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MACROSCOPIC BEHAVIOR OF DIOXINS IN THE SINTERING PROCESS OF IRON ORES

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**Collaborative Research Project for Suppression of Dioxin Emissions
from the Sintering Process (SDD Project), Japan**

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Introduction

A new regulations on the dioxin emissions to the air have been enforced to the iron ore sintering plants and some metallurgical plants/processes in Japan. Although the recent inventory shows that municipal and industrial wastes incinerators are still dominant emission sources in Japan, efforts are required for such plants/processes so as to further suppress the emissions and establish stable operations with sufficiently low emission levels.

In 1997, a collaborative research project was formed by the researchers and engineers of Japanese integrated steel makers and universities, in order to investigate the behaviors of dioxins and relating substances in the sintering process and search for new technological principles for suppression of the emissions rather than waste gas treatments. It has carried out the examination of previous literatures and data, several plant measurements and tests, experiments using process simulators (sinter-pots) and fundamental researches.

The present paper reports a part of the results of the measurements and analyses of the sinter plant equipped with several outlet gas treatment processes. Characteristics of behaviors and flows of dioxins in the sintering bed, windboxes and the gas treatment processes are discussed.

Outline and Operational Conditions of the Subjected Sinter Plant

The sintering machine possesses effective area 210 m² with 15 windboxes and production capacity about 9,600 tons per day. The thickness of sintering bed was kept 660 mm during measurements. It is one of the well-equipped plants in Japan with respect to the treatment processes of outlet gas. Figure 1 shows the flowchart of gas from the sintering machine. It passes dry electrostatic precipitator (D-EP), de-SO_x scrubber, wet electrostatic precipitator (W-EP) and de-NO_x system, and then it is released into the air through a smokestack. Major

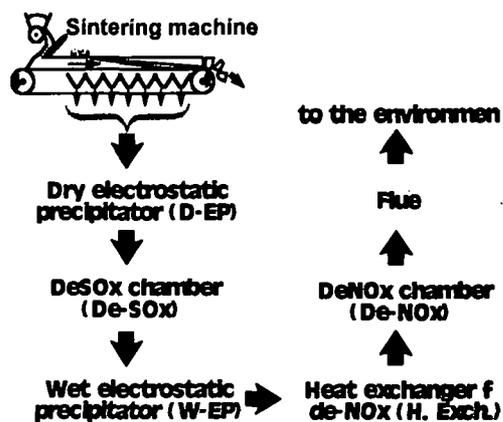


Fig. 1. Outline of outlet gas flow in the p

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operational parameters are listed in Table 1. Significant amounts of recycled materials are utilized such as own D-EP dust, blast furnace dusts, steel converter (LD) slag, mill scale and so forth. Measurements were conducted under a stable condition. Gas samplings for dioxins analysis were made simultaneously at several windboxes and the ducts between gas treatment processes. The sampling time was four hours and concentrations of other gas species were continuously measured. Dusts formed and drain waters discharged from the gas treatment processes and raw materials were also analyzed.

Table 1. Major production parameters of the plant.

Production		9,600 t-dry/d
Raw materials	Blended ore*	10,200 t-wet/d
	Limestone	560 t-wet/d
	Burnt lime	120 t-wet/d
	Coke	310 t-wet/d
	Return sinter	620 t-dry/d
	Ni-slag	70 t-wet/d
Mixing water		230 m3/d
Outlet	D-EP dust	6 t/d
	W-EP water	1,100 m3/d
	De-SOx water	650 m3/d

* Dusts 4%, LD slag 4%, Mill scale 2%, others 4 %

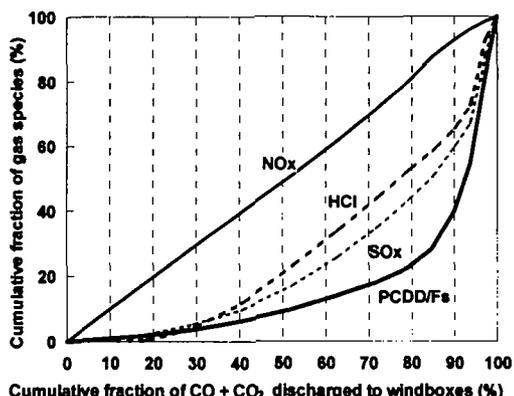


Fig. 4. Relation between cumulative fractions of CO + CO₂ and other gases discharged to windboxes.

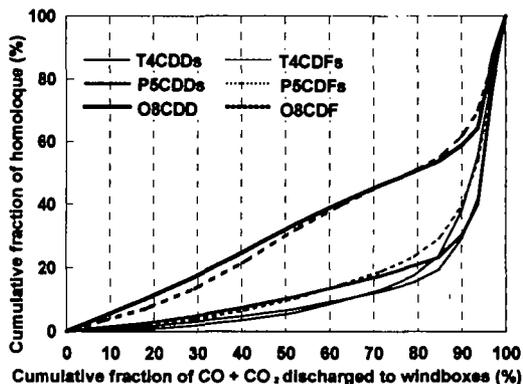


Fig. 5. Relation between cumulative fractions of CO + CO₂ and PCDD/Fs homologues and CPs discharged to windboxes.

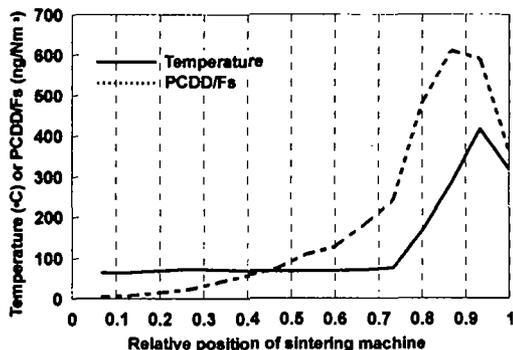


Fig. 2. Profiles of the temperature and PCDD/Fs concentration of outlet gas in the windboxes.

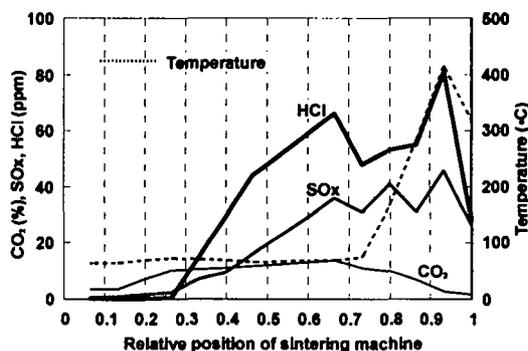


Fig. 3. Profiles of the temperature, CO₂, SO_x and HCl concentration of outlet gas in the windboxes.

Results and Discussions

1) Concentration profiles of outlet gas from the windboxes

Figure 2 shows temperature and PCDD/Fs concentration profiles. Both curves are fairly similar although the peak of the former appears at slightly later position. Such trends are fairly consistent with previous reports^{1,2}. The profiles of CO₂, SO_x and HCl concentrations are shown in Fig. 3. CO₂ starts to decrease at relative position 0.7 while temperature contrary begins to increase at the same point. SO_x and HCl show very low values at earlier position and gradually increase toward the end of sintering. These results suggest that, similar to SO_x, HCl and PCDD/Fs formed in the sintering bed trapped in lower temperature region located at lower bed.

Figure 4 shows the relation between cumulative amount of CO + CO₂, which is an indicator representing the progress of sintering, and those of other gas species discharged to windboxes. It is clear that these gases except for NO_x are discharged in later stage than CO + CO₂. The order of such trends is PCDD/Fs, SO_x and then HCl. The discharged profiles of PCDD/Fs homologues are shown in Fig. 5. The higher chlorinated homologues, *i.e.*, O8CDD/F, are discharged earlier than the lower chlorinated homologues, *i.e.*, T4CDD/Fs and P5CDD/Fs. Such tendency is consistent for all the homologues. This phenomenon is conflict with the fact that the saturated vapor pressures of homologues generally decreases with an increase in the numbers chlorinated³. It may be related to the difference of their solubility to water in wet zone or to the positions in the sintering bed where they mainly form.

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2) Congener profile of PCDD/Fs Emitted from the Sintering Process

Congener profile of PCDD/Fs changes slightly among the windboxes. However, major toxic congener is 23478-PCDF which contributes more than 50 % in terms of TEQ (toxicity equivalent quantity) (see Fig. 6). The profile does not

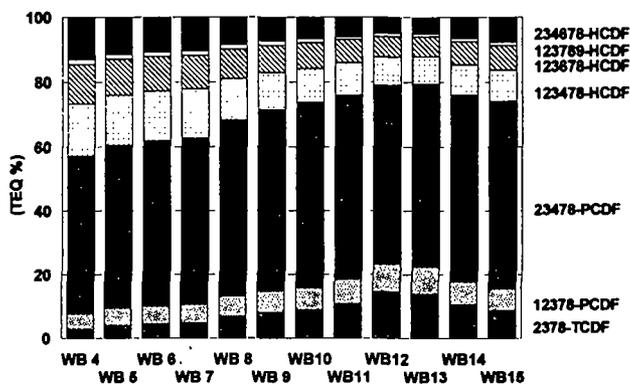


Fig. 6. Toxic congener patterns of outlet gas from windboxes.

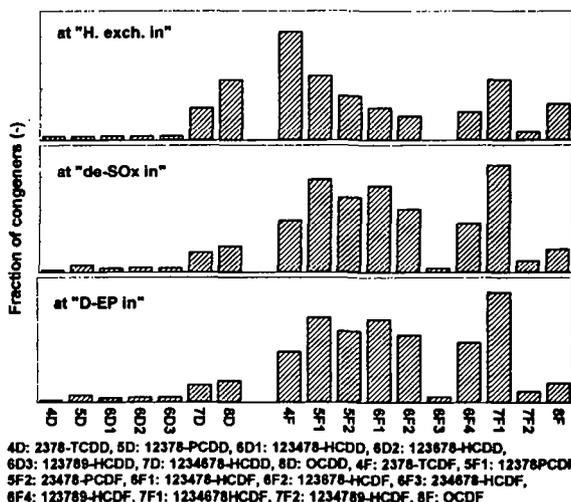


Fig. 7. PCDD/Fs congener profiles measured for the gas at different positions.

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change significantly through the gas treatment processes as shown in Fig. 7. It can be also pointed out that the total fraction of PCDFs is much greater than PCDFs and it agrees well with previously reported data^{1,2}.

3) Macroscopic flow of PCDD/Fs in the sintering plant

Figure 8 shows the changes in PCDD/Fs concentration of gas along the gas treatment processes. It clarifies that PCDD/Fs are mainly removed by three processes, *i.e.*, D-EP, de-SO_x scrubber and W-EP. In de-NO_x system they are further decreased probably by catalytic decomposition. In this condition, PCDD/Fs concentration at the flue was quite low as much as 0.04 ng-TEQ/Nm³.

The raw materials of the sintering process originally contain dioxins to some extent. PCDD/Fs concentration of the EP dust is 28 ng/g (0.7 ng-TEQ/g) and those of other non-recycled materials are less than 0.4 ng/g. The values for returned sinter fine is very low, 0.043 ng/g. Therefore, the EP dust appears to contribute as a certain source of PCDD/Fs in the mixture of raw materials, although its mixing ratio is small, *i.e.*, less than 0.1 mass%. As a result, the mixture contains 0.15 ng/g. In addition, PCDD/Fs concentration of the sinter product is remarkably low, 0.0048 ng/g.

Based on the above measurements, a macroscopic mass balance of PCDD/Fs can be drawn as Fig. 9. Approximately a half of PCDD/Fs removed by the gas treatment processes is recycled as both of solid dust from D-EP and water (probably thin slurry) for the granulation of raw materials. It may be worth to remark that the amount of newly formed PCDD/Fs during sintering, *i.e.*, difference between "Mixture" and "WB total", is relatively smaller than that originally contained in the raw materials. However, the fate of considerable fraction of PCDD/Fs is still unknown. Further investigations are being carried out by the tests using both sinter-pot and practical plants to specify the effect of raw materials and additives for the suppression of the emissions.

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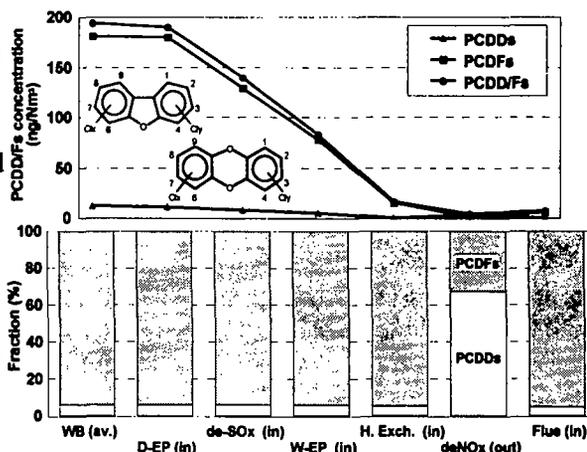


Fig. 8. Distribution of PCDD/Fs concentration and their ratio during gas treatment processes.

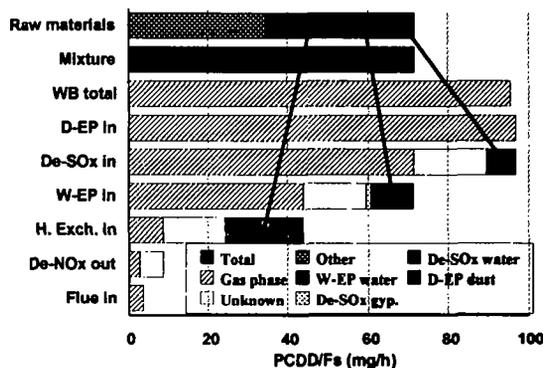


Fig. 9. Flow of PCDD/Fs in the sintering plant.