



# Use of regenerated ferric oxide for CO destruction and suppressing dioxin formation in flue gas in a pilot-scale incinerator

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## Abstract

Catalytic destruction of chlorinated compounds is one of the key methods in reducing pollutant emissions. For the purpose of utilizing waste materials, a catalyst was regenerated from ferric ion sludge, obtained from the addition of iron salts to precipitate heavy metals. The sludge was dewatered, heated (800 °C for 4 h), and ground into smaller particles. The regenerated ferric oxide particles were then used as the oxidation catalyst to destroy CO formation during the combustion of three chlorinated solvents and to suppress dioxin formation in flue gas in a real waste solvent.

In the presence of catalyst, the combustion efficiency (ratio of CO<sub>2</sub> to the sum of CO<sub>2</sub> and CO) for chlorobenzene was more than 98% at 850 °C in a pilot-scale incinerator. The destruction and removal efficiencies of chlorobenzene, 2,4-dichlorophenol and trichlorofluoroethane were more than three nines. In the absence of catalysts, the flue gas emission from a real waste could not meet the regulatory dioxin standard of 0.1 ng-TEQ/N m<sup>3</sup> even with the powdered activated carbon injection. The use of catalyst at either 100 or 300 g/h, however, was able to meet the emission standard.

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## 1. Introduction

Combustion has long been a common alternative for the ultimate disposal of solid and hazardous wastes. In Taiwan, there are 21 regional incinerators developed to manage more than 90% of municipal solid wastes (MSWs). In addition, there are more than 4000 small size incinerators in commercial and industrial sectors for disposal of various industrial wastes and organic sol-

vent. Unfortunately, the dioxin-like compounds emitted in flue gas and present in the solid residues generated after combustion process have become a very sensitive environmental problem. Olie et al. (1977) first described the occurrence of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) from municipal waste incineration. Since then, numerous studies have been performed on the formation of dioxin-like compounds in combustion of a variety of wastes (e.g., Vogg and Stieglitz, 1986; Marklund et al., 1991; Addink and Altwicker, 1996), and reported on concerns over the adverse health effects of PCDD/Fs in the environment. Based on the known information, it is generally agreed that PCDD/Fs are formed via two major pathways: precursor formation and de novo synthesis (Huang and Buekens, 1995; Karasek, 1995).

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With the understanding of formation mechanism (precursor compounds and de novo synthesis) and the associated parameters affecting their formation (e.g., temperature in combustion chamber and subsequent cooling), several technologies for PCDD/F reduction have been developed. The different technologies developed are primarily in response to meeting a stringent emission regulation, e.g., below 0.1 ng-TEQ/N m<sup>3</sup> in flue gas, which is widely used in many countries including Taiwan as the legislative standard (Buekens and Huang, 1998). As an end of pipe technique, the combination of a scrubber and a bag filter coupled with activated carbon adsorption has been introduced. This practice merely transfers the pollutants from the gas phase to a solid stream, and is problematic in terms of treatment and environmental impact. For example, the solid residues need further processing as hazardous wastes (Liljelind et al., 2001); fixed carbon beds can pose fire hazards; and the service lifetime of the adsorber is still in controversy (Siret and Gilman, 1996). Although it is a most effective technique, the use of activated carbon for adsorption of PCDD/Fs in flue gas may not be the best strategy (Weber et al., 2001). Recently, different catalytic filter systems, in lieu of powdered activated carbon, have been demonstrated to be able to destroy more than 99% gaseous PCDD/Fs (Weber et al., 2001; Bonte et al., 2002).

The addition of “inhibitors” (e.g., urea and other inorganic sulfur- and nitrogen-containing compounds) to the fuel/feed has been reported to be a promising means for PCDD/F reduction (Ogawa et al., 1996; Samaras et al., 2000, 2001). An alternative approach for suppressing PCDD/F formation, the so-called primary measure approach, has also received considerable attention lately. This approach includes an external addition of substances (e.g., coke dust or chelating agent) to the flue gas stream (e.g., Addink et al., 1996; Kersting et al., 1997) or using a variety of catalysts under conditions of high or low flue gas temperatures. Nonetheless, studies on the inhibition technique showed the difficulties and the problems (Lenoir et al., 1989). Thus, using catalytic oxidation appears to be a promising control method to reduce the total amount of PCDD/Fs (Altwicker et al., 1992). Several metal materials such as Pd, Pt, PdO, CuO, Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub> and TiO<sub>2</sub> have been reported to exhibit superior oxidation activity in the destruction of dioxin precursors (Weber et al., 1999a). Others (Ide et al., 1996; Weber et al., 1999b) employed a TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst in an NO<sub>x</sub> selective catalytic reactor to decompose the dioxin and related compounds present in MSW flue gas at temperature around 150–210 °C.

Recently, Weber et al. (2002) reported that a model fly ash containing Fe<sub>2</sub>O<sub>3</sub> exhibited the highest dechlorination potential of 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin under oxygen deficiency conditions. Furthermore, Imai et al. (2001) directly applied hematite

(α-Fe<sub>2</sub>O<sub>3</sub>), derived from goethite (α-FeOOH), to promote catalytic oxidation of carbon monoxide and polyethylene. The results showed that 99% CO conversion at 573 K with a significant reduction of dioxin (from 25–30 to 3–4 ng-TEQ/N m<sup>3</sup>), essentially confirming the superior oxidation activity of the hematite catalyst (Imai et al., 1999, 2000a,b).

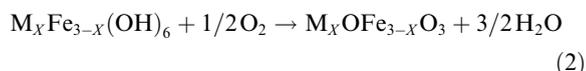
Ferric iron sludge is commonly generated in metal removal facilities and the resultant iron sludge could be regenerated into ferric oxides to be used as a catalyst in combustion processes. If feasible, this would achieve waste reuse and enhance combustion efficiency in general, and reduce dioxin emission in particular. Consequently, this study was undertaken to evaluate the performance of the regenerated iron oxide for oxidizing carbon monoxide and suppressing PCDD/F formation in a pilot-scale incinerator.

## 2. Materials and methods

This study consists two parts: preparation and characterization of regenerated ferric oxides, and catalytic oxidation of chlorinated compounds using the regenerated iron oxide catalyst to suppress dioxin formation.

### 2.1. Preparation of ferric oxide catalyst

The raw ferric iron sludge was obtained from a nearby pilot wastewater treatment plant. In the chemical treatment unit, NaOH was controlled at pH 9–10.5 and ferric sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) was added to form iron hydroxide/oxide precipitates for metal ion removal in a patented process (USA Patent, 1977):



where  $XM^{2+}$  is the amount of divalent metal ions, and  $M_XOFe_{3-X}O_3$  is ferric iron sludge. If only Fe<sup>2+</sup> were present in wastewater (M = Fe and X = 1), the produced sludge would be a pure FeOFe<sub>2</sub>O<sub>3</sub>.

After separation from wastewater by a magnetic process, the ferric iron sludge was initially dried at 105 °C for 30 min and then heat-treated at 800 °C for 4 h. Thereafter, the heat-treated ferric oxide was ground and milled (MB-1, Chuo Kakohki Co., Japan) for 2 h. The final fine particles herein are referred to environ-catalyst, which exhibits a strong magnetic property.

### 2.2. Characterization

The particle size of the environ-catalyst was measured with a laser diameter analyzer (Dry Powder

Module, LS 230 Coulter) and also observed in a scanning electron microscope (SEM, model: Hitachi, S-4700, Type II). A micromeritics instrument (model ASAP2000) was used to measure the BET specific surface area of environ-catalyst. The metallic allotrope pattern of iron oxide morphology was identified by an X-ray powder diffract meter (XRD, Shimadzu XD-5 X-ray XRPD). The chemical compositions of the original ferric sludge and environ-catalyst were analyzed by inductively coupled plasma with a mass spectrometer (ICP-MS, Agilent 7500) and with an atomic emission spectrometer (ICP-AES, USA Jarrel-Ash, ICAP 9000).

### 2.3. Experiments

In the second part of this study, environ-catalyst was initially applied to catalytic oxidation of chlorinated compounds to evaluate its effectiveness. Chlorobenzene was first used to evaluate the optimum combustion operating conditions in terms of its combustion efficiency and the amount of environ-catalyst added. The combustion efficiency is defined as the extent of CO destruction:

$$\text{Combustion efficiency} = \frac{[\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} \times 100\%$$

where [CO] and [CO<sub>2</sub>] are flue gas concentrations in ppm. The CO level has been correlated to the degree of dioxin formation (Hatanaka et al., 2000; Katami et al., 2002); thus, higher combustion efficiencies would indicate a potential dioxin reduction.

Subsequently, destruction and removal efficiencies (DREs) of three compounds, chlorobenzene, 2,4-dichlorophenol and trichlorofluoroethane, were determined to observe the enhanced oxidation capability of environ-catalyst. These chlorinated compounds were selected, as they are potential precursors for dioxin formation (Altwicker et al., 1992). Note that the heptane was used to maintain a relatively constant Cl/C ratio of 5, since most investigators agree that PCDF/Fs are closely related to this ratio (e.g., Tan et al., 2001). Finally, a waste solvent consisting of 90% non-chlorinated compounds and 10% chlorinated compounds was incinerated for investigating the capability of environ-catalyst in reducing dioxin formation in flue gas. The composition and concentration of these chlorinated compounds and the real waste solvent used in the present study are shown in Table 1.

### 2.4. Combustion operation

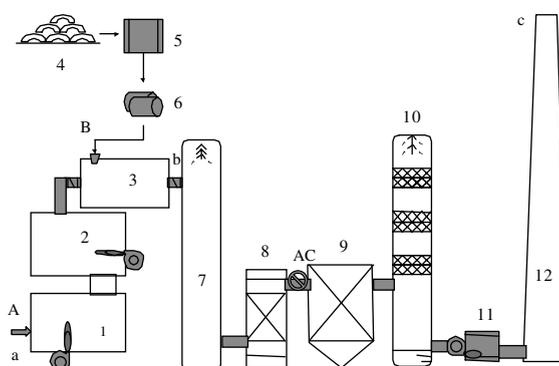
The schematic diagram of the pilot incinerator and the associated air pollution control devices are shown in Fig. 1. The incineration system has two combustion chambers with the upper temperatures controlling at 550

Table 1  
The composition and concentration of chlorinated compounds and real waste solvent

Composition	Concentration (ppm)	Cl/C ratio <sup>a</sup> (%)
Chlorinated compounds		
Chlorobenzene	6640	5
2,4-dichlorophenol	4810	5
Trichlorofluoroethane	14 600	5
Real waste solvent	3050 <sup>b</sup>	

<sup>a</sup> Use of heptane for dilution to maintain the same 5% Cl/C ratio for each chlorinated compound.

<sup>b</sup> Referring to total chlorine content; the solvent also contains 6130 ppm acetate and 11 710 ppm dichloromethane, among other impurity.



A. chlorinated compounds or real waste solvent feed; B. environ-catalyst addition; AC. activated carbon addition.

a. solvent sampling point; b. gas sampling point; c. Dioxin sampling point.

1. first combustion chamber; 2. second combustion chamber; 3. catalytic reactor; 4. ferric iron sludge; 5. dryer/furnace; 6. miller; 7. cooling tower; 8. heat exchanger; 9. bag filter; 10. wet scrubber; 11. reheater (demister); 12. chimney.

Fig. 1. Schematic diagram of the incinerator system.

and 850 °C in chamber 1 ( $V = 1.4 \text{ m}^3$ ) and 2 ( $V = 1.4 \text{ m}^3$ ), respectively. Chlorinated compounds or waste solvent were delivered into chamber 1 at a fixed rate of 20 l/h. Two separate blowers were operated to provide the adequate oxygen to each chamber. The volume of combustion air in chamber 1 and chamber 2 are 12.2 and 0.4  $\text{Nm}^3/\text{min}$ , respectively. The average flue gas rate is about 12.7  $\text{Nm}^3/\text{min}$  to maintain the pressure of chambers under a slight suction condition (negative pressure). The environ-catalyst reaction chamber is located immediately after chamber 2. The environ-catalyst was applied at a preset rate of either 100 or 300 g/h by pulsejet into the reaction chamber ( $V = 0.68 \text{ m}^3$ ). This injection involves no extra air into the reaction chamber. Based on the temperature (close to 850 °C), gas

residence time of about 0.8 s (@  $\text{CO}_2$ ) and turbulence condition (Reynolds number about  $10^6$ ), it is expected that conditions are favorable for the catalytic reactions. As in the case of real incinerator systems, the processes shown in Fig. 1 also include a flue gas cooling system, filter, wet scrubber and a second heating device.

### 2.5. CO, $\text{CO}_2$ , compound and PCCD/F measurements

CO and  $\text{CO}_2$  were continuously monitored in sampling by using a non-dispersive infrared instrument with CO (SIEMENS, ULTRAMAT 23) and  $\text{CO}_2$  (MAIHAK, SIFOR 200) sensors. The gas samples for each individual compound test were collected in a 10 l Tedlar bag after the catalytic reactor (sampling point b in Fig. 1). The compound concentrations were analyzed by a gas chromatography coupled with a mass spectrometry (GC/MS, HP 6890), equipped with a fused silica capillary column (60 m, 0.25 mm ID, 0.25  $\mu\text{m}$  film thickness; J&W Scientific, CA, USA). Prior to analysis, a blank and a quality control samples were prepared to ensure the stability of the retention time and calibration curve, with linear coefficient of each individual >99.5%. The analyses of samples follow the Taiwan standard method A722 (NIEA, 1999).

The stack flue gas (sampling point c in Fig. 1) was sampled (duration of about 4 h) for the analysis of PCCD/F concentrations. Before field sampling, an XAD-2 resin was spiked with isotopically labeled PCDD/F surrogate standards (Wellington laboratories, Ontario, Canada). Trip blank (to check the potential contamination of surrogate standards during storage and transportation) and field blanks (to check the sampling contamination) were also taken and determined. Analyses of PCDD/Fs follow the US EPA modified method 23 (USEPA, 1997). High-resolution gas chromatograph (HRGC) coupled with a high-resolution mass spectrometer was used for the measurement of PCDD/Fs. The HRGC (Hewlett Packard 6970) is equipped with a DB-5MS (J&W Scientific, CA, USA) fused silica capillary column with splitless injection.

## 3. Results and discussion

### 3.1. Characterization of environ-catalyst

After heat-treated at 800  $^\circ\text{C}$  and ground at room temperature, the ferric sludge becomes brownish in appearance. The morphological structures from the SEM photography are shown Fig. 2, with a mean diameter of 1.5  $\mu\text{m}$ , and the BET specific surface area of 5.6  $\text{m}^2/\text{g}$ . Fig. 3 shows the XRD diagrams of the original ferrous/ferric sludge and environ-catalyst, with information provided from the databank of JCPDS (Joint Commit-

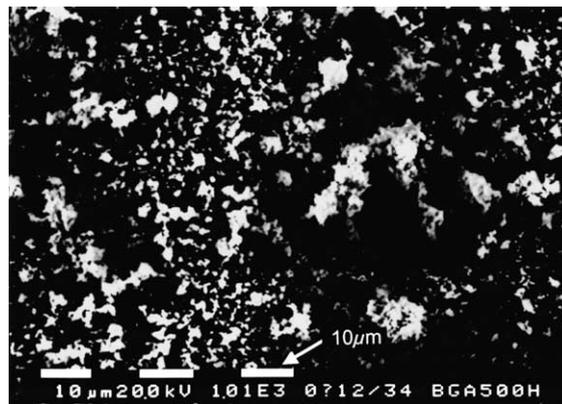


Fig. 2. SEM photographs of environ-catalyst ( $\times 1000$ ).

tee on Powder Diffraction Standards). Clearly, the major component of the ferric iron sludge is magnetite ( $\text{FeFe}_2\text{O}_4$ , Fig. 3(a)), which is the end byproduct in Eq. (2). After heat-treatment, the major component in the environ-catalyst becomes hematite ( $\alpha\text{-Fe}_2\text{O}_3$ , Fig. 3(b)). The magnetic properties of  $\gamma\text{-Fe}_2\text{O}_3$  were also reported by Srivastava et al. (2002). The chemical compositions of the ferric sludge and the environ-catalyst are shown in Table 2. Again, the major constitute of environ-catalyst is  $\alpha\text{-Fe}_2\text{O}_3$  (75%).

### 3.2. Combustion efficiency and DRE

Fig. 4 shows the relationship between combustion efficiency of chlorobenzene and reaction temperature in chamber 2. The combustion efficiency increases steeply from 30% up to 70% (around 550  $^\circ\text{C}$ ), immediately after the addition of the environ-catalyst (300 g/h). The efficiency then slowly increases with increased temperature. The efficiency eventually reaches 98–100% at near 850  $^\circ\text{C}$ , in which the CO concentration is below the detection limit. The experimental conditions at the catalyst dosage of 300 g/h and the chamber temperature 850  $^\circ\text{C}$  were used in the subsequent experiments.

Schwertmann and Murad (1983) reported that the lattice oxygen ion was closely packed in the crystal structure of iron oxides and would be released out in the iron-mediated processes, which involves a variety of oxidative and reductive reaction (Arienzo et al., 2001). The lattice oxygen present in  $\text{Fe}_2\text{O}_3$  was also reported to be a major mechanism for the oxidation of CO on  $\alpha\text{-Fe}_2\text{O}_3$  (Gupta and Tripathi, 2001). In fact, Imai et al. (2001), in evaluating the capability of  $\alpha\text{-Fe}_2\text{O}_3$  to suppress dioxin formation in polyethylene combustion, also reported that the oxidation activity is due to the lattice oxygen generated as well as large numbers of new active sites produced. Therefore, the reason for the increased

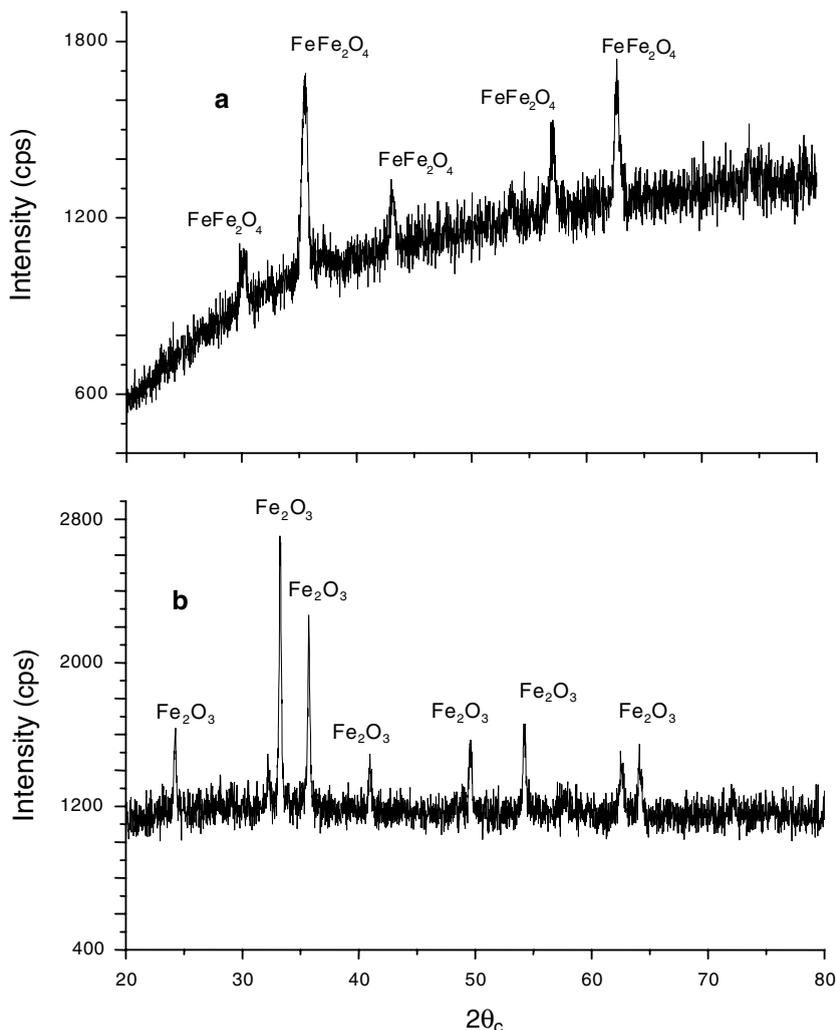


Fig. 3. XRD diagram of samples: (a) original ferrous/ferric sludge, (b) environ-catalyst.

CO oxidation is believed to be the presence and subsequent release of large numbers of lattice oxygen from the structure of environ-catalyst.

The DREs for three chlorinated compounds are shown in Fig. 5 with temperature at 550 °C in the chamber 1 and the catalyst dosage rate of 300 g/h. The DRE ranges from three nines for chlorobenzene and trichlorofluoroethane to five nines for 2,4-dichlorophenol. The lower volatility of 2,4-dichlorophenol may be one of the reasons for the enhanced efficiency. Nonetheless, the environ-catalyst has been demonstrated to be effective for the DREs of these solvents.

### 3.3. Dioxin congeners

To clarify the suppression effect on dioxin formation during combustion of a real waste solvent, five com-

bustion tests were carried out. There were: (1) incinerator start-up test with the chamber 2 temperature below 300 °C (STD1); (2) steady-state test (STD2) (temperatures at chambers 1 and 2 were 550 and 850 °C, respectively); (3) steady-state test with the addition of 100 g/h catalyst (ferrite 1); (4) steady-state test with the addition of 300 g/h catalyst (ferrite 2); and (5) 200 g/h powdered activated carbon injection (carbon). The resultant concentrations of total PCDD/Fs (toxicity equivalent, TEQ) and each dioxin congener for each of five experiments are shown in Table 3. The results clearly indicate that the STD1, STD2 and carbon addition tests were unable to meet the emission standard ( $<0.1 \text{ ng-TEQ/Nm}^3$ ). However, in the presence of the catalyst with two different dosages, the results are below the emission standard. Further, a higher catalyst dosage (ferrite 2 condition) yields the lowest dioxin emissions (Fig. 6).

Table 2  
The chemical composition of the ferric ion sludge and environ-catalyst

M/ferric sludge (mg/kg)	$M_xO_y$ /environ-catalyst (%)	
Fe	376 100	
Na	31 500	
Mn	16 390	
Mg	2260	
Al	1850	
Cr	1170	
Ca	950	
Ti	760	
K	280	
Zn	92	
Ba	72	
Ni	33	
Mo	72	
Sn	15	
Hg	2690	
	Fe <sub>2</sub> O <sub>3</sub>	74.6
	Na <sub>2</sub> O	0.5
	MnO	0.2
	MgO	0.1
	Al <sub>2</sub> O <sub>3</sub>	0.7
	Cr <sub>2</sub> O <sub>3</sub>	0.1
	CaO	0.2
	TiO <sub>2</sub>	0.1
	K <sub>2</sub> O	1.2
	ZnO	0.1
	MoO <sub>3</sub>	0.1
	CdO	0.1
	CuO	0.1
	P <sub>2</sub> O <sub>5</sub>	0.2
	V <sub>2</sub> O <sub>5</sub>	0.2
	PbO <sub>2</sub>	0.3
	SiO <sub>2</sub>	0.1

### 3.4. Ratio of $\sum PCDF/\sum PCDD$

The furan/dioxin ratio from dioxin congeners may indicate which pathway of de novo synthesis and precursor formation is the dominant mechanism of dioxin

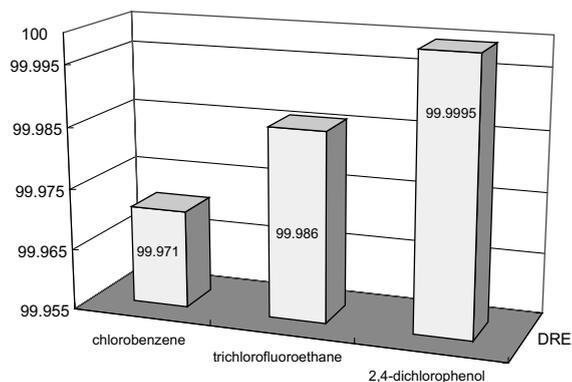


Fig. 5. The DRE of three chlorinated organic compounds.

formation (Huang and Buekens, 1995). The ratio of PCDFs/PCDDs generally ranges from 0.3 to 10 depending on the sampling location (Yamamoto et al., 1989) and the type of the incinerator, among others. Specifically, if the furan/dioxin ratio  $>1$ , de novo synthesis may be the dominant mechanism; and if the ratio is  $<1$ , precursor formation may be the controlling mechanism.

The furan/dioxin ratio for STD1 and STD2 tests are 2.6 and 1.2, respectively. The ratios for the catalyst test, however, are dramatically decreased, 0.7 and 0.6 for

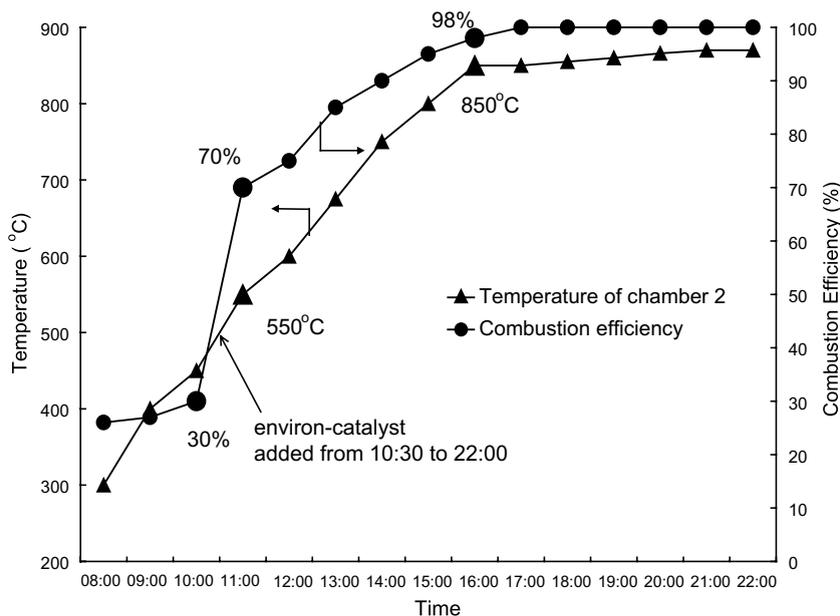


Fig. 4. The relationship between combustion efficiency and reaction temperature in chamber 2 in the presence of environ-catalyst (300 g/h).

Table 3  
PCDD/F concentrations in TEQ and dioxin congeners of real waste solvent in the flue gas

Dioxin congeners	STD1	STD2	Carbon 200 g/h carbon	Ferrite 1 100 g/h environ-catalyst	Ferrite 2 300 g/h environ-catalyst
<b>PCDDs (ng/Nm<sup>3</sup>)</b>					
2,3,7,8-TeCDD	0.01	0.01	0.01	0.01	0.01
1,2,3,7,8-PeCDD	0.03	0.02	0.03	0.01	0.01
1,2,3,4,7,8-HxCDD	0.01	0.02	0.02	0.01	0.01
1,2,3,6,7,8-HxCDD	0.03	0.04	0.03	0.02	0.01
1,2,3,7,8,9-HxCDD	0.03	0.05	0.04	0.03	0.01
1,2,3,4,6,7,8-HpCDD	0.03	0.27	0.10	0.17	0.03
1,2,3,4,6,7,8,9-OCDD	0.30	0.38	0.09	0.33	0.03
<b>PCDFs (ng/Nm<sup>3</sup>)</b>					
2,3,7,8-TeCDF	0.95	0.18	0.27	0.10	0.06
1,2,3,7,8-PeCDF	0.10	0.04	0.04	0.02	0.01
2,3,4,7,8-PeCDF	0.11	0.08	0.07	0.04	0.02
1,2,3,4,7,8-HxCDF	0.26	0.16	0.12	0.09	0.04
1,2,3,6,7,8-HxCDF	0.09	0.08	0.05	0.04	0.02
1,2,3,7,8,9-HxCDF	0.01	0.01	0.01	0.01	0.01
2,3,4,6,7,8-HxCDF	0.08	0.12	0.05	0.05	0.02
1,2,3,4,6,7,8-HpCDF	0.10	0.26	0.13	0.18	0.05
1,2,3,4,7,8,9-HpCDF	0.03	0.08	0.02	0.05	0.01
1,2,3,4,6,7,8,9-OCDF	0.40	0.18	0.04	0.19	0.01
Total PCDD/Fs (ng-TEQ <sup>a</sup> /Nm <sup>3</sup> )	0.23	0.13	0.12	0.07	0.04

<sup>a</sup> TEQ: the TEQs are calculated using international toxic equivalent factors of NATO/CCMS.

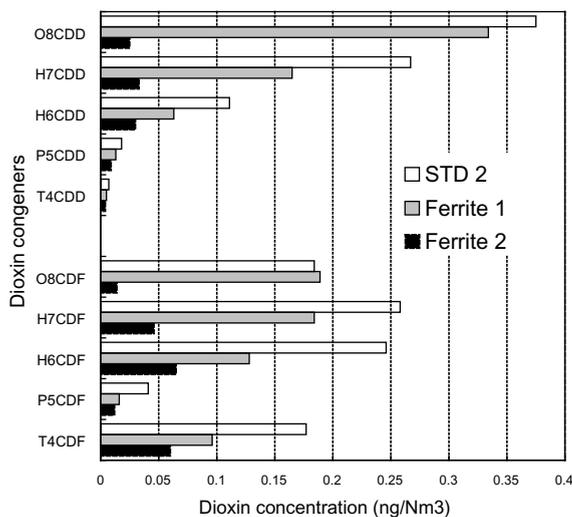


Fig. 6. Distribution of dioxin congeners of ferrite 2 (300 g/h catalyst), ferrite 1 (100 g/h catalyst), and STD2 (without catalyst) under steady-state combustion conditions.

ferrite 1 and ferrite 2, respectively. The reduction in furan/dioxin ratio implies that the excess catalyst may

further reduce dioxins in flue gas. To further comprehend the difference between STD1 and STD2 (absence of catalyst), the log plot of furan/dioxin ratio for several dioxin congeners is presented in Fig. 7. The temperature difference between these two conditions may be responsible for the observed phenomenon. Specifically, TCDF and OCDF concentrations in STD2 have been significantly reduced.

#### 4. Conclusions

For waste reuse, a novel method was developed to regenerate the ferrous/ferric sludge, to be used as a catalyst for suppressing dioxin formation in flue gas during the combustion of three chlorinated organic solvents and a real waste. Experimental results showed that the combustion efficiency of carbon monoxide was more than 98% at 850 °C in the presence of the catalyst. The DRE for three types of chlorinated organic compounds were satisfactory, ranging from 3 to 5 nines. In the presence of the catalyst, the concentration of PCDD/Fs in flue gas is below the emission standard of 0.1 ng-TEQ/Nm<sup>3</sup> for a real waste solvent combustion.

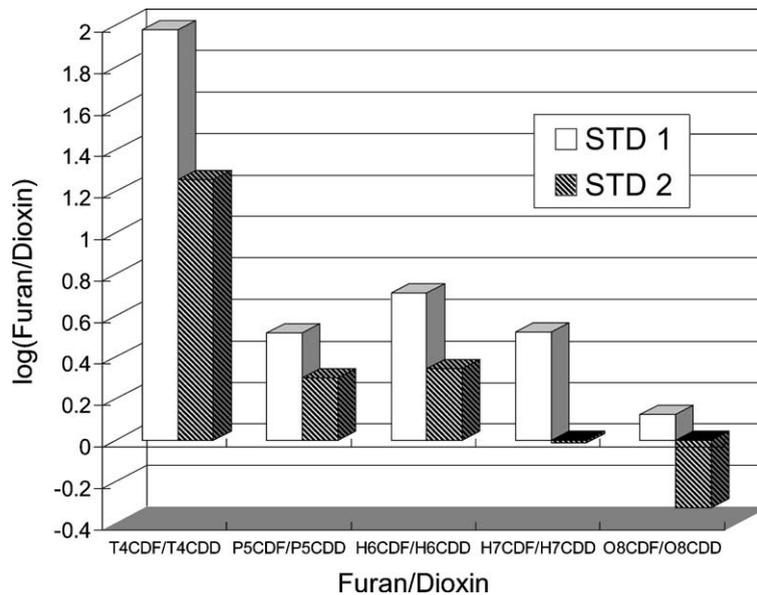


Fig. 7. The logarithmic diagram of furans/dioxins at STD1 (start-up) and STD2 (steady-state) of a real waste solvent combustion.

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### References

- Addink, R., Altwicker, E.R., 1996. Formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans in waste combustion: role of chlorine review. *Organohalogen Compounds* 27 (3), 1–4.
- Addink, R., Paulus, R.H.W.L., Olie, K., 1996. Prevention of polychlorinated dibenzo-*p*-dioxins/dibenzofurans formation on municipal waste incinerator fly ash using nitrogen and sulfur compounds. *Environmental Science Technology* 30 (7), 2350–2354.
- Altwicker, E.R., Konduri, R., Lin, C., Milligan, M., 1992. Rapid formation of polychlorinated dioxins/furans in the post combustion region during heterogeneous combustion. *Chemosphere* 25 (12), 1935–1944.
- Arienzo, M., Chiarenzelli, J., Scudato, R., Pagano, J., Falanga, L., Connor, B., 2001. Iron-mediated reactions of polychlorinated biphenyls in electrochemical peroxidation process (ECP). *Chemosphere* 44 (6), 1339–1346.
- Bonte, J.L., Fritsky, K.J., Plinke, M.A., Wilken, M., 2002. Catalytic destruction of PCDD/F in a fabric filter: experience at a municipal waste incinerator in Belgium. *Waste Management* 22 (4), 421–426.
- Buekens, A., Huang, H., 1998. Comparative evaluation of techniques for controlling the formation and emission of chlorinated dioxins/furans in municipal waste incineration. *Journal of Hazardous Materials* 62 (3), 1–33.
- Gupta, N.M., Tripathi, A.K., 2001. The role of nanosized gold particles in adsorption and oxidation of carbon monoxide over Au/Fe<sub>2</sub>O<sub>3</sub> catalyst. *Gold Bulletin* 34 (4), 120–128.
- Hatanaka, T., Imagawa, T., Takeuchi, M., 2000. Formation of PCDD/Fs in artificial solid waste incineration in a laboratory-scale fluidized-bed reactor: influence of contents and forms of chlorine sources in high-temperature combustion. *Environmental Science Technology* 34 (18), 3920–3924.
- Huang, H., Buekens, A., 1995. On the mechanism of dioxin formation in combustion processes. *Chemosphere* 31 (2), 4099–4114.
- Ide, Y., Kashiwabara, K., Okada, S., Mori, T., Hara, M., 1996. Catalytic decomposition of dioxin from MSW incinerator flue gas. *Chemosphere* 32 (1), 189–198.
- Imai, T., Matsui, T., Nakai, T., 1999. Combustion characteristics of polyethylene added iron oxides (in Japanese). *Kagaku Kogaku Ronbunshu* 25 (5), 935–939.
- Imai, T., Fujii, Y., Matsui, T., Nakai, T., 2000a. Demonstration test of dioxin suppression using an iron oxide catalyst at an intermittently operated incinerator for municipal solid waste (in Japanese). *Journal of Japan Social Waste Management Experts* 11 (2), 67–73.
- Imai, T., Matsui, T., Fujii, Y., Okita, T., Nakai, T., 2000b. Catalytic oxidation of chlorobenzene and benzene over hematite catalyst (in Japanese). *Nippon Kagaku Kaishi* 8 (4), 541–545.
- Imai, T., Matsui, T., Fujii, Y., Nakai, T., Tanaka, S., 2001. Oxidation catalyst of iron oxide suppressing dioxin formation in polyethylene combustion. *Journal of Material Cycles Waste Management* 3 (1), 103–109.
- Karasek, F.W., 1995. An overview of dioxin formation in combustion processes. *Organohalogen Compounds* 23 (2), 315–319.
- Katami, T., Yasuhara, A., Okuda, T., Shibamoto, T., 2002. Formation of PCDDs, PCDFs, and coplanar PCBs from polyvinyl chloride during combustion in an incinerator. *Environmental Science Technology* 36 (6), 1320–1324.
- Kersting, K., Wirling, J., EsserSchmittmann, W., Lenz, U., 1997. Removal of dioxins and furanes from waste gases of a

- sintering plant by using lignite coke. *Stahl und Eisen* 117 (11), 49.
- Lenoir, D., Hutzinger, O., Mützenich, G., Horch, K., 1989. PCDD/F: verhinderung der Entstehung chlorierter dibenzodioxine und-furane bei der Müllverbrennung-inhibierung der katalytischen Bildung. *UWSF—Z. Umweltchem. Ökotox.* 1 (4), 3–6.
- Liljelind, P., Unsworth, J., Maaskant, O., Marklund, S., 2001. Removal of dioxins and related aromatic hydrocarbons from flue gas streams by adsorption and catalytic destruction. *Chemosphere* 42 (5–7), 615–623.
- Marklund, S., Fängmark, L., Rappe, C., 1991. Formation and degradation of chlorinated aromatic compounds in air pollution device for MSW combustor. *DIOXIN* 91 (2), S49–58.
- NIEA (National Institute Environmental Analysis, Taiwan), 1999. Method A722.71B: measurement of gaseous organic compound emission by gas chromatography (in Chinese).
- Ogawa, H., Orita, N., Horaguchi, M., Suzuki, T., Okata, M., Yasuda, S., 1996. Dioxin reduction by sulfur component addition. *Chemosphere* 32 (1), 151–157.
- Olie, K., Vermeulen, P.L., Hutzinger, O., 1977. Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some incinerators in the Netherlands. *Chemosphere* 6 (8), 455–459.
- Samaras, P., Blumenstock, M., Lenoir, D., Schramm, K.W., Kettrup, A., 2000. PCDD/F prevention by novel inhibitors: addition of inorganic S- and N-compounds in the fuel before combustion. *Environmental Science Technology* 34 (24), 5092–5096.
- Samaras, P., Blumenstock, M., Lenoir, D., Schramm, K.W., Kettrup, A., 2001. PCDD/F inhibition by prior addition of urea to the solid fuel in laboratory experiments and results statistical evaluation. *Chemosphere* 42 (5/7), 737–743.
- Schwertmann, U., Murad, E., 1983. Effect of pH on the formation of goethite and hematite from ferrihydrite. *Clays Clay Minerals* 31 (4), 277–284.
- Siret, B., Gilman, K., 1996. A survey of post-combustion PCDD/PCDF control technologies. In: *Proceedings of the International Conference Incineration and Thermal Treatment Technology*, pp. 583–586.
- Srivastava, D.N., Perkas, N., Gedanken, A., Felner, I., 2002. Sonochemical synthesis of mesoporous iron oxide and accounts of its magnetic and catalytic properties. *Journal of Physical Chemistry B* 106 (8), 1878–1883.
- Tan, P., Hurtado, I., Neuschütz, D., Eriksson, G., 2001. Thermodynamic modeling of PCDD/Fs formation in thermal processes. *Environmental Science Technology* 35 (9), 1867–1874.
- USA Patent 3(931), 007, 1977. Fundamental process for wastewater treatment by ferrite-formation, and magnetic separation of precipitated ferrite.
- USEPA, 1997. Method 23: determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from municipal waste combustors. Research Triangle Park Laboratories, Raleigh, NC.
- Vogg, H., Stieglitz, L., 1986. Thermal behavior of PCDD/PCDF in municipal incinerators. *Chemosphere* 15 (2), 1373–1378.
- Weber, R., Sakurai, T., Hagenmaier, H., 1999a. Formation and destruction of PCDD/PCDF during heat treatment of fly ash samples from fluidized bed incinerators. *Chemosphere* 38 (11), 2633–2642.
- Weber, R., Sakurai, T., Hagenmaier, H., 1999b. Low temperature decomposition of PCDD/PCDF, chlorobenzenes and PAHs by TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalysts. *Applied Catalysis B: Environmental* 20 (4), 249–256.
- Weber, R., Plinke, M., Xu, Z., Wilken, M., 2001. Destruction efficiency of catalytic filters for polychlorinated dibenzo-*p*-dioxin and dibenzofurans in laboratory test and field operation-insight into destruction and adsorption behavior of semivolatile compounds. *Applied Catalysis B: Environmental* 31 (3), 195–207.
- Weber, R., Nagai, K., Nishino, J., Shiraishi, H., Ishida, M., Takasuga, T., Konndo, K., Hiraoka, M., 2002. Effects of selected metal oxides on the dechlorination and destruction of PCDD and PCDF. *Chemosphere* 46 (9/10), 1247–1253.
- Yamamoto, T., Inoue, S., Sawachi, M., 1989. Post furnace formation and progressive chlorination of PCDD and PCDF in municipal waste incinerator. *Chemosphere* 19 (1/6), 271–276.