Observation of Behavior of Dioxins and Some Relating Elements in Iron Ore Sintering Bed by Quenching Pot Test

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(Received on September 1, 2004; accepted on October 30, 2004)

Understanding of the formation mechanism of dioxins in the sintering bed is of importance in developing countermeasures to reduce the emission of dioxins from sintering plants. This research has clarified the behavior and the possible mechanism of dioxin formation and the relation to Cl and Cu components in the sintering bed by conducting a series of quenching tests utilizing sintering pots.

The progress of flame front was quenched by terminating the air supply, then introducing N₂ gas in the reverse direction when the sintering process progressed halfway through the test pots, specifically to the position of the thermocouples. The primary specimens were obtained from the raw mixture zone situated beneath the combustion interface for chemical analysis.

Concentrations of dioxins, Cl and Cu were found at the depth of 10–20 mm beneath the combustion interface in raw mixture zone. This was considered to be the site of dioxin synthesis. Slight increase of dioxins in the wet zone was related to dioxin vaporizing from the site of the synthesis, then to be trapped in this zone. Significant amounts of dioxins escaping into the outlet gas at and after burn through point could be explained by both the releasing of trapped dioxins and the acceleration of the synthesizing process attributable to the increased concentration of Cl and Cu.

KEY WORDS: agglomeration; copper; chlorine; dioxins; iron ore sintering; sintering bed.

1. Introduction

The issue of dioxins occurring in the iron-ore sintering process was first posed within the EU. Most of the efforts implemented within the EU were focused on de-dioxin treatments of the waste gas: waste gas circulation (EOS process¹⁾), gas cleaning with water (Air Fine process²⁾), lignite coke injection to the main flue³⁾; other worthwhile attempts of note feature the accretion of urea to the raw mixture.^{4,5)}

In Japan, corresponding to the heightened attention of the general public to the dioxin issue, the law on special measures against dioxins was enacted on July 16, 1999. The law aims to cut-down the domestic emissions by 90 mass% of approximately 7.5 kg-TEQ/year in 1997, and has resulted in the reinforcement of regulations on the exhaust gases of the existing sinter plants to keep less than 1.0 ng-TEQ/Nm³. The sintering plants were relatively large domestic source of dioxins, emitting 135 g-TEQ/year in 1997.⁶⁾ The concentrations of dioxins in waste gases of the sinter plants were ranging from 0.03 to 2.7 ng-TEQ/Nm³.

In order to comply with the regulation, Japanese universities and integrated steel makers organized a committee in 1997, launching a collaborative research project (SDD project). The purpose of this project was to clarify the mechanism of dioxin formation during the sintering process and

proposing techniques to suppress its formation in the bed. The major activities of the project consisted of plant observations, sintering pot tests, quenching pot tests and basic researches, in the chronological sequence.

Plant observations⁷⁾ confirmed that dioxin concentration at wind-box increases with increase in wind-box temperature, and that an increase of Cl concentration of raw mixture leads to larger emissions. The sintering pot tests⁸⁾ have showed the importance of Cl^{9,10)} and Cu¹¹⁾ contents in the raw mixture and the coke properties.¹²⁾ They have also ensured that the suppression effects of nitrogen-bearing inhibitors¹³⁾ on dioxin formation. Although such results seem to be important from the practical point of view, the details of the mechanism on dioxin formation/decomposition and transformation in the sintering bed were remained unknown. Quenching pot tests employed in the present study were designed to cope with such subjects to be resolved, namely the transform/trap behavior of dioxins and related elements.

2. Experimental

2.1. Raw Mixture and Sintering Pot

For the experiments, four iron ores typically used in the Japanese steel works, serpentine, limestone, coke breeze, return fines and additives (Table 1) were used except one

Table 1. Conditions for sintering test.

① Granulation	60s mixing + 180s granulating with water addition using drum mixer of 1m diameter
② Bed Height	600mm including grate and hearth layer
③ Ignition	1100°C × 90s
④ Suction	Constant at 12 kPa

Fig. 1. Apparatus for sintering pot test.

series of experiment, which was conducted to examine the influence of the use of Ore C containing a higher Cu content. The type and quantity of additives were varied according to the purpose of experiment. As the base condition of the experiment, 200 mg/kg NaCl was added to a raw mixture, so as to accelerate the dioxin formation during sintering to a detective extent. The chemical composition of the sintered product aimed for 5.1 mass% as SiO₂, 9.5 mass% as CaO, and 1.9 mass% as Al₂O₃.

The sintering pot was 300 mm in diameter and 600 mm in height. To quench the sintering at a specified position, a thermocouple was inserted into the bed at 400 mm from the top of the bed. Upward N₂ gas flow was applied to stop the combustion of coke and cool the bed when quenching (Fig. 1).

2.2. Procedure of Sintering and Quenching

The raw mixture was mixed for 60 s and granulated with adding water for 180 s in a drum-type mixer of 1 m in diameter. The moisture content was set at 6.5 mass%. The granulated mixture was charged into a pot to form a bed with 560 mm in thickness. The average mass of charges weighed 66 kg. After ignition at 1100°C for 90 s, the sintering process was conducted under a constant suction pressure of 12 kPa.

The quench technique applied in the present study was basically follows after Soma *et al.*¹⁴⁾ Quenching proceeded as follows: when the thermocouple gave the maximum bed-temperature, the main blower was stopped and simultaneously N₂ gas was introduced from the bottom of the pot. For experimental series 1 and 2, the flow rate of the N₂ gas was set at 0.3 Nm/s. It required 2 h to cool the bed. For series 3, 4 and 5, it was set at 0.05 Nm/s. In this case, a half day was needed to cool.

Figure 2 shows time-concentration curves for CO and CO₂, and a time-temperature curve of outlet gas in a preliminary quenching test. The rapid decreases of CO and CO₂ shows that the combustion of coke was quickly stopped. Bed temperature decreased at a rate of 10°C/min. This suggests a possibility that the formation/decomposition of dioxins still proceeds in the course of cooling. The details

Fig. 2. Changes in bed temperature and composition of outlet gas during sintering pot test with quenching operation.

Fig. 3. Sampling positions for solid specimen for chemical analyses.

are discussed later.

The quenched positions were sometimes lower by less than 50 mm than the aimed position. However such deviations were insignificant for the distribution of dioxins and other elements since the position was based on the combustion interface (C/I).

2.3. Sampling and Determination

After cooling, the pot was turned upside-down. Then, samples of wet zone were scooped from the bottom of bed to C/I by every 10 mm thickness. When the sampling reached to C/I, burnt and partially molten particles were taken as the C/I samples. The sintered samples were also obtained by crashing the sinter cake (Fig. 3).

Concentrations of dioxins and related elements such as Cl and Cu in the samples were determined by means of the methods listed in Table 2. In the present study, the term of 'dioxins' means sum of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), excluding polychlorinated biphenyls (PCBs). For financial reason, pentachlorinated dibenzofurans (P₅CDFs), good representative for dioxins, were only determined. Outlet gas composition was not analyzed since dioxin emissions have been reported to be relatively small in the early stage of sintering.⁸⁾

2.4. Experimental Conditions

This research consisted of five series of runs (Table 3). Series 1 was intended to examine the distribution of dioxins in the vertical direction of bed during sintering. It was also aimed to evaluate the validity of the present method to clarify the dioxin distribution. The raw mixture used in Run No. 1 contains 300 mg/kg PVC powder as an accelerator of dioxin formation. Dioxins, Cl and moisture were successfully determined but it was difficult to obtain the stable data regarding oil content.

Table 2. Analytical methods for various elements/substances.

Species	Method
Dioxins	Authorization method of effect to special controlling general waste and special control industry waste (Ministry of health and welfare No.192)
Cl	Combustion method with coulometric titration
Cu	ICP Atomic Emission Spectrometry after acid pretreatment
Total C (TC)	Infrared Spectrometry with combustion in combustion tube
Free C (FC)	Infrared Spectrometry with combustion in combustion tube after acid pretreatment
Combined Water (CW)	Karl Fischer Titration method after Thermal pretreatment
Na, K	Flame Atomic Absorption Spectrometry after acid pretreatment
NH ⁴⁺	Indo-phenol Absorption Spectrophotometry after alkali distilling

Table 3. Peak concentrations of P₅CDFs, Cl and Cu beneath the combustion interface observed under different test conditions.

Series	Run No.	Additives	P ₅ CDFs ng/g	Cl mg/kg	Cu mg/kg
1	1	PVC	PVC 300mg/kg	0.32	980
2	2-1	NaCl	NaCl 330mg/kg (Cl : +200mg/kg)	0.46	879
	2-2	CaCl ₂	CaCl ₂ 310mg/kg (Cl : +200mg/kg)	0.43	1581
3	3-1	Base	NaCl 330mg/kg	0.07	1700
	3-2	CuO	NaCl 330mg/kg; CuO (Cu=400mg/kg)	1.00	1500
	3-3	Ore C	NaCl Cl+200mg/kg	-	920
4	4-1	Base (Cl+200)	NaCl Cl+200mg/kg; CuO Cu+358mg/kg	-	770
	4-2	Cl+400	NaCl Cl+400mg/kg; CuO Cu+358mg/kg	-	1900
	4-3	Cl+600	NaCl Cl+600mg/kg; CuO Cu+358mg/kg	-	2300
	4-4	CuO->CuCl ₂	CuCl ₂ Cl+400mg/kg; Cu+358mg/kg	-	2200
5	5-2	MEA	NaCl 330mg/kg; CuO (Cu=400mg/kg) MEA 2000mg/kg (N=460mg/kg)	0.012	920
	5-3	NH ₄ OH	NaCl 330mg/kg; CuO (Cu=400mg/kg) NH ₄ OH(N=80mg/kg)	0.07	1300
	5-4	Urea	NaCl 330mg/kg; CuO (Cu=400mg/kg) (NH ₂) ₂ CO (N=80mg/kg)	0.06	1300
	5-5	AC	NaCl 330mg/kg; CuO (Cu=400mg/kg)	1.7	2100

- : Not determined

Run No.3-2 is the base run for series 5

MEA: Mono-ethanol-amine, AC: Activated coke, P₅CDFs: Penta chlorinated de-benzo-furans

The raw mixture of series 2 contains 330 mg/kg NaCl or 310 mg/kg CaCl₂. Cl inputs were adjusted to the constant value as 200 mg/kg. Na, K, total carbon (TC), free carbon (FC) and combined water (CW) were determined together with P₅CDFs.¹⁵⁾ TC, FC and CW are convenient indicator for temperature of the bed where it is quenched.

Series 3 aimed to understand the behavior of Cu in the sintering bed. Kawaguchi *et al.*¹¹⁾ have reported that Cu plays an important role in the dioxin emissions during the sintering process. Run No. 3-1 was a base condition, and 200 mg/kg NaCl was added on the basis of Cl. Concentration of Cu in the raw mixture was increased in Run No. 3-2 by adding CuO reagent with the rate of 400 mg/kg. Only Ore C was used for Run No. 3-3 instead of four ores used for the base condition. It increased concentration of Cu in the raw mixture by 30 mg/kg.

Addition of Cl to the raw mixture were varied in series 4 from 200 to 600 mg/kg while Cu input was fixed to 385 mg/kg. CuO reagent was used as Cu source in Runs Nos. 4-1, 4-2, 4-3. They were designed to clarify the effect of Cl on the transport of Cu in the sintering bed.

Series 5 was designed to examine the effects of nitrogen-bearing compounds and activated coke (AC) on the dioxin emissions. Kawaguchi *et al.*^{11,12)} have reported that such additions give significant effect to reduce the dioxin emissions during sintering.

CuO and CuCl₂ reagents were added to raw mixture as they were. NaCl and CaCl₂ were dissolved with water controlling the moisture of the raw mixture.

3. Results and Discussion

3.1. Distribution of Dioxins, Cl and Cu in the Vertical Direction of Sintering Bed

Figure 4 shows distributions of dioxins, Cl, Cu and moisture content in the sintering bed. The data for the Cu are obtained from Run No. 3-1 and others are from Run No. 1. The moisture content is low from C/I to the depth of 30 mm (dry zone), and it gradually increases from 30 to 100 mm (transit zone), and becomes constant value of 6 mass% (wet zone). The dioxin concentration showed a clear peak at dry zone, and decreases slightly in the transit zone. It further lowers to the similar value to the initial concentration of raw mixture. Cl and Cu also showed the peaks in the dry zone.

Such distributions lead to a following hypothesis on the dioxin formation in sintering bed:

- 1) Cl and Cu concentrate in the course of vaporizing in the melting zone and condensing in the dry zone.
- 2) Their increases promote the formation of the dioxins in the dry zone.
- 3) Dioxins formed in the dry zone are partly evaporated and subsequently trapped in the transit and wet zones where the temperature is rather low.

3.2. Behavior of Cl

Table 4 shows Cl balances for a pot before and after quenching experiment. Sum of the amounts of Cl in the sintered and transit/wet zones after the experiment was almost same as the initial Cl input to raw mixture. It suggests that

Fig. 4. Distributions of dioxins, Cl, Cu and moisture contents. Data are from Run No. 1 except Cu which is from Run 3-1. S: Sintered zone, C/I: combustion interface, 1–19: the number of layer of 10 mm thickness from C/I, Mix: initial raw mixture).

Table 4. Mass balance of Cl estimated by determining Cl content of each layer before and after experiment (Run No. 1).

Before/after experiment	Layer	Thickness of layer, measured (mm)	(e) Weight of layer, measured (kg)	(f) Cl content of layer, measured (mg/kg)	(g) Cl amount of layer, calc. (g)	(h) Ratio, calc. (-)
Initial	Raw mixture (a)	560	66	130	8.6	1.0
After quenched	Sintered zone (b)	370	40	35	1.4	0.16
	Transit/Wet zone (c)	190	22	351	7.7	0.90
	Missing (=b+c-a)				-0.5	-0.06

(g): = (e)*(f), (h): = (g)/8.6.

Fig. 5. Relation between the amount of Cl input to the raw mixture and peak concentration of Cl observed at quenched bed (Run No. 4).

Fig. 6. Variation of removal ratio of Cl as functions of initial concentration in raw mixture and the form of the added chloride.

most of Cl vaporized at melting zone was trapped in the lower bed. **Figure 5** shows the change in peak concentration of Cl in dry zone with the amount of Cl input to raw mixture. Naturally, the increase in the Cl input enhances the peak concentration of Cl.

Difference in removal ratio of Cl among various chlorides, *i.e.* PVC, NaCl, CaCl₂, CuCl₂, as defined in the equation shown in **Table 5**, was not clear because of the large deviation (**Fig. 6**). Moreover, the position of the peak and its concentration of Cl in the dry zone were almost same regardless of the type of added chloride (**Fig. 7**). These results suggest that the cations of chlorides do not significantly affect the movement of Cl in the sintering bed.

Figure 8 shows molar-concentration distribution of chlorides beneath C/I. NaCl and KCl were determined by chemical analysis; still surplus Cl existed there, the paired cation (X) of which remained unidentified. The possible elements for X seem to be Fe, Ca, H or hydrocarbons. Fe and Ca were the major components in the raw mixture. Moisture in

the air could react to alkali chloride to produce HCl at elevated temperatures. Chlorinated hydrocarbon itself could also function as the carrier X during the vaporization/condensation process. The determination of the X remains as a further problem.

The behavior of Cl in the sintering bed are summarized as follows:

- (1) Introduction of Cl into the Raw Mixture Derived from Revert Materials, Ores and Coke Breeze

EP dust (dust collected from main flu gas of the sintering machine) contained a certain concentration of Cl mainly in the form of KCl, according to the XRD analysis. Oils adhering to the dust and scale were suspected to be chlorinated. Ores usually contain about 200 mg/kg of Cl on the average though the form of Cl has not identified yet. Coke also contains approximately 100 mg/kg of Cl. Kawaguchi *et al.*¹⁰⁾ reported that most of the Cl is water-soluble.

Fig. 7. Comparison of distribution of Cl concent among the form of the added chloride. (a) Comparison between NaCl and CaCl₂ (Run No. 2), (b) comparison between NaCl and CuCl₂ (Run No. 4).

Fig. 8. Distribution of chlorides beneath C/I (Run No. 2-2).

(2) Evaporation of Cl as KCl, NaCl and Others at Melting Zone

The initial vaporization of Cl is multiplying, depending on its original form. Alkali chlorides could directly vaporize (Eq. (2)). Metallic chlorides (M-Cl) such as FeCl₃, CaCl₂ with vapor pressure lower than NaCl could vaporize by substituting its cation (M) with K or Na (Eq. (3)); and/or, by reacting with water vapor to produce HCl (Eq. (4)). Chlorinated hydrocarbons (HC) could also decompose, and release HCl (Eq. (5)).

(3) Condensation of Cl in the Dry Zone as KCl, NaCl and Others

Gaseous alkali chlorides could condense when the temperature decreases (Eq. (6)). HCl could be trapped to form iron or calcium chlorides (Eq. (7)).

(4) Repetition of Vaporization/Condensation Process with Transferring Cl Component toward Lower Layers

During the subsequent vaporization cycles, the reactants were fixed to be KCl, NaCl and XCl. Such fixation probably allows Cl to behave in a similar manner in the bed re-

gardless of its initial form, resulting in the same position and height for condensation peaks of Cl.

3.3. Behavior of Cu

Minor quantities of Cu vaporized during the sintering process. The removal ratio for Cu ranged from 0 to 0.43 (Table 5).

Cu also shows a peak beneath the C/I (Fig. 9). In the case of no Cu addition as the base condition, the increase in peak concentration was approximately 30 mg/kg (Run No. 3-1); sintering of Ore C single yielded a slightly higher peak (Run No. 3-3); a 400 mg/kg addition as CuO reagent increased the peak height to approximately 50 mg/kg. It should be noted that the increase in the peak height for the Cu was much smaller than those for the Cl as shown in Fig. 5. This seems to partially arise from the smallness of the Cu removal ratio.

Figure 10 show the effect of Cl input on the vaporization/condensation behavior of Cu. Increasing Cl input accelerates the removal of Cu from sintered zone (Fig. 10(a)), and increases the peak concentration of Cu in the dry zone (Fig. 10(b)). These results suggest that Cu vaporizes in the form of Cu chlorides.

The influence of anions combined to Cu remained in vogue. Figure 10(a) suggests no difference between CuO and CuCl₂ during the evaporation process of Cu. In contrast, CuCl₂ seems to show higher concentration peak than CuO.

The behavior of Cu in sintering bed are summarized as follows:

(1) Introduction of Cu into the Raw Mixture Derived from Scales and Ores

Scales inevitably contain Cu component originated from scrap materials. Some ores contain up to twice the quantity of Cu. Kasai estimated the form of Cu contained in an ore to be a sulfide based on EPMA analysis.¹⁶⁾

(2) Vaporization of Cu as CuCl₂ in Melting Zone

Based on the above-mentioned discussion, Cu is here assumed to vaporize as chlorides, *i.e.* after the oxidation of Cu from sulfide into oxide (Eq. (8)), the Cu is then chlorinated and vaporizes. The candidates for Cl supplier are HCl, NaCl and KCl since their contents in the sintering mixture are sufficiently large for the chlorinating reactions, Eqs. (9)–(11).

Table 5. Calculated removal ratios of Cl and Cu for sintered zone.

		1 PVC	2-1 NaCl	2-2 CaCl ₂	3-1 NaCl	3-2 NaCl CuO	3-3 NaCl C Ore	4-1 NaCl CuO	4-2 NaCl CuO	4-3 NaCl CuO	4-4 CuCl ₂
Cl	Raw mixture (mg/kg) (a)	130	224	276	240	255	260	270	370	630	460
	Sinter (mg/kg) (b)	35	31	150	130	125	30	30	80	110	70
	Removal ratio (-) (d)	0.76	0.87	0.61	0.51	0.55	0.90	0.90	0.73	0.84	0.86
Cu	Raw mixture (mg/kg) (a')				30	365	80	230	220	270	280
	Sinter (mg/kg) (b')				33	370	50	295	265	260	265
	Removal ratio (-) (d')				0	0.8	0.43	(-0.16)	(-0.10)	0.12	0.14

(d) Removal Ratio (-) = $[1 - [(b)/(1.1 \times (a))]]$, (d') = $[1 - [(b')/(1.1 \times (a'))]]$ **Fig. 9.** Comparison of Cu concentration among the casis with different form of Cu component (Run No. 3).

(3) Condensation of Cu in the Dry Zone

CuCl₂ vapor condensed in dry zone. It is unclear if the main compounds that condense is CuCl₂ (Eq. (12)) or CuO (Eq. (13)).

(4) Vaporization/Condensation Cycles for Transferring Cu to Lower Layers

For the subsequent vaporization processes, the fixation of reactants (either CuCl₂ or CuO) occurs as well as the case for Cl, resulting in the independence of Cu behaviors in bed on its initial form.

3.4. Dioxin Formation

Changes in CW, FC and TC contents possibly estimate the temperature at the sampling position; CW begins to decompose at about 300°C; FC starts to decrease at approximately 600°C owing to combustion; decomposition of CaCO₃ decreases TC from approximately 900°C. **Figure 11** illustrates the results obtained from Run No. 2. It indicates a minor decrease of CW but the FC and TC at the position 10 to 20 mm below the C/I scarcely decrease from their initial values while P₅CDFs shows its peak. This analysis suggests that the temperature at the P₅CDF peak position ranged from 300 to 600°C; the range includes the temperature of around 400°C at which vigorous *de-novo* synthesis of dioxins occurs.¹⁷⁾

Figure 12 shows homologue profile for Run No. 1 together with those of outlet gas obtained in a pot test conducted under a similar conditions for Run No. 1 by Hosotani *et al.*¹⁸⁾ The profile of dioxins remaining at the peak, as shown (2) in Fig. 12, indicates clear difference in PCDDs from that of raw mixture, (mix). It means that the dioxins existing at the peak position were newly formed during sintering process. The homologue profile of dioxins located at (8) position in Fig. 4 are closely agreed with that of the peak. It suggests that the dioxin at (8) position transferred from the peak position. The profile for the outlet gas, designated (gas) in Fig. 12, shows similarity to those of bed samples rather than the raw mixture, implying that the dioxins newly formed in the bed dominates the dioxin emissions from the outlet gas.

The above findings lead a hypothesis of dioxin formation process in the sintering bed as indicated in **Fig. 13**. It is quite similar to the process described in the work by Antoine *et al.*¹⁹⁾:

- 1) Both of Cl and Cu condense beneath C/I, descending toward lower layers.
- 2) Coke combustion generates soot consisting of carbon, hydrocarbons.
- 3) Dioxins are synthesized beneath C/I from soot and/or Cl component,²⁰⁾ where Cu may acts as a catalyst in the reaction.
- 4) Progress of flame front kills part of dioxins remaining at C/I, but the rest moves to be trapped in the wet zone.
- 5) When flame front is approaching the bottom of the bed, the wet zone disappears. Dioxins trapped in the wet zone and those newly formed beneath C/I are released into the outlet gas.

It still remains uncertain whether the dioxins of outlet gas originated in the homogeneous formation across the bed and consequent accumulation in the wet zone or in the intensive formation at the bottom of the bed owing to the enriched content of Cl and Cu. This is an important question in the development of countermeasures. In the former case, inhibitors should be positioned homogeneously throughout the bed; in the latter case they need be concentrated in the lower layers of the bed. Kawaguchi *et al.*¹³⁾ failed to decrease dioxin emission by intensive charging of inhibitors to the lower layer, which supports the former process. In contrast, the 13C-O₈CCD/2378-T₄CDF spiked in raw mixture was almost decomposed during sintering,⁹⁾ which supports the latter one.

3.5. Major Factors Affecting Dioxin Formations

The discussion below is based on the peak concentrations of dioxins beneath C/I though the most concern is on their concentrations in outlet gas. We assume that the peak

Fig. 10. Effect of the amount of Cl input to raw mixture on (a) the Cu concentration in sintered zone and (b) its peak beneath C/I.

Table 6. Factors and effects on peak concentrations of dioxins beneath Combustion Interface.

Factors	Effects	Bases
Quenching speed	-0.3	Comparison Run2-1 and Run3-1
Amount of Cl input	Increase	Fig.11
Kind of cations combined with Cl	Small	Comparison among Run1,2
Amount of Cu input	0.9	Comparison Run3-1 and Run3-2
Kind of anions combined with Cu	-	(No measurements)

Fig. 11. Concentration distributions of (a) P₅CDFs and (b) TC, FC, CW observed in Run No. 2-1.

Fig. 12. Homologue profiles of dioxins for raw mixture, dry and wet zones (sampling position 2, 8) for Run No. 1 (PVC=300 mg/kg) with an outlet gas cited from a literature (PVC addition 1800 mg/kg).

concentrations have positive correlation to those in the outlet gas.

3.5.1. Cooling Speed at Quenching Operation

The peak concentrations of dioxin in Run No. 2-1 and Run No. 3-1 differed by one order in spite of the use of the same additive. The only condition different between the runs was the flow rate of the N₂ gas used for the quenching operation. Apparently, the N₂ flow either decomposed the dioxin or carried it away from the site of the formation. This phenomenon made it difficult to compare directly the dioxin data beyond the series of experiments.

Fig. 13. Possible reactions and phenomena occur in the sintering bed.

Fig. 14. Relation between peak concentrations of Cl and P₅CDFs.

3.5.2. Cl and Cu Components

Figure 14 shows the relationship between peak concentrations of P₅CDFs and those of Cl in series 1, 2 and 3. Here, the influence of cooling speed is corrected within the plot by subtracting 0.3 ng/g from the P₅CDFs value in series 1 and 2. The plot showed a positive correlation, confirming the influence of the Cl on dioxin formation.

Comparing Run No. 3-1 and No. 3-2 (Table 3) shows that CuO addition increased P₅CDFs peak concentration, also confirming the influence of the Cu.

Comparing Run No. 2-1 and No. 2-2 (Table 3) shows that the variety of Cl sources exerted insignificant differences in the resulting dioxin formation. This seems to be

Fig. 15. Comparison of concentration distributions of (a) Cl and (b) Cu among cases using metallurgical coke and activated coke (AC).

explained by the fact that the variety did not affect the Cl behavior in the bed as discussed in Sec. 3.2.

Kobayashi *et al.*²¹⁾ proved that the alkali vaporizes as chlorides and its vapor pressure rules the amount of vaporization. According to their findings, Cl vaporization should proceed in the sequence of: $\text{CuCl}_2 > \text{NaCl} > \text{CaCl}_2$. The order is indirectly confirmed in measurements provided by Kawaguchi *et al.*⁹⁾ on dioxin concentrations in the outlet gas from the test pot with varying chlorides; the sequence indicated in the study was: $\text{KCl} > \text{NaCl} > \text{CaCl}_2$. The present work, in contrast, showed no clear tendency for the influence of different chlorides on dioxin formation, probably because the difference is small owing to the above-mentioned fixation mechanism and also because the determination of Cl and dioxin contained in solids is more difficult than the contents of gases. Nevertheless, it seemed at least the effect of the chloride type is relatively small when compared to the amount of Cl input.

3.5.3. Coke Properties

Kawaguchi *et al.*¹²⁾ have tested the properties of solid fuel on dioxin concentration in outlet gas, reporting that the replacement of metallurgical coke with activated coke (AC) suppressed the emission of dioxin. In the present work, however, Cl and Cu peaks obtained from AC were almost the same as the height of the peaks produced by metallurgical coke (Fig. 15), and P_5CDF peak for AC (1.7 ng/g from Run 5-5) was no lower than the peak for the metallurgical coke (1.0 ng/g from Run 3-2) (Table 3), meaning that AC had insignificant advantage in dioxins suppression as far as the peak concentration of dioxins beneath C/I. A common interpretation for the superficially different results is that AC has not advantage in reducing the amount of dioxins formed beneath C/I but has an ability to adsorb and decompose dioxins transferring toward lower layer in the bed.

3.5.4. Effects of Nitrogen-bearing Inhibitors

Inhibitors containing nitrogen, *e.g.* ammonia, urea, amines are capable of suppressing the dioxin formation during the sintering process. Kawaguchi *et al.*¹¹⁾ pot-tested many types of such inhibitors successfully; Southern *et al.*⁴⁾ was the first to succeed in suppressing the emission of dioxin from sintering plants by adding urea to the raw mixture. Two possible mechanisms are that the inhibitors release NH_3 , which combines with Cl to reduce chlorinating potential, and that they adsorb on Cu by means of forming N-Cu complexes, thus poisoning the Cu catalysis. We compared

Fig. 16. Comparison of concentration distribution of NH_4^+ among the case of addition of nitrogen-bearing reagents.

Fig. 17. Changes in peak concentration of Cl and Cu with the amount of input N to the raw mixture as different forms.

here ammonia aqua's solution (NH_4OH), urea and monoethanolamine (MEA).

Figure 16 shows the comparison of NH_4^+ concentration in bed distribution among various N-containing additives. NH_4^+ existed in the transit and wet zones, showing no distinct difference attributable to the type of inhibitors.

The inhibitors affected peak heights of Cl; the increase of N input decreased the height of the peak; type of inhibitor indicated no difference in the peak concentration (Fig. 17). In contrast, the inhibitors did not change the peak concentration of Cu (Fig. 17).

Figure 18 shows the effects of the inhibitors on the index of dioxin decomposition ratio (the ratio of dioxin peak concentration with inhibitor to that without inhibitor) on the basis of inhibitor usage; the solid line in the figure shows Southern's data⁴⁾; the broken line is obtained by multiplying the solid line by 0.1, which is arbitrary chosen so that the broken line comes close to the plots for peak concentration data. The plots showed that inhibitors obviously decrease the peak concentration of dioxins. The data for NH_4OH and urea coincide at the same point; the datum for MEA was

Fig. 18. Effect of the amount of input N-bearing material and its form on the suppression ratio of dioxins.

superior to others. The superiority of MEA derived mainly from excess N input.

In summary, the inhibitors decreased the concentration of Cl and dioxins beneath C/I, but no evidences of their differences in in-bed behaviors were detected in spite of differing chemical properties. These results, therefore, lead to a conclusive function of the N-containing inhibitors; *i.e.* they remove Cl from the synthesis zone, though their function to Cu remains as a further problem.

4. Conclusion

In order to clarify the dioxin formation process in the sintering bed, and the vaporization/condensation behaviors of dioxins and related elements were investigated by means of quenching pot test. Results are summarized as follows:

(1) Cl vaporized by alkali metal and trapped in the dry zone, forming a concentration peak 0–20 mm below from the combustion interface. The peak height increased in correspondence to the increase of the Cl input but remained unchanged regardless of the type of chlorides.

(2) Cu probably vaporized in the form of chlorides and condensed in dry zone forming a peak. The peak height increased mainly in correspondence to the increase of the Cl input.

(3) Dioxins peaked in the dry zone where the temperature ranged between 300 and 600°C suitable for dioxin formation. Partly vaporized and trapped, minor quantities of dioxins concentrated in the transit and wet zones.

(4) NH₄OH, urea and monoethanolamine decreased the peak concentration of Cl in the dry zone. Thereby, they inhibited the in-bed formation of dioxins.

(5) Activated coke (AC) scarcely differed from metallurgical coke so far as its influence on the behaviors of dioxins, Cl and Cu in the dry zone are concerned; therefore, the effect of AC in suppressing the emission of dioxin was presumed to be the result of absorption–decomposition function.

The collaborative research project (SDD project) has provided a lot of findings practically useful in controlling dioxin emission from sintering plants: the influence of various operating factors, and the effects of inhibitors. However, details of transfer phenomena and formation mechanism of dioxins and related elements remains still unknown. Further basic researches focused on the mechanism from a more basic point of view are desirable. The SDD project ended in March 2002; further activities will be continued to the next project, to be implemented under the ISIJ foundation.

We wish to thank the Steel Industry Foundation for the Advancement of Environmental Protection Technology for the fund to this research and all members participating in the SDD project for many contributive advices and opportunities for discussions.

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