

Formations and controls of HCl and PAHs by different additives during waste incineration

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Abstract

This study employed a laboratory-scale fluidized bed incinerator to investigate the formations and controls of hydrogen chloride (HCl) and polycyclic aromatic hydrocarbons (PAHs) by adding different additives in the feedstock during waste incineration. The effects of different organic and inorganic chlorides on the formation and control of HCl and PAHs were also studied. Additionally, the thermodynamic equilibrium modeling was also carried out to interpret and compare with the experimental results.

Experimental results showed that the formation of HCl was related to the potential of chlorine released from the combustion of different chlorides. Organic chloride PVC had greater potential to form HCl than inorganic chloride NaCl. The performances of additives were affected by incineration temperature. Increasing temperature decreased the control efficiency of additives because the emission yields of HCl and Cl₂ were increased with temperature. The control efficiencies for HCl and Cl₂ by calcium based additives (Ca(OH)₂, CaO, CaCO₃) were better than that by magnesium based additive (Mg(OH)₂) and CaO was the best additive. The control efficiencies of PAHs by adding CaO in the feedstock were not apparent because the fluidization quality in the fluidized bed incinerator was decreased.

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1. Introduction

Municipal solid waste usually contains a lot of moisture, plastics and kitchen garbage in Taiwan. Most chlorine present in the waste plastic PVC and salty kitchen garbage will be released during incineration and reacts with hydrogen to form hydrogen chloride (HCl) [1,2]. Some products of incomplete combustion (PICs) may combine with HCl to form dioxins or chlorine-containing aromatic compounds through metal catalysis on the fly ash [3,4]. As these pollutants are released into the atmosphere, they will be harmful to the environment and human health. Some researchers used absorbents or inhibitors such as sulfur, amine (NH₃, urea), activated carbon, and alkaline materials (calcium based or magnesium based) to control the acid gas and dioxins in flue gas by different physical and chemical mechanisms. They found that these additives could effectively suppress the formations of HCl, organic

chloride pollutants and dioxins and reduce the emissions of these pollutants from waste incineration [3,5–13].

Most researches investigated the controls of HCl and organic chloride pollutants by post combustion or by conventional air pollution devices such as dry scrubber, spray-dryer, and wet scrubber incorporated with activated carbon injection. However, these conventional methods usually had the problems of producing secondary pollution [14]. The controls of acid gas and organic chlorides by adding additives in the feedstock during waste incineration were rarely studied before. The control efficiencies of these pollutants by different additives were distinct. The operating conditions such as combustion temperature and feedstock composition not only influenced the formations of acid gas and organic pollutants, but also influenced the performances of additives. Consequently, this study employed different additives and artificial feedstock with different chlorides to investigate the control efficiencies for HCl and PAHs at different operating conditions. The species, behaviors, and characteristics of pollutants were analyzed and the influences of different operating conditions were also discussed. Experimental results were summarized and compared with the results of thermodynamic equilibrium

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modeling. Suggestions on controlling HCl and PAHs during waste incineration were finally provided.

2. Thermodynamic equilibrium simulation

The aspect of thermodynamic equilibrium is carried out to study the formation of HCl and Cl_2 under various incineration conditions. The method of element potentials combined with the atom population constraints is used to minimize the Gibbs energy of the system [15]. The computer model used for the equilibrium calculation was written by Cruise [16] and subsequently modified by Ulrich [17], Mudgett [18], and Desrosiers [19]. For convenient and extensive application, the interface modification and the thermodynamic data of species of interest were incorporated into this computer program. The thermodynamic data for each species, such as heat capacity (C_p), entropy (S), and enthalpy (H), were obtained from a reference book [20] and then established in the model. The concentrations of each composed element in the artificial feedstock were first estimated by the unit of gram. These concentrations of input elements, operating temperature and pressure (1 atm) were then input to perform the equilibrium calculation. The simulation results were finally checked and compared with the experimental results. The detailed simulation procedure of thermodynamic equilibrium could refer to our previous study [21].

3. Experimental

3.1. Apparatus

A laboratory-scale fluidized bed incinerator, as shown in Fig. 1, was used in this study. The main combustion chamber was 5.5 cm inner-diameter, 60 cm height, and was made of stainless steel. The combustion chamber was preheated

electrically to the required temperature before operation. Two thermocouples (Pt87%/Rh13%) were used to monitor the temperature in the sand bed and freeboard. The combustion gas was treated by a wet scrubber and an activated carbon adsorption tower, and then released into the atmosphere.

3.2. Preparation of artificial feedstock

The feedstock used in this study contained organic chloride PVC, inorganic chloride NaCl, sawdust, and five different additives $\text{Ca}(\text{OH})_2$, CaO, CaCO_3 , $\text{Mg}(\text{OH})_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. For avoiding the interferences of complex compositions in real waste on the results and emphasizing the roles of different chlorides in waste, we decided to use simulated waste as feedstock in this study. The compositions of simulated waste were determined referring to the average compositions of municipal solid waste (MSW) in Taiwan. According to the report of Taiwan EPA [22], the weight percents (wet basis) of different compositions in MSW were paper 36%, cloth and fiber 4%, wood, straw and leaves 3%, kitchen garbage 13%, plastics 21%, leather and rubber 2%, and the others 8%. The sawdust (43%) in our simulated waste was used to represent the paper, cloth and fiber, straw and leaves, and kitchen garbage in MSW. Most of them were composed of cellulose, fiber and lignin. The plastics (31%) in our simulated waste were used to represent the plastics, leather and rubber paper, and the others. Most of them were composed of artificial organic polymer and leathers. The different salts (12–24%) in our simulated waste were especially added to serve as additives for the control of HCl, Cl_2 and PAHs. The amounts of these additives were determined from equal stoichiometric ratio of calcium and chlorine ($\text{Ca}/\text{Cl}=1$) in every tests, the weight percents of these additives were therefore different. Each material of feedstock was mixed and enclosed by a paper bag. Table 1 listed the compositions of feedstock and operating conditions.

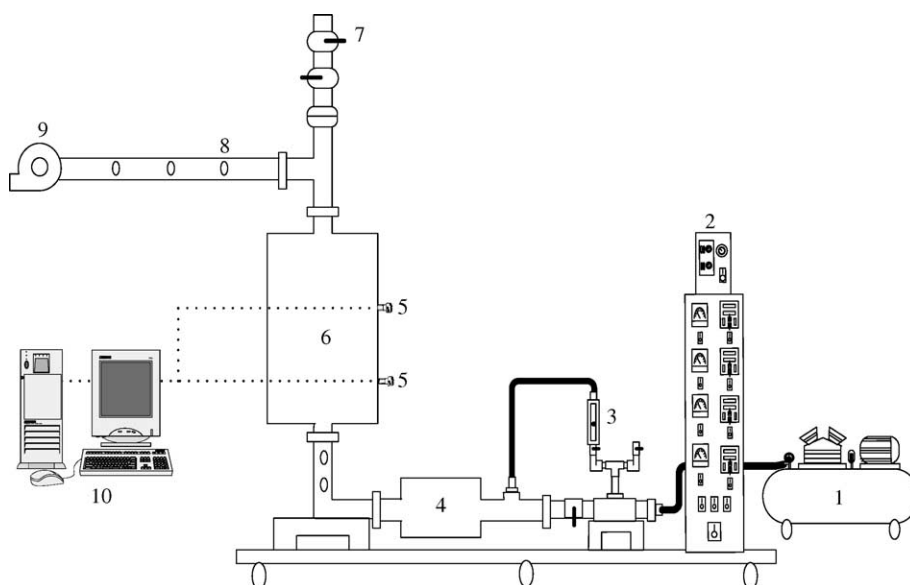


Fig. 1. Experimental apparatus. Explanation: (1) air compressor; (2) temperature feedback controller; (3) flow meter; (4) air preheated chamber; (5) thermocouples; (6) combustion chamber; (7) feeder; (8) sampling site; (9) induced fan; (10) computer.

Table 1
Operating temperature and compositions of the feedstock

Run	Temperature (°C)	Sawdust (g)	Paper (g)	PVC (g)	NaCl (g)	Ca(OH) ₂ (g)	CaO (g)	CaCO ₃ (g)	Mg(OH) ₂ (g)
1–3	600, 700, 800	–	0.2	4.8	–	–	–	–	–
4–6	600, 700, 800	–	0.2	4.8	–	2.41	–	–	–
7–9	600, 700, 800	–	0.2	4.8	–	–	1.82	–	–
10–12	600, 700, 800	–	0.2	4.8	–	–	–	3.25	–
13–15	600, 700, 800	–	0.2	4.8	–	–	–	–	1.89
16–18	600, 700, 800	6.46	0.2	–	3.8	–	–	–	–
19–21	600, 700, 800	6.46	0.2	–	3.8	2.41	–	–	–
22–24	600, 700, 800	6.46	0.2	–	3.8	–	1.82	–	–
25–27	600, 700, 800	6.46	0.2	–	3.8	–	–	3.25	–
28–30	600, 700, 800	6.46	0.2	–	3.8	–	–	–	1.89

3.3. Experimental procedure

The combustion chamber was preheated before experiments and the auxiliary air was passed through the preheated chamber to increase the temperature and then injected into the combustion chamber. The artificial feedstock was fed into the incinerator at the rate of one bag per 20 s. Hydrogen chloride (HCl), chlorine (Cl₂) and PAHs were sampled and analyzed during the experiment. When the experiment was finished, the combustion chamber was cooled down and the residuals in the sand bed was collected and examined by X-ray diffraction (XRD) analysis. The X-ray tube target was Cu K α and the working voltage and current were 30 V and 20 A, respectively.

3.4. Sampling and analysis

The adsorption and sampling apparatus for PAHs was modeled on US EPA modified method 5 (MM5). The sampling gas was isokinetically drawn out of the flue pipe by a stainless steel sampling probe, and passed through a heated filter (120 °C) with glass fiber to remove fine particles and a cooling tube (5 °C) to capture gas-phase organic compounds by XAD-4 adsorbents. The sampling time was lasted for 10 min. The XAD-4 adsorbents containing gas-phase PAHs and the glass-fiber filter containing solid-phase PAHs were respectively extracted for 18 h by the Soxhlet extraction process, and the extraction solution was concentrated to 1 ml by a KD evaporative concentrator. Finally, the concentrated solutions were stored in brown vials at 4 °C and analyzed by a GC/FID detector. The concentrations of each species of gas-phase and solid-phase PAHs were analyzed.

The concentration of HCl and Cl₂ in the gas stream were determined by a spectrophotometer according to R.O.C. NIEA method A412.70A and R.O.C. NIEA method A410.70A, respectively [23]. The impingers filled with 100 ml 0.1 M NaOH and 50 ml 3,3-dimethylbenzidine dihydrochloride were used to absorb HCl and Cl₂, respectively. The absorption solutions were analyzed by colorimetry. Mercury (II) thiocyanate and ammoniummisen (III)-sulfate was used to react with HCl to produce a salmoncolored complex compound of iron (II) thiocyanate.

The quantification analyses of PAHs, HCl and Cl₂ in our study were all performed with duplicate or triplicate samples. The instruments were also calculated using at least six standards and the correlation coefficient of the calibration curve was requested >0.995. For the repeatability test the relative standard deviation ranged from 2 to 10% and the results of the accuracy test showed that for most of the PAHs, HCl and Cl₂ amounts were within $\pm 15\%$.

Table 2 showed some data of chlorine mass balances in the experiments. Because this study focused on the emissions and controls of HCl, Cl₂ and PAHs in the flue gas under various operation conditions, the contents of chlorine in the fluidized media (silica sand) and additives were not measured. Therefore, the chlorine mass balances were not complete. Nevertheless, the results of organic chloride experiment displayed good recovery in chlorine mass balance. The low recovery of chlorine in inorganic chloride experiment was attributed to most chlorine being present in the sand bed.

4. Results and discussions

4.1. Simulation results of thermodynamic equilibrium modeling

For better understanding the reaction characteristics of different chlorides and additives in the feedstock at different incineration conditions, the thermodynamic equilibrium simulation was first carried out in this study. The influences of different chlorides on the formation of pollutants were examined. When the feedstock contained organic chloride (PVC), the major products were HCl and Cl₂ and their emission yields were high, because organic chloride could offer more free hydrogen to react with chlorine to form HCl. Cl₂ were usually formed from the surplus chlorines which were contained in the waste and did not react with hydrogen. When the feedstock contained inorganic chloride (NaCl), the major species were HCl, Cl₂ and NaCl_(g). The emission yields of HCl and Cl₂ were much lower than that as the feedstock contained PVC because inorganic chloride could not offer free hydrogen. From the formation constants (K_p) of HCl from different inorganic chlorides (Table 3), we could note that chloride would transfer to HCl easily as the equilibrium constant was quite great [24,25]. On the other hand, less HCl was formed as the equilibrium constant become smaller at

Table 2
Data of chlorine mass balance in the experiments

Feedstock	Organic chloride			Inorganic chloride		
	600	700	800	600	700	800
Operation temperature (°C)						
Total Cl input (g)	2.302	2.302	2.302	2.302	2.302	2.302
HCl in flue gas (g)	1.463	2.271	2.010	0.0001	0.0001	0.0004
Cl ₂ in flue gas (g)	0.008	0.004	0.002	ND	ND	ND
Total Cl output (g) ^a	1.479	2.279	2.014	0.0001	0.0001	0.0004
Recovery (%) ^b	63.9	98.8	87.4	0.004	0.004	0.02

^a Total Cl output (g) was calculated from [HCl] + 2 [Cl₂].

^b Recovery (%) of Cl was calculated from [Total Cl output]/[Total Cl input] × 100.

Table 3
Formation constants (K_p) of HCl from different inorganic chlorides at different temperatures [24]

	Temperature (°C)					
	300	500	700	800	900	1000
NaCl	3×10^{10}	4×10^5	6×10^2	5×10	7	1
KCl	7×10^{10}	9×10^5	1×10^3	1×10^2	2×10^{10}	5
MgCl ₂	2×10^{17}	4×10^{10}	5×10^6	2×10^5	1×10^4	6×10^3
CaCl ₂	5×10^{16}	1×10^{10}	1×10^6	5×10^4	4×10^3	6×10^2

Formation mechanism: $2\text{NaCl} + \text{SO}_2 + 0.5\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ (Hargreaves equation).

higher temperature. Previous researches also indicated that NaCl was not completely decomposed and was left in the bottom ash during incineration or some NaCl was decomposed slowly so that the released chlorine could not react with hydrogen to form HCl. Therefore, the formation of HCl from organic chloride was much higher than that from inorganic chloride at high temperature. The formation of HCl was increased with temperature while the formation of Cl₂ was decreased no matter what types of chlorides was input.

Considering the influences of different additives on the formations of air pollutants, simulation results revealed that the major species were CaCl_{2(c)} and MgCl₂ if the feedstock contained organic chloride and calcium based additives (Ca(OH)₂, CaO, CaCO₃) and magnesium based additive (Mg(OH)₂), respectively. When the feedstock contained inorganic chloride, the major species were NaCl_(c), CaO_(c) and MgO_(c) if adding calcium based additives and magnesium based additives, respectively. Moreover, whatever organic or inorganic chlorides were present in the feedstock, the formation of HCl was increased with temperature and

the formation of Cl₂ was decreased. Comparing the removal efficiency of HCl and Cl₂ by different additives showed that calcium based additives had better performances than magnesium based additive in the case of organic chloride feedstock (Fig. 2). The removal efficiency of HCl and Cl₂ followed the sequence of CaO > Ca(OH)₂ > CaCO₃ > Mg(OH)₂. In the case of inorganic chloride feedstock, additives did not have apparent effects on the removal of HCl and Cl₂. But adding CaO had significant effect on the removal of Cl₂ at the temperature of 600 °C (Fig. 3). This phenomenon was resulted from that the reaction tendency of CaO and Cl₂ at 600 °C is especially significant from the view of thermodynamic.

When copper compound was added into the organic chloride feedstock, the major species become HCl, Cl₂ and Cu₃Cl₃. When the temperature was increased, the formation of HCl also increased but the formations of Cl₂ and Cu₃Cl₃ were reduced. When the feedstock contained inorganic chloride, the major species was copper oxide CuO_(c) and NaCl_(c). The formations of copper chloride, HCl and Cl₂ were not apparent.

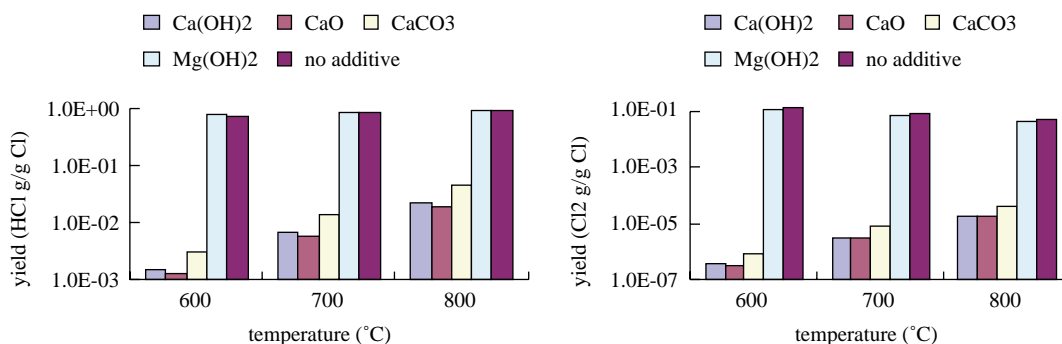


Fig. 2. Emission yields of HCl and Cl₂ in the combustion of organic chlorides and different additives by thermodynamic equilibrium modeling.

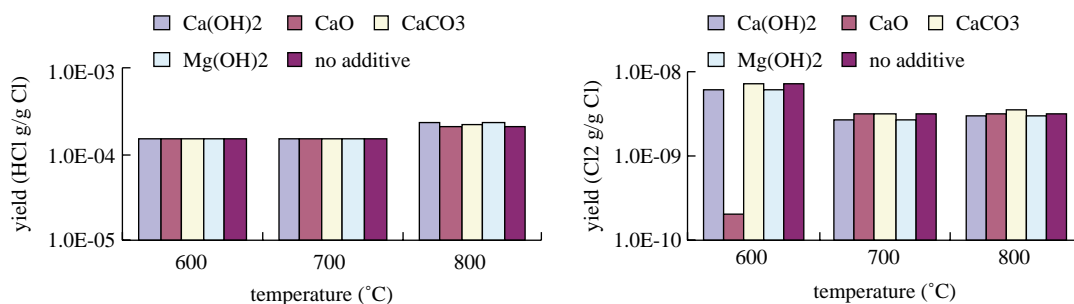


Fig. 3. Emission yields of HCl and Cl_2 in the combustion of inorganic chlorides and different additives by thermodynamic equilibrium modeling.

In addition, the formations of HCl and Cl_2 were decreased as the feedstock contained copper compounds. HCl may be transformed into Cl_2 and H_2O by the catalysis of copper through Deacon reaction, after which a serial chloride reactions proceed and some dioxin precursors were produced [26]. The other reason why the formations of HCl and Cl_2 were decreased should be resulted from the chlorine being reacted with copper to form Cu_3Cl_3 . As the feedstock contained inorganic chloride, the formations of HCl and Cl_2 were decreased at 600 and 700 °C but were increased at 800 °C. This was attributed to NaCl being decomposed easily at 800 °C than 600 and 700 °C or attributed to the sintering of sodium with calcium at high temperature, so that more chlorine was released from NaCl to react with hydrogen to form HCl.

4.2. Experimental results

This section discusses the influences of different operating parameters, such as temperature, additives, and copper compounds, on the formation and removal efficiency of HCl and PAHs as the feedstock contained organic and inorganic chlorides. The pollutants were sampled and analyzed at three periods and no apparent differences were found in each test, indicating our experiments were sufficiently stable. In addition, the concentration of Cl_2 was not obtained in the experiment of inorganic chloride due to its concentration was much lower than the detection limit of analytical method. They were not included in the following discussion.

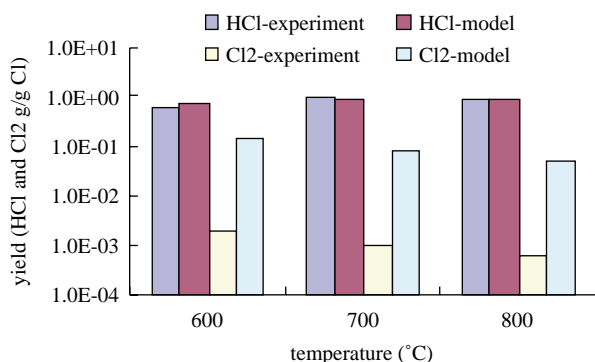


Fig. 4. Emission yields of HCl and Cl_2 in the combustion of organic chloride by experiments and thermodynamic equilibrium modeling.

4.2.1. Influences of different chlorides on the formations of pollutants

Fig. 4 showed the results of experiment and simulation as the feedstock contained organic chloride at different temperature. The figure indicated that the formation of HCl was increased with temperature but not that of Cl_2 . This result was in agreement with the reference [27], which pointed out that the formation of HCl was increased with temperature in thermal pyrolysis of polyvinyl chloride (PVC). When the feedstock contained inorganic chloride, as shown in Fig. 5, the formation of HCl also increased with temperature. This finding was agreed with the result of simulation. On the other hand, the yields of Cl_2 in experiments and model also had similar trends with the operation temperatures whether the feedstock contained organic chloride or inorganic chloride (Figs. 4 and 5). However, the yields of Cl_2 in experiment were lower

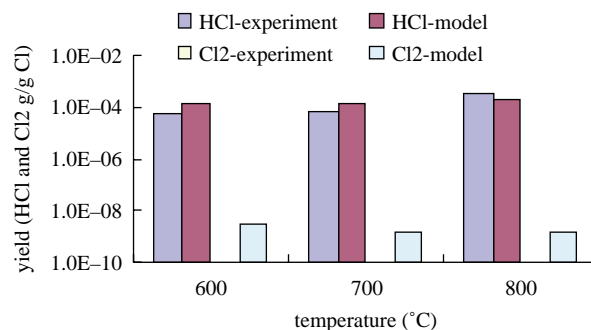


Fig. 5. Emission yields of HCl and Cl_2 in the combustion of inorganic chloride by experiments and thermodynamic equilibrium modeling.

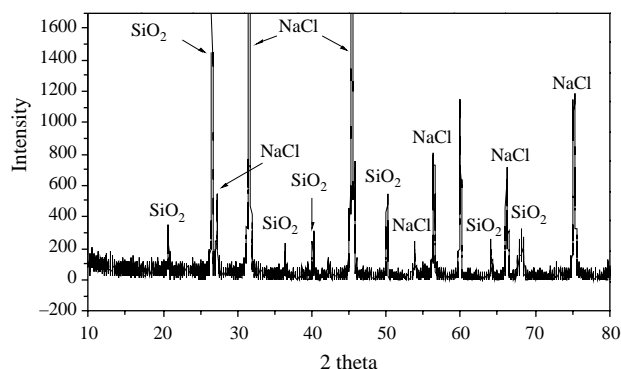


Fig. 6. XRPD spectra of the bottom ash formed in the combustion of inorganic chloride.

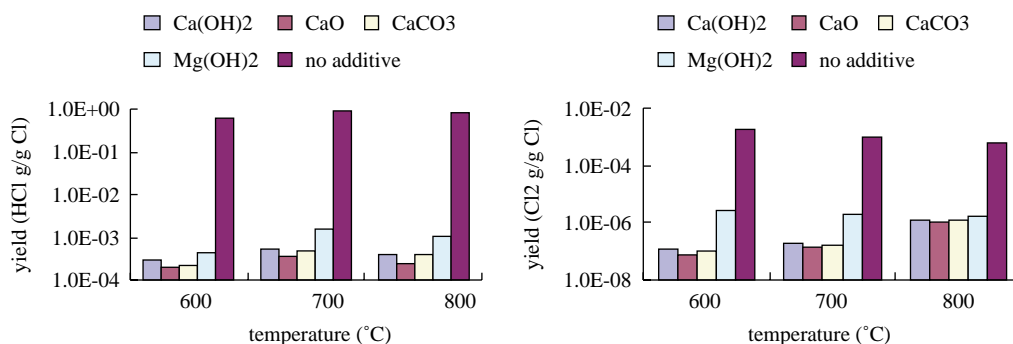


Fig. 7. Emission yields of HCl and Cl_2 in the combustion of organic chlorides and different additives.

than that in model. This result indicated that thermodynamic simulation, which assumed a complete reaction system, can provide some important information about reaction tendency, but cannot actually reflect the real situations in such waste incineration processes. Furthermore, the emission yield of HCl and Cl_2 in organic chloride feedstock was found to be higher than inorganic chloride. Wang et al. [28] also pointed out that organic chloride PVC had more potential to form HCl than inorganic chloride NaCl at high temperatures. Emission yields HCl and Cl_2 were lower with inorganic chloride feedstock because some NaCl did not decomposed completely and remained in the bottom ash, or because the released yield of chlorine from NaCl was slower so that the released chlorine

cannot react with hydrogen to form HCl. In addition, the affinity of chlorine and sodium is higher than that of chlorine and hydrogen. The formation of NaCl was easier than HCl. This finding was confirmed by the XRPD spectra in Fig. 6. The peaks of NaCl were identified in the XRPD spectra of inorganic chloride feedstock and their diffraction intensities were higher, indicating NaCl was present in the bottom ash.

4.2.2. Removal efficiency of HCl and Cl_2 by different additives

Fig. 7 showed the emission yield of HCl with different additives in organic chloride feedstock. The emission yield of HCl with each additive was much lower than that with no additive. The emission yield of HCl tended to increase with

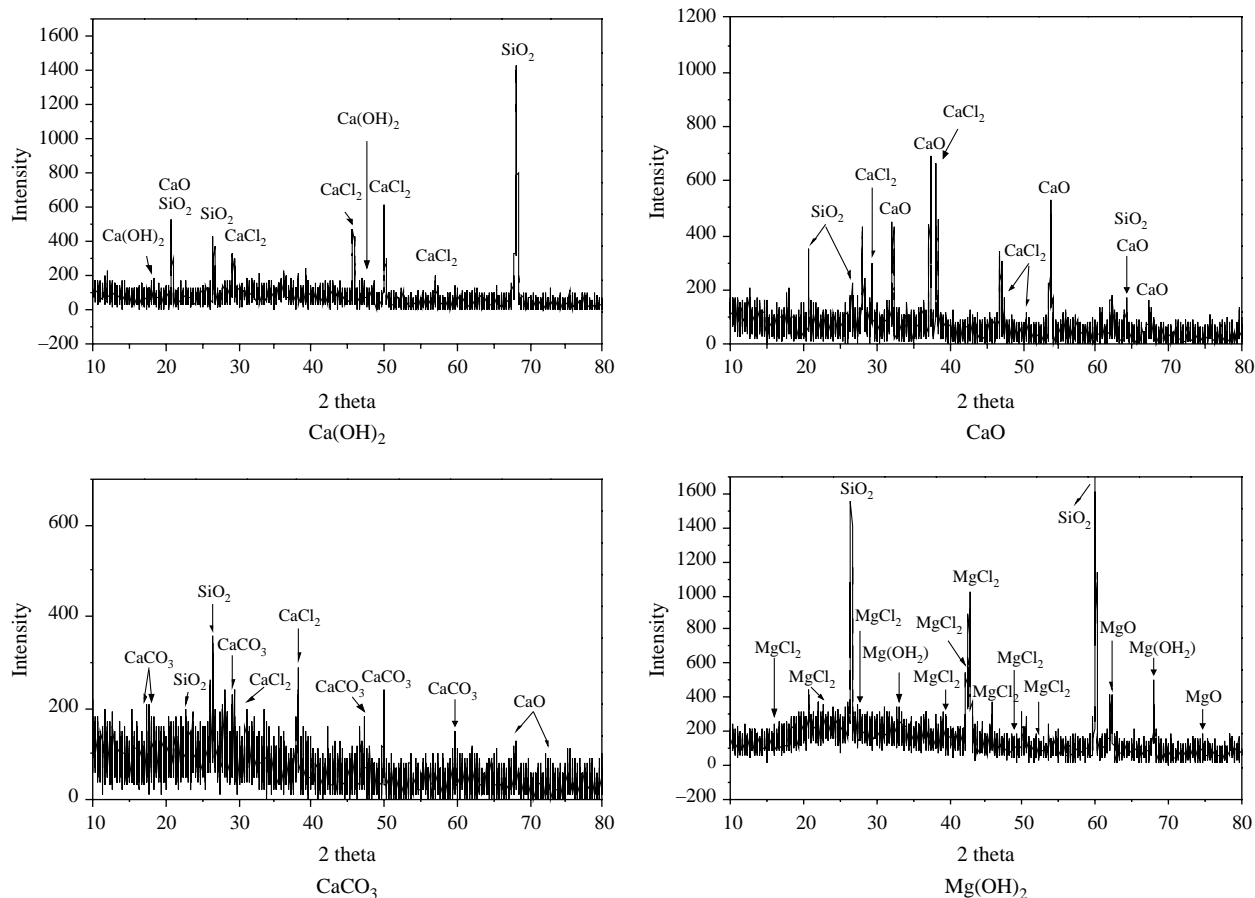


Fig. 8. XRPD spectra of the bottom ash formed in the combustion of organic chloride and different additives.

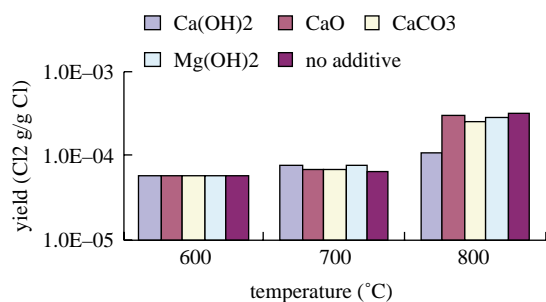


Fig. 9. Emission yield of HCl in the combustion of inorganic chlorides and different additives.

temperature. Weinell et al. [29] indicated that the optimum temperature for calcium absorbent to react with chlorine hydrogen to form CaCl_2 was lower than 600 °C. The emission of HCl would be lower at 600 °C and this agreed with our experimental result. Comparing the control efficiency of HCl by different additives indicated that calcium based additives have better performances than magnesium based additive and CaO was the best additive to control HCl and Cl_2 . Duo and Kirkby [5] used CaCO_3 , CaO, Ca(OH)_2 and other salts to reacted with simulated exhaust gas containing HCl in a fixed bed reactor; Their results showed that the removal efficiency of CaO was the best, Ca(OH)_2 was the second, and CaCO_3 was the least. Their results also agreed with the present study. Because CaO could directly and easily react with HCl and Cl_2

to form CaCl_2 , while Ca(OH)_2 , CaCO_3 and Mg(OH)_2 are usually decomposed to CaO and MgO at high temperature and then react with chlorine to form CaCl_2 and MgCl_2 , their performances were therefore poor than CaO.

Considering the control efficiency of Cl_2 by different additives also showed that the emission yield of Cl_2 was significantly reduced by adding different additives and calcium based additives have better performances than magnesium based additives. The performance of different additives followed the sequence of $\text{CaO} > \text{CaCO}_3 > \text{Ca(OH)}_2 > \text{Mg(OH)}_2$. Both calcium based additives and magnesium based additives can effectively decrease the emissions of HCl and Cl_2 . From the identifications of XRPD spectra, CaCl_2 and MgCl_2 were present in bottom ash (as shown in Fig. 8).

Fig. 9 showed the emission yield of HCl with different additives in inorganic chloride feedstock. The control efficiency of HCl with every additive was not apparent at the temperatures of 600 and 700 °C, even the emission yield of HCl was increased slightly at 700 °C. When the temperature rose to 800 °C, the control efficiencies of additives were recognized and Ca(OH)_2 was especially prominent. This may be attributed to the H_2O generated from the decomposition of Ca(OH)_2 at high temperature 800 °C was beneficial to retard the sintering of silica sand as the feedstock contained inorganic chloride. From the identifications of XRPD spectra, as shown in Fig. 10, NaCl was present in bottom ash and its higher diffraction intensity indicated that the concentration of NaCl

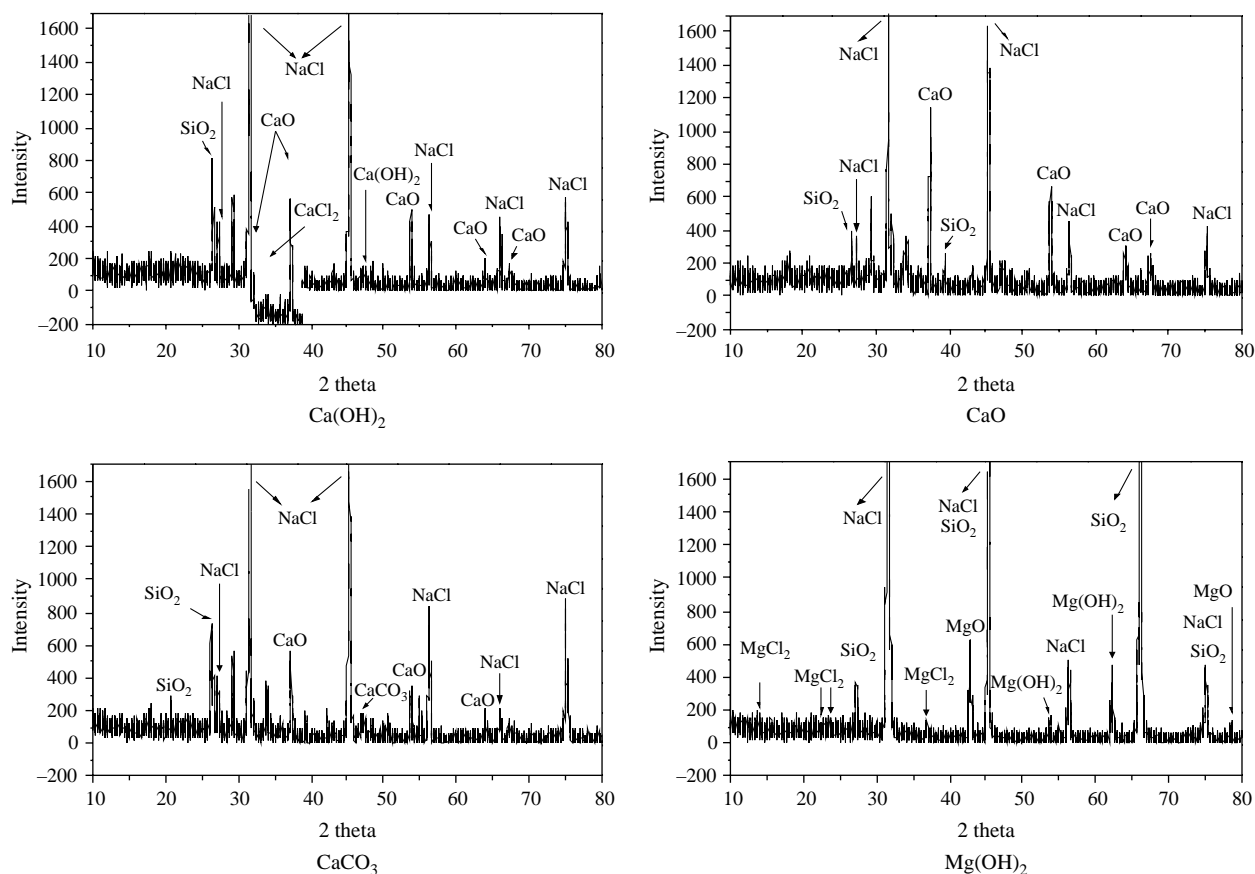


Fig. 10. XRPD spectra of the bottom ash formed in the combustion of inorganic chloride and different additives.

Table 4

Concentration of gas-phase PAHs formed in the combustion of organic chloride with and without CaO additive at different temperatures

Additive temperature	No additive			CaO additive		
	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C
NaP	ND	0.07	ND	31068.2	36607.8	0.05
AcPy	ND	ND	ND	ND	ND	ND
Acp	ND	ND	0.04	0.11	0.06	ND
Flu	ND	0.04	0.08	0.13	0.10	ND
Pha	ND	73.2	234.05	0.077	78.30	ND
Ant	ND	ND	0.05	0.06	0.04	ND
FluA	ND	0.07	0.14	0.14	ND	ND
Pyr	ND	ND	0.09	ND	ND	ND
B(a)A	ND	ND	ND	0.28	ND	ND
Chr	ND	0.55	ND	ND	ND	ND
B(b)F	ND	ND	0.10	1319.9	279.520	ND
B(k)F	ND	ND	ND	ND	ND	ND
B(a)P	ND	ND	ND	2494.8	440.7	77.2
DbA	ND	ND	288.4	0.26	0.12	120.7
B(ghi)P	ND	ND	ND	ND	ND	ND
InP	ND	ND	ND	419.1	0.06	ND

Unit of concentration: $\mu\text{g}/\text{N m}^3$; ND, non-detected.

should be high. The peaks of CaCl_2 and MgCl_2 were also found in the XRPD spectra. With the formation of NaCl , CaCl_2 , and MgCl_2 , the reaction between chlorine and hydrogen to form HCl was suppressed and the emission yield of HCl and Cl_2 was low in inorganic chloride feedstock.

4.2.3. Control efficiency of PAHs by CaO additive

From the above experimental results, we found that using additives can effectively suppress the emission of HCl and Cl_2 and CaO was the best additive. This section further discussed the control efficiency of PAHs by CaO additive at different temperatures.

Tables 4 and 5 showed the concentrations of gas- and solid-phase PAHs at different temperature as the feedstock contained organic chloride and CaO additive. The formation of gas-phase

Table 5

Concentration of solid-phase PAHs formed in the combustion of organic chloride with and without CaO additive at different temperatures

Additive temperature	No additive			CaO additive		
	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C
NaP	ND	ND	ND	ND	ND	ND
AcPy	ND	ND	ND	ND	ND	ND
Acp	0.131	0.42	1.10	0.24	0.49	0.19
Flu	1306.2	6790.7	ND	1964.3	8004.5	6557.4
Pha	1646.8	ND	ND	ND	ND	ND
Ant	541.6	ND	ND	801.9	ND	ND
FluA	251.5	ND	ND	263.0	ND	ND
Pyr	216.8	ND	ND	258.3	ND	ND
B(a)A	189.9	3.27	ND	213.3	4.74	ND
Chr	164.4	ND	ND	157.7	ND	ND
B(b)F	0.17	ND	ND	252.0	ND	ND
B(k)F	ND	7169.4	ND	ND	6461.8	11584.7
B(a)P	171.8	ND	ND	119.5	ND	ND
DbA	0.04	ND	ND	ND	ND	ND
B(ghi)P	ND	ND	ND	ND	ND	8708.2
InP	ND	948.1	ND	ND	1006.1	1834.1

Unit of concentration: $\mu\text{g}/\text{N m}^3$; ND, non-detected.

Table 6

Concentration of gas-phase PAHs formed in the combustion of inorganic chloride with and without CaO additive at different temperatures

Additive temperature	No additive			CaO additive		
	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C
NaP	0.43	0.14	0.07	0.15	0.05	ND
AcPy	0.06	ND	ND	ND	ND	ND
Acp	0.15	ND	ND	0.09	ND	ND
Flu	200.3	ND	0.06	0.06	246.4	ND
Pha	225.1	ND	43.16	109.5	295.4	33.50
Ant	103.4	55.50	65.47	0.04	83.0	ND
FluA	0.21	0.13	ND	0.10	0.06	ND
Pyr	0.09	0.04	ND	ND	0.06	ND
B(a)A	ND	ND	ND	ND	ND	ND
Chr	0.96	ND	0	ND	ND	ND
B(b)F	840.6	ND	578.57	ND	256.2	ND
B(k)F	ND	ND	0	ND	ND	ND
B(a)P	1361.1	ND	947.15	ND	ND	ND
DbA	0.15	276.0	ND	59.17	33.4	ND
B(ghi)P	ND	602.1	ND	ND	ND	ND
InP	134.2	ND	79.19	ND	ND	ND

Unit of concentration: $\mu\text{g}/\text{N m}^3$; ND, non-detected.

PAHs was less than that of solid-phase PAHs. The formation of gas-phase PAHs was increased by adding CaO at 600 and 700 °C, but was decreased at 800 °C. The control efficiency of solid-phase PAHs by adding CaO was also bad at each operating temperature; in some cases, there were even inverse effects. This result which may be attributed to the combustion efficiency of fluidized bed incinerator was influenced by the addition of CaO . Alkaline and alkaline-earth metals such as Na, K, Ca, Mg are easily sintered with silica sand and decrease the fluidization quality of a fluidized bed incinerator [21,23]. The phenomena of sintering and aggregation of silica sand were observed in this experiment, and the combustion efficiency was therefore decreased.

Tables 6 and 7 showed the concentrations of solid- and gas-phase PAHs at different temperature as the feedstock contained inorganic chloride and CaO additive. The formation of gas-phase

Table 7

Concentration of solid-phase PAHs formed in the combustion of inorganic chloride with and without CaO additive at different temperatures

Additive temperature	No additive			CaO additive		
	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C
NaP	4.12	0.81	ND	0.57	0.45	ND
AcPy	1.81	0.06	ND	0.12	0.06	ND
Acp	0.38	0.16	ND	0.22	0.20	ND
Flu	6340.3	3.14	460.6	0.68	1.44	484.3
Pha	2018.7	5372.0	622.3	780.0	2187.6	1323.5
Ant	1051.5	3087.6	207.6	378.3	642.3	433.4
FluA	0.11	2005.9	115.3	1273.9	925.6	717.0
Pyr	0.32	2255.2	121.9	0.25	1007.7	687.5
B(a)A	0.21	0.63	ND	0.10	0.27	ND
Chr	0.08	0.56	ND	0.87	0.23	0.11
B(b)F	405.0	719.7	ND	237.4	472.8	266.2
B(k)F	ND	ND	ND	ND	ND	ND
B(a)P	ND	980.2	ND	216.8	310.4	223.9
DbA	ND	1992.3	ND	ND	873.4	0.07
B(ghi)P	ND	ND	ND	ND	ND	ND
InP	0.26	ND	ND	ND	ND	ND

Unit of concentration: $\mu\text{g}/\text{N m}^3$; ND, non-detected.

PAHs with inorganic chloride was more than that with organic chloride, and was effectively suppressed by CaO additive at 600 and 800 °C. The formation of solid-phase PAHs was more than gas-phase PAHs, and was effectively suppressed by CaO additive at 600 and 700 °C. The control efficiency of solid-phase PAHs by CaO additive was poor at 800 °C, but the control efficiency of gas-phase PAHs was good. This result was identical with that in organic chloride feedstock, and indicated that CaO additive could suppress the emission of gas-phase PAHs at higher temperature but increased the formation of solid-phase PAHs. The later was resulted from the sintering of silica sand with CaO and the combustion efficiency was decreased.

5. Conclusions

This study investigated the formations and controls of HCl and PAHs in the incinerations of organic and inorganic chlorides by different additives. The formation of HCl was related to the potential of chlorine released from the combustion of different chlorides. Organic chloride PVC had great potential to form HCl than inorganic chloride NaCl. The performances of additives were affected by incineration temperature. Increasing operating temperature decreased the performances of additives because the emission yields of HCl and Cl₂ were increased with temperature. Calcium based additives (Ca(OH)₂, CaO, CaCO₃) had better performances than magnesium based additive Mg(OH)₂ on the controls of HCl and Cl₂. CaO had the best performance in our experiments. The control efficiencies of PAHs by adding CaO additives in the feedstock were not apparent because the fluidization quality in the fluidized bed incinerator was decreased.

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