Dechlorination of organochlorine compound in flue gas from municipal solid waste incinerator using metal compound added activated clay

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1. Introduction
Flue gas treatment techniques for municipal solid waste incinerators (MSWIs) have continued to develop to meet the emission standards for environment pollutant substances such as acid gases, heavy metals, dioxins, etc. as well as to improve energy performance in operations. High temperature dust collection method at 300°C using a ceramic filter is expected to decrease energy and cost consumption of MSWIs by elimination of unnecessary cooling and re-heating processes in flue gas treatment system. In our previous research, thirteen kinds of activated clays were investigated as a substitute of activated carbon to remove dioxins including organochlorine compounds at 300°C, the operation temperature of high temperature dust collection process¹. Among them, six kinds of activated clays showed an effect on removal of mono-chlorobenzen (MCB) by dechlorination. In this study, it is investigated that the improvement of dechlorination effect of activated clay by adding various metal compounds at 300°C.

2. Material and Methods
Mizuca-Ace #400 (Mizusawa Industrial Chemicals Ltd.) was chosen as a base material among activated clays which have been proven effective in dechlorination of MCB in previous research¹. Mizuca-Ace #400 was called as #400 for short in this work. Table 1 shows the physicochemical property of #400. Meanwhile, eight metal compounds such as sodium bicarbonate, calcium hydroxide, calcium oxide, iron, iron (III) oxide, copper, copper oxide, and titanium oxide were selected as additives and mixed to #400 by 2.5-5wt%.

Table 1 Physicochemical property of #400

<table>
<thead>
<tr>
<th>Si [wt%]</th>
<th>Al [wt%]</th>
<th>Fe [wt%]</th>
<th>Mg [wt%]</th>
<th>Ca [wt%]</th>
<th>K [wt%]</th>
<th>Na [wt%]</th>
<th>Ti [wt%]</th>
<th>BET specific surface [m²/g]</th>
<th>Average pore diameter [Å]</th>
<th>Pore volume [cc/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.8</td>
<td>8.7</td>
<td>2.1</td>
<td>1.8</td>
<td>0.60</td>
<td>0.33</td>
<td>0.18</td>
<td>0.15</td>
<td>106</td>
<td>125.0</td>
<td>0.34</td>
</tr>
</tbody>
</table>

MCB removal experiment was performed using a lab scale of equipment. Temperature of diffusion tube containing MCB in Permeater™ (PD-1B, GASTEC Co.) was adjusted at 40°C and flow rate of pure air was set to 500mL/min to generate MCB standard gas in concentration of 0.08-0.55mg/L. Temperature of reactor (size: ø18mm x 80mm) with 5g of #400+metal compound was maintained at 300°C and then MCB gas was injected to reactor for 40 min. To confirm the input and output MCB mass, MCB gas was absorbed by n-hexane solution at an interval of 10 min. MCB concentration was measured by GC-FID (GC-14B, Shimadzu Co.). MCB removal rate (η) was calculated using a following equation, \[ η(\%) = \left(1 - \frac{m_{\text{out}}}{m_{\text{in}}}\right) \times 100 \] where \( m_{\text{in}} \): MCB input mass (mg) and \( m_{\text{out}} \): MCB output mass (mg).

When MCB removal experiment finished, #400+metal compound in reactor was entirely collected to extract chloride ion and organic compound from it using a simultaneous ultrasonic-assisted extraction method. 50ml distilled water and 50ml n-hexane was used as extraction solvent and extraction time was 40 min. After solid-liquid separation, distilled water and n-hexane was collected separately to analyze chloride ion and organochlorine compounds including MCB respectively. The concentration of chloride ion in each solution was measured by anion chromatography (AS-8020, TOSOH Co.). Organochlorine compounds were analyzed by GC/MS (GC: HP 7890 series; MS: JEOL JMS-T100GCv).

From the result of MCB removal experiment, MCB detected in n-hexane solution at outlet of reactor was determined as “unreacted one”. While chloride detected in distilled water obtained by simultaneous ultrasonic-assisted...
extraction of metal compound added #400 was determined as “dechlorinated MCB”, MCB extracted in hexane solution was determined as “adsorbed one”.

3. Results and discussion
3.1 MCB removal rate depending on additive types

Figure 1 shows the input and output of MCB mass and MCB removal rate per ten minutes at 300°C depending on the types of metal compound additives. Each metal compound was added to #400 by 5wt%. MCB removal rates were similar levels or increased comparing to that of #400 without metal compound addition (Fig.1a). In particular, MCB was almost not detected for copper addition (Fig.1g). MCB removal rates for sodium bicarbonate and calcium oxide additions were higher than that of #400 without metal compound addition too. However, if the adsorption got involved in MCB removal, MCB removal rate might increase as its concentration increased. As shown in Fig. 1b and Fig. 1d, input mass of MCB were about 40% higher than other runs. Thus, it could not be excluded the possibility of increase of MCB removal rate by higher input concentration of MCB for above two cases.

Fig.1 Input and output of MCB mass and MCB removal rate per ten minutes at 300°C depending on the types of metal compound (addition ratio: 5wt%)

3.2 Confirmation of MCB dechlorination by ultrasound-assisted extraction of #400+metal compound

Simultaneous ultrasound-assisted extraction of #400 was performed as a blank test. As a result, 31.5±12.7μg-Cl/g was determined as chloride content of #400 and was reflected to estimation of dechlorination amount of MCB in each experiment. Figure 2 shows the mass balance of MCB removal experiment at 300°C. There was some difference between MCB input mass and sum of dechlorinated, adsorbed, and unreacted MCB. According to GC/MS spectrums of n-hexane solution in absorption bottles (as “unreacted MBC”) and extract solution of #400+metal compound, there was no organochlorine compound except for MCB. Therefore, the difference between two values might be caused by fluctuation of input MCB mass and some loss of unreacted MCB. Comparing to the dechlorination amount of #400