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Operating condition influences on PCDD/Fs emissions from sinter pot tests with hot flue gas recycling

Yongmei Yu^{1,2}, Minghui Zheng^{1,*}, Xianwei Li², Xiaolei He²

1. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China. E-mail: yuyongmei@baosteel.com

2. Research Institute of Baoshan Iron & Steel Co., Ltd., Shanghai 201900, China

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Abstract

This study was designed to clarify the influence of operating conditions on the formation and emissions of polychlorinated-*p*-dibenzodioxins and dibenzofurans (PCDD/Fs) from a sintering process with hot flue gas recycling. A pilot scale sinter pot with simulated flue gas recycling was developed, and four key operational parameters, including temperature, oxygen content of the simulated waste flue gas, the coke rate of the sintering mixture, and the quicklime quality, were selected for exploring PCDD/Fs formation. The results showed that the temperature of the recycled flue gas had a major affect on PCDD/Fs formation, and a high temperature could significantly increase their formation during sintering. A clear linear correlation between the temperature of recycling flue gas and PCDD/Fs emission ($r = 0.93$) was found. PCDD/Fs could be reduced to a certain extent by decreasing the level of oxygen in the recycled flue gas, while sintering quality was unchanged. The coke rate had no significant influence on the formation of PCDD/Fs, but the quality of quicklime used in the sintering mixture could affect not only the amount of PCDD/Fs emissions but also the sintering productivity. Compared with a benchmark sinter pot test, PCDD/Fs emissions markedly decreased with improvements to quicklime quality. However, the reduction in PCDD/Fs emissions realized by using high-quality quicklime was limited by the temperature of the inlet gas. The highest reduction achieved was 51% compared with conventional quicklime when the temperature of the inlet gas was 150°C.

Key words: PCDD/Fs; sintering; recycling flue gas; formation mechanism

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Introduction

Polychlorinated-*p*-dibenzodioxins and dibenzofurans (PCDD/Fs) can be formed unintentionally in industrial processes such as waste incineration, metallurgy and other thermal processes (Lv et al., 2011). According to a Chinese national inventory on PCDD/Fs release, emissions from the metallurgical industry in 2004 accounted for 45.6% of total emissions of PCDD/Fs in China. Furthermore, sintering was one of the largest industrial sources of PCDD/Fs, accounting for 57% of the emissions from the metallurgical industry (Geng et al., 2010). In order to reduce PCDD/Fs emissions from iron ore sintering processes, effective technical measures other than end-of-pipe technologies are needed (Arion et al., 2002; Fisher et al., 2003).

A number of technologies for sintering with hot flue gas recycling have been developed to save energy and control pollution, such as the emission optimized sintering process (EOS, Chen et al., 2008a; Menad et al., 2006), environmental process optimized sintering (EPOSINT,

Fleischanderl et al., 2007) and low-emission and energy-optimized sintering process (LEEP, Eisen et al., 2004). The EOS system was developed in 1994 in an attempt to reduce emissions of SO₂, NO_x, and PCDD/Fs in the Hoogovens sintering plant (the Netherlands). Because the large quantity of flue gas emitted was strongly reduced, the results obtained were considered very promising (Menad et al., 2006). About 63% of PCDD/Fs was destroyed by thermal decomposition in the sintering layer without any negative effects on the production capacity or the quality of the sinter product. The recycled CO resulted in a decrease in fuel consumption. Based on this technology, Siemens VAI and the Linz Steelworks developed a new approach, EPOSINT, to reduce environmental impacts to an absolute minimum (Fleischanderl et al., 2007). Using a selective waste gas recirculation system, waste gas generated during sintering can be substantially reduced, while part of the waste heat of the recycled gas portion is used, thus decreasing fuel costs. The implementation of selective waste gas recirculation also resulted in lower emissions of SO_x and NO_x. Furthermore, PCDD/Fs and mercury concentrations in the flue gas were significantly reduced and specific coke consumption was also reduced. The total emission could be

* Corresponding author. E-mail: zhengmh@rcees.ac.cn

reduced by approximately 30% using this new technology, while productivity was unchanged. LEEP technology was developed by Huttenwerke Krupp Mannesmann GmbH (HKM) in Duisburg, Germany, with the goal of reducing emissions and optimizing energy consumption (Eisen et al., 2004). At the heart of the new process was a system that recycled the waste gas of the sinter strand sections with the highest exhaust emissions and the largest heat content, reducing solid fuel consumption and especially emissions, without influencing the sintering quality. Although the results of both of the above technologies were promising, studies on the influence of operating conditions on PCDD/Fs emissions from the sintering bed with flue gas recycling are very limited.

Furthermore, Chen (2008b) employed the Taguchi experimental design process to identify the optimal operating conditions for reducing PCDD/Fs formations during the iron ore sintering process. Four operating parameters, including the water content, suction pressure, bed height, and type of hearth layer were selected and it was found that the resultant optimal combination could decrease the emission factor of total PCDD/Fs up to 62.8% in reference to the current operating conditions of a real-scale sinter plant. Through ANOVA analysis, they also found that water content was the most significant parameter for the formation of total PCDD/Fs, but the operating conditions would be changed significantly after some part of the hot waste gas was recycled into the sinter process. Some other operating parameters, such as the temperature and oxygen content of the waste flue gas, are also very important not only to the quality of sinter product but also to the formation of PCDD/Fs. Further research is needed for PCDD/Fs emission control.

In this study, a pilot scale sinter pot with a simulated flue gas recycling stream was developed to simulate the sintering process with hot flue gas recycling. Four important operating parameters, the temperature and oxygen content of the waste flue gas, the coke rate, and the effects of quicklime quality on the formation of PCDD/Fs were

selected for exploring PCDD/Fs formation. The sintering productivity and sinter strength were examined to evaluate the effects of flue gas recycling on the sinter product quality and to further validate the appropriateness of the operating parameters.

1 Materials and methods

1.1 Raw materials and experimental apparatus

The raw material used in this study contained iron ore fines (65.4 wt.%), coke breeze (3.7 wt.%), quicklime (2.9 wt.%), limestone (4.2 wt.%), serpentine (0.8 wt.%), dolomite (2.5 wt.%), sinter return fines (15.2 wt.%), and recycled materials containing iron and coke (5.3 wt.%), which is consistent with raw material for an industrial-scale sinter plant. The mean granular size range of the above raw material was 1.98 to 2.50 mm. According to the requirements of the sintering, the coke breeze rate in the mixture could be changed to comply with the variety of flue gas recycle temperatures.

To simulate a full-scale sintering process with hot flue gas recycling, a pilot scale sinter pot with a simulated hot flue gas source was developed (Fig. 1), consisting of a simulated flue gas recirculation section, a sinter pot (I.D. 300 mm, H 800 mm), a flue gas exhaust section and a sampling section. The simulated flue gas was generated by combustion of coke oven gas (COG). The temperature was easily controlled by adjusting the volume of COG. Oxygen content in the simulated flue gas was adjusted by injecting the desired volume of pure oxygen. The sinter mixture was charged into the sinter pot and ignited by an ignition burner above the bed. After 2 min ignition, the burner was moved aside and the hood supplying simulated flue gas was lowered simultaneously.

The simulated flue gas was then introduced to the sinter bed surface via a gas distributor and was drawn through the sinter bed by a suction fan. At the same time, the flame front was propagated by drawing gas through the bed. When the temperature of the exhaust gas in the wind box

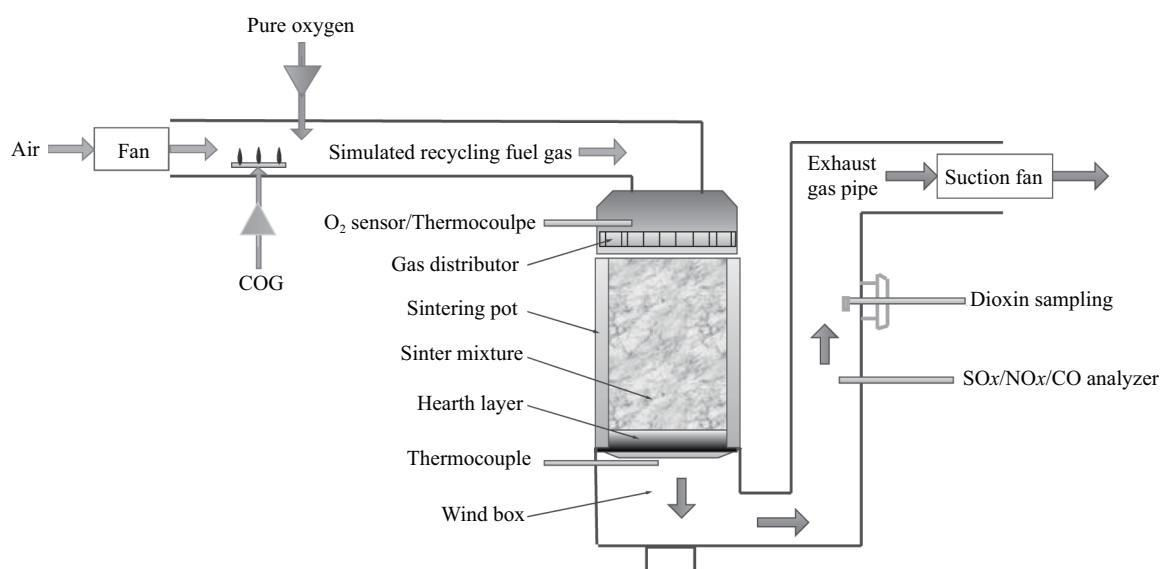


Fig. 1 Schematic of the sintering pot system.

reached 100°C, the hood was moved aside and fresh air was drawn through the bed. The remaining sintering and cooling process was completed with fresh air. Typically, the sintering time for each pot test was about 35 min. The sintering conditions were kept constant for all experiments. The pot test conditions are shown in Table 1.

Table 1 Conditions of the sinter pot tests

Granulation	60 sec mixing + 180 sec granulation with water addition using drum mixer (1 m diameter)
Bed height	750 mm including grate and hearth layer
Ignition	890°C × 120 sec
Ignition suction	8.83 kPa
Sintering suction	14.71 kPa
Water content of sinter mixture	7.2%

1.2 Variable factors examined in pot tests

Table 2 shows the factors used in each pilot study run. The temperature and oxygen content of the recycled flue gas were the key factors in the sintering process. The amount of heat recovered from the sintering process by flue gas recirculation depends on the temperature of the recycle gas. The sintering productivity and sinter quality may be influenced by oxygen content and heat transfer. On the other hand, the temperature and oxygen content of the recycling gas are the important factors affecting PCDD/Fs emissions during sintering.

In addition, the sintering operation often involves adjustments to the coke content of the sinter mixture to maintain optimal performance (Nakano and Okazaki, 2007). The reduction of coke content caused by utilizing the waste heat from flue gas recycling can directly affect the energy consumption of the sintering process. Thus, the coke contents shown in Table 2 were varied widely and were below the coke ratio of real production. The variety of coke contents used in this study was similar to that in the experiments by Nakano and Okazaki (2007).

1.3 Sampling and analysis

The PCDD/Fs sampling port is shown in Fig. 1. Samples were collected from the flue gas duct according to US EPA Method 23. The sampling train (Graseby Andersen, Bedfordshire, UK) was composed of a heated, glass-lined sampling probe and filter equipped with a glass fiber filter and a water-cooled XAD-2 sorbent trap. Samples were collected through a heated, glass-lined sampling probe, and particulates were collected on a glass fiber filter contained in a heated filter box, while gaseous PCDD/Fs were trapped on a XAD-2 resin (Supelco Ltd., USA) contained within a water-cooled trap. XAD-2 sampling kits were previously spiked with five surrogate target compounds (Wellington Laboratories, Guelph, Ontario, Canada). The analytical samples consisted of the filter, XAD-2 resin, and solvent washings from the glassware of the sampling train. All samples were tightly wrapped in aluminum foil to minimize contamination and loss. At the end of each sampling cycle, the samples were immediately transferred

to a refrigerator, where they were stored until analysis.

Analysis of PCDD/Fs was carried out based on U.S. EPA Method 23. Briefly, samples were spiked at the time of analysis with known amounts of $^{13}\text{C}_{12}$ -PCDD/Fs internal standards (Wellington Laboratories, Canada). They were then extracted in a Soxhlet apparatus (Universal Extraction System, B-811, BÜCHI, Switzerland) with toluene for 24 hr and the extracts were then concentrated with a rotary evaporator. The concentrated sample extracts were then subjected to a series of cleanup steps by adsorption chromatography, including a 44% sulfuric acid silica column and a multilayer silica gel column. PCDD/Fs and the other organic compounds were fractionated on a basic alumina column. Finally, the fractions were reduced to about 20 μL by rotary evaporator and a gentle stream of nitrogen. The final samples were spiked with a known amount of $^{13}\text{C}_{12}$ -labeled PCDD/Fs recovery standards (Wellington Laboratories, Canada) and analyzed by high-resolution gas chromatography, combined with high-resolution mass spectrometry (HRGC–HRMS) (Waters AutoSpec Premier, UK) equipped with a DB5 ms column (60 m × 0.25 mm × 0.25 μm). The analyzer mode of selected ion monitoring with a resolving power of 10,000 was used. The electron energy was set to 35 eV, and the source temperature was set to 280°C. All data were analyzed using the Mass Lynx version 4.0 software (Micromass, Manchester, UK).

The sampling recoveries of five $^{13}\text{C}_{12}$ -PCDD/Fs surrogate standards were measured relative to the $^{13}\text{C}_{12}$ -PCDD/Fs internal standards. Recoveries were in the range 70%–115% for the five surrogate $^{13}\text{C}_{12}$ -labeled PCDD/Fs sampling standards. The recoveries of nine $^{13}\text{C}_{12}$ -labeled PCDD/Fs internal standards ranged from 60% to 105%.

Each level of the test was repeated at least three times to ensure the reproducibility of the pot test. The average value of each level was used in the analysis.

2 Results and discussion

2.1 Influence of simulated recycled flue gas temperature on PCDD/Fs emission

In sintering processes with selective flue gas recirculation, the temperature of the recycled flue gas is below 300°C. The temperatures of recycle waste gas were designed to be 20, 150, 190 and 240°C in the pot tests. The waste heat content of the simulated flue gas is utilized during the sintering process. As shown in Fig. 2, PCDD/Fs emission from the sinter bed increased with increasing flue gas temperature. A clear linear correlation ($r = 0.93$) was observed between the temperature of the recycling gas and the amount of PCDD/Fs formed. The baseline for PCDD/Fs formation was set at a recycling gas temperature of 20°C, with the levels of PCDD/Fs increasing to 34%, 59% and 52% as the temperature of simulated recycled gas was 150, 190 and 240°C, respectively.

The PCDD/Fs profiles in two runs of the pot test are compared in Fig. 3. One was a baseline pot test without gas recycling and the other was a pot test run with simulated

Table 2 Variable factors for the sinter pot test

Factor						
Temperature of simulated recycling flue gas (°C)	20	150	190	240		
O ₂ content of simulated recycling flue gas (%)	19	21	22	23.7		
Coke content of sinter mixture (wt.%)	2.60	2.67	2.72	3.00	3.20	3.60
Quicklime of sinter mixture	High content of CaO			Low content of CaO		

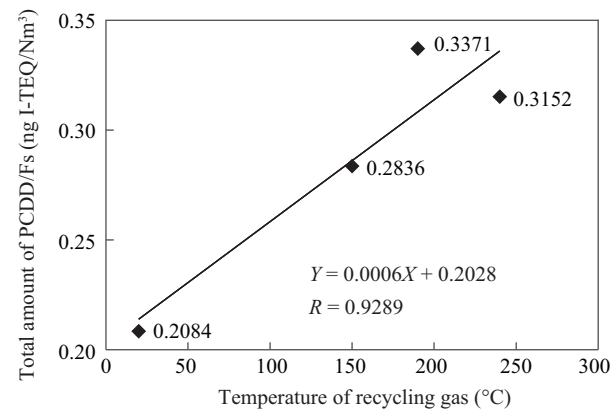


Fig. 2 Influence of recycle gas temperature on PCDD/Fs emission.

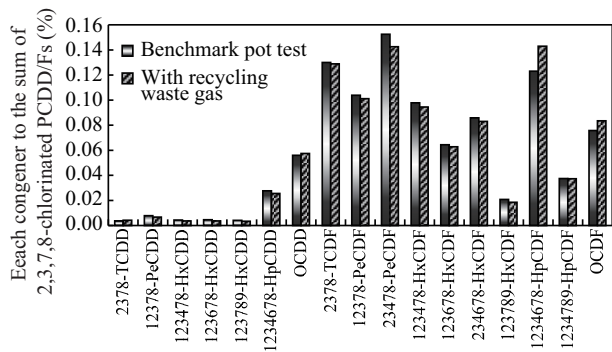


Fig. 3 PCDD/Fs profiles in two runs of the pot test.

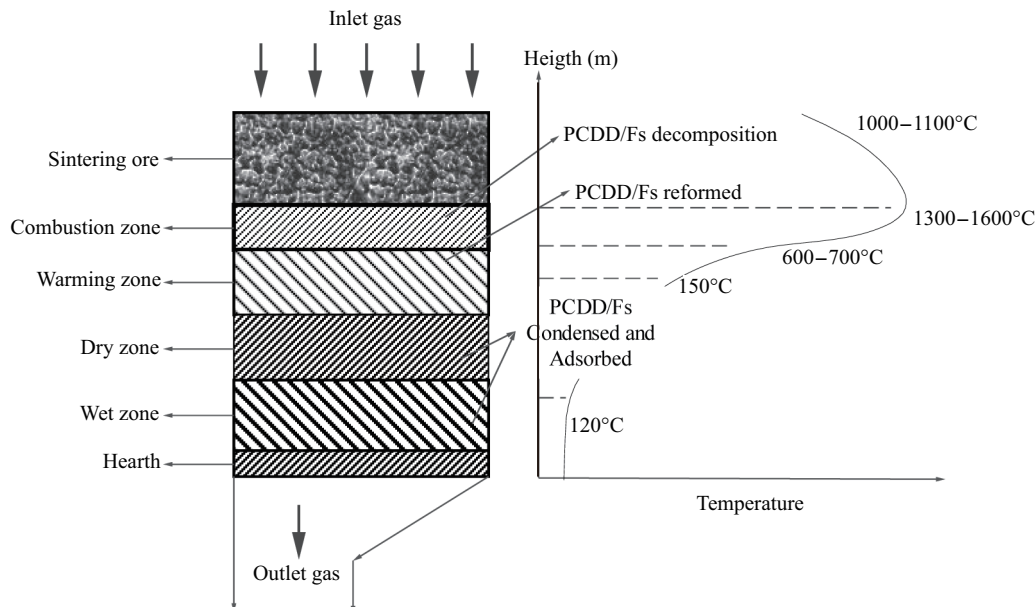


Fig. 4 Formation and decomposition of PCDD/Fs in the sinter bed.

flue gas recycling at 240°C. The similar distribution of each homologue suggests the same mechanism for PCDD/Fs formation under different operating conditions.

Fleischanderl et al. (2007) and Eisen et al. (2004) stated that PCDD/Fs could be destroyed by thermal decomposition in the sintering layer. Harjanto et al. (2002) studied the behavior of PCDD/Fs during thermal remediation in the zone combustion process by spiking ¹³C-O₈CCD/2378-T₄CDF in a raw mixture, and the experiment results showed that this was almost completely destroyed during sintering. Nakano et al. (2005) also observed in a quenching pot test that PCDD/Fs formed in the sintering bed dominate the PCDD/Fs emissions from the outlet, indicating that regardless of whether or not the recycling flue gas contained PCDD/Fs, these would be destroyed by high temperature during the sintering process. Figure 4 shows the formation and decomposition of PCDD/Fs in the sinter bed (Zhou and Kong, 1989; Kasai et al., 2001; Harjanto et al., 2002). When flue gas is recirculated to the sintering bed, any PCDD/Fs present would be destroyed in the combustion zone. PCDD/Fs would be mainly formed again beneath the combustion interface and released into the outlet gas. However, the temperature distribution from the top to the bottom of the sintering bed was altered by the flue gas recirculation technology. An increase in the formation of PCDD/Fs may result from that the temperature of the flue gas is increased.

Figure 5 shows temperature curves for the outlet gas under different conditions. One test was the benchmark

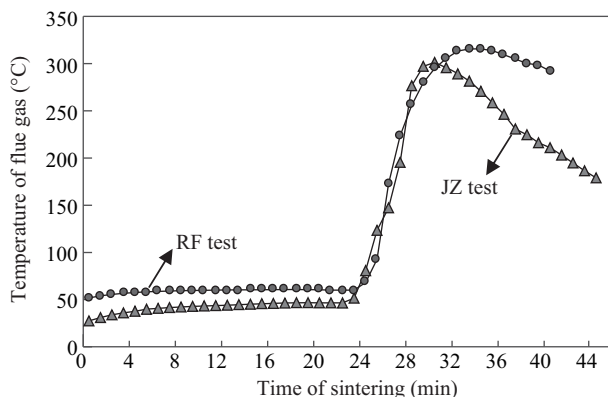


Fig. 5 Temperature curves for the outlet gas.

sinter pot test (JZ test) and the other was under simulated recycle gas operation (RF test). This shows that the outlet gas temperature of the RF test was 10°C higher than that of the JZ test before the exhaust gas temperature increased and indicates that the sintering temperature distribution may be altered by the flue gas recirculation technology, probably resulting in the increase in temperature of the wet and dry zones or their ranges being expanded. Because PCDD/Fs formed tend to be desorbed from the surface of carbonaceous particles at higher temperatures (Suzuki et al., 2004), more PCDD/Fs would be desorbed and released into the outlet gas. On the other hand, if the temperature zone from 200 to 400°C in the bed was expanded, it would enable more opportunities for PCDD/Fs synthesis. This may explain why there was a higher PCDD/Fs content in the outlet gas compared with the benchmark sinter pot test. This means that any reduction of PCDD/Fs emissions gained through adoption of sintering technology with flue gas recirculation would be decreased as the temperature of the recirculated flue gas increased.

2.2 Influence of simulated recycled flue gas oxygen content on PCDD/Fs emission

Figure 6 illustrates the influence of simulated recycled flue gas oxygen content on PCDD/Fs emissions in the sinter pot test. The oxygen content in the recycled flue gas in this series of sinter pot tests was adjusted by injecting pure oxygen. Four levels of oxygen content were selected, representing three sintering conditions: oxygen-deficiency (O_2 content 19%), conventional oxygen supply conditions (O_2 content in the air, 21%) and oxygen-enriched (O_2 contents 22% and 24%). The results show that enhancing the oxygen content in the inlet gas resulted in increas-

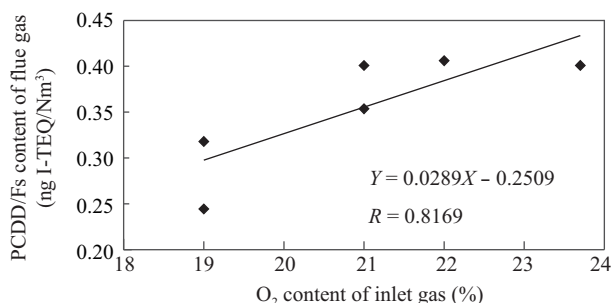


Fig. 6 Influence of flue gas oxygen content on PCDD/Fs formation.

ing PCDD/Fs emissions in the outlet gas. This can be explained by O_2 favoring de novo synthesis of chloro-organic compounds within the sintering bed, as reported by Buekens et al. (2001).

Oxygen is a very important operating parameter for the sintering process. Once the flue gas is recycled in the sintering process, the oxygen content in the gas remains below 21%. The experimental results showed (Fig. 7) that enhancing the oxygen content had no obvious influence on sinter tumbler strength or productivity if the oxygen content was higher than 19%, indicating that PCDD/Fs formation could be reduced by a lower recycle flue gas oxygen content.

2.3 Influence of sintering mixture coke rate on PCDD/Fs emissions

Coke breeze is generally recognized as the best fuel for iron ore sintering. On the other hand, coke is also the source of carbon in the process for de novo synthesis of PCDD/Fs (Suzuki et al., 2004; Xhrouet and de Pauw, 2004; Fisher et al., 2003). The relationship between sintering mixture coke rate and PCDD/Fs emissions from the sintering bed in this study is shown in Fig. 8.

It can be seen that reducing the sintering mixture coke rate did not significantly influence PCDD/Fs emissions. Nevertheless, some states with higher coke rates showed lower PCDD/Fs emissions. The higher PCDD/Fs emissions for some states with lower coke rates may be caused by an increase in the inlet gas temperature. The results are

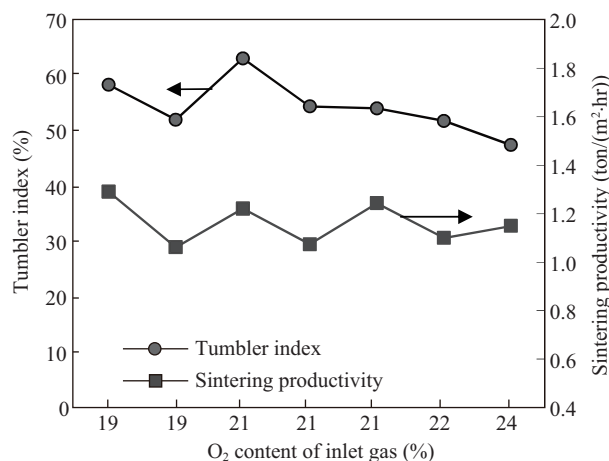


Fig. 7 Influence of inlet gas O_2 content on sinter tumbler strength and productivity.

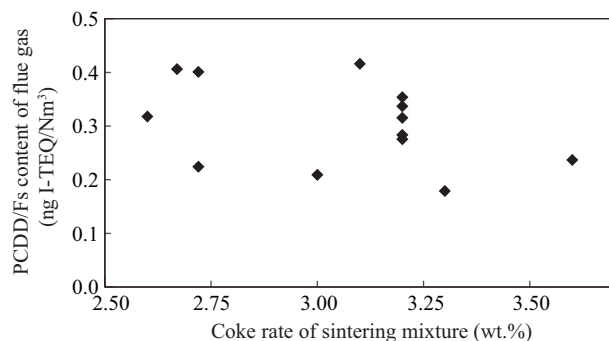


Fig. 8 Influence of sintering mixture coke rate on PCDD/Fs emissions.

Table 3 Quicklime compositions (wt.%)

	Quicklime 1	Quicklime 2
S	0.05	0.08
SiO ₂	0.90	5.13
Al ₂ O ₃	0.39	1.24
CaO	91.72	71.91
MgO	2.42	1.48
TiO ₂	0.10	0.10
P ₂ O ₅	0.10	0.10
TFe (total Fe)	0.15	0.23
LOI (loss on ignition)	4.27	19.53
TC (total carbon)	0.60	4.50

consistent with some studies that show that the type of fuel has no significant effects on PCDD/Fs emissions (Fisher et al., 2003; Xhrouet et al., 2004; Suzuki et al., 2004; Kasai et al., 2001).

2.4 Influence of quicklime quality on PCDD/Fs formation

When the sintering pot test was run under simulated flue gas recycling, sintering productivity decreased in comparison with the benchmark pot test (Fig. 9a). To increase sintering productivity, higher quality quicklime was introduced as an economical binder. Chemical compositions for two batches of quicklime are shown in Table 3.

By utilizing high-quality quicklime, sintering productivity was improved over that of the benchmark pot test

(Fig. 9b). On the other hand, increasing the temperature of the inlet gas decreased the sintering productivity compared with the benchmark pot test. The optimal operating temperature of the recycled flue gas was from 150 to 240°C.

Quicklime can act as a PCDD/Fs suppressing agent in the sintering process, as reported by Nakano et al. (2005, 2009), through reducing the chlorination atmosphere by reacting HCl to CaCl₂. Experimental results were very encouraging in this regard. The results of sinter pot tests are shown in Fig. 10 for runs with two types of quicklime with differing CaO content.

The curve in Fig. 10 represents quicklime quality. The histogram in the figure represents the PCDD/Fs emissions for each experimental run. Tests 1, 2 and 3 were triplicate benchmark test runs without flue gas recycling. Tests 4, 5 and 6 were conducted with flue gas recycling at different temperatures but with the lower quality quicklime. Test 7 used higher quality quicklime but without flue gas recycling. Tests 8, 9 and 10 were conducted with flue gas recycling at different temperatures with higher quality quicklime. It can be seen that PCDD/Fs emissions were greatly decreased when the lime quality was improved. Compared with the benchmark sinter pot test, reductions of up to 51% were obtained under the condition of flue gas recycling at 150°C. However, PCDD/Fs emission reductions decreased with increasing flue gas temperature. When the temperature of the recycling flue gas was increased to

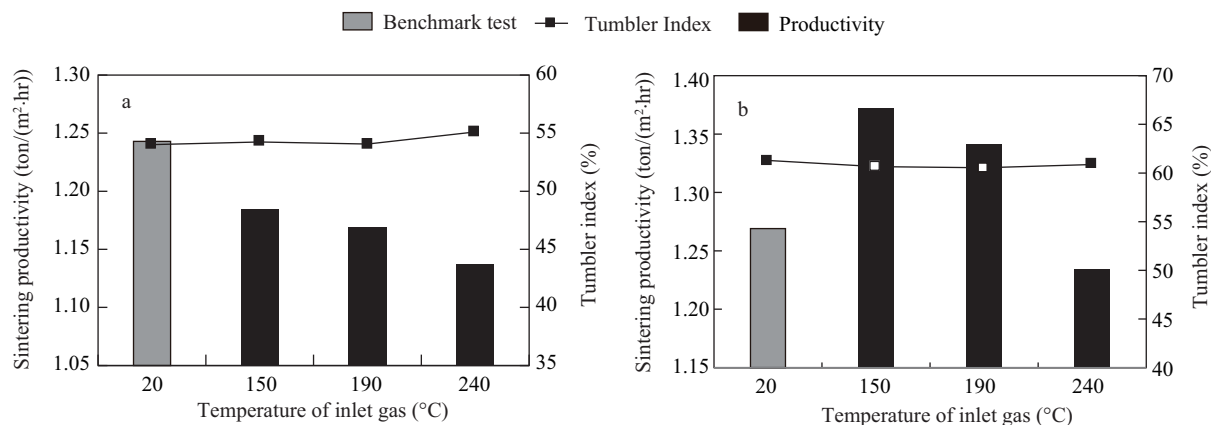


Fig. 9 Effect of recycled waste gas temperature on productivity and tumbler index. (a) utilizing poor-quality quicklime; (b) utilizing high-quality quicklime.

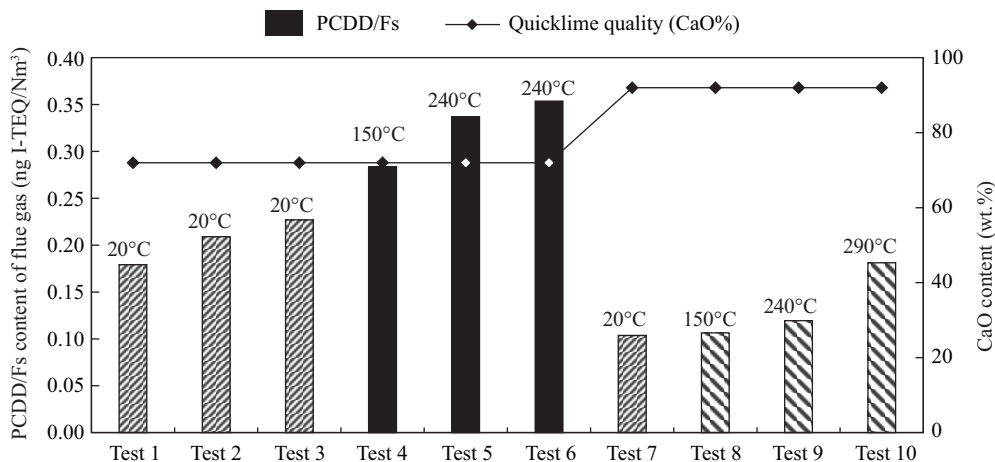


Fig. 10 Influence of quicklime quality on PCDD/Fs emission.

240°C, the level of PCDD/Fs emissions reduction decreased to 47%. If the temperature continued to rise above 290°C, the level of PCDD/Fs reduction decreased to 20%. This suggests that improving the quicklime quality can significantly reduce PCDD/Fs formation.

3 Conclusions

To clarify the influence of operational conditions on PCDD/Fs emissions from a sintering process with flue gas recirculation technology, a pilot scale sinter pot with simulated flue gas recycling was used to simulate various sintering conditions. Several related parameters affecting PCDD/Fs emission were investigated and the results are summarized as follows: (1) Recycling flue gas at higher temperature probably caused a significant increase in the formation of PCDD/Fs during the sintering process. The main influencing factor was the temperature of the recycled flue gas. PCDD/Fs formation in the sinter bed increased with temperature of the recycled flue gas, indicating that a reduction of PCDD/Fs in the exhaust gas from the sinter bed could likely be obtained if the recycled flue gas with lower temperature was introduced. The other factor influencing PCDD/Fs emissions was the oxygen content of the recycled flue gas. PCDD/Fs formation could be suppressed by lower oxygen content in the recycled flue gas. (2) The quality of quicklime added into the sintering mixture could affect not only the amount of PCDD/Fs emissions but also sintering productivity. Compared with a benchmark sinter pot test, PCDD/Fs emissions were greatly decreased through the use of high-quality quicklime.

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