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The influence of flue gas components and activated carbon injection on mercury capture of municipal solid waste incineration in China

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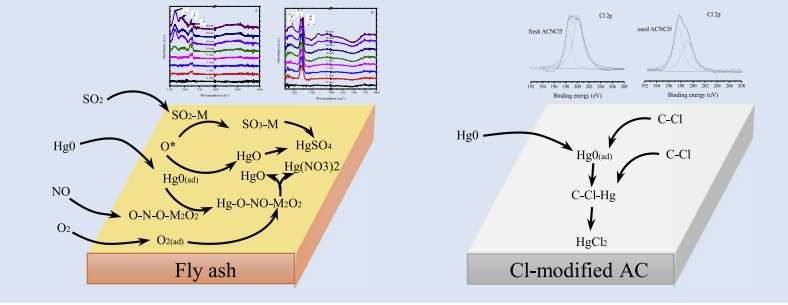
HIGHLIGHTS

- The SO_2 can form effective group SO_3-M on Lewis acid site.
- The NO addition forms NO_2-M group oxidizing Hg^0 into HgO and $Hg(NO_3)_2$.
- The HCl addition fails to promote mercury removal.
- The Cl-modified AC performs excellent mercury capture ability in various flue gases.
- Cl-modified AC is recommended to be the optimal method for mercury removal.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the influence of flue gas components and original/modified activated carbon (AC) injection on mercury removal to obtain a suitable mercury removal method for typical municipal solid waste (MSW) incineration plants in China. The field test was conducted to research the mercury emission characteristics of a typical plant. The result shows that the mercury concentration of before and after air pollution control devices (APCDs) is 91.28 ± 47.98 and 25.67 ± 18.13 μg m^{-3}, respectively, and the average mercury removal efficiency is 71.9%. Based on actual APCDs condition, the flue gas components (O_2, SO_2, HCl and NO), fly ash, activated carbon and NH_4Cl-modfied AC were used to further remove the mercury of flue gas. The O_2 and HCl slightly promoted mercury removal while the SO_2 and NO addition decreased mercury concentration from 50 μg m^{-3} to 35.8 and 13.7 μg m^{-3}, respectively. The increase of AC injection amount failed to decrease emission concentration to desired value and imposed heavy financial burden to plants. The method of 2.5 wt% Cl-modified AC addition reduced mercury concentration to below 5 μg m^{-3} in various flue gas condition and did not need to change any existing APCDs or operating parameters, which was considered as the optimal method for mercury removal in MSW incineration. Reaction mechanism of SO_2, NO and Cl-modified AC was explored by TPD, XPS and *in situ* Diffuse Reflectance Fourier Transform (DRIFT). The SO_2 and NO formed effective active groups of SO_3-M and NO_2-M, and their reaction mechanism follows Langmiur-Hinshelwood mechanism and Eley–Rideal mechanism, respectively. The Cl modification effectiveness was ascribed to C-Cl group formation.

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1. Introduction

The pollution of mercury, in both inorganic and organic forms, is an important public health and environmental concern due to its persistent, toxic and bioaccumulative properties [1]. The mercury emission reduction from various anthropogenic sources is increasingly attracting public attention. Municipal solid waste (MSW) incineration is one of the five major mercury emission sources in Minamata Convention [2]. In China, annual growth rate of burning capacity is 23.5% in 2008–2013 and 20–30% of MSW was treated by incineration [3]. The capacity increase of MSW incineration possibly enhanced the mercury emission. The incineration temperature can reach 850–1200 °C, at which the mercury all releases into gas phase in the form of Hg^0. The gas mercury was captured via subsequent APCDs. In China, the typical MSW incineration plants use the APCDs combination: a dry/semidry scrubbing system for removing acidic gases, an activated carbon injection system for capturing dioxins, and a fabric bag filter. This APCDs combination shows over 60% mercury removal efficiency [4,5]. According to previous studies, the average mercury concentration of stack outlet was at the range of 9.5–26.4 $\mu g\,g^{-1}$ in the MSW incineration plants of Guangzhou, Chongqing, and Wuhu [6], which is far higher than 0.05–4.56 $\mu g\,m^{-3}$ in Japan [7], 1.96–4.71 $\mu g\,m^{-3}$ in Korea [8] and 3.7 $\mu g\,m^{-3}$ in US [9]. Moreover, individual monitoring data of some MSW incineration plants was very unstable and varied in the range of 8.7–133.6 $\mu g\,g^{-1}$ [10]. This result indicates that it is necessary to further investigate more stable pollution control methods for mercury capture.

With a view to the fact that the APCDs transformation and upgrading needs high fees, reducing mercury emission via slightly operational adjustment under the condition of existing equipments will be better accepted by MSW incineration plants. The increase of the oxidable components of incineration flue gases, such HCl, SO_2 and NO, is a commonly applied method [11]. Nishitani's study indicated that the proportion of $HgCl_2$ to total Hg increased with the increasing of HCl concentration [12]. The study of Wang also showed that the HCl addition improved the mercury removal performance of coal-fired fly ash [13]. The NO can transform into NO_2 and then oxidize Hg^0 into bivalent mercury [14–16]. The Hg^{2+} was easier to remove by the wet flue gas desulfurization devices (WFGDs). Previous studies suggested that the presence of SO_2 and O_2 in the flue gas led to mercury oxidation and adsorption on the sorbents or fly ash [17–20]. The objects of these studies are coal-fired flue gases and fly ash while few studies focus on the mercury emission reduction of MSW incineration. Compared with coal-fired plant, the APCDs of MSW incineration do not contain WFGDs in China, thus the mercury removal efficiency of APCDs in MSW incineration was possibly not as effective as in coal-fired incineration. Moreover, the flue gas of MSW incineration includes higher HCl content and thus the fly ash usually included higher Cl content (20%) [21,22], so the HCl addition possibly fails to effectively promote mercury removal as coal-fired flue gas. It is necessary to research whether the elemental mercury can be oxidized by acidic gases and then captured on fly ash or AC.

Another effective method of mercury abatement is activated carbon (AC) injection. Though AC was wildly used to clean flue gas of MSW incineration, few plants take mercury emission control into consideration in the processing of AC injection [23,24]. It is necessary to investigate the relation between AC injection amount and mercury abatement effectiveness. In addition, the modified reagents shows great promotional effect on the removal efficiency of AC in coal-fired flue gas, such as sulfur, halogen, etc. [25,26]. Ie' s study showed that the sulfur-impregnated AC had great performance for $HgCl_2$ removal via simulation experiment of MSW incineration flue gas [27]. But this study failed to consider the AC injection amount and the influence of acidic gas and fly ash. In our previous study, the NH_4Cl modification greatly promoted the mercury adsorption capacity of sorbents and the acidic gases were also beneficial to the mercury removal [15,28]. The NO, SO_2 and HCl have high content in flue gas of MSW incineration, hence the Cl-impregnated AC is possibly suitable to mercury removal in MSW incineration industry.

This study investigated the influence of flue gas components and original/modified AC injection on mercury removal to find a stable mercury controling method in existing APCDs of typical MSW incineration in China. In order to reflect mercury emission characteristics, this study conducted field test to the mercury concentration of a typical MSW incineration plant in China. Meanwhile, the fly ash and AC were sampled for further simulation experiments of mercury removal. According to the actual component of flue gas, the effect of O_2, HCl, NO and SO_2 was investigated on the mercury removal. Moreover, the effect of AC injection amount and NH_4Cl-modified AC is also investigated on the mercury capture. The influence mechanism of acidic gases and AC was illustrated via TPD, *in situ DRIFT* and XPS analysis.

2. Material and methods

2.1. Field test

Field test was conducted on a 550 $t{\cdot}d^{-1}$ incineration line in a Chinese MSW incineration plant, which is located in Fujian Province. The air pollution control devices of flue gases contain: activated carbon injection, dry/semidry scrubbing system and fabric filter. This is a typical device combination and its installing percent is over 90% in Chinese MSW incineration plants. The detailed description of the tested plant, sampling procedures, analysis methods, quality assurance and quality control (QA/QC) were presented in the Supporting Information. The flue gases before and after pollution control facilities were sampled and analyzed with the Ontario Hydro Method (OH method) [29]. The solid samples (fly ash, activated carbon) were also sampled simultaneously with the flue gas samples.

2.2. Solid sample preparation

This study contains four solid samples: original fly ash (FA), heated fly ash (FAH), original activated carbon (AC) and modified activated carbon (ACNCl5). The samples were prepared as follows:

In order to remove adsorbed mercury on fly ash, the fly ash sampled in 2.1 was heated to 850 °C and remained for 1 h. The original and heated fly ashes were denoted as FA and FAH, respectively.

The original activated carbon sampled in 2.1 was mixed with 1 wt% NH_4Cl solution in a ratio of 1 g: 5 ml. The mixture was stirred for 12 h and then dried at a water bath at 80 °C until the water vanished. The mixture was further dried at an oven for 12 h at 105 °C. The original and modified activated carbons were denoted as AC and ACNCl5, respectively.

2.3. Characterization techniques

The proximate analysis of fly ash and AC was measured according to the method of GB/T212-2008. The ultimate analysis of fly ash and AC was measured by Elementar EA3000 (LEEMAN, China) and X-ray diffraction (XRD). The scanning electron microscope (SEM) was used to measure the surface image of fly ash by ProX (Phenom, Netherlands). The element (Cl, N, O, S and Hg) valence state was analyzed by X-ray photoelectron spectroscopy (XPS) by