Study on Drying of Island Domestic Waste and Dechlorination of Flue Gas by Shells

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Abstract. This paper reports an island domestic waste disposal method that uses diesel flue gas to dry waste and shells to purify the gas from waste incineration. Applying this method, the energy consumption of waste incineration can be reduced, and the pollution can be alleviated. The experimental results show that island domestic waste drying process is divided into an adjustment section and a deceleration section, and the waste is dried up after heating for 30 minutes. The study also finds out that shells can replace calcium-based adsorbent to purify the flue gas, and the best dechlorination temperature for shells is 700°C.

1. Introduction

With the continuous development of China's islands, the traditional island domestic waste disposal method could not adapt to the rapid growth rate of domestic waste. How to make island domestic waste reduced, recycled and harmless has become the main issue to be solved on islands. As a waste treatment technology, the waste incineration method can reduce the volume of waste by more than 85% and reduce the weight by more than 75% [1]. It is suitable for remote and small regions such as islands. However, the island domestic waste is collected without classification, which brings difficulties to the local waste incineration: (1) the moisture content of waste is generally higher than 50%, which lowers the calorific value of waste, hence make waste incineration inefficient. (2) Plastics and rubber contain chlorine. The HCl gas generated during the waste incineration will cause the boiler to corrode and form acid rain [2, 3]. At the same time, chlorine is a precursor of highly toxic substances such as polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofurans (PCDFs) [4, 5]. Therefore, the key issue of in-situ island waste incineration is to reduce the moisture content of the waste and remove HCl from flue gas.

Waste drying technologies include drying waste in the incinerator furnace, biological drying, and residual heat drying. Under atmospheric pressure, energy consumed during the drying by reducing the waste moisture content from 48.5% to 43.3% is 1000 kJ/kg, which equaled to 15 kg standard coal (5500 kcal/kg) [1]. The technology of drying waste in incinerator has high thermal intensity, but the power consumption is so high that requires additional fuel. Bio-drying technology has low energy requirements in contrast. However, it has a long composting cycle and complicated technical process. The residual heat drying technology can reasonably utilize the exhaust flue gas, and the cost is low. Municipal solid waste (MSW) dechlorination mainly relies on the addition of calcium-based chlorine adsorbent, but the cost is high and it is not suitable for remote islands.
After investigated on some islands, we found that island's electricity consumption depends on diesel generators, and the shellfish in domestic waste account for a relatively high proportion. The main component of shells is calcium carbonate, which is able to dechlorinate. Based on the characteristics of islands, this paper proposes an island domestic waste disposal method by drying with residual heat of diesel engine flue gas and incinerating with shells. Drying curves of the waste at different temperatures were obtained through the drying experiment. Based on the principle of reaction kinetics, drying mathematical model and Arrhenius equations were obtained. Shell, Ca(OH)$_2$ and CaCO$_3$ were used as experimental objects to study their HCl adsorption capacity in simulated flue gas at different temperatures, and reaction products were analyzed by X-ray diffraction (XRD). Then, different Ca/Cl molar ratio conditions were set to get the optimal chlorine removal condition by shells.

2. Materials and methods

2.1. Survey on island domestic waste component

The constituent of island domestic waste is complex and affected by many factors such as natural conditions and development levels. Through investigations and on-site samplings in some Zhuhai islands, basic data of waste were obtained. Island domestic waste sampling method was referred to the "Sampling and Analysis Methods for Domestic Waste" (CJ/T313-2009). The moisture content of waste was measured by a blast drying oven (THG-9078A). The calorific value of waste was measured by an oxygen bomb calorimeter (ZDHW-7B).

2.2. Drying experiments of island domestic waste

For this part, we took Wailingding island domestic waste as the research object, and the waste was divided into plastic, wood and bamboo, fabric, paper, glass and metal. In order to ensure the homogeneity of the samples, the domestic waste was crushed and mixed up, and the particle size was less than 1cm. The waste drying process was simulated in a blast drying oven, and the waste drying characteristics at high temperatures were studied.

2.3. Experiments of shell removal HCl

The reaction device is shown in Figure 1. The compositions of simulated flue gas referred to the waste incineration exhaust [6]: O$_2$ accounted for 5%, CO$_2$ accounted for 15%, and the rest of flue gas was N$_2$. The total flue gas flow was 200 ml/min. By controlling the concentration of hydrochloric acid, the concentration of HCl in the flue gas was 0.09-0.1 mol/m$^3$. The concentration of chloride ions in the NaOH absorbent was measured by a chloride ion meter (PXS-CL), and the HCl removal rate was calculated by formula (1).

$$Y = \left\{ \frac{[\text{Cl}^-]_a - [\text{Cl}^-]_b}{[\text{Cl}^-]_a} \right\} \times 100\% / [\text{Cl}^-]_a$$

(1)

Here, $Y$ is the HCl removal rate; [Cl$^-$]$_a$ is the concentration of chloride ions in the NaOH solution before passing through the quartz tube; [Cl$^-$]$_b$ is the concentration of chloride ions in the NaOH solution after passing through the quartz tube.
The composition information of reaction products were analyzed by an X-ray diffractometer (D8 ADVANCE). Finally, the different Ca/Cl molar ratio conditions were set to get the best dosage of shells at 700 °C.

3. Results and discussions

3.1. Characteristics of island domestic waste

According to the characteristics of domestic waste in China, it could be divided into nine categories: kitchen waste, shellfish, plastic, paper, wood, fabric, metal, glass and others. Through investigation and on-site sampling analysis, the composition of island domestic waste (by weight) was obtained.

| Island           | Kitchen waste | Shellfish | Plastic | Paper | Wood | Fabric | Metal | Glass | Others |
|------------------|---------------|-----------|---------|-------|------|--------|-------|-------|--------|
| Nanao island     | 43.36         | 8.01      | 11.98   | 18.04 | 8.91 | 3.17   | 1.26  | 2.72  | 2.58   |
| Wanshan island   | 34.33         | 5.24      | 16.75   | 20.45 | 7.01 | 3.52   | 3.69  | 4.29  | 4.73   |
| Wailingding island | 35.08       | 11.06     | 14.55   | 14.23 | 11.37| 3.61   | 5.3   | 2.58  | 2.21   |
| Dongao island    | 37.45         | 8.34      | 14.16   | 16.65 | 7.13 | 2.34   | 2.57  | 2.08  | 9.29   |

Figure 1. Fixed bed dechlorination reactor

Figure 2. Island domestic waste moisture content and calorific value
From table 1 and figure 2, we can get the following characteristics of island domestic waste:

1. Kitchen waste is a dominant component in waste, which account for more than 30%. Especially in Nanao Island, the proportion of kitchen waste is as high as 43%. This situation is related to the general development of tourism on islands, and the tourists generate large amounts of kitchen waste.

2. Plastic, paper and wood account for large proportions, and water content of paper and wood are high. The calorific value of the waste will increase after drying and incinerate easily.

3. Shellfish waste is a unique component in island. Various shells and fish bones are the main ingredients of shellfish waste, and their compositions are mainly CaCO₃.

4. Island domestic waste has a high moisture content and low calorific value, which poses a problem for waste disposal.

In order to remove the chlorine from flue gas which generated by waste incineration, 5%-10% calcium-based adsorbents are added into refuse derived fuel (RDF) [7]. Similarly, adsorbents can be added into island domestic waste to reduce the pollution caused by the incineration. However, the island is so far from the mainland that raises costs for freight. If the traditional calcium-based adsorbents are added, the cost of waste incineration will be relatively expensive. The island is rich in shellfish, and the main component of the shell is calcium carbonate. Therefore, it is conceivable to replace the traditional calcium-based adsorbent with shells.

3.2. Drying characteristics of island domestic waste

![Figure 3](image_url)  
**Figure 3.** Drying rate of island wood waste at different temperature versus time

Since the kitchen waste is treated by the composting method in island, metal and glass waste cannot be incinerated. This part mainly studies the combustible components of waste, such as wood, paper, plastic and fabric.

Wood waste is hygroscopic porous material, which contains both bound-water and unbound-water. The proportion of bound-water is large. Figure 3 shows the change of mass loss rate of island wood waste with time. When the gas flow rate in the drying oven is constant, the temperature plays a positive role in the removal of unbound-water. As the temperature rises, the unbound-water evaporates quickly. The effect of temperature on the combined water is two-way: When the temperature rises, the mass transfer rate increases, which is conducive to water vaporization, meanwhile, the waste shrink and agglomerate at high temperatures, hindering the removal of the combined water. When the temperature is lower than 200°C, High temperature is good for waste dehydration. When the temperature is higher than 200°C, the factors that hinder the evaporation of water predominate, and the drying rate of waste decreases when the temperature increases.
Comparing figure 3 with figure 4, the effect of temperature on the drying speed of wood and paper waste is different. The drying speed of paper waste increases when the drying temperature increases, while the wood is different. Because the water content of paper waste is mainly unbound-water. For unbound-water, the temperature difference between the surface of the paper and the flue gas is the main influencing factor of heat transfer and mass transfer. The temperature difference becomes large, so that the driving force for drying becomes large, and the drying rate of paper waste becomes fast. The moisture content of plastic and fabric waste is also unbound-water, and its drying law is similar with paper waste.

![Figure 4](image_url)

**Figure 4.** Drying rate of island paper waste at different temperature versus time

The wood waste spontaneously combusted when dried for 25 min at 260°C. The paper waste spontaneous combusted when dried for 10 min at 220°C, and plastic waste would produce odor at 220°C. Therefore, the drying temperature of island domestic waste should not exceed 220°C.

![Figure 5](image_url)

**Figure 5.** Drying rate of island domestic waste at 200°C versus time

As shown in figure 5, the effect of time on the drying rate of different types of island domestic waste is the same. All types of waste reached the highest drying rate at 5 minute and completely dehydrated at around 30 minutes. From figure 6, the temperature has the same effect on all kinds waste drying process. At high temperatures, the waste drying process can be divided into an adjustment section and a deceleration drying section, and there is no constant speed section.
Comparing different types of waste, wood waste is the most difficult to dry because of its high moisture content. Next is fabric waste, which has abundantly small porosity. For plastic waste and paper waste, which mainly contain unbound-water, dehydration is much easier.

3.3. Drying dynamics analysis of island domestic waste

The drying process of domestic waste can be considered as the process that water in the waste changes to gas from liquid, in which water molecule energy increases. The process can be described as below:

\[ A(l) \rightarrow B(g) + C(s) \]  \hspace{1cm} (2)

The main factor affecting the drying rate of waste is temperature. For isothermal drying process, the drying rate can be expressed as formula (3):

\[ \frac{dMR}{d\tau} = k(1 - MR)^n \]  \hspace{1cm} (3)

Where \( k(\text{s}^{-1}) \) is the drying rate constant; \( \tau \) (min) is the drying time; \( n \) is the reaction series and can be taken as 1; \( MR(\%) \) is the water loss rate of waste, which can be calculated by the formula (4):

\[ MR = \frac{M - Md}{Mw - Md} \]  \hspace{1cm} (4)

Where \( M(\%) \) is the moisture content at certain point; \( Md(\%) \) is the moisture content of dried waste; \( Mw(\%) \) is the moisture content of undried waste. \( Md \) is so small compared to \( M \) and \( Mw \) that it can be ignored. Therefore formula (4) can be simplified to formula (5):

\[ MR = \frac{M}{Mw} \]  \hspace{1cm} (5)

The formula (6) below is obtained by integrating formula (5):

![Figure 6. Drying rate of island domestic waste at 200°C versus moisture content](image-url)
\begin{equation}
\ln(1 - MR) = -k \tau + k 0
\end{equation}

Where \( k 0 \) is the integral constant.

According to the formula (6) and the experiment results on \( \tau \) and \((1-MR)\), the drying rate constants \( k \) of paper waste and wood waste under different temperature conditions were obtained (Table 2).

**Table 2. Drying rate constants of paper waste and wood waste versus temperature**

| Temperature / °C | \( k_1 \) (Wood) / s\(^{-1}\) | \( k_3 \) (Paper) / s\(^{-1}\) |
|------------------|-----------------|-----------------|
| 160              | 0.02189         | 0.02147         |
| 180              | 0.03125         | 0.02666         |
| 200              | 0.04067         | 0.02849         |
| 220              | 0.06584         | 0.03137         |
| 240              | 0.06139         | --              |
| 260              | 0.05556         | --              |

The relation between drying rate constant and temperature can be certained by Arrhenius equation showed below:

\begin{equation}
\ln k = -\frac{E_a}{RT} + \ln A
\end{equation}

Where \( E_a \) (J/mol) is the activation energy of dehydration, which is a constant within a certain temperature range; \( R \) [J/(mol·K)] is the molar gas constant; \( A \) (min\(^{-1}\)) is the pre-exponential factor.

Combined with the data in table 2, \( E_a \) and \( A \) can be obtained.

The Arrhenius equation of paper waste dehydration is as below:

\begin{equation}
\ln k = -\frac{776.84}{RT} - 1.07
\end{equation}

In this research, the drying rate constant of wood waste in the temperature range of 160-260°C don’t completely conform to the Arrhenius equation. The constant get smaller when temperature is higher than 220°C, because wood waste may shrink and agglomerate at high temperatures. Hence the Arrhenius equation of wood waste dehydration shown below are obtained by the experimental data at 160-220°C.

\begin{equation}
\ln k_1 = -\frac{5149.17}{RT} + 0.0031
\end{equation}

According to formula (8) and (9), the activation energy of paper waste dehydration is lower than that of wood waste dehydration, which illustrates that paper waste is easier to be dried than wood waste.

### 3.4. Dechlorination of flue gas by shells

Flue gas is able to react with adsorbent more sufficiently in lab conditions because of its slow velocity, which leads to a higher removal rate of HCl. Chlorination processes using shells, Ca (OH)\(_2\) and CaCO\(_3\) are affected by temperature (Figure. 7). Their optimum temperatures are 700°C, 600°C and 600°C respectively, which can be determined due to the fact that HCl removal rate increased first then get lower. Their maximum HCl removal rates are 89.89%, 91.58% and 75.08% respectively.
When temperature are above 600 °C, the comparison of dechlorination abilities of those three adsorbents illustrates a better performance of shells, which contrasts Ca (OH)₂ and CaCO₃. The volume of CaCl₂ is 1.5 times that of Ca (OH)₂ when their mole are same. So the generated CaCl₂ will be coated on the surface of adsorbents and then block the diffusion of HCl into internal pores. Hence, the coated product CaCl₂, as well as melt and condensation of adsorbents, are supposed to be the reason why HCl removal rate of Ca(OH)₂ descends when temperature get higher. CaCO₃ possesses a lower density than that of CaCl₂, so the descent of its HCl removal rate may be attributed to its melt and condensation. On the contrary, shells adapted to high temperatures well in spite of negative influence above, which benefited from its abundant pores and solid structure. So the optimum dechlorination temperature of shells is higher than that of Ca (OH)₂ and CaCO₃. The removal efficiency of HCl by those three adsorbents is reduced when the reaction temperature is 800 °C.

The experimental results show that shells are better dechlorination adsorbents than CaCO₃. Although the HCl removal rate by shells is 63.88% at 300 °C, but it could be guaranteed more than 80% when reaction temperature get higher. Therefore, the advantage of shells as chlorine removal absorbents is that good dechlorination ability can be ensured even at high temperatures.

CaCO₃ can be divided into calcite, aragonite and vaterite according to its crystal structures. The main component of shells is CaCO₃, which consist of aragonite (Figure 8). Aragonite can be
converted to calcite due to its instability at high temperatures, which can be proved by XRD results showed in figure. 9.

![XRD results](image)

**Figure 9.** Diffraction pattern of action products versus temperature

From figure. 9, HCl is mainly adsorbed by CaCO₃ in shells at 400℃ and 600℃. CaO diffraction peaks don’t appear in the 600℃ shell samples. Hence the HCl removal rate by shells is lower than that of Ca (OH)₂ at 600℃. When the reaction temperature rises to 800℃, CaCO₃, as well as CaO which is decomposed by CaCO₃, removed HCl from flue gas.

In the purification practice of waste incineration flue gas, Ca (OH)₂ is not supposed to directly react with HCl. It’s CaO and CaCO₃ converted from Ca (OH)₂ in CO₂ atmosphere that react with HCl to generate CaCl·6H₂O [8]. So it’s reasonable to use shells, which consist of CaCO₃, to remove HCl from flue gas rather than Ca (OH)₂.

The reasons why the adsorbent dosage is usuall y higher than the theoretical value in the dechlorination process are below:

1. The release rate of HCl is often rapider than the adsorption rate by adsorbents [9].
2. Incomplete contact between adsorbents and HCl leads to the waste of adsorbents.
3. Excessive adsorbents are needed in order to prevent thermolabile CaCl₂ from decomposition and hence promote the adsorption of HCl.

It’s common to dose a certain amount of adsorbents so that the Ca/Cl molar ratio is 1.2-6.0, which is based on the consideration of cost and calorific value.

![Derivative Y](image)

**Figure 10.** Removal rate of HCl by shell at 700℃ versus Ca/Cl molar ratio
With the increase of Ca/Cl molar ratio, the HCl removal efficiency from flue gas by shells get better (Figure. 10). But the promotion in removal efficiency get slightly when the ratio is larger than 3. Considering that the low calorific value of shells would lead to the suppression of waste incineration, the Ca/Cl molar ratio is not recommended more than 3.

The shell dosage in the waste incineration process can be calculated by the formula (10).

$$ms = \frac{m(Cl) \times M(CaCO_3)}{M(Cl) \times W \times a}$$  (10)

Where $ms$ is the shell dosage; $m(Cl)$ is the chlorine content in waste, which is 1.52% [10,11]; $M(Cl)$ is the atomic weight of chlorine and equals to 35.5; $M(CaCO_3)$ is the molecular weight of CaCO$_3$ and equals to 100; $W$ is the CaCO$_3$ content in shells, which is 95%; $a$ represents Ca/Cl molar ratio.

According to the formula, shell dosage should be 13% when Ca/Cl molar ratio is 3, and 9% when Ca/Cl molar ratio is 2.

4. Conclusion
Islands are rich in residual heat and shells. Therefore, it’s feasible to pretreat flammable components in waste by the flue gas of diesel to reduce moisture and improve incineration conditions. Shells in waste are able to remove chlorine from flue gas and hence reduce the pollution in the incineration process.

The drying rate of island waste reaches the maximum value when it has been dried for 5 min. After 30 min, the dehydration process nearly comes to the end. To avoid self-ignition of waste, the drying temperature should not be higher than 220°C. The Arrhenius equation and activation energy of island waste dehydration were obtained as below:

Wood waste:

$$\ln k1 = -\frac{5149.17}{RT} + 0.0031, \quad E = 5149.17 \text{ J/mol}$$

Paper waste:

$$\ln k = -\frac{776.84}{RT} - 1.07, \quad E = 776.84 \text{ J/mol}$$

Shells in island waste are able to adsorb HCl from flue gas produced by waste incineration. X-ray diffraction patterns illustrated mechanisms of dechlorination as below:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

The optimum reaction temperature of dechlorination using shells was 700°C. The removal efficiency of chlorine by shells is better than that by CaCO$_3$ overall, as well as that by Ca (OH)$_2$ when temperature get higher than 700°C. Therefore, the adaptability of shells’ dechlorination ability at high temperature makes shells possible to be used as chlorine adsorbents in incineration process. The structural stability of shells under high temperature conditions is the reason of its high chlorine removal efficiency. The best shell dosage was 9%~13% of total waste in order to control the Ca/Cl molar ratio within 3.

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References
[1] A. Li, D. Li, X. Xu. A, Discussion on pretreatment to improve MSW incineration, J. Chinese
Journal of Environmental Engineering. 2.6 (2008) 830-834.

[2] Valente. T, Fireside corrosion of superheater materials in chlorine containing flue gas, J. Journal of Materials Engineering & Performance 10.5 (2001) 608-613.

[3] J. M. Brossard, I. Diop, X. Chaucherie, et al, Superheater fireside corrosion mechanisms in MSWI plants: Lab - scale study and on - site results, J. Materials & Corrosion. 62.6 (2015) 543-548.

[4] C. K, L. S, L. D, Emissions of PCDDs/DFs and dioxin-like PCBs from small waste incinerators in Korea, J. Atmospheric Environment. 42.5 (2008) 940-948.

[5] C. M, L. T, W. L, et al, The PCDD/F removal efficiency of a medical waste incinerator dual-bag filter system, J. Aerosol and Air Quality Research. 14.4 (2014) 1223-1231.

[6] X. X, X. Li, Experimental study on drying domestic waste by waste heat from cement production, J. Environmental Sanitation Engineering. 24.3 (2016) 6-8.

[7] V. N, D. Filippis P, Reaction kinetics of hydrogen chloride with sodium carbonate, J. Chemical Engineering Science. 61.22 (2006) 7487-7496.

[8] Y. Lin, D. Chen, P. Wei, et al, Investigation of gaseous HCl high temperature scrubbing from incineration flue gas with modified CaCO₃ alternative to Ca(OH)₂, J. Journal of Tongji University (Natural Science). 34.10 (2006) 1389-1393.

[9] T. Zhu, Y. Xiao, F. Chen, et al, A fundamental study of circulating fluidized bed for removing hydrogen chloride, J. Acta Scientiae Circumstantiae. 21.2 (2001) 194-197.

[10] F. D. Hernandez-Atonal, C. Ryu, V. N. Sharifi, et al, Combustion of refuse-derived fuel in a fluidised bed, J. Chemical Engineering Science. 62.1 (2007) 627-635.

[11] Z. Wang, H. Huang, H. Li, et al, HCl Formation from RDF pyrolysis and combustion in a spouting-moving bed reactor, J. Energy & Fuels. 16.3 (2002) 608-614.