



## Migration of inorganic chlorine during thermal treatment of mineralized waste



Wenxiang Li<sup>a</sup>, Dongyun Liu<sup>a</sup>, Dongsheng Shen<sup>a</sup>, Lifang Hu<sup>b</sup>, Jun Yao<sup>c</sup>, Yuyang Long<sup>a,\*</sup>

<sup>a</sup> Zhejiang Provincial Key Laboratory of Solid Waste Treatment and Recycling, School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

<sup>b</sup> College of Quality and Safety Engineering, Institution of Industrial Carbon Metrology, China Jiliang University, Hangzhou 310018, China

<sup>c</sup> College of Life Science, Taizhou University, Linhai 317000, China

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### ABSTRACT

Chlorine is a common element in the environment where it mostly exists in an inorganic ionic state that is highly mobile and non-degradable. It is important to investigate the potential release of chlorine into the environment from mineralized waste (MW) for stable landfill reclamation. In this study, inorganic chlorine in the MW migration process was explored during thermal treatment for chlorine pollution control. The temperature and chlorine greatly affected the distribution of inorganic chlorine in the thermally treated products. Below 800 °C, more than 60% of the inorganic chlorine remained in the bottom slag. Above 900 °C, volatilization caused the release of chlorine from the MW and more than 75% of the inorganic chlorine was deposited inside the furnace. The mass of inorganic chlorine deposited in the thermal treatment furnace was significantly correlated with the actual temperature. At 1000 °C, the masses of inorganic chlorine deposited under pyrolysis, incineration, and gasification atmospheres were 7.69, 5.81, and 5.68 mg, respectively. The greatest deposition of inorganic chlorine inside the furnace occurred during pyrolysis. The chlorine migration process must gain more sight during MW thermal processing.

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### 1. Introduction

The global municipal solid waste (MSW) production is estimated at 1.3 billion tons per year and is expected to reach 2.2 billion tons by 2025 (Hoornweg and Bhada-Tata, 2012). Sanitary landfill always plays an important role for waste disposal around the world due to its relative low technical requirements (Kollikkathara et al., 2009). Unfortunately, landfill site overload operation has become a more and more common phenomena with the fast growth of MSW volume (Zhao et al., 2006). It is urgent to find an alternative volume reduction strategy for MSW management.

After several years of degradation inside the landfill site, the MSW physicochemical proportion reach a stable (i.e., harmless) state and it is referred to as mineralized waste (MW) (Li and Zhao, 2000). The MW has flammable components and potential for safe mining and recycling (Zhang et al., 2012). Typically, thermal treatment method is a better choice for the further volume reducing for MW.

Chlorine in MSW is always neglected because of its relative low direct pollution risk, especially when landfilling. However, it was reported that most of the chlorine still remain in the landfill after years of operation (Long et al., 2018). It should be gained insight once the MW is subjected to further thermal processing because of the possible corrosion and dioxin formation risk.

The organic and the inorganic states are the two main forms of chlorine in MW. In which, the organic chlorine is mainly contained in C–Cl bonds with low bond energy. The C–Cl bond can be thoroughly broken once the temperature is higher than 200 °C (Ma et al., 2010). However, the inorganic chlorine is mainly combined with alkali metal elements and has high bond energy. Theoretically, it cannot be decomposed if the temperature is lower than 850 °C (Jiang et al., 2005). In a word, the chlorine can be released at different state and amount during the whole MW thermal processing. The released chlorine can easily combine with hydrogen as HCl during the thermal treatment like incineration, pyrolysis, or gasification. It also indicates that if sufficient oxygen and catalyst are available, HCl may trigger the further synthesis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Matsuda et al., 2005), which are toxic in the environment (Ma et al., 2019). Therefore, the chlorine in MW is no longer a negligible problem.

\* Corresponding author.

E-mail address: [longyy@zjgsu.edu.cn](mailto:longyy@zjgsu.edu.cn) (Y. Long).

There are numerous studies related to the distribution of chlorine during the thermal treatment of solid wastes and the associated challenges (Du et al., 2014), but few studies have reported the effects of chlorine migration from MW during thermal treatment. Liu investigated HCl concentrations in the flue gas from a simulated incinerator at different temperatures and found the ratio of HCl in the flue gas to the total chlorine input increased significantly with increasing temperature (Liu and Pan, 2000). During pyrolysis, Cl and S in the waste easily enter the pyrolysis gas in the form of HCl and H<sub>2</sub>S, which can cause high temperature corrosion of equipment (Pan et al., 2007). However, it still cannot answer the question of chlorine detailed migration during the thermal process. Moreover, the main components of MW are humus soil (Marousek et al., 2019), plastics, and inert materials such as stones and metals (Krook et al., 2012), which differ with raw MSW significantly. It is hard to evaluate the chlorine migration behavior in MW by direct comparing it with MSW.

In this research, the detailed migration of inorganic chlorine during thermal treatment of MW was investigated. It aims to provide useful reference information for the further MW thermal processing pollution control.

## 2. Materials and methods

### 2.1. Distribution of MW

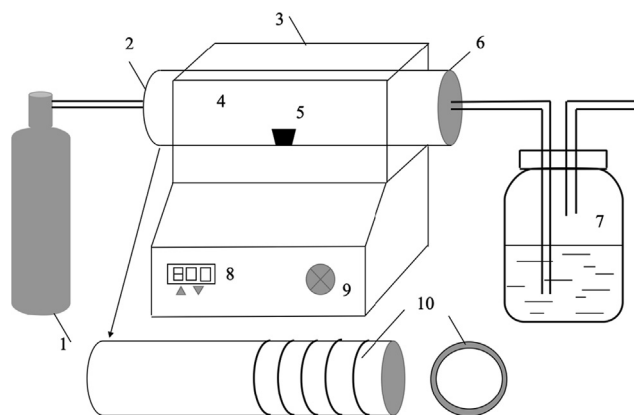
The MW used in this study was taken from a stabilized anaerobic simulated landfill reactor that had been in use for more than 5 years. Details of the MW are given in our previous paper (Long et al., 2018). Visible inert materials such as glass and metal were removed quickly after taking the MW out of the reactor. A sample of the MW (50 g) was used to determine the water content and the remaining material was dried in an oven at 70 °C for 24 h. The dried MW was cooled to room temperature, ground to a particle size of less than 2 mm with a crusher (SM2000, Retsch, Germany), and placed in a sealed bag. The properties of the tested MW are listed in Table 1.

### 2.2. Experimental system

The experimental system (Fig. 1) consisted of four parts: a carrier gas, a gas flow control system, a tubular furnace, and a flue gas absorption device. The tubular furnace acted as a reactor for thermal treatment of the MW. The carrier gas could be switched to simulate incineration, pyrolysis, and gasification scenarios. The tube was made of corundum and had the following dimensions: length, 90 cm long; central heating zone length, 30 cm; inner diameter, 5.4 cm; and outer diameter, 6 cm.

### 2.3. Experimental design

Details of the experimental design are given in Table 2. Nitrogen, air, or a mixture of nitrogen and oxygen was introduced into the tubular furnace to simulate a pyrolysis, incineration, or gasification atmospheres, respectively. The gas flow rate was 600 mL min<sup>-1</sup>. The temperature range was 300–1000 °C, with a gradient of 100 °C and heating rate of 10 °C min<sup>-1</sup>.



**Fig. 1.** Schematic of the tube furnace: 1, gas cylinder; 2, air inlet; 3, furnace; 4, furnace tube; 5, quartz boat; 6, air outlet; 7, absorption bottle; 8, temperature controller; 9, flow controller; and 10, stainless steel rings.

The procedure included the following steps:

- (1) The tube furnace inlet port was connected to the carrier gas. The pipeline was checked for air tightness, the gas flow rate was fixed at 600 mL/min, and the temperature program was set. The tubular furnace outlet was connected to a 250 mL gas absorption bottle that contained 0.1 M sodium hydroxide (60 mL) as the absorbent.
- (2) The MW (1.50 g) was placed in a quartz boat. When the desired temperature was reached, the inlet of the tubular furnace was opened and the quartz boat with the sample was quickly pushed into the central point of the tube from the inlet. The inlet was sealed immediately.
- (3) To investigate deposition of inorganic chlorine on the tubular furnace wall, stainless-steel rings were placed inside the tubular furnace. The outer diameter of each stainless-steel ring (5.3 cm) was slightly less than the inner diameter of the tubular furnace (5.4 cm), and its length was 2 cm. The stainless-steel rings were placed in the flue gas flow direction from the central heating point to the tubular furnace outlet at intervals of 5 cm. After each thermal treatment, the rings were washed carefully to collect the deposited inorganic chlorine. The amount of inorganic chlorine deposited on each ring was calculated as follows:

$$m_i = (m_j + m_{j+5}) \times 5/2, \quad (1)$$

where  $m_i$  is the mass of inorganic chlorine deposited on ring  $i$  (mg),  $m_j$  is the mass of inorganic chlorine deposited at a distance of  $j$  cm from the quartz boat (mg), and  $m_{j+5}$  is the mass of inorganic chlorine deposited at a distance of  $j + 5$  cm from the quartz boat.

- (4) After heating for 30 min, the quartz boat was removed and immersed in ultrapure water (50 mL) for 24 h. The extract was passed through a 0.22 μm filter and then the Cl<sup>-</sup> concentration was determined by ion chromatography (882 Compact IC plus, Metrohm AG, Herisau, Switzerland).

**Table 1**  
The characteristics of the tested MW after removal of the visible inert fraction.

Index	Moisture content (%)	Inorganic chlorine (mg/g)	Organic chlorine (mg/g)	Combustible chlorine (mg/g)	Non-combustible chlorine (mg/g)	Volatile matter (%)
Content	65.86	7.40	0.64	4.65	2.75	50.69

**Table 2**  
Experimental design.

Gas	Gas composition	Temperature (°C)	Time (min)	Gas flow rate (mL/min)	Simulated atmosphere
Nitrogen	1	300–1000	30	600	Pyrolysis
Air	1	300–1000	30	600	Incineration
Oxygen/Nitrogen	1/9	300–1000	30	600	Gasification

- (5) The  $\text{Cl}^-$  concentration in the absorption bottle was determined after the liquid in the absorption bottle had been passed through a 0.22- $\mu\text{m}$  filter.
- (6) The five stainless-steel rings were removed from the tubular furnace and soaked in ultrapure water (100 mL) for 24 h to remove deposited  $\text{Cl}^-$ . The  $\text{Cl}^-$  concentration in each extract was determined.

#### 2.4. Sample analysis

The MW inorganic chlorine content was determined by leaching in ultrapure water for 24 h, and the concentration of  $\text{Cl}^-$  in the solution was determined by ion chromatography. The organic chlorine content was determined with a solid-to-liquid ratio of 1:10 for leaching, and the remaining solid was dried in an oven at 105 °C. The sample was placed on filter paper and burned completely in a combustion bottle filled with oxygen and sodium hydroxide solution. The concentration of chlorine in the absorption solution was determined. The sample was placed in an oxygen flow in the tubular furnace and incinerated, and the tail gas was absorbed by the sodium hydroxide solution. The  $\text{Cl}^-$  in the absorption liquid was flammable chlorine. The  $\text{Cl}^-$  present after leaching of the remaining bottom slag was non-flammable chlorine (Ma et al., 2011). The temperature field distribution of the tubular furnace was monitored using a thermocouple until the temperature was stable. Each experiment was repeated three times.

### 3. Results and discussion

#### 3.1. Flow characteristics of inorganic chlorine under different thermal treatment conditions

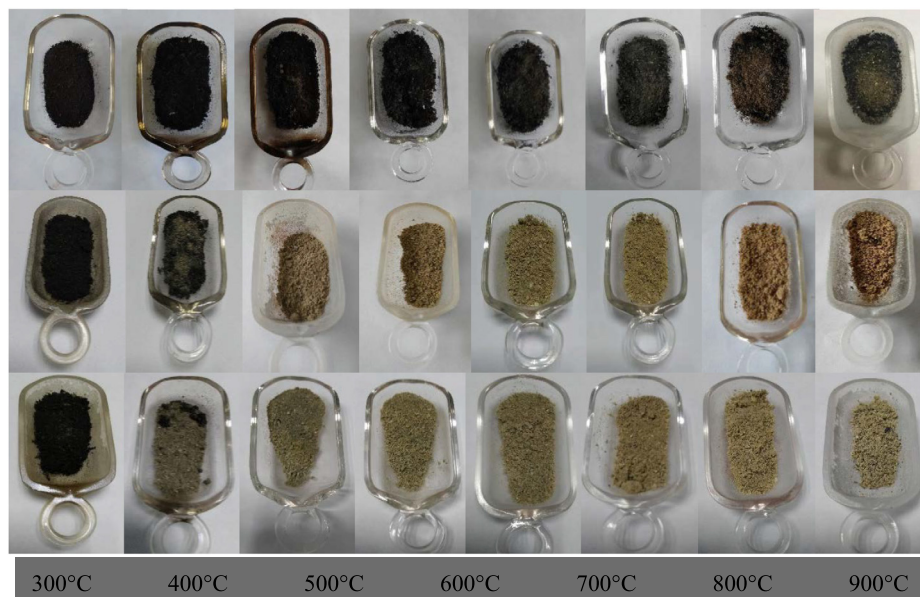
The decomposition behavior of the MW varied with changes in the reaction gas atmosphere. The oxygen concentration greatly

affected the MW feature after thermal treatment (Fig. 2). In a nitrogen atmosphere, thermal treatment did not significantly change the MW feature, and its color remained black. In the two oxygen-containing atmospheres, the MW was rapidly oxidized to a yellow.

When the temperature increased above 200 °C, C–Cl bonds were broken, and chloride salts volatilized or decomposed. Most of the chlorine was released in the form of HCl, and some of the chlorine may have combined with alkali metals to form metal chlorides. When the temperature reaches 850 °C, the metal chlorides decompose. After thermal treatment of MW, the inorganic chlorine was distributed among three thermal treatment products: flue gas, bottom slag, and furnace sediment. The proportions of inorganic chlorine in these three products were compared for the different atmospheres and temperatures (Fig. 3). The conversion and migration of inorganic chlorine was greatly affected by the temperature and form of chlorine.

In the low-temperature zone (300 °C–600 °C), more than 90% of the inorganic chlorine remained in the thermally treated bottom slag, and the masses in the flue gas and the furnace were small. The decomposition temperature of organic chlorine was between 300 °C and 600 °C. The background values (Table 1) showed that the organic chlorine content of the MW used in this study was 0.64 mg g<sup>-1</sup>; therefore, the organic chlorine input was 0.96 mg and accounted for only 8% of the total chlorine input. This may be the main reason for the low quantities of inorganic chlorine in the flue gas and furnace sediments in the low-temperature zone (300 to 600 °C).

At temperatures above 700 °C (the high-temperature zone), the inorganic chlorine in the MW began to degrade or volatilize. The inorganic chlorine input was 11.1 mg, which was 92% of the total chlorine content. The volatilization or decomposition of inorganic chlorine in the MW led to increases in the amounts of flue gas and inorganic chlorine in the furnace with increasing temperature.



**Fig. 2.** Sample images after thermal treatment in different atmospheres. The images in the rows from top to bottom are for samples from pyrolysis, gasification and incineration atmospheres.

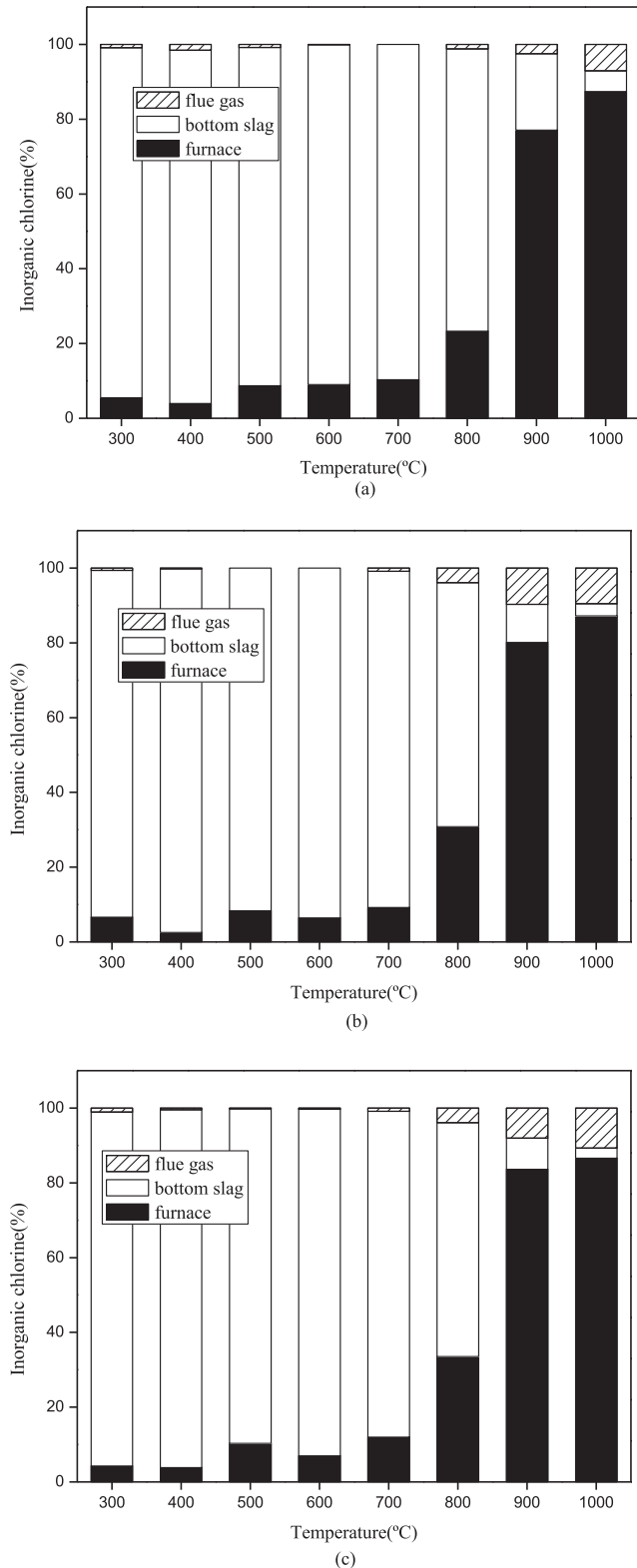


Fig. 3. Percentage of inorganic chlorine in flue gas, bottom ash, and furnace in pyrolysis (a), incineration (b), gasification atmosphere (c).

When the temperature reached 800 °C, the proportions of inorganic chlorine in the bottom slag in the pyrolysis, incineration, and gasification atmospheres were 75%, 65%, and 63%, respectively. At 900 °C, the corresponding percentages of inorganic chlorine in the bottom slag decreased to 20%, 10%, and 9%, and deposition in the furnace increased to 77%, 80%, and 83%. These data clearly

indicate that an aerobic environment promotes the release of organic chlorine. The data also indicate that a large quantity of chlorine was released from the MW at 800–900 °C, and most of it was deposited in the furnace, with small quantities in the flue gas and bottom slag. This may be because the melting points of most chloride salts (e.g., NaCl and KCl) are between 700 °C and 800 °C and when the temperature reaches the melting point, evaporation of the chloride salts accelerates.

Chlorine in the MW was released into the flue gas or deposited inside the furnace during thermal treatment. The risk of inorganic chlorine conversion and migration could be reduced by controlling the temperature and chlorine form.

### 3.2. Distribution of inorganic chlorine in the flue gas

The mass of inorganic chlorine in the absorption bottle was used as the inorganic chlorine content of the flue gas. The inorganic chlorine concentration in the flue gas was calculated as follows:

$$C_g = \frac{m_g}{600 \text{ mL/min} \times 30 \text{ min}} \times 10^6 \text{ mL/m}^3, \quad (2)$$

In the low-temperature zone, the concentration of inorganic chlorine in the flue gas was relatively low ( $<6.65 \text{ mg m}^{-3}$ ), in all cases (Fig. 4). Under the pyrolysis atmosphere, the concentration of inorganic chlorine in the flue gas was slightly higher than under the other two atmospheres. When the temperature reached 500 °C, the concentrations of inorganic chlorine in the flue gases under the incineration and gasification atmospheres were 0.00 and  $1.14 \text{ mg m}^{-3}$ , respectively. Under the pyrolysis atmosphere, the concentration of inorganic chlorine reached  $5.48 \text{ mg m}^{-3}$ .

In the high-temperature region, as the temperature increased, the inorganic chlorine concentration in the flue gas also increased. At this time, the inorganic chlorine concentration under the pyrolysis atmosphere was lower than those under the other two atmospheres. At 700 °C, the masses of inorganic chlorine in the flue gases under the three atmospheres were 0 (pyrolysis), 0.08 (incineration), and 0.05 mg (gasification), and the concentrations were 0 (pyrolysis), 45 (incineration), and  $33 \text{ mg m}^{-3}$  (gasification). The concentrations of inorganic chlorine in the flue gases increased rapidly with increasing temperature and reached maximum values of 34.4 (pyrolysis), 35.2 (incineration), and  $39.1 \text{ mg m}^{-3}$  (gasification) at 1000 °C.

The results show that the concentrations of inorganic chlorine in the flue gas under the incineration and gasification atmospheres were significantly different from that under the pyrolysis

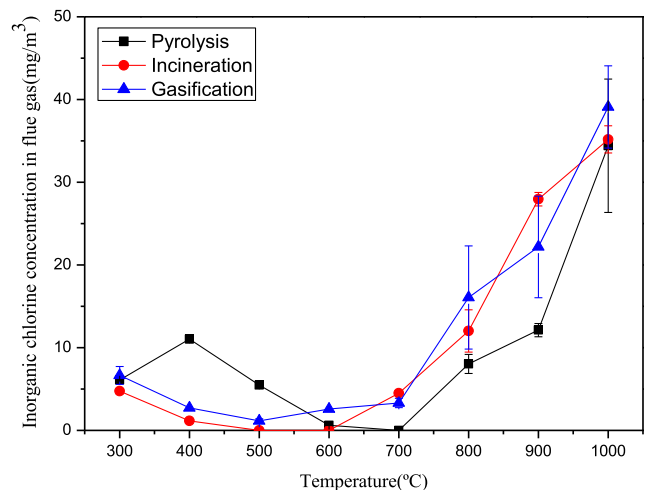


Fig. 4. Concentration of inorganic chlorine in the flue gas.

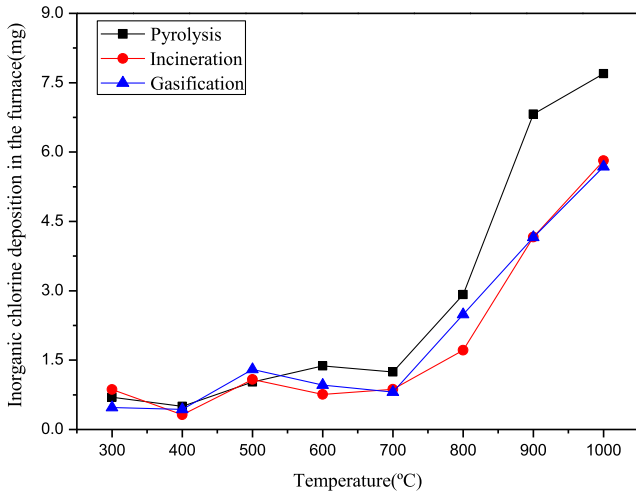


Fig. 5. Inorganic chlorine deposition in the furnace.

atmosphere. This indicates that the presence or absence of oxygen affects the concentration of inorganic chlorine in the flue gas. However, under the incineration and gasification atmospheres, the concentrations of inorganic chlorine in the flue gas were similar, which indicates that the oxygen concentration has little effect on the concentration of inorganic chlorine in the flue gas. In the low-temperature zone, the concentrations of inorganic chlorine in the flue gas under the incineration and gasification atmospheres were lower than that under the pyrolysis atmosphere. In the high-temperature zone, the results showed the opposite and the concentrations increased with increasing temperature.

### 3.3. Distribution of inorganic chlorine inside the furnace

The mass of inorganic chlorine deposited inside the furnace was also affected by the temperature and presence of oxygen (Fig. 5). Compared with the high-temperature zone, less inorganic chlorine was deposited inside the furnace in the low-temperature zone, and the differences among the masses deposited in the three atmospheres were not significant. In the high-temperature zone, the mass deposited increased rapidly with increasing temperature. When the temperature reached 1000 °C, the masses of inorganic chlorine deposited under the pyrolysis, incineration, and gasification atmospheres reached 7.69, 5.81, and 5.68 mg, respectively. The mass deposited under the pyrolysis atmosphere was 1.5 times the masses deposited under the other two atmospheres.

The relationship between the temperature and the distribution of inorganic chlorine in the furnace was investigated by determining the temperature field distribution in the tubular furnace. The temperature required for the experiments was reached at a distance of 40 to 50 cm from the air inlet (Fig. S1). The temperature on both sides gradually decreased with increasing distance, which showed that the temperature distribution was parabolic.

The actual temperatures at a fixed positions in the furnace were significantly correlated ( $P < 0.05$ ) with the masses of inorganic chlorine deposited under the three atmospheres (Fig. 6). The mass of inorganic chlorine deposited in the furnace increased exponentially with increasing temperature.

At the same temperature and location, inorganic chlorine deposition was higher under the pyrolysis atmosphere than under the incineration and gasification atmospheres. This phenomenon was more obvious at higher actual temperatures. For example, at an actual temperature of 422 °C, the mass of inorganic chlorine

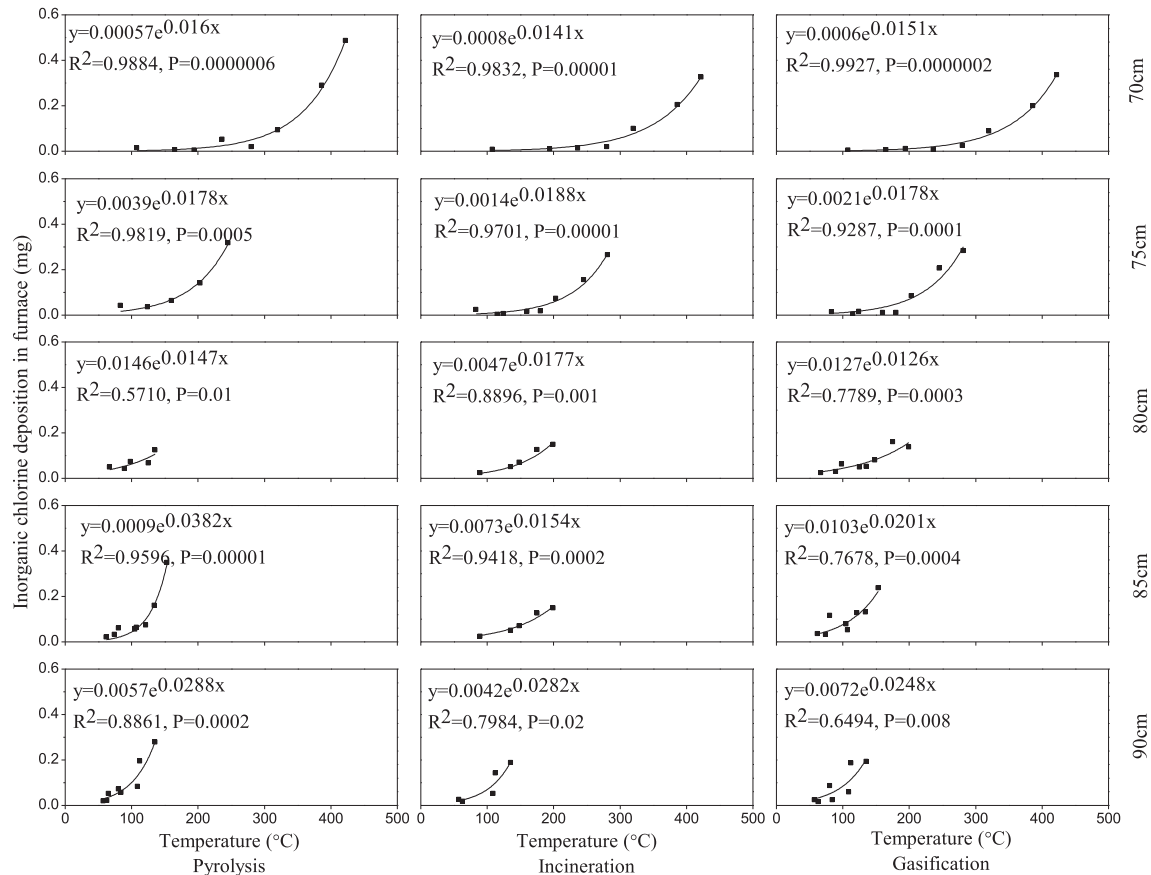


Fig. 6. Correlation analysis of the actual temperature and inorganic chlorine deposition in furnaces under different atmospheres.

deposited 70 cm in the furnace under the pyrolysis atmosphere was 0.49 mg. By comparison, the masses of inorganic chlorine deposited under the incineration and gasification atmospheres were 0.33 and 0.34 mg, respectively. For a given atmosphere, the exponent and coefficient in the fitting equation increased with increasing distance. On the basis of the exponential function, it could be inferred that at the same actual temperature, the risk of inorganic chlorine deposition increased with increasing distance from the sample heating zone. For example, under the nitrogen atmosphere, if an actual temperature of 100 °C was assumed and put into the equation, the calculated masses of deposited inorganic chlorine at 70, 75, 80, 85, and 90 cm were 0.008, 0.017, 0.068, 0.063, and 0.098 mg, respectively. These calculated results are consistent with the actual measured results. In practical applications, direct measurement of the mass of inorganic chlorine deposited inside a furnace is difficult. Model analysis shows that the temperature can directly reflect the mass of inorganic chlorine deposited at a certain position inside the furnace. Therefore, the mass of deposited inorganic chlorine can be obtained by measuring the temperature at the required position. This enables estimation of the corrosion rate of the heating equipment and corresponding protective measures can be taken.

#### 4. Conclusions

In thermal treatment of landfill-stabilized MW, the greatest inhibition of the release of inorganic chlorine occurs in high-temperature (>700 °C) anaerobic environments. Below 800 °C, more than 60% of the inorganic chlorine remains in the bottom slag, and above 900 °C, more than 75% of the inorganic chlorine is deposited inside the furnace. The actual temperature inside the furnace is correlated with the mass of deposited inorganic chlorine, and this mass increases exponentially with increasing temperature. At the same temperature and position, the deposition of inorganic chlorine inside a furnace under a pyrolysis atmosphere is higher than that under an incineration or gasification atmosphere. In a given atmosphere, inorganic chlorine deposition increases with the distance from the concentrated heat zone. The chlorine migration process must gain more sight during MW thermal processing.

#### Declaration of Competing Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2020.01.012>.

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