Removal Elemental Mercury from Simulated Syn-Gas over Manganese-based Absorbents

H. W. Cheng, Y. S Lin, and C. T. Yu

Abstract—In this study, a layered carbonate sorbent was prepared by manganese metal and anions with co-precipitation method. There CO, CO$_2$, H$_2$, and CH$_4$ gases were mixed within 48.5ppb concentration elemental mercury and used as simulated syn-gas. The mercury removal sorbent was tested in a fixed reactor operation in simulated syn-gas environment. To understand the effects of different temperatures on the removal of elemental mercury, a thermal adsorption test was performed to observe the effect of different temperatures on removal effect. The study found that the Mn-based absorbent performed best efficiency at 100°C and still remained 98.3% removal rate after continuous eight hours, which was higher than 83.6% of the adsorption capacity at 25°C. With the increase of adsorption temperature, mercury removal rate has an increasing trend. However, when the temperature rises above 200°C, the reducing gas such as CO, H$_2$ in the simulated gas may react with the manganese metal on the surface of the material to reduce the oxidizing ability of the mercury removal agent for elemental mercury, thereby affecting the mercury removal amount.

Index Terms—Elemental mercury removal, syn-gas, Mn-based absorbents.

I. INTRODUCTION

Mercury as a major heavy metal contaminant has attracted globally attention and was present in most fossil fuels such as coal naturally. The recent research has found that most of mercury generated from coal combustion remains in flue gas and ash for approximately 39% and 42%, respectively [1]. The mercury emission from the combustion of fossil fuel is one of the most serious environmental problems and a huge risk to human health because of its bio-accumulation. The U.S. Environmental Protection Agency (EPA) updated the emission limits of mercury and other toxic gas pollution for new power plants under the Mercury and Air Toxics Standards (MATS) on March 28, 2013, and the mercury emission limit for the new power plants and new integrated gasification combined cycle (IGCC) units was 0.003 lb/MWh [2]. Otherwise, the EU has also made progress to decrease 4.5% gasification new power plants under the Mercury and Air Toxics emission limits of mercury and other toxic gas pollution for U.S. Environmental Protection Agency (EPA) updated the coal naturally. The recent research has found that most of risk to human health because of its bio-accumulation. The one of the most serious environmental problems and a huge Mn-based absorbents.

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Al(NO₃)₃·9H₂O, NaOH and Na₂CO₃ was purchased from Merck Chemical Co. LTD. The Mn–Al powder was prepared by co-precipitating method with Mn(NO₃)₂·4H₂O and Al(NO₃)₃·9H₂O in an alkaline NaOH/Na₂CO₃ solution that contains 0.3 mole Mn²⁺ and 0.1 mole Al¹³⁺ in deionized H₂O treated with 0.2 mole NaOH and 0.05 mole Na₂CO₃. The mixtures were stirred to mix the acidic solutions with the alkaline solution at constant pH to form precipitates of Mn–Al for 8 h after dried and processed through solid-liquid separation. The mixtures were then dried in an oven for 8 h at 110 °C. The product was denoted as Mn–Al layered carbonate.

B. Mercury Removal Test Apparatus

Mercury removal test apparatus was built specifically for measuring mercury concentration from fix-bed reactor. The testing reactor contains of a 2.5cm-diameter quartz reactor tube that has a carrier plate of 200 mesh aperture to support powders. A 1kW single-stage furnace chamber surrounding the reactor is used to provide the heat. The synthetic flue gas contains gases that mix with CO, CO₂, CH₄, and H₂. Mercury was introduced using permeation tubes (VICI Inc., CA) by blending trace amounts of mercury into the synthetic flue gas. Hg⁰ is immersed in a temperatures-controlled permeation oven and the inlet Hg⁰ concentration was set at 60 ppb and the total flow rate was controlled at 0.1 L/min. 1 gram of the prepared sorbent was well mixed with 4g quartz sand and the bed height of sorbent/sand mixture was about 1cm. The Hg⁰ concentration at the outlet of the reactor bed was continuously monitored with an on-line mercury analyzer (EMP-2, Nippon Instrument Corporation, Japan). Fig. 1 shows the schematic of the test apparatus.

With the temperature-controlled mercury removal analysis system at the end of the adsorption fix-bed reactor, the breakthrough curve of mercury removal can be obtained immediately and the residual gas concentration data can be calculated.

![Fig. 1. Schematic of the experimental apparatus.](image)

The mercury concentration and mercury removal ratio were calculated according to the Eq. (1)(2) below:

\[
W_t = \int_t^\infty (C_0 - C(t)) \times V \times dt \tag{2}
\]

C. Characterization of Sorbents

The samples were scanned by X-ray powder diffraction (XRD) analysis (D8advance, Bruker, USA) to understand the crystal phase structure. The information of elemental composition of sorbents was measured by XRF spectroscopy (MES-50, Horiba, Japan) and the surface property was determined using a Micrometerics ASAP 2020 N₂ adsorption apparatus.

III. RESULTS

A. Characterization of Sorbents

The XRD pattern is shown in Fig. 2 below. There are both MnO₂ and Mn₂O₃ were detected on the surface of Mn–Al layered carbonate. Fig. 3 shows an SEM image of a Mn–Al layered carbonate, which is sticky-like at a magnification of 5000 times. After being magnified to 10,000 times, the agglomerated particle size is approximately 5–10 µm. The surface area of Mn–Al layered carbonate is mesoporous size distribution and pore characteristics are shown in Table II. The crystalline and non-porous characterization of Mn–Al is clearly observed as having higher surface areas and pore volumes than Mn₂O₃. The concentration of Mn, Al was measured by XRF in Table III.

![Fig. 2. XRD patterns of the samples.](image)

![Fig. 3. SEM image of a Mn–Al layered carbonate.](image)

**TABLE II: BET ANALYSIS OF SORBENTS**

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Surface area (m²/g) (Multi-BET)</th>
<th>Pore volume (c.c/g) (BJH)</th>
<th>Pore radius Dv(1) (BJH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>6.05</td>
<td>0.008</td>
<td>15.523 Å</td>
</tr>
<tr>
<td>Mn-Al</td>
<td>24.86</td>
<td>0.039</td>
<td>19.235 Å</td>
</tr>
</tbody>
</table>

**TABLE III: XRF ANALYSIS OF SORBENTS**

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>MnO₂ (%)</th>
<th>Al₂O₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>99.98</td>
<td>0.008</td>
</tr>
<tr>
<td>Mn-Al</td>
<td>85.10</td>
<td>14.89</td>
</tr>
</tbody>
</table>

B. Effect of Temperature and Atmosphere on Removal of Hg

With the temperature-controlled mercury generation source analysis system, the breakthrough curve of mercury removal can be obtained and get the residual gas concentration data immediately.
Equilibrium mercury adsorption equivalent (μg Hg adsorbed/g adsorbent) were determined by summing the mass of mercury removed from the gas stream based on the acquired breakthrough curves.

As shown in Fig. 4, the results clearly demonstrated that Mn-Al 3:1 was effective than MnO for elemental mercury removal at 200°C. The mercury removal rate of MnO dramatically declined to 50% comparing with 100% of Mn-Al. Furthermore, Mn-Al can still maintain a removal rate of more than 90% after 6 hours continuous experiment.

In Fig. 5, the phenomenon of mercury adsorption equivalent of manganese-based absorbents is reported to increase progressively as the temperature increases from 25 to 300°C, and decrease at higher temperature. Temperature of adsorption is a critical parameter and has a significant impact on the adsorption of elemental mercury removal efficiency. Manganese-based absorbents showed a best mercury adsorption equivalent 247μg /g in 300°C.

The influence of temperature on the adsorption efficiency of the manganese-based absorbents was studied at temperature 25-300°C and with flowing Hg content as 48.5ppb. The testing results of mercury removal on different atmosphere were showed in Fig. 6. When the temperature was increased to 200 and 300°C, the Hg removal efficiency remain to nearly 100% at N₂. As shown in Figure 5, with ratio of syn-gas increasing, adsorption capacity of Mn–Al absorbent samples decreased dramatically. The capacity of Mn–Al absorbent has dropped 53-60% with ratio of syn-gas increasing from 10% to 20% at 300°C.

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IV. CONCLUSIONS

The study found that the Mn–Al absorbent after metal modification performed best at 200°C and still had 98.3% of the adsorption capacity after eight hours, which was higher than 83.6% of the adsorption capacity at 25°C. With the increase of adsorption temperature, mercury removal rate has an increasing trend. However, when the temperature rises above 200°C, the reducing gas such as CO, H₂ in the simulated gas may react with the manganese metal on the surface of the material to reduce the oxidizing ability of the mercury removal agent for elemental mercury, thereby affecting the mercury removal amount.

Compared with precious metal absorbents, the Mn–Al absorbent can reduce the cost of synthesis and achieve the
purpose of improving the working temperature and the removal efficiency. This research may contribute immediate use for mercury removal in coal and cement industry to meet mercury regulations.

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REFERENCES


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