DIOXIN EMISSIONS IN THE SINTERING PROCESS

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Introduction

A major source of dioxins in the iron and steel making industry are sintering process[1]. In the sintering process, a mixture of iron ore, additives and iron containing recycled materials of steel work are agglomerated. Usually coke serves as a fuel for the sintering.

In the sintering process, it has been assumed that a significant proportion of dioxins are produced via the de Novo synthesis[2]. It has been known that the recycled materials are main source of organic compounds which generate dioxins. Typical oil-containing recycled materials are mill scale generated during rolling of hot steel and blast furnace dust. Measurements at sinter plants have shown a proportional correlation between hydrocarbons in the sinter feed mixture and dioxin emissions in the flue gas[2,3].

In the present work, the dioxin emissions in the sintering process have been extensively studied. We investigated the influence of the sinter feed composition on the dioxin formation. The factors influencing the dioxin emissions in the sintering process were also discussed.

Materials and Methods

The tests were performed in the sinter plant of POSCO. Sintering generates a huge flow of waste gas, composed of the combustion products from the sinter feed mixture. The waste gas is only treated with EP(electrostatic precipitator) for the dedusting.

The sampling and analysis were carried out according to the Korea standard methods. Samples were taken from the sampling ports positioned at stack, and if necessary, at ahead of EP simultaneously. The quantitative and qualitative analyses of dioxins were made by a High Resolution GC/MS. For convenience, the analysis results on the dioxin concentration are expressed by the toxic equivalent.

Results and Discussion

Effect of sinter feed composition on the dioxin formation

It has been known that the recycled materials such as mill scale and blast furnace dust are main source of the dioxin formation in the sintering process[3]. A detailed investigation was carried out to examine the influence of the sinter feed composition during the sintering. Thus, the mixing ratio of mill scale, blast furnace dust and anthracite, which is used as a fuel as well as coke, was changed and the effect on the dioxin formation was studied as shown in Table 1. The sampling was done in the flue gas before EP. Total fuel amount of anthracite and coke was adjusted to 5.2 ~ 5.6% and the ratios of anthracite and coke were changed.

The increase in the amounts of blast furnace dust slightly increased the concentration of dioxins(test 1 and 2). The cut off of anthracite into the sinter feed mixture significantly decreased the concentration of dioxins(test 2 and 3). Generally, it is known that anthracite contains significant amounts of volatile hydrocarbons. We measured the concentration of hydrocarbons in the flue gas. The concentration of hydrocarbons changed from about 28 ppm to 5 ppm by the cut off of anthracite. On the other hand, the increase in the amount of mill scale did not show significant effect on the dioxin formation(test 1 and 4).

Table 1. Effect of sinter feed mixing ratio on the dioxin formation.

Test No.	Feed mixing ratio	Dioxin emission before EP ($ngTEQ/Nm^3$)
1	Anthracite 2.3% Coke 3.2% Blast furnace dust 0.02% Mill scale 0.02%	0.513
2	Anthracite 1.0% Coke 4.6% Blast furnace dust 2.3% Mill scale 0.02%	0.636
3	Anthracite 0% Coke 5.6% Blast furnace dust 2.32% Mill scale 0.02%	0.347
4	Anthracite 1.0% Coke 4.2% Blast furnace dust 0.01% Mill scale 3.4%	0.528

Dioxin and dust emissions

Fig. 1 shows the correlation between the dust and dioxin concentration in the flue gas of the stack. It is evident that as the concentration of dust in the flue gas increases the dioxin concentration also increases.

The distribution of dioxins between the gas and particulate phases has significant meaning because the dioxins bound to particulate phase could be removed by dust collector such as EP. Fig. 2 shows the results of the analysis made on the gas and particulate phase. The particulate phase contains much hexa-, hepta-, and octa chlorinated dioxins and furans of higher molecular weight. In the gas phase, on the other hand, much tetra- and penta chlorinated dioxins and furans existed.

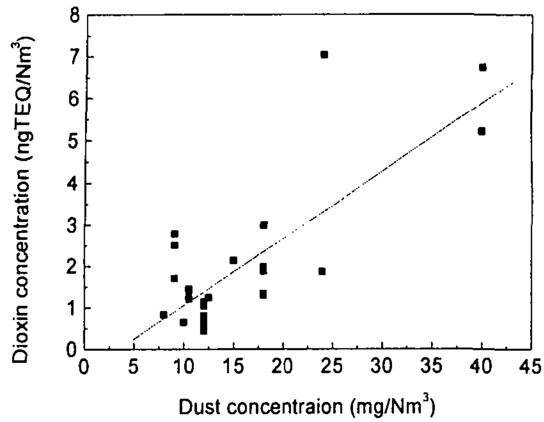

Fig. 1. Correlation of the dust and dioxin emissions.

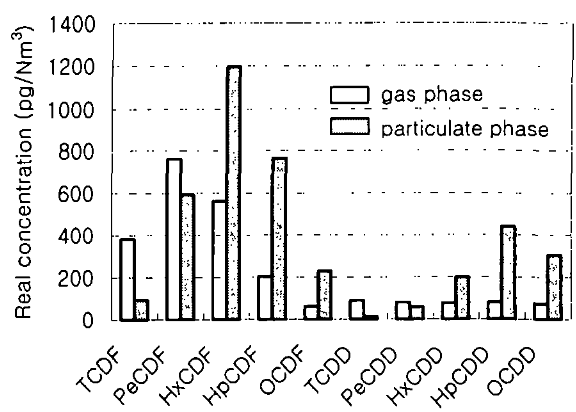

Fig. 2. Distribution of dioxins between the gas and particulate phases

The dioxins could be condensed to the particulate phase as the temperature is reduced because of the decease of the vapor pressure. Fig. 3 shows the effect of temperature on the gas phase ratio of dioxins. The increase in the temperature increased the dioxin amounts in the gas phase. Especially, this relationship was well correlated for 2,3,7,8-TCDD.

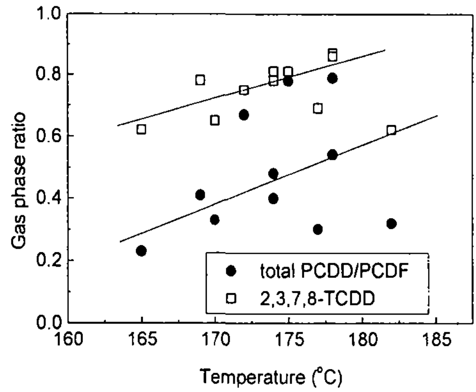

Fig. 3. Gas phase ratio of dioxins with temperature.

Dioxin formation in the electrostatic precipitator

During the measurements, the concentrations of dioxins after EP sometimes exceed those measured before EP. This indicates the dioxin formation in the EP. The increase in the flue gas temperature enhanced the formation of dioxins as shown in Fig.4.

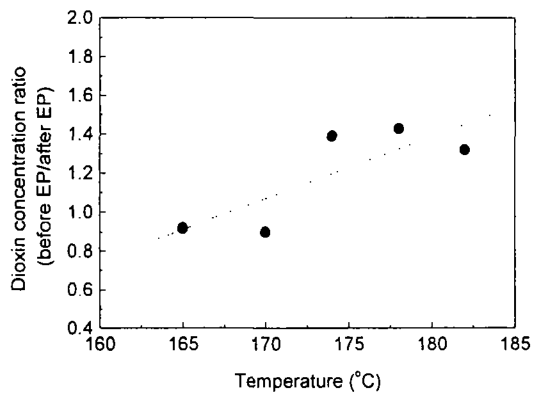

Fig. 4. Dioxin concentration ratio before and after electrostatic precipitator.

References

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