

Effects of calcium-based sorbents on PCDD/F formation from pentachlorophenol combustion process

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Abstract

Calcium-based sorbents are widely employed to reduce the acidic gases emission from combustion processes, and also have effects on trace organic pollutants formation and emission. Batch experiments were conducted to investigate the effects of calcium-based sorbents on pentachlorophenol (PCP) forming PCDDs/Fs during high temperature combustion processes. The results indicated that highly chlorinated PCDD/F homologues were the predominant dioxin products from PCP thermo decomposition, and only minor increasing of PCDDs happened when Ca/Cl ratio was lower than 1, while a major jump occurred when Ca/Cl ratio increased from 1 to 2. The CaO addition clearly promoted the production of all chlorinated dibenzo-*p*-dioxins homologue and 4–7DFs homologue. Comparison of total PCDD/F emission and its I-TEQ for three different calcium-based sorbents addition (CaO, CaCO₃, basic fly ash) indicated that CaO and fly ash containing CaO had almost the same promotion effects on PCDDs/Fs originated from PCP, while CaCO₃ inhibit PCDD/F formation greatly with inhibition efficiency up to 70%. Such effects may be partly proved by the observed clearly different micro-surface structures of their reaction residues. The mechanism of CaO on condensation and dechlorination reactions for PCP forming PCDDs and acid–base interaction were proposed to speculate the promotion effects of CaO, and the reaction precedence was used to speculate the inhibition effects of CaCO₃ on PCDDs/Fs originated from PCP. The results of the present paper might be useful for the industrial application of calcium-based sorbents to control PCDD/F emission.

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1. Introduction

PCDD/F emission from municipal solid waste (MSW) incinerators has caused serious public concern because it is carcinogenic and hazardous to human health since Olie et al. [1] first detected the PCDDs/Fs in fly ash from a MSW incinerator in Amsterdam.

Three main formation mechanisms of PCDDs/Fs in the MSW incinerators were reported as: (1) PCDDs/Fs in raw MSW were not decomposed and appeared in flue gas; (2) gas phase formation due to the products of incomplete combustion (PICs); (3) heterogeneous reaction on fly ash surfaces in post-combustion zone [2,3]. The last two mechanisms were much important during MSW incineration process, but till now it is still uncertain which one is the main PCDD/F formation mechanism during incineration process [4–8]. A general explanation could be con-

cluded that PCDDs/Fs in flue gas are mainly formed from the PICs when bad combustion happens and from heterogeneous reaction in post-combustion cooling process. The techniques to control PCDD/F emission focuses on the optimal design “3-Ts” principle, operational optimization of incinerators and adoption of advanced flue gas cleaning system [9–12].

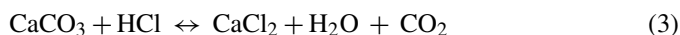
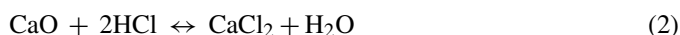
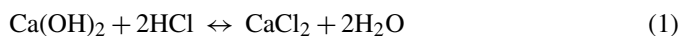
In PCDD/F formation process, Cl₂ is considered as the main source of chlorine and has more effective substitution reactivity than HCl [13]. However, Addink et al. [14] found in experiments on PCDDs/Fs that chlorination caused by HCl and Cl₂ does not follow the same route; amounts of PCDDs/Fs formed with either Cl₂ or HCl from carbon/fly ash mixture are fairly equal. Anyway, the chlorine sources in flue gas are helpful for the forming of PCDDs/Fs through chlorination action.

Generally, it is supported most widely that the depletion of chlorine agent either Cl₂ or HCl could inhibit PCDD/F formation. That means, the measures of adding basic additives, such as CaO, CaCO₃, Ca(OH)₂, Mg(OH)₂, NaOH, Ba(OH)₂, BaCO₃, etc. to remove HCl and Cl₂ in flue gas or fly ash could reduce the PCDD/F formation and emission expectably [15–17].

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The addition of calcium-based sorbents, such as CaO, Ca(OH)₂ and CaCO₃ are generally injected into furnace chamber or post-combustion zone of an incinerator system in order to reduce the pollution of acidic gases, such as SO₂, HCl and even Cl₂. However, some literature reported the inhibition effects [18,19] of SO₂ on PCDD/F emission, so the addition of basic additive perhaps could not favor the inhibition of PCDD/F emission. Some study showed that basic additive might reduce the concentration of Cl⁻ in post-combustion zone, and consequently affect the chlorination reactions during PCDD/F formation process [20].

The capture reactions of Cl⁻ in flue gas by calcium-based sorbents are as follows [16,11,17,18].



Many experiments of injecting basic additives (CaO, Al₂O₃ and MgO) into furnace or flue gas in order to reduce the effect of acid gas on PCDD/F formation have been studied [15,21]. The formation of PCDD/F through adding different ratio of basic oxide studied by Roland et al. [22] shown that the addition of basic additive could reduce the formation of PCDD/F under de novo condition. It was reported recently that calcium oxide (CaO) could inhibit PCDD/F formation from precursors, such as PCP, HCB and 2,3,4,5-T4CP at temperature range between 280 and 450 °C [23]. Test of adding basic substance to waste incinerator carried out by some researchers showed that the concentration of HCl reduced, but the PCDD/F emission may keep invariable, increasing or decreasing. When adding 51 kg dolomite/t-waste to the furnace chamber of fluidized-bed, PCDD/F emission did not change. When adding 158 kg dolomite/t-waste, PCDD/F emission decreased by 94% below emission standard. When adding CaCO₃ or Mg(OH)₂, PCDD/F emission increased remarkably [24,25].

In this study, combustion experiments on pentachlorophenol (PCP) and calcium-based sorbents or fly ash at high temperature in a lab-scale quartz tubular furnace was conducted to investigate the effects of calcium-based sorbents addition on PCDDs/Fs originated from PCP. All the results are expected to be useful for

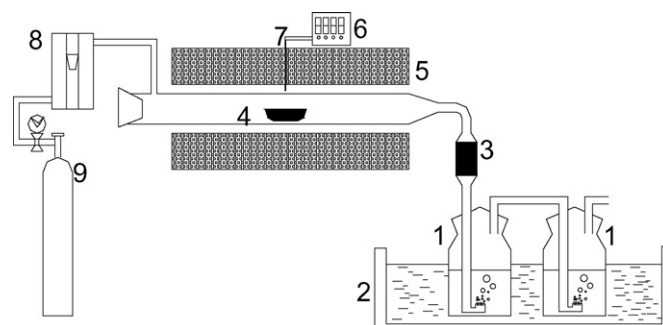


Fig. 1. Schematic diagram of a bench-scale tubular furnace reaction system for heating and sampling experiments. (1) Toluene impingers; (2) ice bath; (3) XAD-2 resin; (4) quartz pipe and reactants; (5) electric heating tubular furnace; (6) temperature controller; (7) thermal couple; (8) flow meter; (9) compressed air source.

further understanding of PCDD/F formation from chlorophenol precursors and its emission control in industrial incinerators or other combustion processes.

2. Experiments and methods

2.1. Experiments in bench-scale tubular furnace

Schematic diagram of a bench-scale tubular furnace system purchased from Shanghai Laboratory Electric Furnace Works was described as Fig. 1. The control temperature range for this tubular furnace is 200–1200 °C (±2 °C). The laboratory reactor consists of a quartz tube with i.d. of 16 mm and a length of 400 mm, which is placed centrally into the electric heating furnace for about 250 mm of its total length. The residence time of the combustion gas in the furnace is estimated on average to be 1.0 s with air flow 300 ml/min. In this set up, the mixture of 0.025 g PCP and calcium-based additives was put in the mid of quartz tube after the furnace temperature reached 850 °C. The amounts of calcium-based additives based on the molar ratio of Ca/Cl (0, 0.5, 1, 2 and 3) in the mixed reagents are showed in Table 1. The molar ratio of Ca/Cl was adapted to indicate the ability of calcium-based additives capturing the chlorine agent produced from reaction process. Reaction time for each test was 45 min. PCDDs/Fs in the flue gas were absorbed by XAD-2 resin and toluene. The residue in ceramic boat, XAD-2 resin, toluene

Table 1
Reaction parameters for heating runs of PCP and calcium-based sorbent mixtures

Reactant	Additives	Molar ratio of Ca/Cl ^a	Weight of calcium-based sorbent (g)	Temperature (°C)	Air flux (ml/min)	Sample number ^a
PCP 0.025 g	–	0 (0)	0(0)	850	300	Ca-1A (B)
	CaO	0.49 (0.49)	0.013 (0.013)	850	300	Ca-2A (B)
	CaO	0.99 (1.01, 1.01)	0.026 (0.027, 0.027)	850	300	Ca-3A (B, C)
	CaO	2.05 (2.05, 1.99)	0.054 (0.054, 0.052)	850	300	Ca-4A (B, C)
	CaO	3.01 (3.04, 2.98)	0.079 (0.080, 0.078)	850	300	Ca-5A ^b (B, C)
	CaCO ₃	2.10 (2.00)	0.098 (0.094)	850	300	Ca-6A (C)
	Fly ash	1.93	0.066	850	300	Ca-7A

^a Duplicate or triplicate experiments as noted A, B and C were done for each test run, which A and B for PCDD/F formation determination, C for SEM (scanning electron microscopy) analysis to observe the microstructure of the residue in ceramic boat; the numbers in the bracket of molar ration of Ca/Cl column are corresponding to sample number B and C.

^b Accidental loss of toluene fraction in impingers happened to Ca-5A during sample collecting process, the PCDD/F analysis results of Ca-5B was employed in this paper.

Table 2
Comparison of PCDD/F emission for different calcium-based sorbents addition

Comparison items	Relative emission factors for different calcium-based sorbents			
	Ca/Cl = 0 ^a		Ca/Cl ≈ 2 ^a	
	No sorbent	CaO	CaCO ₃	Basic fly ash
PCDDs	1	2	0.33	1.31
PCDFs	1	1.80	0.043	0.56
Total PCDDs/Fs	1	1.95	0.26	1.13
I-TEQ	1	29.06	0.24	25.66

^a The emission factor for Ca/Cl=0 was set to be 1, the emission factors for Ca/Cl ≈ 2 were the relative value compared to that of Ca/Cl=0.

in impingers and toluene elutes from quartz tube and connectors are collected and mixed together for the next PCDD/F determination process. Conditions for all test runs were listed in Table 1.

The calcium-based additives employed in experiments were CaO (AR, purity >99%, >200 mesh), CaCO₃ (AR, purity >99%, >200 mesh) and basic fly ash (raw MSWI fly ash; CaO: 76.8%; SiO₂: 1.7%; Al₂O₃: 1.1%; Fe₂O₃: 0.6%; CuO: 9.6%; ZnCl₂: 7.4%; P₂O₅: 0.7%; K₂O: 2.2%). Emission factors were calculated by PCDD/F amount per unit of PCP gram for each test run. The results were also compared to evaluate the effects of three calcium-based additives on PCDD/F emission at the same reaction condition with Ca/Cl=2 as shown in Table 2. In our experiments, we did not analyze PCDDs/Fs in gas phase or residue phase separately, and all emission factor results were expressed in gas and residue phases together.

2.2. Sample pretreatment and analysis

Each sample contained the fractions of residue in ceramic boat, XAD-2 resin, toluene in impingers and toluene elutes from quartz tube and connectors. The mixed sample was spiked by 10 μl five ¹³C isotope internal standards (¹³C-2,3,7,8-TCDD, ¹³C-2,3,7,8-TCDF, ¹³C-1,2,3,6,7,8-HxCDD, ¹³C-1,2,3,4,6,7,8-HpCDF, ¹³C-OCDD) and then extracted by 250 ml toluene for 24 h (4–5 circulations/h) using traditional Soxhlet extraction method. The extract was concentrated to 1–2 ml by rotary evaporation. The concentrated solution, which has to be purified by multistage chromatography columns, i.e. acidic/alkaline silica gel column, acidic alumina column and another small acidic alumina column [26]. The cleaned-up elute was kept in clean beaker and concentrated to 1–2 ml, then transferred into a centrifugal tube and gently blown to dry by high purity nitrogen. Added 10 μl recovery standards (¹³C-1,2,3,4-TCDD; ¹³C-1,2,3,7,8,9-HxCDD) to the dry centrifugal tube and vibrated the tube using ultrasonic equipment for 15 min. ¹³C-1,2,3,4-TCDD is used to calculate the amount of Te-PeCDD/Fs, ¹³C-1,2,3,7,8,9-HxCDD for Hx-OCDD/Fs.

All analyses were performed on a low resolution Finnigan Voyager mass spectrometer (LRMS) with a trace 2000 high-resolution gas chromatograph (HRGC). Chromatographic separations were carried out on a 60 m DB-5 silica-fused capillary column with i.d. of 0.25 mm and a stationary phase film

thickness of 0.25 μm. The temperature program for GC oven was: initial temperature 100 °C, held for 2 min; 100–200 °C at 25 °C/min; 200–280 °C at 3 °C/min; 280 °C held for 20 min. Carrier gas: helium (99.999%), 1 ml/min. Splitless sample injection. Mass spectrum condition: electron impact ionization 70 eV; electron multiplier voltage 420 V; ion source temperature 220 °C; interface temperature 250 °C; SIM (selected ion monitoring mode). All the isotope standards were purchased from Wellington laboratories, Canada or Cambridge Isotope Laboratory, USA. The toxicity of the sample is presented in terms of PCP weight using TEF in USEPA Method 8280B [26].

Scanning electron microscope (SEM) analysis was always conducted to determine the physical property changes and chemical species distributions within the aimed materials [27–29]. In this paper, the residues in ceramic boat of the experiments C series in Table 1 were collected to do the microstructure analysis in a SEM instrument JEM-2010 made by JEOL. The residue was first transferred to a small sample plate, and then the sample was coated with a layer of platinum in a vacuum coating machine. The coating sample was then detected by a SEM with an accelerating voltage of 20 kV. The same magnification (5000×) SEM pictures of residues from experiments Ca-3C, Ca-4C, Ca-5C and Ca-6C were presented to compare the microstructure differences of reaction residues after reaction of calcium-based sorbents and PCP.

3. Results and discussion

3.1. Effects of CaO on PCDD/F emission in bench-scale tubular furnace

Figs. 2–4 showed the impact of different Ca/Cl ratio on the emission of PCDDs, PCDFs and total dioxins during the co-reaction of CaO and PCP at 850 °C. It had to be mentioned that the indicated data points with arrowhead at Ca/Cl = 3 in Figs. 2–4 were conducted only once, the duplicated data were not obtained because the toluene in first impingers of the Ca-5A test run was lost. For those Ca/Cl molar ratios from 0 to 2, the duplicated results are acceptable.

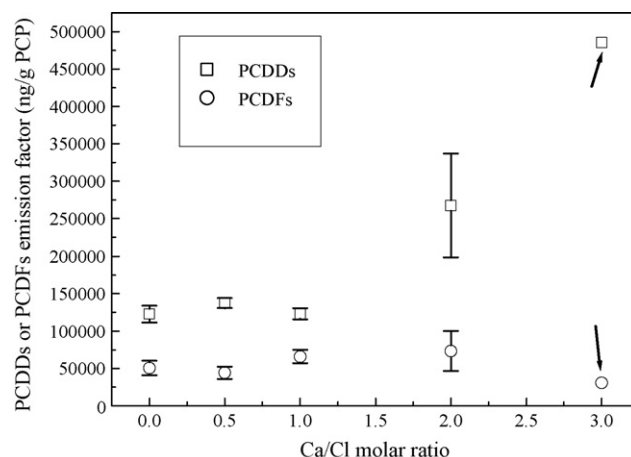


Fig. 2. Relationship between Ca/Cl molar ratio and PCDDs or PCDFs emission.

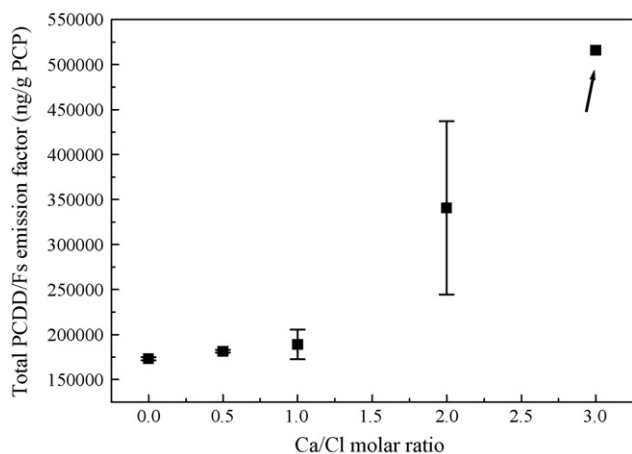


Fig. 3. Relationship between Ca/Cl molar ratio and total PCDD/Fs emission.

From Fig. 2, the amount of PCDDs increased sharply with the increase of Ca/Cl ratio. The amount of PCDFs showed no clear increase from Ca/Cl=0 to 3. In Fig. 3, we see that the total PCDD/F emission could be mainly caused by the PCDDs increase. The same rising trend occurred with I-TEQ emission in Fig. 4 except in the case of Ca/Cl=3. One of the interesting phenomenon in Figs. 2–4 was that only a minor increase occurred when Ca/Cl increased from 0 to 0.5 and 1, while a steep rise from three to four times occurred when the Ca/Cl ratio changed from 0 to 1 and 2. That meant one of the Ca/Cl value among the ratio 1–2 could be considered as the critical point of the high promotion impact of CaO on the emission of PCDDs/Fs when co-firing with PCP.

Fig. 5 showed the PCDD/F homologue profiles for different Ca/Cl molar ratios in test series runs B. The concentration of OCDD (8DD) hardly changed with the Ca/Cl ratio in range of 0–2, and increased greatly at Ca/Cl=3. The emission of tetra- to hepta-CDD (4–7DD) had the same change as the variation of Ca/Cl ratio, and amount of 4–7DD were the most abundant in case of Ca/Cl=2 and 0.5. From columns in Fig. 5, it could be seen that CaO addition into the PCP thermo decomposition process promoted the production of all chlorinated dibenzo-*p*-

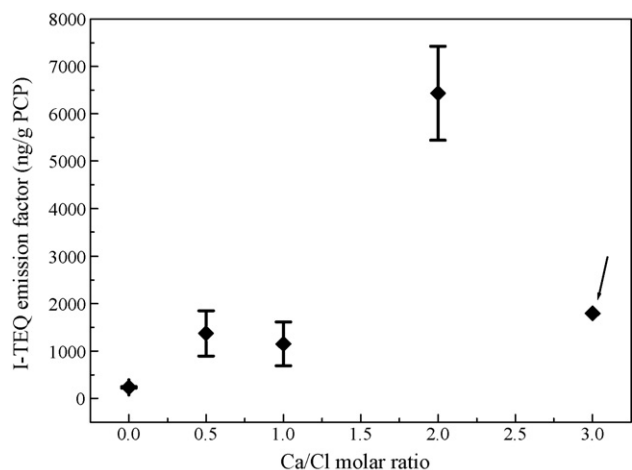


Fig. 4. Relationship between Ca/Cl molar ratio and I-TEQ emission.

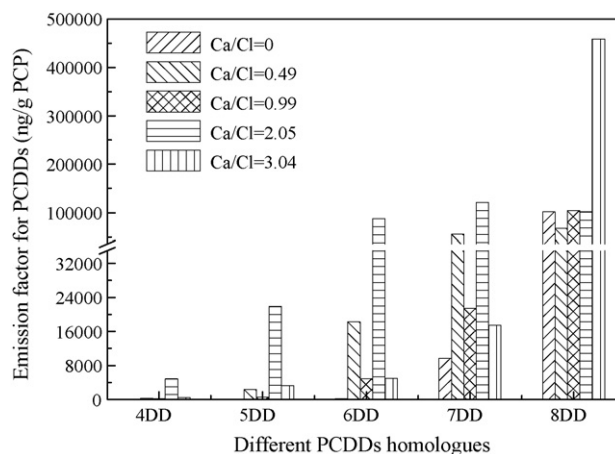


Fig. 5. PCDDs homologue profiles for different Ca/Cl molar ratios.

dioxins. For dibenzofurans formation in Fig. 6, the effect of CaO on PCP decomposition was different. The most abundant emission of tetra- to octa-CDF (4–8DF) was at Ca/Cl=2. All cases of CaO addition promoted 4–7DFs formation clearly, while two cases of Ca/Cl=1 and 2 promoted 8DF formation, and the other two cases of Ca/Cl=0.5 and 3 suppressed 8DF formation. With comparison of Figs. 5 and 6, the production of 4–8DF was one order of magnitude lower than that of 4–8DD. That meant PCDDs were the predominant dioxin products after PCP thermo decomposition [30,31]. This also indicated that the micro-pore surface of CaO might provide large dispersion and decomposition space for PCP at high temperature, and also CaO might capture the decomposed chlorine and promote PCP decomposition to form dioxins. It could be calculated that 0.016% PCP converted to PCDDs/Fs when no CaO added, and the conversion percent increased to over 0.048% with CaO addition.

We also listed the 2, 3, 7, 8-substituted toxic PCDD/F production for Ca/Cl=1 and 2 in Figs. 7 and 8. For those toxic tetra- to hepta-DD/Fs, the amount for Ca/Cl=2 was two or more times of that for Ca/Cl=1. Even though the octa-DD/F production for Ca/Cl=2 was a little bit lower than that for Ca/Cl=1, the I-TEQ quantity for Ca/Cl=2 in Fig. 4 remained

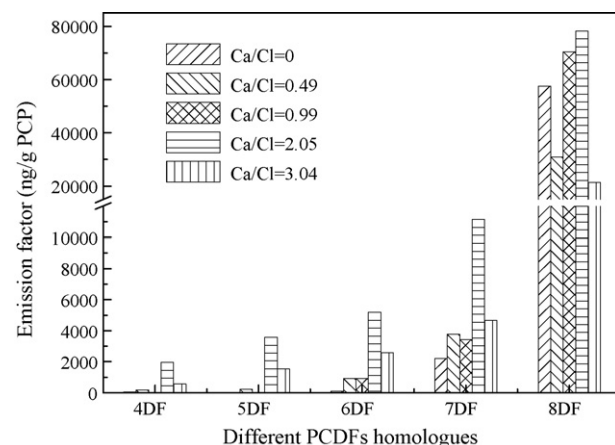


Fig. 6. PCDFs homologue profiles for different Ca/Cl molar ratios.

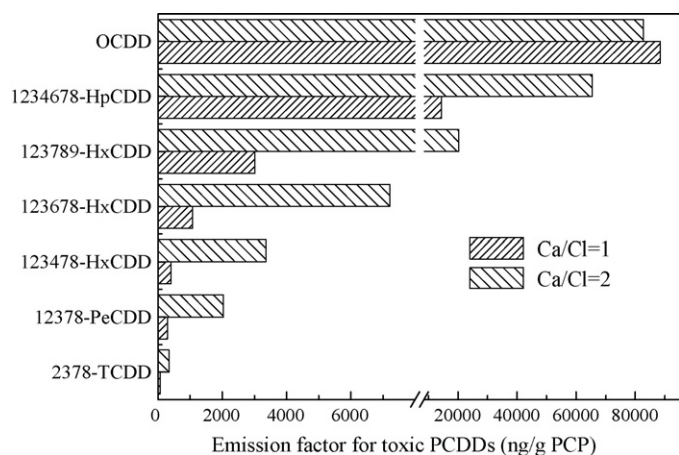


Fig. 7. Comparison of toxic PCDDs emission factor for Ca/Cl=1 and 2 of test runs B.

much higher than that for Ca/Cl=1 because of a I-TEF as low as 0.001 for octa-DD/F. From the above results, we hypothesize that much more supply of CaO during PCP heating process (with Ca/Cl ratio up to 2) facilitated octa-DD/F decomposing to low chlorinated tetra- to hepta-DD/Fs. Such results and hypothesis were completely reversed from the suppressing effect on PCDD/F formation from mix-heating of 1 mg PCP and 30 mg CaO (Ca/Cl molar ratio could be calculated as a result of 28.5) at low temperature 280–340 °C for 2 h, the suppressing efficiencies could be up to over 90% [32]. It could be found that the most abundant PCDD/F products in Figs. 7 and 8 were octa-DD and DF, which indicated the main decomposition mechanism for PCDDs/Fs originated from PCP. The second abundant products were 1, 2, 3, 4, 6, 7, 8-hepta-DD/Fs, most of which could be the further decomposing products of octa-DD and DF [32–34].

3.2. Effect of different calcium-based sorbents on PCDD/F emission in bench-scale tubular furnace

Comparison of total PCDD/F emission and its I-TEQ for different calcium-based sorbents addition (CaO, CaCO₃ and

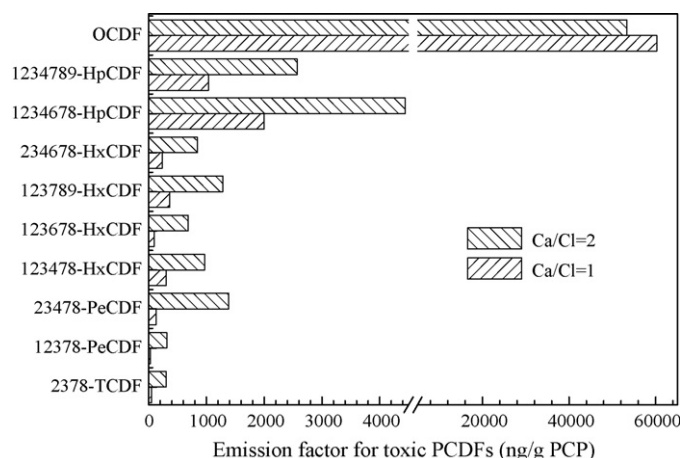


Fig. 8. Comparison of toxic PCDFs emission factor for Ca/Cl=1 and 2 of test runs B.

basic fly ash) was listed in Table 2. In contrast to Ca/Cl=0, the emission factor of CaCO₃ was the lowest at Ca/Cl=2, the total emission was one order of magnitude lower than that of CaO and basic fly ash and the I-TEQ was two orders of magnitude lower at least. The emission factor of CaO was close to basic fly ash because the calcium-based compounds in basic fly ash mainly existed in form of CaO, which accounts for 76.75%. Even transition metal compound of Cu, Fe included in the fly ash might promote the formation of PCDDs/Fs at the reaction temperature 850 °C, the promotion effect of CaO on PCDDs/Fs originated from PCP was higher than that of basic fly ash according to the test results.

The results in Table 2 showed that the effect of CaCO₃ on PCP forming PCDD/F was completely different from that of CaO and basic fly ash containing CaO. CaO and basic fly ash promoted I-TEQ increase by almost 30 times. In addition, CaCO₃ inhibited the reaction of PCDDs/Fs originated from PCP and the efficiency could be up to 70%. In another lab-scale PVC incineration tests at 450 °C by Sun et al. [35], it was found that addition of definite amount of CaCO₃ could reduce the emission of PCDDs/Fs from PVC in the gas phase reaction, but the PCDD/F concentration in solid residue increased. They made the following hypothesis to explain the above phenomenon: CaCO₃ had good absorbability to chlorophenol precursor of PCDDs/Fs and HCl, and most of the precursors and HCl were absorbed in solid residue phase, thus the emission of gas phase PCDD/F reduced and that of solid phase increased [35]. It could be generally concluded from our experimental condition that PCDDs/Fs were predominantly in gas phase because all reactants should be in 850 °C zone for 45 min. So the hypothesis from Sun et al. on good absorbability of CaCO₃ to chlorophenol precursors at comparatively low temperature does not explain well the results of this paper. Such interesting inhibition effect of CaCO₃ on PCDD/F formation from PCP would be discussed in Section 4 and need further study.

3.3. Comparison of microstructures of reaction residue for CaO and CaCO₃ in tubular furnace

Another series of parallel experiments labeled runs C had been carried out to observe the microstructures of reaction residues. The residue samples were analyzed by electron microscopic scanner JEM-2010 (HR). Figs. 9–12 showed the surface structures for PCP and calcium-based mix-heating residues. Many attached small particulates could be found on residues from CaO and PCP mix-heating, while no such particulates were found on CaCO₃ and PCP mix-heating. Small particulates in Figs. 9–11 might be the deposit build-up of CaCl₂ crystals when the residues cooled to the room temperature and adsorbed the moisture in atmosphere. Only very little of such crystals were found in Fig. 12; it could be suggested that only small part of CaCO₃ was chlorinated to be CaCl₂, and large amount of particles were retained as CaCO₃ or CaO. Previous study on high temperature capture of HCl by calcium-based sorbents in a lab-scale drop-tube furnace with fluidizing indicated that, the HCl removal efficiency for CaO and CaCO₃ at 850 °C were 40 and 50% separately [17]. It means that the HCl capture abilities

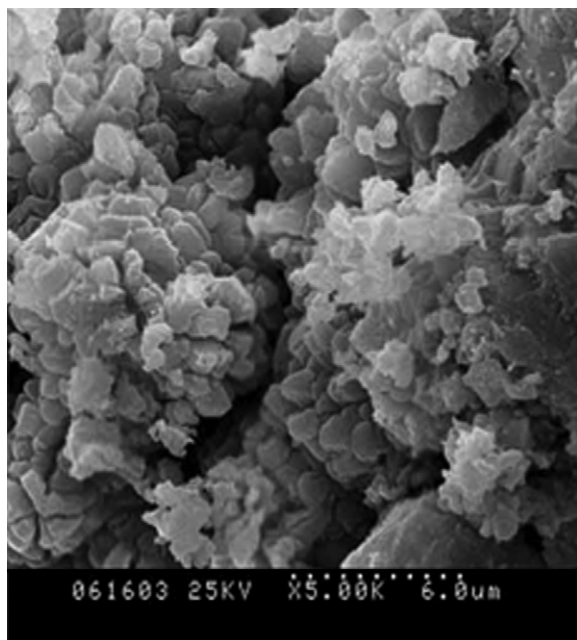


Fig. 9. SEM graph for CaO residue for test Ca-3C with Ca/Cl=1 ($\times 5000$).

for CaO and CaCO₃ at 850 °C are almost comparable, while CaCO₃ seemed a little bit higher. The complete different effects of CaCO₃ and CaO on PCDD/F formation from PCP could be attributed to their effects on possible mechanisms of PCDD/F formation from PCP, which would be discussed in the following section.

4. Discussion

In our experiments at 850 °C, the reactions of mixed reactant containing CaO and PCP included, the volatilization and

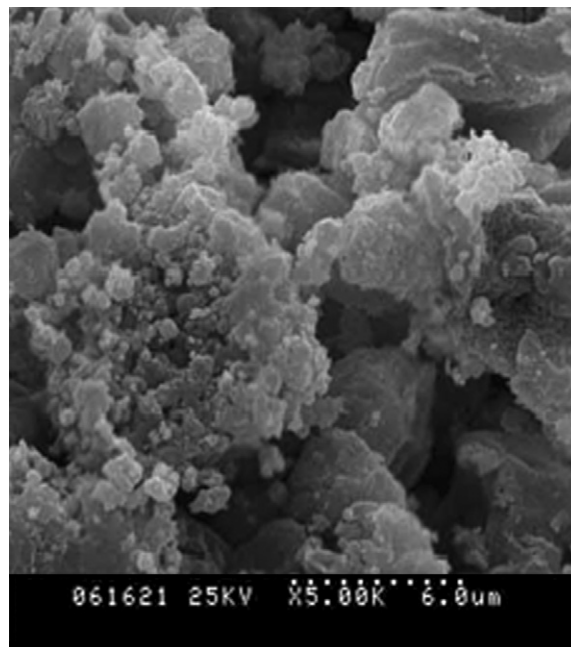


Fig. 11. SEM graph for CaO residue for test Ca-5C with Ca/Cl=3 ($\times 5000$).

decomposition reactions of PCP in gas phase; PCP and incomplete decomposing products absorbed in the micro-pore surface of CaO as well as the further extensive decomposition via heterogeneous reactions; CaCl₂ generation by absorbing HCl and again partly decomposing to CaO and HCl at high temperature; the desorption of CO₂ from CaCO₃ at high temperature and CaO and surface micro-pore structure was obtained. The different results using CaO and CaCO₃ could be attributed to the above reaction pathways.

It has been revealed in our experiments that PCP predominantly produced PCDDs. The possible reaction pathways could

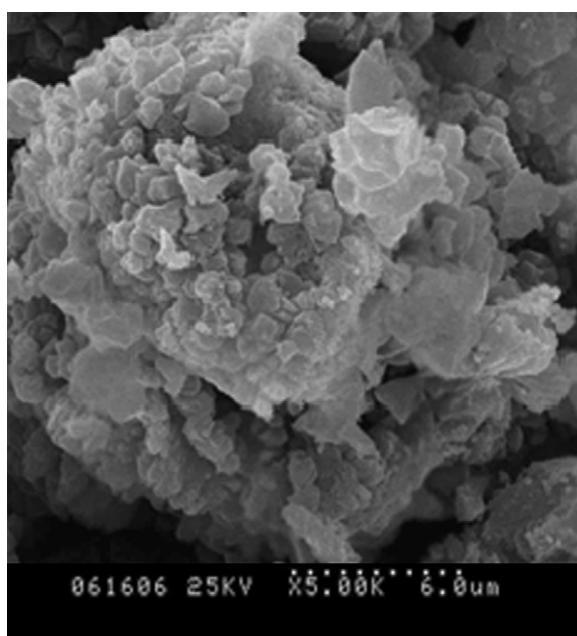


Fig. 10. SEM graph for CaO residue for test Ca-4C with Ca/Cl=2 ($\times 5000$).

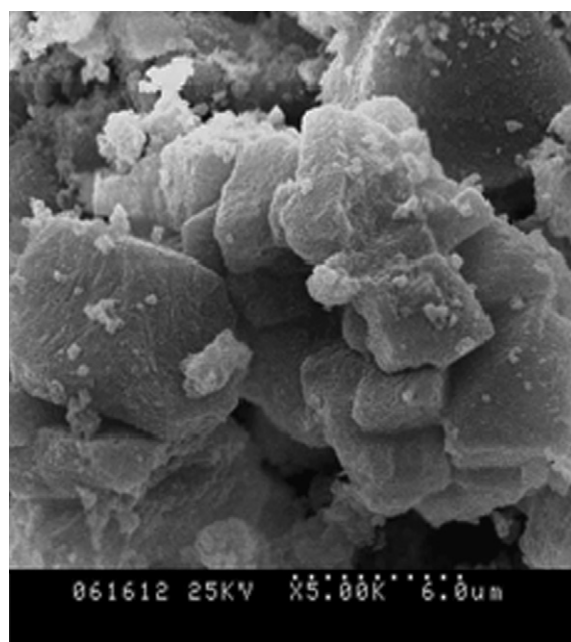


Fig. 12. SEM graph for CaCO₃ residue for test Ca-6C with Ca/Cl=2 ($\times 5000$).

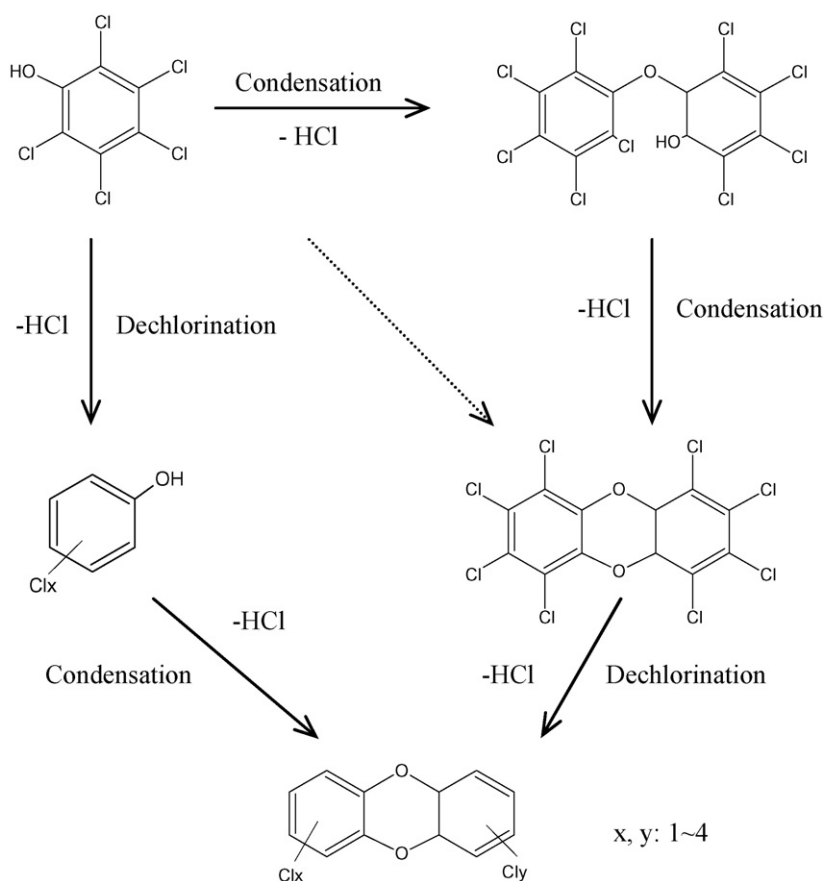


Fig. 13. Schematic diagram of PCP decomposing to PCDDs.

be described as Fig. 13. The processes of PCDDs formation were mainly the condensation and dechlorination reactions, and each step in Fig. 13 accompanied the production of HCl. The capture of HCl and supply of reacting surface or site by CaO could dramatically promote the condensation and dechlorination steps and produce much more PCDDs. If enough CaO was supplied, the PCDDs production from PCP might have a steep increase. Such hypothesis had been exactly proved in the present experiments by the great PCDD/F production difference between $\text{Ca}/\text{Cl}=2$ and 3 and $\text{Ca}/\text{Cl}=1$. Some researchers had proposed the acid–base interaction, as could be seen in Fig. 14, and atomic parameter (Z/r , charge to radius ratio) to speculate the inhibition effect of CaO on PCDDs/Fs originated from PCP at low temperature 280–340 °C [32]. The acid–base interaction in Fig. 14 also could be used to speculate the promotion effect of CaO on PCDDs/Fs originated from PCP at 850 °C. The anion in Fig. 14 could mostly serve as intermediates in PCP conden-

sation reactions described in Fig. 13. More production of such anion, more PCDDs formed.

The reaction precedence order was assumed to explain the inhibition effect of CaCO_3 on PCDDs/Fs originated from PCP. It was supposed that the PCP volatilization and decomposition reactions happened, as well as the CaCO_3 calcining reaction with CO_2 desorption or emission at particulate surface or micro-pore sites. Such CO_2 desorption or emission from the CaCO_3 particulates prevented the adsorption and dispersion of macromolecular, such as benzene rings or chlorinated intermediates onto the micro-pore surface. Most of these intermediates was driven away from CaCO_3 or CaO surface to gas phase and further oxidized to CO_2 and little chlorinated compounds. This made it less potential for PCDDs/Fs originated from PCP at high temperature up to 850 °C. Anyway, the detail mechanisms for CaCO_3 inhibiting PCDDs/Fs originated from PCP need further experimental or model studies.

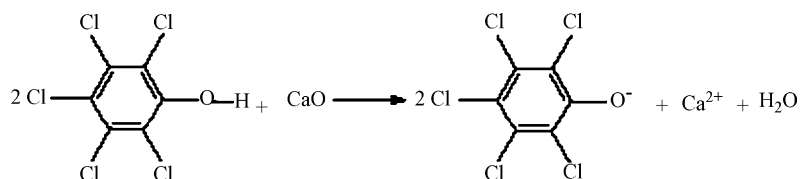


Fig. 14. Schematic diagram of acid–base interaction [33].

5. Conclusion

According to the results of lab-scale combustion experiments, the completely different effects for CaO and CaCO₃ on PCDDs/Fs originated from PCP at high temperature up to 850 °C were reported and discussed. CaO was found to promote PCDDs/Fs originated from PCP obviously, and with the increasing molar ratio of Ca/Cl from 1 to 2, the dramatic promoting to PCDD/F formation happened. This could be the result of the capture of HCl capture and supply of large reaction sites by CaO. The comparison of the impact of the three likely kind of calcium-based additives (CaO, CaCO₃ and basic fly ash; Ca/Cl ≈ 2) on PCDD/F formation show that CaCO₃ can inhibit the formation of PCDDs/Fs remarkably, the inhibiting efficiency was over 70%. The fly ash was found the same promotion effect on PCDDs/Fs originated from PCP because of its CaO containing and other potential catalytic reasons.

In industrial processes, such as fluidized bed combustion, calcium-based sorbents are always injected into the high temperature combustion furnace to capture the acidic gas, such as SO₂ and HCl. Even though the macro-effect of acidic gas capture for different calcium-based sorbents are almost same, the completely different effect of trace organic pollutants formation, such as PCDDs/Fs may be existed. The results of the present paper are expected to be useful for the industrial application of calcium-based sorbents to control PCDD/F emission.

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