DIOXIN'S REMOVAL FROM COMBUSTION GAS BY GAS INJECTION INTO WATER

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ABSTRACT
The purpose of the present study is to develop a simple removal method of dioxins/furans (dioxins) from a combustion gas at low cost. Removal method of suspended matters in gas (as a cold model) and dioxins in exhaust gas (as a hot model) has been investigated by gas injection into water; the mechanism is that the suspended matters in the gas gather on gas-liquid interface.

In the cold model, the removal ratio of fine particles ($R_P$) by injecting gas into water was correlated well by the following equation: $R_P (\%) = 100 \times \left(1 - \exp\left(-0.8 \cdot S_s \cdot t_C\right)\right)$, where $S_s$ (1/cm) designates a specific surface area of bubbles, and $t_C$ (s) a residence time of bubbles in water.

In the hot model under combustion experiments of poly vinyl chloride, the removal ratio of dioxins ($R_D$) by injecting the exhaust gas into water was estimated as: $R_D (\%) = 100 \times \left(1 - \exp\left(-0.8 \cdot S_s \cdot t_C \cdot C_{DO}^{0.67}\right)\right)$, where $C_{DO}$ (ng/cm\textsuperscript{3}(s.t.p.)) designates dioxin's concentration in the exhaust gas before injection into water.

KEYWORDS: Removal of dioxins, Fly carbonaceous matters (C*), Removal of fly C*, Gas Injection into water

INTRODUCTION
The main release source of dioxins/furans (dioxins) is combustion processes such as a municipal and an industrial waste incinerators, and the causes of dioxins formation in the incineration processes are locally incomplete combustion in a combustion zone and a de novo synthesis [1] at c.a. 573 K within a flue.

One of the countermeasures for the suppression of dioxins release in Japan is the removal of poly vinyl chloride (PVC) products [2]. In the incineration processes, the suppression methods against dioxins formation are adopted “3T” [2, 3] which stands for a rise in combustion temperature (Temperature), a complete mixing of combustion gas (Turbulence), and a long residence time at high temperature zone (Time). On the countermeasures against a de novo synthesis in the cooling process of an exhaust gas, there are many methods [2] such as quenching of an exhaust gas with a water spray, decrease in the working temperature of an electrostatic precipitator and improvement of the removal ratio of fine fly ash from an exhaust gas with a bag filter. The amount of dioxins emission in air from municipal and industrial waste incinerators has been decreased drastically from 7,000 g-TEQ/year in 1997 to 400 g-TEQ/year in 2004 [4] in Japan by those countermeasures. However, in middle- and small-scale municipal and industrial waste incinerators, the countermeasure against dioxins release still lags and many of their incinerators are fallen into discontinuance or are dismantled, because the above-mentioned countermeasures need high running and facility costs and much space.

The purpose of the present study is to develop a simple removal method of dioxins by injecting combustion gas into water at low cost.

The complete combustion experiments [5] with PVC powder fully satisfying “3T” were done by the combustion temperature of 1073 K, the residence time of 22 s at 1073 K and the enhancement of combustion with Al\textsubscript{2}O\textsubscript{3} balls bed at 1073 K (see Fig.1). Even under such combustion conditions, the fly carbonaceous matters (C*) of various sizes with micron order, namely unburned matters were found in the exhaust gas (see SEM photographs in Fig.2). In the fly C*, precursor such as phenol, benzene, biphenyl, naphthalene, anthracene, and their chlorides have been detected by chemical analysis with gas chromatography-mass spectrometry (GC-MS) [5]. Wang et al. [6] have also reported that chlorinated polycyclic aromatic hydrocarbons have been formed.
in the combustion of PVC. Figure 3 reveals that total dioxin's concentration in the exhaust gas has a good correlation with the number of fly C* remaining in the exhaust gas [5]. From fundamental studies [5] on combustion experiments and thermodynamic evaluations, it was inferred that dioxins are mainly formed under the thermodynamically heterogeneous sites with high CO/CO₂ ratio, which are the boundary layer on the surfaces of the fly C* remaining in combustion gas (see Figs.4 and 5). Thus, the main cause of dioxins formation is supposed to be the fly C* in the exhaust gas.

Figure 6 summarizes effects of chlorine sources and forms on the formation concentration of dioxins under combustion furnace (see Fig.1) at 1073K [7]. The combustion of powder mixture of the thermodynamically stable chloride, NaCl, and organic compound, polyethylene (PE), under the complete
Combustion conditions suggest very low dioxin's concentration. The formation of dioxins is high in the case of the combustion using PVC as an organochlorine compound. Even in the case of the thermodynamically stable NaCl, dioxin's concentration is formed by the existence of the hydrate as shown hinoki cypress and flour in Fig.6. Chlorine sources and forms are also important factors in the formation of dioxins. The concentration of dioxins is greatly governed by whether active Cl exists or not on the surface and in itself of the fly C* formed in the combustion processes [7].

Therefore, it can be expected that dioxin's concentration in the exhaust gas is considerably decreased by the removal of those fly C* alone. We have considered a floatation technology of inclusions within liquid by injecting gas bubbles into liquid [8].

In the present study, a simple removal method of dioxins from the combustion gas by injecting the exhaust gas into water has been investigated with cold and hot models.

**EXPERIMENTAL METHOD**

**PVC Combustion Experiments**

Figure 1 shows a schematic layout of the combustion furnace. The reaction tube, made of SUS 316 with 157 mm I.D., was heated by an electric furnace composed of three-divided heating parts to obtain a long isothermal zone through controlling each temperature separately. The temperature in the reaction tube was controlled at 1073K, which is a general combustion temperature in municipal waste incineration. What we call “the isothermal zone” at

1073±10K was 250 mm long as shown in Fig.1. PVC powder with a size of 200 μm was fed together with O2-N2 gas mixture by the fixed quantity feeder, which was installed in the upper part of the reaction tube. PVC feed rates were controlled to burn out with the amount of 5 vol%O2 in the supplied O2-N2 gas mixture. The combustion zone is designed to be composed of the primary and the secondary combustion parts. This primary combustion part is for preheating, gasification and combustion of the combustion materials and the secondary combustion part is within a bed packed with Al2O3 balls, where gas and unburnt materials are well mixed and combusted by heat exchange. Gas flow rates of O2 and N2 were controlled by the respective mass flow controllers.

**Removal Experiments**

(a) Removal of Fine Particle by Gas Injection into Water (Cold model at R.T.)

Removal experiments of the suspended matter in gas at R.T. were carried out by using experimental apparatus shown in Fig.7. Two kinds of gas washing bottle were used and filled with a various volume of distilled water as listed in Table 1. Although the residence time of bubbles in water differed not a little depending on the injection rate of gas, the volume of water in a bottle and a kind of gas washing bottle, much longer residence time was achieved by the increase in the number of gas washing bottle. The suspended matter was then fine Al2O3 particle with a mean size of 0.5 μm, and the fine particle was mixed with N2 gas. The number of the suspended matter before and after injection of gas mixture into water was measured by using a particle counter (KANOMAX, Model 3886, Max 70,000 piece/(L/min) (s.t.p.)).

**Fig.7. Experimental apparatus of gas injection into water.**
Table 1. Characteristics of bubbles generated by gas injection into gas washing bottle filled with water.

<table>
<thead>
<tr>
<th>Gas washing bottle (cm³)</th>
<th>Volume of water in a bottle (cm³)</th>
<th>Q₀ (cm³/min) (s.t.p.)</th>
<th>h (cm)</th>
<th>N (1/s)</th>
<th>r (cm)</th>
<th>v (cm/s)</th>
<th>tₑ (s)</th>
<th>Sₑ (cm²/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2,000</td>
<td>14</td>
<td>13</td>
<td>0.84</td>
<td>44</td>
<td>0.32</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>5,000</td>
<td></td>
<td>22</td>
<td>0.96</td>
<td>48</td>
<td>0.29</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>3,600</td>
<td></td>
<td>20</td>
<td>0.74</td>
<td>27</td>
<td>0.29</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>4,000</td>
<td></td>
<td>35</td>
<td>0.75</td>
<td>34</td>
<td>0.23</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>5,000</td>
<td></td>
<td>38</td>
<td>0.75</td>
<td>39</td>
<td>0.21</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>6,000</td>
<td>8.0</td>
<td>39</td>
<td>0.80</td>
<td>46</td>
<td>0.17</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>2,000</td>
<td></td>
<td>39</td>
<td>0.85</td>
<td>54</td>
<td>0.15</td>
<td>3.5</td>
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</tr>
<tr>
<td>800</td>
<td>5,000</td>
<td></td>
<td>8.1</td>
<td>1.25</td>
<td>54</td>
<td>0.22</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td>8.4</td>
<td>1.33</td>
<td>55</td>
<td>0.22</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

h: height from orifice to water surface  
N: number of generated bubbles per second  
Q₀: gas flow rate  
r: average radius of bubbles  
Sₑ: specific surface area of bubbles  
tₑ: average residence time of bubbles in water  
v: average rising velocity of bubbles

The characteristics of bubbles generated by gas injection into water are summarized in Table 1. The characteristics of bubbles, which were the number of bubbles per second (N (1/s)), average radius of bubbles assumed an equivalent radius to a sphere (r (cm)), specific surface area of bubbles (Sₑ (cm²/cm³)), average residence time of bubbles in water (tₑ (s)), and average rising velocity of bubbles (v (cm/s)), were measured by an image analysis using a high-speed camera (NAC, HSV 500).

(b) Dioxin’s Removal by Combustion Gas Injection into Water (Hot model)

Many kinds of the exhaust gas with different concentration of dioxins were made by the variation of the supplied gas concentration of O₂ and PVC feed rate. The exhaust gas from PVC combustion at 1073K was injected into gas washing bottles filled with distilled water, which were the same apparatus as the cold model (see Fig.7), in order to remove dioxins from the exhaust gas. The removal ratio of dioxins was calculated from the difference of dioxins’ concentration before and after injection of the exhaust gas into water. Although the characteristics of bubbles generated by injecting the exhaust gas into gas washing bottle were also measured by an image analysis using a high-speed camera, their characteristics were almost the same as those of the cold model (see Table 1).

RESULTS AND DISCUSSION

Removal of Fine Particle by Gas Injection into Water (Cold model at R.T.)

The removal rate of fine particles within gas by gas injection into water was assumed as Eq.(1) on the basis of the removal rate of inclusions from liquid by injection of gas bubbles into molten steel [8], which frequently has been using in the steel industry.

\[-\frac{dC_p}{dt} = k_s \cdot A \cdot C_p^* \cdot C_b\]  

where, A: surface area of bubbles (cm²)  
Cₚ: number of bubbles per unit volume (1/cm³)  
Cₚ*: inclusion’s concentration in molten steel (1/cm³)  
kₛ: hypothetical inclusion’s concentration on a surface of a bubble (1/cm³)  
t: time (s)

Since Eq.(1) is applied for the migration of inclusion from liquid to gas-liquid interface, A, Cₚ, and Cₚ* in Eq.(1) are transformed to apply to the migration of the suspended matter from gas to gas-liquid interface in the present study as follows:

\[A \cdot C_b = Sₚ\]  
\[C_p^* = C_p\]

where, Cₚ: concentration of fine Al₂O₃ particles in gas (1/L (s.t.p.))  
Sₑ: specific surface area of bubbles (cm²/cm³).
Therefore, the removal rate of fine particles in gas can be rewritten as follows:

\[-dC_p/dt = k_s \cdot S_s \cdot C_p\] (4)\\n
The concentrations of fine particle on a bubble surface and in a bubble are assumed to be the same. Integration of Eq.(4) with \(t\) yields the following change of the concentration of fine particle in gas:

\[C_p = C_{p0} \cdot \exp (-k_s \cdot S_s \cdot t_c)\] (5)

where, \(C_{p0}\): concentration of fine Al2O3 particles in gas before gas injection into water (1/L (s.t.p.))
\(t_c\): residence time of bubbles in water (s).

The removal ratio of fine particle (\(R_p\)) is defined as
\[R_p (\%) = 100 \times \frac{(C_{p0} - C_p)/C_{p0}}{, and written from Eq.(5) as follows:
\[R_p = 100 \times \left[1 - \exp(-k_s \cdot S_s \cdot t_c)\right]\] (6)

Figure 8 shows the removal ratio of fine particles in gas by gas injection into water as a function of \(S_s \cdot t_c\). The value of adhesion rate constant \((k_s)\) in Eq.(6) can be determined by the least square method of experimental data, and the resultant value is 0.8 (cm/s):

\[R_p = 100 \times \left[1 - \exp(-0.8 \cdot S_s \cdot t_c)\right]\] (7)

As shown in Fig.8, Eq.(7) reproduces the experimental results well. It is recognized that the removal ratio \((R_p)\) of fine particles increases with increasing in \(S_s \cdot t_c\), that is, \(R_p\) increases with an increase in specific surface area of bubbles and/or the residence time of bubbles in water [8].

Dioxin's Removal by Combustion Gas Injection into Water (Hot model)

The removal ratio of dioxins \((R_D)\), which was defined as \(R_D (\%) = 100 \times \frac{(C_{D0} - C_D)/C_{D0}}{, was calculated from the difference of dioxin's concentration before \((C_{D0})\) and after \((C_D)\) injection of the exhaust gas into water.

Equation (7) for the cold model was tried to apply to \(R_D\) obtained by the hot model. Experimental values of \(R_D\) have a correlation to \(S_s \cdot t_c\) as \(R_p\), but are a little lower than \(R_p\). The main cause of such a difference is considered to be the saturated vapor pressure of dioxins [9,10], that is, vaporous dioxins pass through water without trap. Therefore, the removal ratio of dioxins \((R_D)\) is expected to be affected by dioxin’s concentration of the exhaust gas \((C_{D0})\), and so \(R_D\) is assumed as Eq.(8) by taking \(C_{D0}\) into consideration in Eq.(7).

\[R_D = 100 \times \left[1 - \exp(-0.8 \cdot S_s \cdot t_c \cdot C_{D0}^n)\right]\] (8)

The value of \(n = 0.07\) can be determined by the least square method of experimental data of \(R_D\). Therefore, \(R_D\) by the injection of the exhaust gas into water is written as follows:

\[R_D = 100 \times \left[1 - \exp(-0.8 \cdot S_s \cdot t_c \cdot C_{D0}^{0.07})\right]\] (9)
It is seen from Fig. 9 that experimental data of $R_D$ agree rather well with calculated value. Consequently, it is found that $R_D$ greatly depends on the specific surface area of bubbles ($S_b$) and the residence time of bubbles in water ($t_c$), and is affected a little by dioxin's concentration of the exhaust gas ($C_{DD}$).

**Removal of Dioxins from Wastewater**

It is very important problem to remove dioxins from wastewater. We have developed a simple removal of dioxins from wastewater [11]. The removal mechanism of dioxins from wastewater is that fly C* including almost all dioxins is adsorbed on the polyolefin surface by the electrostatic effect. Therefore, the removal effect of dioxins from wastewater has examined by using a fluidized bed packed with PE particle. Experimental results reveal that dioxin more than 95% can be removed easily from wastewater by this method [11].

**CONCLUSIONS**

Dioxin's removal from gas by the exhaust gas injection into water has been investigated using the exhaust gas of PVC combustion. The conclusions obtained are as follows:

1. Injection of the exhaust gas into water is very effective method for the removal of dioxins in the exhaust gas.

2. Predictive equation for $R_D$ is as follows:

   $R_D(\%) = 100 \times [1 - \exp(-0.8 \cdot S_b \cdot t_c \cdot C_{DD}^{0.97})].$

3. $R_D$ greatly depends on the specific surface area of bubbles ($S_b$) and the residence time of bubbles in water ($t_c$), and is affected a little by dioxin's concentration of the exhaust gas before injection ($C_{DD}$).

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**REFERENCES**


