

DIOXIN REDUCTION BY SULFUR COMPONENT ADDITION

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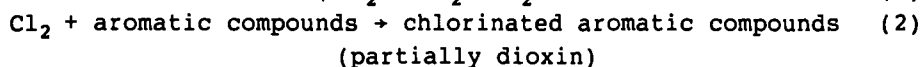
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1. INTROCUCTION

Griffin has suggested that an addition of certain sulfur compounds to the fuel is effective for dioxin reduction¹⁾. This study focused its attention to such sulfur addition and SO₂, coal and pure sulfur were selected as sulfur sources.

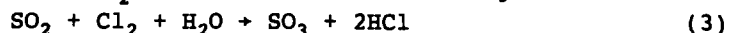
2. CONCEPTION

According to Griffin, the following 2 steps of reaction could be considered as one of formation process of dioxin¹⁾. That is,



HCl is oxidized by O₂ and Cl₂ is formed. (Reaction formula (1)). The reaction (1) is the so-called Deacon reaction and is known that the reaction proceeds with such transition metal compound as CuCl₂ as catalyst²⁾. Since Cl₂ has high reactivity, it chlorinates the unburnt aromatic compounds in the combustor (reaction formula (2)). At this time, dioxin may be formed.

According to the above assumption, most effective procedure is to control the second reaction step. Therefore, a supply of sulfur to the combustor could be feasible. The sulfur content is converted into SO₂, and it reduces Cl₂ to HCl with the following reaction:



therefore, dioxin can be reduced.

EMCO

3. EXPERIMENT

Fig. 1 shows a flow sheet of fluidized bed combustor system used in this experiment. The test fluidized bed combustor is mainly composed by mullite of 205mm ϕ \times 4m, and silica sand was used as a fluidizing medium.

In this experiment, gas components (HCl, SO₂, CO, CO₂, O₂) and inside temperature of the combustor, etc. were continuously measured. The mixture with the wood saw dust and PVC were fed to the combustor as a fuel. The wood saw dust contains lignin as the source of dioxin structure and PVC was expected as the source for chlorine. Sulfur was fed in the following modes within their molar ratio 0.075 to 3.8;

CASE A : Gaseous SO₂ was fed directly.

CASE B : Coal containing sulfur was fed.

CASE C : Coal and sulfur reagent were fed.

Our experimental conditions were shown in Table 1. The blank test in Table 1 meant the sulfur free condition and was used as our standard for comparing the other experimental conditions.

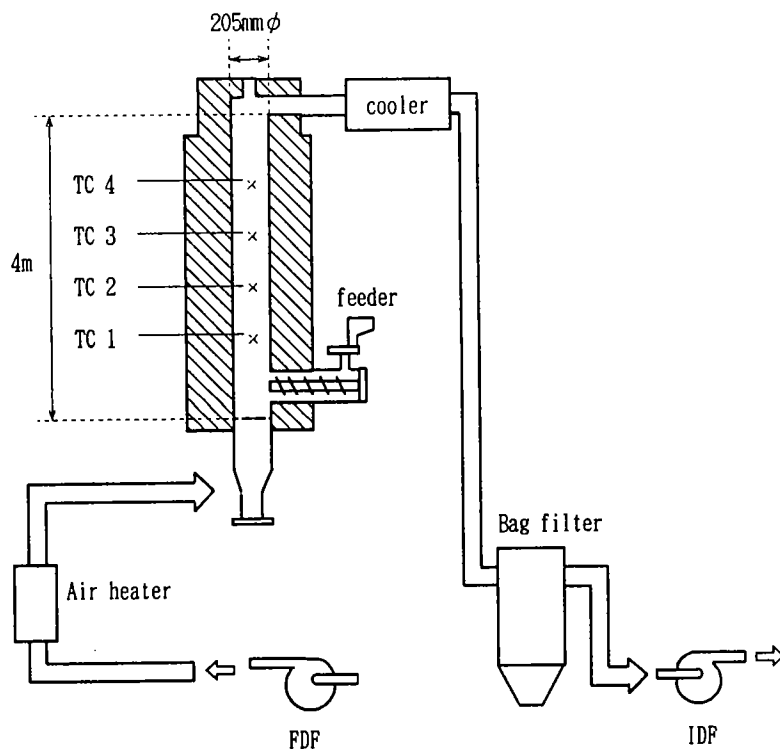


Fig. 1 Flow sheet of FBC test system

The following incineration conditions were employed in this experiment;

- ① O₂ (at exit flue gas) = 8%
- ② combustor temperature = 1000°C
- ③ fuel feed rate = 0.10~0.15 kg/min

Flue gas sampling method and dioxin analysis were completely along to the procedure established by the JAPAN WASTE RESEARCH FOUNDATION.

4. RESULTS AND DISCUSSION

All data are summerized in Table 2.

4.1 Effects of gaseous SO₂ addition (CASE A)

Fig. 2 shows that the more SO₂ is fed, the less dioxin is formed. This result shows the reaction by formula (3) probably occurred and the results show that SO₂ in the abated gas is less than SO₂ in the unabated gas (Table 3). It also shows that the reaction defined by formula (3) occurred.

4.2 Effects of coal addition (CASE B)

In this case, coal (containing sulfur) was added to the fuel. The results are shown in Fig. 3. It indicates that an addition of coal greatly reduced an amount of dioxin. This means that gaseous SO₂ which was oxidized by O₂ in the combustor reduced dioxin by formula (3).

The reason for greater reduction effects by addition of coal than by addition of gaseous SO₂ is considered an active intermediate. It was generated in the combustor and worked on Cl₂ more actively than SO₂ did. But details remain unknown.

4.3 Effects of addition of coal+pure sulfur reagent (CASE C)

All data including results of CASE C are plotted in Fig. 4. The results of CASE B show that an addition of coal was very effective. Therefore, in CASE C, pure sulfur reagent was further added to CASE B3 for much greater dioxin reduction. However, much greater effect for dioxin reduction could not be found, compared with CASE B. These data also show that the reduction effect varies depending on the mode of sulfur added into the fuel.

5. CONCLUSION

Small scaled combustion tests were carried out with an addition of gaseous SO₂, coal, pure sulfur reagent to the fuel, and the following conclusions are obtained:

- (1) Dioxin reduction occurs by gaseous SO₂ addition to the fuel.

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- (2) Dioxin reduction occurs by coal addition to the fuel and this effect is greater than the case of gaseous SO₂ addition. It indicates that effect of dioxin reduction varies depending on the mode of sulfur addition.
- (3) Coal+pure sulfur reagent were added to the fuel for effect of dioxin reduction. However, further effect of dioxin reduction was not noted.

This combustion tests revealed that a presence of sulfur largely affect a reduction of dioxin. However, there are phenomena which can not yet be explained. Further basic studies are necessary for reduction of dioxin in the combustor.

REFERENCES

- 1) R.D. Griffin, *Chemosphere*, Vol. 15, Nos. 9-15, 1987(1986).
- 2) Tadimitsu Kiyoura, Kenji Yoshida, Kiyoshi Shikai, Takayuki Mitani, Yasuaki Totsuka, *J. Chem. Soc. Jap.*, No. 9, 1672(1987).

Table 1 Test conditions

		blank test	SO ₂ CASE A			coal CASE B			coal+S powder CASE C	
			A1	A2	A3	B1	B2	B3	C1	C2
H ₂ O	%	15	15	15	15	8.3	8.5	8.4	8.5	8.5
O ₂	%	8.0	8.3	8.0	8.0	8.3	8.1	8.4	8.2	8.6
CO ₂	%	13	12	12	13	12	12	12	11	12
CO	%	50	44	39	80	150~450	100~400	120	100~350	100~400
SO ₂	ppm	0.52	20	40	390	250	250	250	660	1050
NO _x	ppm	72	68	70	66	220	250	250	290	260
HC ℓ	ppm	1290	1360	1490	1310	1140	380	260	220	150
PCDDs	ng/Nm ³	1400	1200	1000	470	14	15	6	15	3.5
PCDFs	ng/Nm ³	5100	3300	2400	1300	27	18	7.6	24	5.6
total	ng/Nm ³	6500	4500	3400	1800	41	33	14	39	9.1

Table 2 Test results

		blank test	CASE A			CASE B			CASE C	
			A1	A2	A3	B1	B2	B3	C1	C2
S/Cl	mol/mol	0.075	0.17	0.29	0.51	0.096	0.44	0.65	2.4	3.8
SO ₂	Nl/min.	0	0.16	0.33	0.65	-	-	-	-	-
PVC	%	3.3	3.3	3.3	3.3	4.0	0.92	0.57	0.56	0.56
coal	%	-	-	-	-	55	57	57	56	56
S Powder	%	-	-	-	-	-	-	-	0.68	1.3

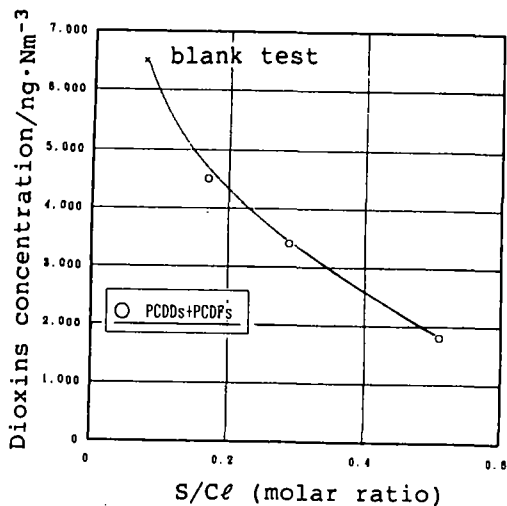


Fig. 2 Influence of SO₂ gas

Table 3 Sulfur balance (CASE A)

S/Cl	0.17	0.29	0.51
Input SO ₂ /ppm	310	530	950
Output SO ₂ /ppm	18	35	390

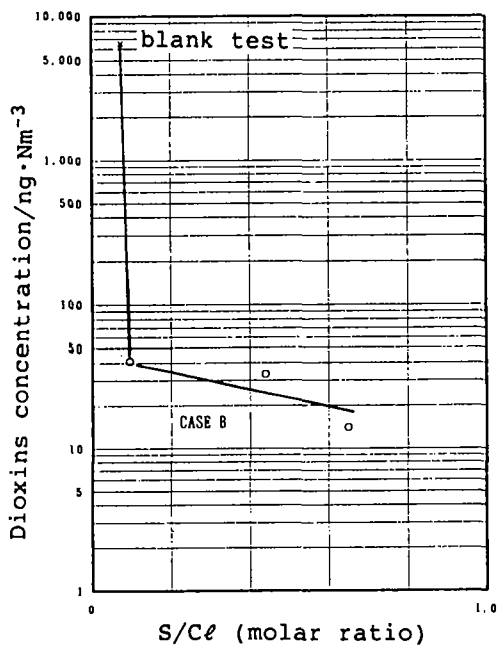


Fig. 3 Influence of coal

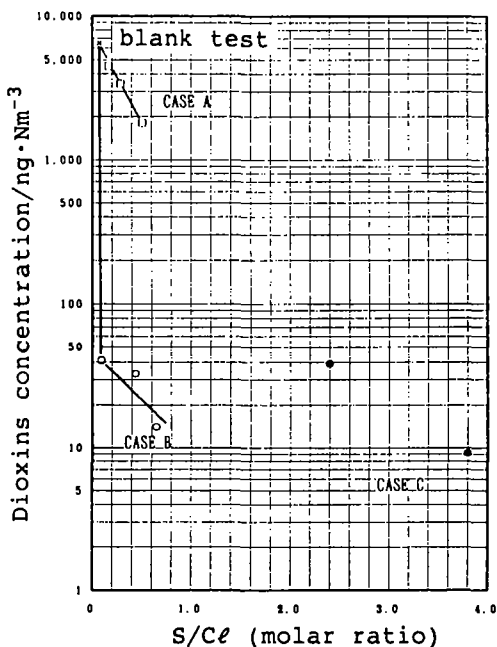


Fig. 4 Influence of sulfur