



Hydrothermal treatment of municipal solid waste incineration fly ash for dioxin decomposition

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ABSTRACT

Hydrothermal treatment of MSWI fly ash was performed in this paper with a purpose to reduce its dioxin content. First a hydrothermal reactor was set up with a mixture of ferric sulphate and ferrous sulphate serviced as the reactant, then the effects caused by reaction conditions such as reaction temperature, pre-treatment by water-washing and reactant dosage were checked; the results showed that as a promising technology, hydrothermal treatment exhibited considerable high efficiencies in decomposition of PCDDs/PCDFs and good stabilization of heavy metals as well. Experimental results also showed that for dioxin destruction, higher reaction temperature is the most important influencing factor followed by Fe addition, and pre-treatment of raw fly ash by water-washing increased the destruction efficiencies of dioxins only very slightly. Finally with help of Gaussian software chemical computational simulation was performed to investigate the mechanism of dioxin decomposition based on quantum chemistry calculation. The calculation results were supported by the experimental data.

The leaching toxicities of hydrothermal products were higher than upper limits defined in the latest Chinese standard GB 16889-2008 for sanitary landfill disposal, thus an auxiliary process is suggested after the hydrothermal treatment for heavy metal stabilization.

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1. Introduction

Incineration is one of thermal treatment method of municipal solid waste, which can reduce the mass and volume of municipal solid waste greatly resulting the saving of landfill capacity, as well as recovering energy for electricity generation and district heating. However, municipal solid waste incineration (MSWI) also generates residues which may be grouped into bottom ashes (BA) and fly ashes (FA) [1]. BA are not classified as hazardous waste and can be reused as construction materials for civil engineering applications. MSWI fly ashes are contaminated with toxic components, including organic compounds such as polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) and heavy metals such as Pb, Cd, Cr and Hg etc.; thus they are defined as hazardous wastes and require special disposal.

According to statistics, 74 municipal solid waste incineration (MSWI) plants have been set up in China until 2008 and the total incineration capacity reaches more than 50,000 ton/day, accounting 16% of total amount of innocent treated municipal solid wastes [2]. Amount of fly ash generated is 1500–2500 ton/day. With the

rapid development of MSWI in China, it is estimated that by the end of 2010, there will be more than 100 MSWI plants. As the number of incineration facilities increases, the amount of MSWI fly ashes increases quickly. Finding a solution to safely dispose of the fast growing MSWI fly ashes has become an increasing necessitous task.

The stabilization of heavy metals in fly ashes under normal atmospheric temperatures has been explored extensively; the typical methods include cement solidification, chemical stabilization using organic chelators or inorganic chemicals [3], or combination of organic and inorganic reagents [4]. However, there are very few studies on the decomposition of PCDDs/PCDFs in fly ashes under non-refractory conditions, except for some reports related to catalyst utilization [5]. Catalysts are easy to be poisoned when contacted with fly ashes and most of them are very expensive.

Hydrothermal condition is relatively mild compared to high-temperature refractory conditions and it is more energy saving since steam produced in incineration heat recovery boiler can be used as the heating sources. Studies on hydrothermal treatment of fly ashes with the purpose of heavy metal stabilization showed that reduction of metal leaching concentrations could be observed, which might caused by the incorporation of metals in phases with low solubility [6,7]. The elimination of the PCDDs/PCDFs under hydrothermal condition has been explored by some Japanese scientists. Results showed that PCDDs/PCDFs

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would completely decompose when the hydrothermal reactions took place under 573 K for 20 min in a solvent of 1 N NaOH solution containing 10 vol% methanol and when the treated fly ash toxicity of PCDDs/PCDFs decreased to 0.03 ng-TEQ/g [8]. Although a good decomposition of PCDDs/PCDFs was obtained in their work, the reagent methanol that they used was poisonous and the alkaline environment would result in caustic brittleness of the reaction wall which works under high pressure. In order to enhance decomposing PCDDs/PCDFs during hydrothermal process, a strong reductant carbonylhydrazide also was studied under the temperatures of 518 K and 533 K, the decomposition rates of PCDDs/PCDFs were over 80% and 90%, respectively by total concentration. However their toxic equivalent (TEQ) decreased only slightly or even increased [9].

Iron oxides (Fe_xO_y) have been tested as good catalysts in catalytic oxidation of gaseous PCDD/Fs at temperature below 200 °C in the presence of ozone [10]. AC-supported iron was also used as a catalyst to decompose PCB-153 under an atmosphere of either air or N_2 [11]. In chemical stabilization, FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ solution reacted with scrubber ashes to decrease the releasing of heavy metals [12]. The objective of this study is to introduce the ferric/ferrous sulphate into hydrothermal processing with the purpose of destruction of PCDDs/PCDFs and stabilization of heavy metals.

2. Experiment materials

MSWI fly ash was from a full scale operating incinerator in southeast of China having capacity of 1050 ton/day and using spraying-dry flue gas scrubbing system followed by a bag filter. The total PCDDs/PCDFs content of raw fly ash was 11463.3 ng/kg and its toxicity equivalents (TEQ) was 628.8 ng/kg. Its elemental composition is listed in Table 1.

A mixture of ferric sulphate and ferrous sulphate was introduced as the reactant to enhance the decomposition of PCDDs/PCDFs during hydrothermal process, in which the ratio of Fe(III)/Fe(II) is 2. Ferrous sulphate used in this study was a kind of light blue monoclinic crystal, and ferric sulphate was a kind of white or light yellow powder. They were of analytical purity produced by Sinopharm Chemical Reagent Co. Ltd.

3. Methods

3.1. Experiment method

An autoclave produced by Shandong Shuguang Company was used for the study, with volume of 3 L, maximum temperature of 583 K and maximum pressure of 10 Mpa. For each experiment batch, 800 g of raw MSWI fly ash or the pre-treated fly ash (on dry basis) and 1600 g of deionized water were mixed at liquid/solid ratio in the range of 2.5–3. The liquid/solid ratio was selected according to the classic Ferrox-process. Some kind of suspension was formed in a container. The reactant was also dissolved into the suspension according to specially defined dosages. Three dosages of Fe sulfate were adopted which made Fe concentrations in the fly ash of 1 wt%, 2 wt% and 3 wt%. Then the suspension was pumped into an autoclave to be heated to pre-set temperatures, 518 K, and 563 K (with corresponding pressures of 3.46 MPa and 7.44 MPa respectively).

Table 1
List of Chemical composition of MSWI fly ash (wt%).

Element	Al	Fe	P	Ca	Mg	K	Na	As	Pb	Ni	Sn	Cr
Content	2.15	1.42	0.45	30.15	1.12	4.31	2.53	0.01	0.27	0.01	0.06	0.02
Element	Mn	Co	Cl	Zn	Cd	Ba	Sb	Cu	Li	Sr	B	
Content	0.09	0.00	13.36	0.45	0.01	0.10	0.05	0.10	0.01	0.03	0.02	

The treated fly ash after hydrothermal processing was recovered from the autoclave and filtrated to separate water. Filter cakes from the experiments were dried at 353 K for 2–3 days. The dried filter cakes obtained by parallel experiments were mixed, a part of which was sent to state key laboratory of clean energy utilization in Zhejiang University, which is authorized by CMA (China Metrology Accreditation, Certification Number: 2009001014K), for analysis of PCDDs/PCDFs concentrations. Ashes samples were pre-treated according to USEPA method 1613, and then analyzed by the HRGC-HRMS (High Resolution Gas Chromatography/High Resolution Mass Spectrometry) (JMS800D). The steps of the process were shown in Fig. 1.

The decomposition efficiency was defined as the ratio of total PCDDs/PCDFs concentration reduction by hydrothermal processing to total original PCDDs/PCDFs concentrations in experimental fly ashes. The destruction efficiency was defined as the ratio of the reduced I-TEQ value to original I-TEQ value.

The leaching toxicities of hydrothermal products were tested according to Chinese solid waste extraction procedure for leaching toxicity-acetic acid buffer solution method [13]. Eluate samples from leaching tests were filtrated through 0.45 μm polypropylene membrane filters and acidified with concentrated nitric acid to a pH less than 2, and then stored at 278 K until analysis. All liquid samples were analyzed for concentrations of selected heavy metals by inductively coupled plasma optical emission spectrometry (ICP) method.

X-ray diffraction (XRD) analysis was performed using Cu $K\alpha$ monochromated radiation in an X-ray polycrystalline diffractometer (D/max-2550VB/PC). The accelerating voltage was 45 kV, and the current was 100 mA. The scan parameters ($5\text{--}80^\circ 2\theta$ in 0.020° increments, 10–15 s/step) were selected as required for observation. A software MDI jade 5 (Materials Data Inc.) involving ICDD-PDF database as a source of reference data was used to identify possible crystalline phases in the ash samples. It is impossible to determine the mineral phases of heavy metal elements whose concentration in fly ashes were below 0.1 wt%.

3.2. Chemical computational simulation

The chemical computational simulation in this research was done in order to establish the pathway of decomposition of PCDDs/PCDFs, and find evidences to support the experimental results. Gaussian 03 was used, which is a popular and widely used electronic structure program based on quantum chemistry and licensed by Gaussian Inc. [14].

Step 1 was used GaussianView (a visualization program for data generated by the Gaussian) to obtain the molecular structure of investigated congener of dioxin; the Optimization (OPT) function was done with HF method to obtain optimal molecular structure. Step 2 was based on the results of the OPT job. Frequency calculation (Freq) started; the thermodynamic parameters in certain pressure and temperature could be obtained. Then POP = FULL was added into the OPT command line. The new OPT calculated the molecular orbital (or MO) which is a mathematical function describing the wave-like behavior of an electron in a molecule. The target results were LUMO (Lowest Unoccupied Molecular Orbital) and HOMO (Highest Occupied Molecular Orbital). The LUMO and HOMO can be inspected by importing chk file into GaussianView.

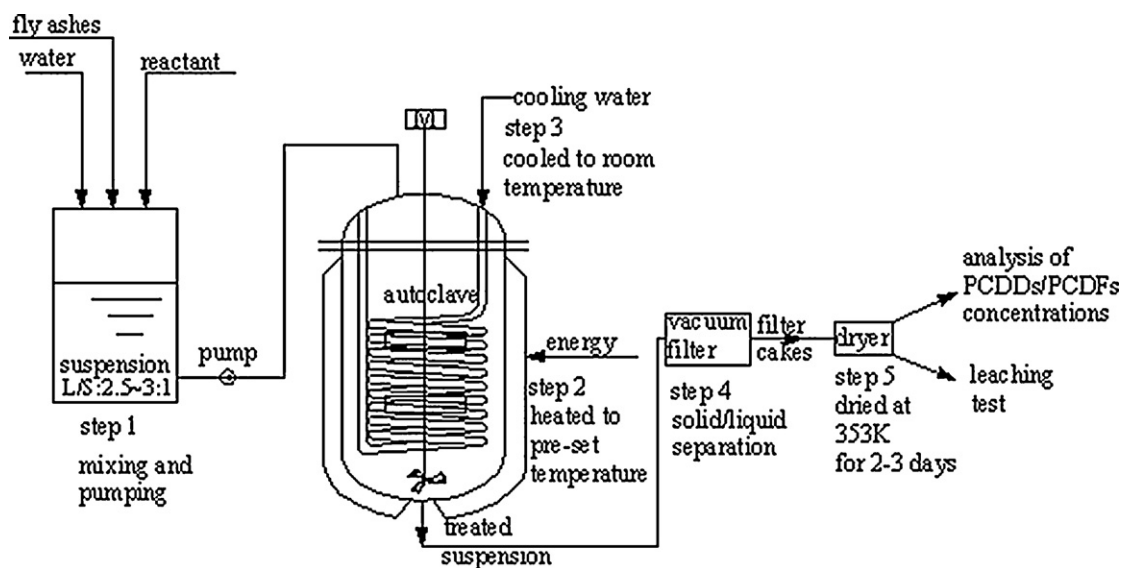


Fig. 1. Process of hydrothermal treatment.

The two steps above were used to obtain the characteristic parameters of the target compounds.

In step 3, the model of decomposition reaction of PCDDs/PCDFs was established according to some studies [15–17]. The decomposition reaction of PCDDs/PCDFs was generally considered as de-chlorination hydrogenation reaction, which was assumed as an electrophilic substitution reaction between H atom and Cl atom on the benzene ring. The pathway of reaction was assumed as following:

Reactant \rightarrow transition state1(TS1) \rightarrow σ complex compound

\rightarrow transition state 2(TS2) \rightarrow π complex compound \rightarrow product

Finally, the functions in step 3 were involved to look into the reaction process and mechanism. Among these functions, the Potential Energy Surface Scan and Transition State were often used in this research. Potential Energy Surface was applied in the reaction in which the Potential barrier did not exist. Add Scan into OPT command line; the energy changes (the energy required to destruct the bond) were obtained. On the basis of the information about this reaction, the guess on the reaction pathway was created and verified by the calculation results. By adding QST2 (Quadratic Synchronous Transit 2) into OPT command line, the transition state was located. The calculation results of transition state were verified by Freq function. If there was only one imaginary frequency, the results would be seen as a transition state. Otherwise, the model needed to be adjusted. Completed all the steps above, the energy changes between reactants, resultant and several transition states were made into potential energy profile.

4. Results and discussion

4.1. Effect of Fe dosage

Fig. 2 showed the dependence of decomposition and destruction efficiency of PCDDs/PCDFs on Fe dosage. The processing condition is under 563 K, and pre-treated fly ashes by water washing were used.

It was shown that without addition of ferric/ferrous sulphate, the decomposition efficiency and destruction efficiency of PCDDs/PCDFs were 80.03% and 46.17%, respectively. When Fe-sulphate was used, the decomposition efficiency of PCDDs/PCDFs raised a little to a range of 81.88–92.30%, while the destruction efficiency of PCDDs/PCDFs increased dramatically to a range of

80.82–89.59%. Fe addition improved the decomposition efficiency by 2.31–16.13%, with the increment of destruction efficiency by 75.05–94.04%. It seemed that the effect of addition of Fe compound on decomposition of PCDDs/PCDFs in MWSI fly ashes was limited, but the addition could enhance the destruction efficiency greatly.

With the increase of Fe dosage, the corresponding efficiencies were shown fluctuating changes in the range of 80–90%, which seemed that the dosage of Fe did not play significant influence on the decomposition and destruction efficiency. Iron oxides (Fe_xO_y) have been tested as good catalysts in oxidation of gaseous PCDD/Fs and decomposition of PCB [9,10]. The mineral analysis of product obtained by hydrothermal treatment with Fe addition showed that Fe_3O_4 was formed (more details could be found in part 3.5). Since the dosage of Fe might not influence the decomposition of dioxins greatly, Fe_3O_4 also might be serviced as catalysts in the decomposition reaction of PCDDs/PCDFs.

4.2. Influence of reaction temperature

Table 2 listed the decomposition/destruction efficiencies of raw fly ashes by hydrothermal processing with 1% Fe dosage

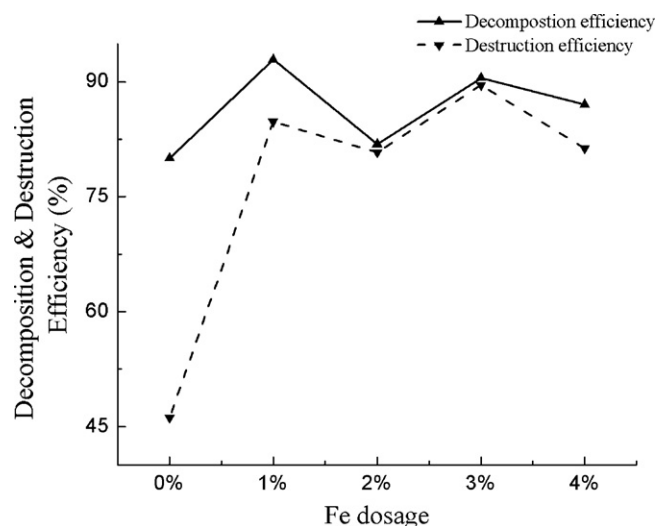


Fig. 2. Decomposition & destruction efficiency of PCDDs/PCDFs vs. Fe dosage.

Table 2
Comparison decomposition/destruction efficiencies of raw fly ashes hydrothermal-treated under 518 K and 563 K.

	518 K		563 K	
	C (ng/g)	I-TEQ (ng/g)	C (ng/g)	I-TEQ (ng/g)
Total	4.0148	0.9773	1.8914	0.1036
Decomposition efficiency		65.37%		83.69%
Destruction efficiency		-75.15%		81.44%

at 518 K and 563 K, separately. It was found from Table 2 that the effect of reaction temperature change on dioxins' decomposition/destruction efficiency was distinct. The decomposition and destruction efficiencies of dioxin at 563 K were higher than those at 518 K. Especially the destruction efficiency at 518 K was a minor value, which meant that the concentration of 2378-TCDD increased, resulting in the toxicity of treated fly ash increased rather than decrease. It was clear that higher reaction temperature benefited decomposition of 2378-TCDD and could improve the destruction efficiency of dioxin. These phenomena also appeared in Yamaguchi' researches [8]. The improved effect on PCDDs/PCDFs decomposition/destruction with the increased temperature seemed to cause by the change of water properties' at high temperature and pressure. When the temperature and pressure was high, the water could ionize and then the water could dissolve and oxidize many organics including PCDDs/PCDFs [8], especially around 523 K water ionic product reached maximum and hydrolytic decomposition of dioxins could happen [18].

Fig. 3 showed distribution of PCDDs/PCDFs congeners in the raw fly ash and hydrothermal-treated fly ashes at the temperatures of 518 K and 563 K. The results revealed that the decomposition of different congeners was different. Most of the congeners were decomposed to a large extent after hydrothermal treatment at discussed temperatures; while for some congeners, reaction temperature influenced the decomposition manner significantly. For the treated fly ashes at the temperatures of 518 K, its concentrations of the most toxic congeners 2,3,7,8-TCDD and congener 2,3,7,8-TCDF increased dramatically, resulting its I-TEQ value risen, even

the total PCDDs/PCDFs contents decreased greatly. This may be due to the fact that these two congeners have the fewest chlorination positions compared to the other congeners. When de-chlorination of other highly chlorinated congeners were occurred, 2,3,7,8-TCDD or 2,3,7,8-TCDF might be the most possible products of decomposition of highly chlorinated congeners. Besides, the concentration of OCDF also increased after hydrothermal treatment at 518 K. This might be because that the boiling point of OCDF is about 533 K [19], it could not turn into gaseous status during the hydrothermal treatment at 518 K, therefore the decomposition of OCDF might not happen. When reaction temperature reached 563 K, the concentration of each congener in treated products was less than that of treated fly ash at 518 K, which meant that high temperature could enhance the decomposition of every congeners of dioxin. For 2,3,7,8-TCDD and 2,3,7,8-TCDF, the concentrations were even below that of raw fly ash, which suggested that the decompositions of these two congeners started resulting in a decrease in I-TEQ of fly ashes.

4.3. Influence of pre-treatment

MSWI fly ash was pre-treated by water washing, which was done with expectation of washing out most of chlorine in fly ash to enhance dioxin congener de-chlorination in hydrothermal process. Generally, pre-treatment did change the total content and congener distribution of dioxins in fly ash. When the raw fly ash and washed fly ash undergone hydrothermal treatment taking place at 563 K with 1% Fe addition, concentration of PCDDs/PCDFs congeners of the two treated fly ashes were shown in Table 3.

It was shown in Table 3 that pre-treatment of raw fly ash by water-washing increased the decomposition and destruction efficiency of PCDDs/PCDFs by 11.05% and 4.13%, respectively, compared to those of raw fly ash under same hydrothermal treatment condition. The influence of pre-treatment on decomposition efficiency was greater than on destruction efficiency.

The degrees of improvement of pre-treatment on decomposition of PCDDs/PCDFs (η) were varied with different congeners. For most investigated congeners, η values were positive, with the maximum value of 62.97% for OCDD in PCDD congeners and 77.53% for OCDF in congeners. But there was not definite dependence of the number of chlorine atom in congeners on the η value. Furthermore, η values for 12378PeCDD, 123478HxCDD, 123789HxCDD and 123789HxCDF were minor. It seemed that the pre-treatment did not influence the decomposition of 12378PeCDD, 123789HxCDD and 123789HxCDF a lot since the η values of corresponding three congeners were less than -10%. For 123478HxCDD, the η value was -68.70%, which meant the water-washing had significant negative influence on decomposition of this congener.

4.4. Mechanism of de-chlorination hydrogenation reaction

Based on the models has been built, the molecules of OCDD and 2378TCDD was analyzed by means of computational chemical stimulation with 1234679-TCDD and 237-TCDD as product, respectively.

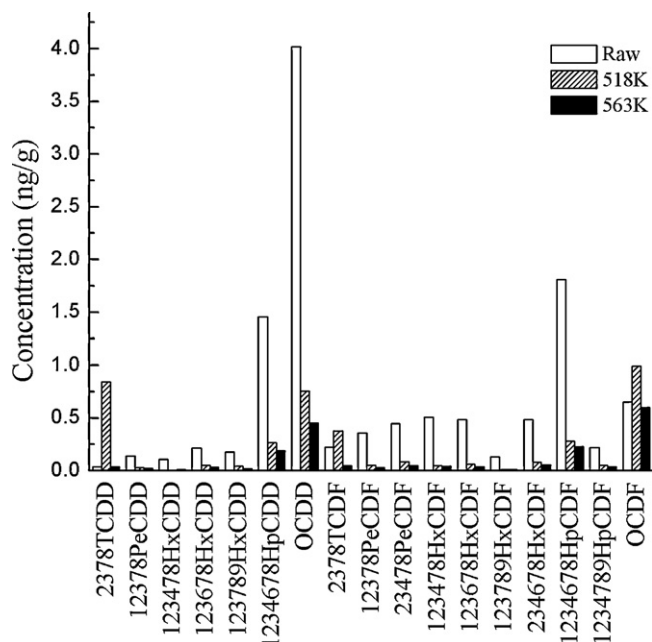


Fig. 3. PCDDs/PCDFs congeners in the raw fly ash and hydrothermal-treated fly ashes.

Table 3
PCDDs/PCDFs congeners in the raw fly ash and water-washed fly ash after hydrothermal treatment at 563 K with 1% Fe addition.

Compound	TEF	RAW	RAW.H ₂ O	$\eta = \frac{C_1 - C_2}{C_1}$
		C ₁ (ng/g)	C ₂ (ng/g)	%
2378TCDD	1	0.0383	0.0356	7.11%
12378PeCDD	0.5	0.0203	0.0210	-3.53%
123478HxCDD	0.1	0.0090	0.0152	-69.70%
123678HxCDD	0.1	0.0303	0.0221	27.08%
123789HxCDD	0.1	0.0197	0.0200	-1.14%
1234678HpCDD	0.01	0.1925	0.0923	52.04%
OCDD	0.001	0.4526	0.1676	62.97%
2378TCDF	0.1	0.0453	0.0162	64.35%
12378PeCDF	0.05	0.0289	0.0216	25.15%
23478PeCDF	0.5	0.0467	0.0326	30.27%
123478HxCDF	0.1	0.0412	0.0407	1.20%
123678HxCDF	0.1	0.0386	0.0350	9.46%
123789HxCDF	0.1	0.0088	0.0093	-5.54%
234678HxCDF	0.1	0.0537	0.0302	43.83%
1234678HpCDF	0.01	0.2283	0.1011	55.71%
1234789HpCDF	0.01	0.0384	0.0246	35.94%
OCDF	0.001	0.5987	0.1345	77.53%
Total concentration		1.8914	0.8196	
Decomposition efficiency		83.69%	92.93%	
Destruction efficiency		81.44%	84.80%	

Decomposition reaction pathway of OCDD:

Reactant(Cl atom on the No. 8 position was attacked by H atom)

- TS1 → σ complex compound → transition state 2(TS2)
- π complex compound → product(1234679-TCDD)

Decomposition reaction pathway of 2378-TCDD:

Reactant(Cl atom on the No. 8 position was attacked by H atom)

- TS1 → σ complex compound → transition state
- 2(TS2) → π complex compound → product(237-TCDD)

The potential barriers in every single step in the reaction pathways were compared. The resulting potential energy profile was shown in Fig. 4. For OCDD, the elemental reaction from reactant to σ complex compound was neither endothermic nor exothermic with the potential barrier of 204.32 kJ/mol; the elemental reaction from σ complex compound to π complex compound was endothermic with the heat of 50.52 kJ/mol in which the potential barrier was 209.87 kJ/mol; the elemental reaction from π complex compound

to product was exothermic with the heat of 37.75 kJ/mol, but without potential barrier. For 2378-TCDD, the corresponding first step was an exothermic reaction with the heat of 7.89 kJ/mol in which the potential barrier was 410.42 kJ/mol; the second step was also an exothermic reaction with the heat of 27.1 kJ/mol in which the potential barrier was 397.77 kJ/mol; the final step was an endothermic reaction with the heat of 35.24 kJ/mol without potential barrier. From the potential energy profile, it could be seen that the both reactions were endothermic. The heat which needed to decomposition of OCDD was 12.77 kJ/mol was higher than that of 2378-TCDD which was 0.2533 kJ/mol. But the potential barriers in first and second elemental reaction of decomposition of 2378-TCDD were twice of those of OCDD, which meant that much more activation energy was needed to break potential barrier to complete the decomposition of 2378-TCDD, and OCDD had more possibility to complete de-chlorination. This result was supported by the evidence found in the experiments that the congeners with higher number of Cl atom had higher decomposition efficiencies than those with lower number of Cl atom.

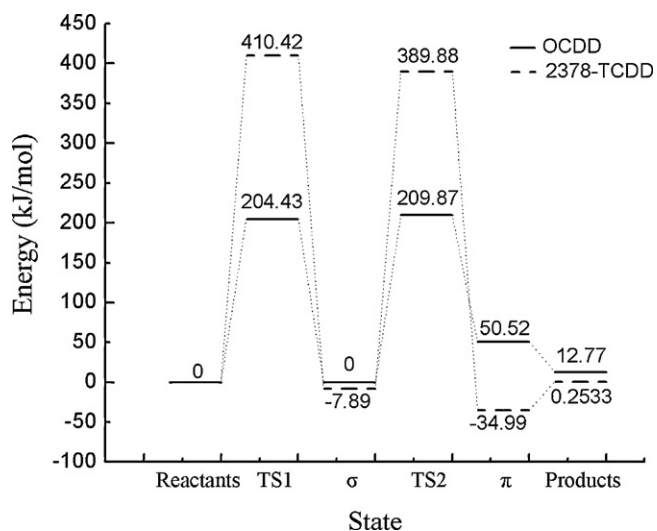


Fig. 4. Potential energy profile of de-chlorination hydrogenation reaction of 2378-TCDD and OCDD.

4.5. Mineral phase analysis

XRD analysis was performed for raw fly ash, water-washed fly ash, the product which was water-washed, and then went through hydrothermal treatment without Fe addition (blank experiment), and the product which was water-washed, and then went through hydrothermal treatment 4% Fe addition, the results showing in Fig. 5.

It was found in Fig. 5 that anhydrite (CaSO₄) and calcite (CaCO₃) were very common in all investigated ash samples, which were products of air pollution control process. Raw fly ash contained a lot of soluble salts, such as halite (NaCl) and sylvite (KCl) which could be found in Fig. 5(a). The presence of a lot of soluble salts made heavy metals such Pb and Cd easy to be released from fly ashes because the formation of dissolved complexes as PbCl⁻, PbCl₂⁰, and CdCl⁻ and CdCl₂⁰. After water washing, almost all soluble salts were removed, which was confirmed by Fig. 5(b). It was found in previous work of the authors that the water washing process would remove 90% soluble salts from fly ashes. Compared Fig. 5(c) and Fig. 5(d), it seemed that magnetite (Fe₃O₄) was generated in hydrothermal process, while hematite (Fe₂O₃) and lepidocrocite (FeOOH) could hardly be found in the product of hydrothermal treatment. It was

Table 4
Heavy metal concentrations in leachates of different fly ashes (mg/L).

Element	As	Zn	Pb	Cd	Ni	Ba	Cr	Cu
Upper limits defined in GB 16889-2008	0.3	100	0.25	0.15	0.5	25	1.5	40
RAW	0.108	23.61	2.534	0.942	0.289	0.577	0.053	1.310
RAW, 533 K*	0.824	7.089	2.889	0.233	0.144	0.233	0.057	2.477
RAW.H ₂ O	ND	27.76	3.069	0.996	0.168	0.354	0.113	3.619
RAW.H ₂ O, 533 K*	0.017	10.21	4.524	0.392	0.1	0.137	0.161	3.064
RAW, 518 K*, 1% Fe	0.069	30.94	9.276	1.547	0.094	0.466	0.271	6.334
RAW, 563 K*, 1% Fe	0.042	46.85	8.353	2.348	0.071	0.863	0.275	8.47
RAW.H ₂ O, 563 K*, 1% Fe	0.158	40.49	18.19	1.397	0.311	0.624	0.713	16.96
RAW.H ₂ O, 563 K*, 2% Fe	0.015	37.54	10.63	1.833	0.312	0.984	0.316	11.32
RAW.H ₂ O, 563 K*, 3% Fe	0.011	41.94	7.444	2.306	0.17	1.011	0.294	9.34
RAW.H ₂ O, 563 K*, 4% Fe	0.103	24.870	1.193	1.059	0.083	1.053	0.093	17.770

* Temperature shown here means the hydrothermal treatment temperature.

Fe₃O₄ that improved the decomposition of PCDDs/PCDFs as a catalyst.

4.6. Stabilization of the heavy metals during hydrothermal process

In this work, heavy metals' stabilization in the hydrothermal process was checked by the leaching tests of the treated fly ashes according to the standard [13]. The leachates obtained were checked for heavy metal concentrations and the results were compared with limits required in the Chinese national standard for pollution control on the landfill site of municipal solid waste [20], as shown in Table 4.

It presented that leaching concentrations of Pb and Cd from raw fly ash were higher than the upper limits of GB 16889-2008, which seemed to be the most stringent standards by now and was quite hard to be satisfied by most of technologies reported [4]. Pre-treatment of raw fly ash by water washing could not improve the

leaching characteristics of raw fly ash. On the contrary, except for As, Ni and Ba, water washing of raw fly ash to different extents caused increase of heavy metals leaching.

The hydrothermal treatment with the mixture of ferric and ferrous sulfate was only favorable to stabilize few heavy metals such as As, and Ni contained in MSWI fly ashes, which were not necessary to be stabilized since the leaching concentrations of such metals did not exceed the limit values. But hydrothermal treatment with Fe sulfate showed negative effects on stabilizing most of heavy metals, such as Zn, Pb, Cd, Ba, Cr, and Cu. Compared to leaching of raw fly ash, deterioration of leaching of Pb and Cd was very serious. With the increase of Fe dosage, the leaching of Pb and Cd reduced and increased, respectively. It seemed that the leaching of Pb was controlled by the formed Fe₃O₄ in hydrothermal process. Improvement of the leaching characteristic of Pb could be achieved by increasing of Fe dosage. However, the leaching of Cd might be controlled by pH value; additional measurements should be taken to stabilize Cd, which might be during or after hydrothermal process.

5. Conclusion

MSWI fly ash was treated under hydrothermal conditions with intention of destruction its dioxin contents, and a mixture of ferric and ferrous sulphate was used as an auxiliary chemical to enhance dioxins' decomposition, which also could service as a stabilizing agent for heavy metals.

The investigation results showed that temperature was the most important factor influencing the destruction efficiency of PCDDs/PCDFs and a higher reaction temperature was preferred when possible. Pre-treatment of raw fly ash by water-washing could also improve the decomposition of dioxins slightly. Usage of ferric and ferrous sulfate seemed to enhance dioxin destruction. However, increasing Fe dosage only helped increase the destruction efficiencies of dioxins slightly. Meanwhile, the effect of Fe addition is less than that of temperature in the decomposition of PCDDs/PCDFs.

The results of computational chemical stimulation showed that the decomposition of OCDD and 2378-TCDD were endothermic reactions. The heat which needed to decomposition of OCDD was 12.77 kJ/mol was higher than that of 2378-TCDD which was 0.2533 kJ/mol. But the potential barriers for decomposition of 2378-TCDD were about twice of those of OCDD, which meant that decomposition of 2378-TCDD was more difficult than that of OCDD.

At the same time the leaching behaviors of heavy metals contained in the MSWI fly ashes were changed. Leaching tests of hydrothermal products showed that the leaching concentrations of most heavy metals were higher than those of the raw fly ash especially for Pb and Cd, which indicated that the hydrothermal processing seemed to increase the mobility of the heavy metals in

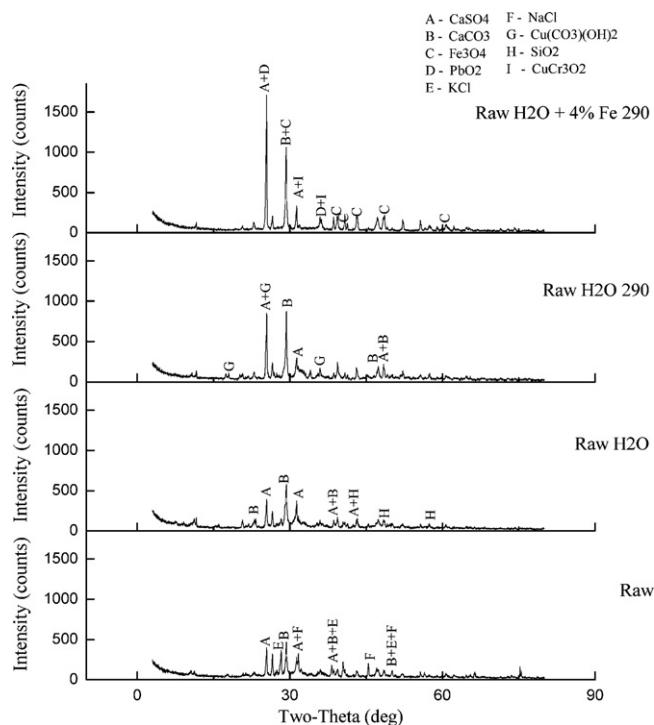


Fig. 5. XRD patterns of preformed for raw fly ash (RAW), (a) water-washed fly ash (RAW.H₂O), (b) the product which was water-washed, (c) and then went through hydrothermal treatment without Fe addition (RAW.H₂O 290), (d) and the product which was water-washed, and then went through hydrothermal treatment 4% Fe addition (RAW.H₂O + 4% Fe 290).

MSWI fly ash. As a result, the hydrothermal products would require an auxiliary process for heavy metal stabilization.

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References

- [1] T. Sabbas, A. Poletini, R. Pomi, T. Astrup, O. Hjelmard, P. Mostbauer, G. Cappaie, G. Magelf, S. Salhofer, C. Speiserg, S. Heuss-Assbichler, R. Kleinh, P. Lechner, Management of municipal solid waste incineration residues, *Waste Manage.* 23 (2003) 61–88.
- [2] China Statistics Press, *China Statistical Yearbook 2009*, Beijing, 2009.
- [3] J.Q. Margarid, C.B. Joao, M.Q.F. Rosa, Treatment and use of air pollution control residues from MSW incineration: an overview, *Waste Manage.* 28 (2008) 2097–2121.
- [4] B. Zhou, Y.Y. Hu, D.Z. Chen, Selection and development of chemical stabilization technologies for MSWI fly ash treatment to meet the new landfill standard, *Acta Sci. Circumst.* 29 (1) (2009) 2372–2377 (in Chinese).
- [5] Z.J. Yang, C.H. Xia, Q. Zhang, J.P. Chen, X.M. Liang, Catalytic detoxification of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in fly ash, *Waste Manage.* 27 (2007) 588–592.
- [6] Y.Y. Hu, D.Z. Chen, T.H. Christensen, Chemical stabilization of incineration fly ash with FeSO₄ under hydrothermal conditions, *Environ. Pollut. Control* 29 (1) (2007) 4–8 (in Chinese).
- [7] A.P. Bayuseno, W.W. Schmahl, T. Müllejans, Hydrothermal processing of MSWI fly ash-towards new stable minerals and fixation of heavy metals, *J. Hazard. Mater.* 167 (2009) 250–259.
- [8] H. Yamaguchi, E. Shibuya, Y. Kanamaru, K. Uyama, M. Nishioka, M. Yamasaki, Hydrothermal decomposition of PCDDs/PCDFs in MSWI fly ash, *Chemosphere* 32 (1) (1996) 203–208.
- [9] J.L. Xie, Y.Y. Hu, D.Z. Chen, B. Zhou, Hydrothermal treatment of MSWI fly ash for simultaneous dioxins decomposition and heavy metal stabilization, *Front. Environ. Sci. Eng. China* 4 (1) (2010) 108–116.
- [10] C.W. Hou, H.C. Shu, C.H. Pao, F.H. Jyh, B.C. Moo, Catalytic oxidation of gaseous PCDD/Fs with ozone over iron oxide catalysts, *Chemosphere* 71 (2008) 388–397.
- [11] Y.F. Sun, M. Takaoka, N. Takeda, T. Matsumoto, K. Oshita, Kinetics on the decomposition of polychlorinated biphenyls with activated carbon-supported iron, *Chemosphere* 65 (2006) 183–189.
- [12] S.H. Hu, Stabilization of heavy metals in municipal solid waste incineration ash using mixed ferrous/ferric sulfate solution, *J. Hazard. Mater.* 123 (1–3) (2005) 158–164.
- [13] HJ/T 300-2007, Solid waste-extraction procedure for leaching toxicity-acetic acid buffer solution method, Environmental Protection Agency of China, Beijing, 2007.
- [14] A. Frisch, *Gaussian 03 User's Reference*, Gaussian Inc., Wallingford, 2003.
- [15] M.B. Smith, J. March, *March Advanced Organic Chemistry: Reactions, Mechanisms and Structures*, sixth ed., Wiley, New York, 2006.
- [16] J.B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, second ed., Gaussian Inc., Pittsburgh, PA, 1996.
- [17] X.H. Qu, The study on mechanisms of formation and decomposition of typical toxic organic pollutants by quantum chemistry methods, Ph.D. thesis, Shandong University, 2009.
- [18] N. Yamasaki, G. Sekiyu, Recycling possibilities of organic waste by hydrothermal process, *J. Jpn. Pet. Inst.* 41 (3) (1998) 175–181.
- [19] B.F. Rordorf, Prediction of vapor pressures, boiling points and enthalpies of fusion for twenty-nine halogenated dibenzo-p-dioxins and fifty-five dibenzofurans by a vapor pressure correlation method, *Chemosphere* 18 (1989) 783–788.
- [20] GB 16889-2008, Standard for pollution control on the landfill site of municipal solid waste, Environmental Protection Agency of China, Beijing, 2008.