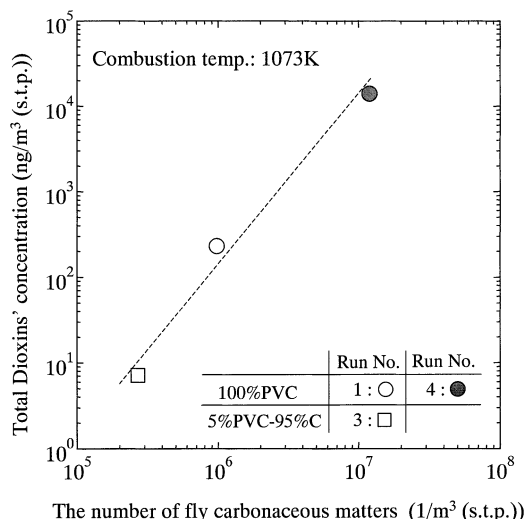


Fig. 4. Relation between total Dioxins' concentration and the number of the fly carbonaceous matters in exhaust gas.

the relation between the total Dioxins' concentration and the number of fly carbonaceous matters. Total Dioxins' concentration increases as the number of fly carbonaceous matters increases in the exhaust gas. Therefore, one of the important points on the formation/suppression of Dioxins is to control the existence of the fly carbonaceous matters remained in the combustion gas at high temperature.

3.4. Microscopic Observation of the Fly Carbonaceous Matters

To observe and chemically analyze the fly carbonaceous matters, the fly carbonaceous matters were collected from the exhaust gas by the capturing equipment with the filter papers. **Figure 5** shows some examples of the photographs of the fly carbonaceous matters observed by an optical microscope. The small amount of the fly carbonaceous matters with the size from 0.5 to 30 μm was detected in the exhaust gas of 30 l under the complete combustion conditions (Fig. 5(a)), and under the incomplete combustion conditions the large amount of the fly carbonaceous matters having the size from 0.5 to 40 μm was detected in the exhaust gas of only 4 l (Fig. 5(b)).

Figure 6 shows some photographs of 7500 magnifications of the fly carbonaceous matters by SEM under the complete combustion conditions (Run No. 1). Although various sizes of the fly carbonaceous matters attached on silica fiber were found, their surface is smooth such as liquid. From chemical analysis by gas chromatography-mass spectrometry (GC-MS), precursor such as phenol, benzene,

biphenyl, naphthalene, anthracene, and their chloride *etc.* have been detected in the fly carbonaceous matters. Wang *et al.*²²⁾ have also reported that chlorinated polycyclic aromatic hydrocarbons have been formed in the combustion of PVC.

Dioxins and precursor are formed even at combustion temperature as high as 1073 K under the existence of the fly carbonaceous matters. Generally, the fly carbonaceous matters should be, however, decomposed thermally at the combustion temperature of 1073 K.²³⁾ Therefore, the inner temperature of the fly carbonaceous matters may be lower than the combustion temperature, because their decomposition occurs under endothermic reactions. The further examinations on this subject have to be carried out in detail.

4. Thermodynamic Evaluations on the Formation of Dioxins

In order to evaluate the formation and the decomposition behaviors of Dioxins at high temperature of 1073 K, the thermodynamic evaluations were carried out using the thermodynamic software, MALT 2.¹⁹⁾ The thermodynamic data for Dioxins¹⁷⁾ and precursors²⁴⁾ were the same as that of Yazawa *et al.*, in which the species having the same molecular formula and the same toxic equivalent factor were summated. The carbon deposition was neglected in the thermodynamic evaluations of Dioxins, because Dioxins were not formed under low CO/CO₂ ratio with the carbon coexisted.

Figures 7 and 8 show the calculated results for the influence of the mol quantity of O and C on the formation of

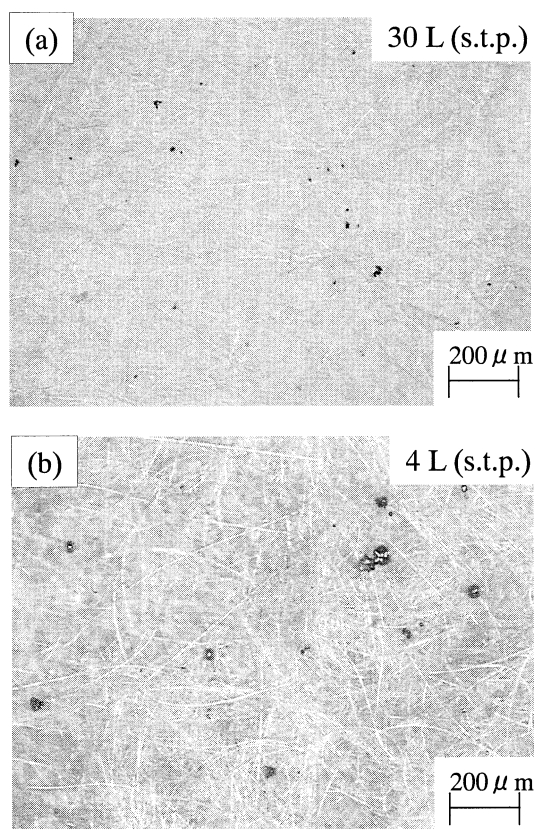


Fig. 5. The fly carbonaceous matters captured by the ceramic filter paper from the exhaust gas (1073 K, 100 mass% PVC, Al₂O₃ ball bed). (a) Under the complete combustion conditions (Run No. 1). (b) Under the incomplete combustion conditions (Run No. 4).

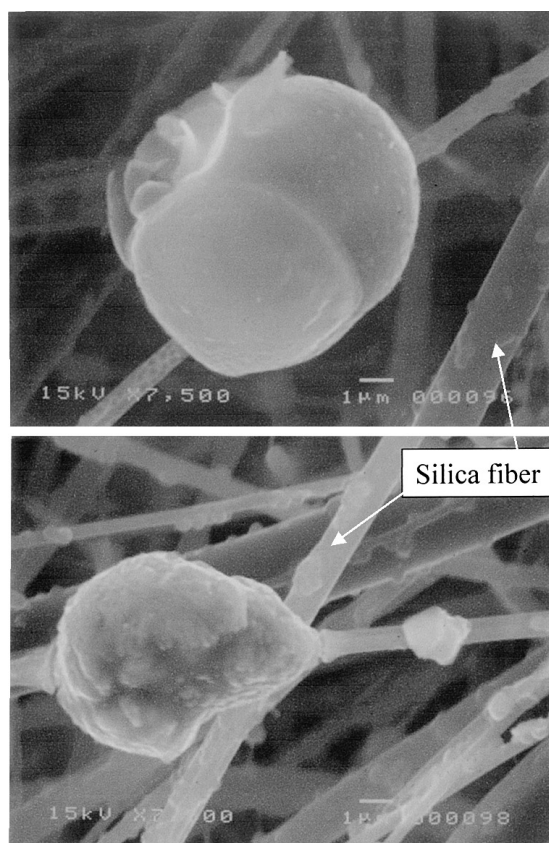


Fig. 6. SEM photographs of the fly carbonaceous matters shown in Fig. 5(a).

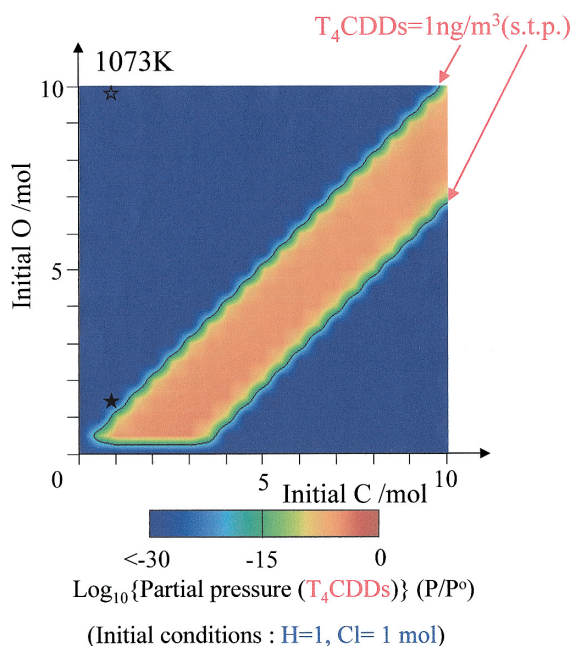


Fig. 7. Influence of O and C on the formation of T_4CDDs at 1073 K (P^0 : standard pressure).

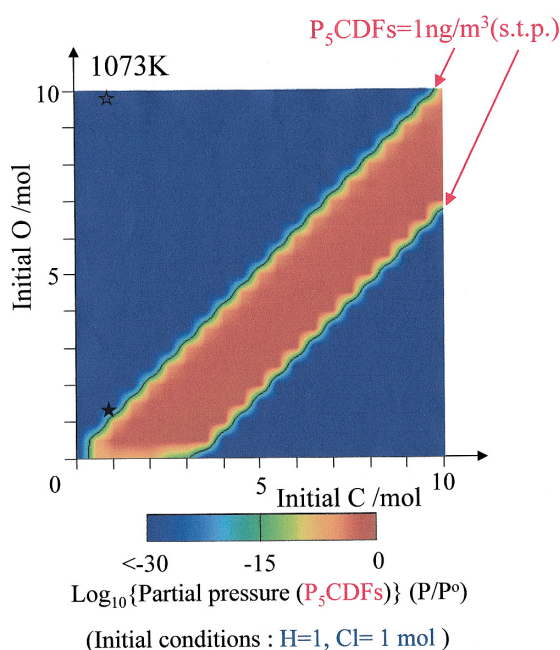


Fig. 8. Influence of O and C on the formation of P_5CDFs at 1073 K (P^0 : standard pressure).

T_4CDDs and P_5CDFs under the initial conditions of 1 mol H and 1 mol Cl at 1073 K. The profiles of the formation for other dioxins/furans were similar to those for T_4CDDs and P_5CDFs . The change of CO/CO_2 ratio under the same conditions as Figs. 7 and 8 is shown in Fig. 9. These results in the present estimations can be applied to the limited region near the surface of the fly carbonaceous matters. The symbol ☆ and ★ in Figs. 7 and 8 indicate the complete combustion and the incomplete combustion conditions under the present experiments, respectively. Dioxins and furans are actively formed in the regions of red and orange (Figs. 7 and 8), where CO/CO_2 ratio is very high (Fig. 9), but dioxins and furans are hardly formed in the region of blue under

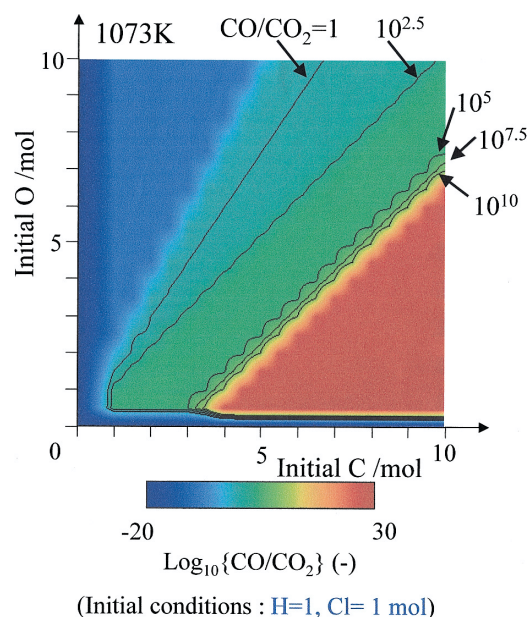


Fig. 9. Influence of O and C on CO/CO_2 ratio at 1073 K.

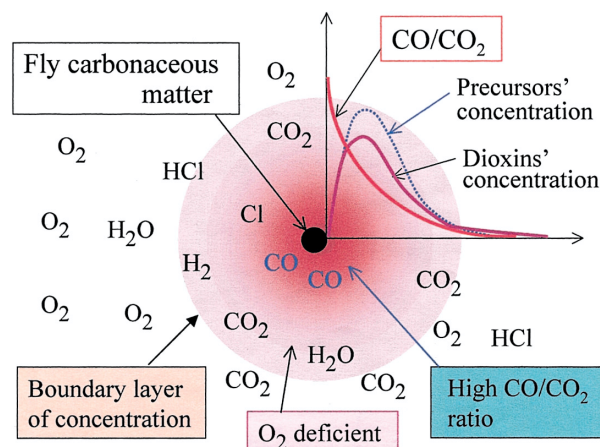


Fig. 10. Mechanism of Dioxins formation at high temperature.

the oxidized or very strongly reduced atmosphere.

The thermodynamic evaluations show that Dioxins are never formed with O_2 surplus conditions, because high CO/CO_2 ratio cannot be obtained in thermodynamically homogeneous equilibrium state of gas phase under O_2 surplus conditions. On the other hand, as mentioned above, the experimental results represent that Dioxins are formed under the existence of the fly carbonaceous matters, which are caused by the microscopically incomplete combustion even in the complete combustion conditions. Dioxins may be considered to be formed when the heterogeneous site with high CO/CO_2 ratio exists.

Although the reactions of ① $2CO \rightarrow C + CO_2$ (carbon deposition) and ② $C + CO_2 \rightarrow 2CO$ (CO formation; oxidation of the fly carbonaceous matter by CO_2) occur in the site of high CO/CO_2 ratio around the fly carbonaceous matters, Dioxins may be formed by assuming that (1) the heterogeneous site with high CO/CO_2 ratio is kept by the reaction of CO formation, and/or (2) the rate of the formation of Dioxins is a little higher than the rate of the carbon deposition. The kinetics of the formation of Dioxins is one of the

important factors to decide the amount of Dioxins. The fundamental studies on this subject should be investigated in the near future.

5. Mechanism of Dioxins Formation at High Temperature

From the present investigations described above, the mechanism of Dioxins formation at 1073 K may be considered as follows: the fly carbonaceous matters with the size of 0.5–40 μm are moving together with the bulk flow, where Reynolds number Re based on the particle becomes much smaller than 1 because the relative velocity between the fly carbonaceous matters and the bulk flow is nearly zero. Then, Stokes flow is formed around these fine particles and the flow almost stagnates. Thus, the boundary layer becomes very thick on the surface of the fly carbonaceous matters. CO/CO_2 ratio becomes high in this boundary layer. As shown in Fig. 10, it can be estimated that Dioxins are mainly formed in the boundary layer on the surface of the fly carbonaceous matters with high CO/CO_2 ratio. It was reported that polycyclic aromatic compounds including precursors were detected in the fly carbonaceous matters from the chemical analysis and were quickly made up under the microscopically incomplete combustion.^{22,25,26} It may be considered that Dioxins and precursors decompose at the high temperature when some Dioxins and precursors diffuse to the outside of the boundary layer, but the other Dioxins and precursors are still keeping in the layer. These formation and decomposition reactions are repeated around the boundary layer. Dioxins in the boundary layer are carried with a combustion gas stream and are exhausted from the combustion furnace when the fly carbonaceous matters are still existing in the exhaust gas. It can be considered that the formation of Dioxins is mainly attributed to the fly carbonaceous matters in the combustion gas. Therefore, one of the important points on the zero formation of Dioxins can be considered to burn out the fly carbonaceous matters in the furnaces by more enhancement mixing with combustion gases.

6. Conclusions

The combustion experiments, in which PVC powder was mainly used as combustion materials, were carried out with the electric furnace in laboratory scale at 1073 K. The experimental and the thermodynamic studies on Dioxins in the combustion process at 1073 K lead to the following conclusions:

- (1) Dioxins are formed even at combustion temperature of 1073 K when there exist the fly carbonaceous matters.
- (2) A little Dioxins may be formed even in the condition without the organic matters when there are four elements of C, H, Cl and O for Dioxins.
- (3) Dioxins' concentration in the exhaust gas has the correlation with the number of the fly carbonaceous matters.
- (4) Dioxins may be considered to be formed when the heterogeneous site with high CO/CO_2 ratio exists, for example in the boundary layer on the surface of the fly car-

bonaceous matters.

- (5) One of the important points on the zero formation of Dioxins can be considered to burn out the fly carbonaceous matters in the furnaces by more enhancement mixing with combustion gases.

Acknowledgments

Present study was supported by Japanese Ministry of Education, Culture, Sports, Science and Technology, Collaborative Research Center for Advanced Science and Technology in Osaka University, Sumitomo Metal Industries, Ltd., Sumitomo Metal Technology, Inc., Sumitomo Heavy Industries, Ltd. and Hitachi Zosen Corp. We wish to thank members for helpful discussions and their financial assistance. We thank Miss E. Nakayama at the Sumitomo Metal Technology Inc., Mr. T. Tanii and Mr. M. Tanabe of graduate student of Osaka University for their experimental supports.

REFERENCES

- 1) H. Ismo, T. Kari and R. Juhani: *Chemosphere*, **34** (1997), 2649.
- 2) A. Buekens, H. Huang and L. Stieglitz: *Organohalogen Compounds*, **41** (1999), 109.
- 3) M. Hiraoka: *Science and Industry (Kagaku to Kogyo)*, **72** (1998), 319.
- 4) H. Vogg and L. Stieglitz: *Chemosphere*, **15** (1986), 1373.
- 5) H. Hagenmaier, M. Kraft, H. Brunner and R. Haag: *Environ. Sci. Technol.*, **21** (1987), 1080.
- 6) H. Vogg, M. Metzger and L. Stieglitz: *Waste Management & Research*, **5** (1987), 285.
- 7) L. Stieglitz and H. Vogg: ISWA 88 Proc. of the 5th Int. Solid Wastes Conf., Vol. 1, Academic Press, London, (1988), 331.
- 8) E. Kasai, T. Aono, Y. Tomita, M. Takasaki, N. Shiraishi and S. Kitano: *ISIJ Int.*, **41** (2001), 86.
- 9) T. Takasuga, T. Makino, K. Tsubota and N. Takeda: *Chemosphere*, **40** (2000), 1003.
- 10) K. Takasuga, F. Baba, T. Kobayashi, M. Sato, M. Kurata and M. Kokado: *Organohalogen Compounds*, **40** (1999), 275.
- 11) M. Morita: Introduce to Dioxin (U.S. EPA Research Reporting Series "Dioxins"), Japan Environmental Sanitation Center, (1997), 5.
- 12) R. L. Rawls: *Chem. Eng. News*, **12** (1979), Feb., 23.
- 13) H. Kawabata, T. Usui, K. Marukawa and S. Hara: ICSS 2000 Proc. of the Int. Conf. on Steel and Society, ISIJ, Tokyo, (2000), 162.
- 14) Y. Miyashita and K. Marukawa: *CAMP-ISIJ*, **11** (1998), 993.
- 15) M. Hiraoka, N. Takeda, S. Sakai, S. Okajima, K. Sakamoto, M. Yamaguchi and E. Shibuya: *Organohalogen Compounds*, **3** (1990), 81.
- 16) H. Vogg, H. Hunsinger, A. Merz and L. Stieglitz: *Chemosphere*, **25** (1992), 149.
- 17) A. Yazawa, S. Nakazawa and N. Menad: *Chemosphere*, **39** (1999), 2419.
- 18) E. Shibata, S. Yamamoto, E. Kasai and T. Nakamura: *Organohalogen Compounds*, **46** (2000), 221.
- 19) H. Yokogawa, S. Yamauchi and T. Matsumoto: *Thermochem. Acta*, **245** (1994), 45.
- 20) I. Fangmark, B. Stromberg, N. Berge and C. Rappe: *Environ. Sci. Technol.*, **28** (1994), 624.
- 21) K. Kawamoto, K. Umabuchi and N. Takeda: Proc. the 10th Annual Conf. Japan Society of Waste Management Experts, JSWME, Tokyo, (1999), 818.
- 22) D. Wang, M. Piao, S. Chu and X. Xu: *Environ. Contam. Toxicol.*, **66** (2001), 326.
- 23) T. Okufuji: PPM, The Nikkan Kogyo Shinbun Ltd., **3** (1992), 30.
- 24) W. M. Shaub: *Thermochim. Acta*, **55** (1982), 59.
- 25) M. Frenklach, S. Taki and R. A. Matula: *Combust. Flame*, **49** (1983), 275.
- 26) B. S. Haynes and H. G. Wagner: *Prog. Energy Combust. Soc.*, **7** (1981), 229.