

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, CO₂, H₂, and CH₄ 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 adsorbent 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, 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.

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% to global mercury emissions to air in 2010 (AMAP/UNEP, 2013) [3]. It can be noted that effective technologies to govern mercury emission from coal-fired power plants require to be developed.

Hg compounds from coal combustion sources mainly consist of gaseous elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particular mercury (Hg_p). The methods to remove gas-phase mercury mostly in common are using existing electrostatic precipitator (ESP), wet flue gas

desulfurization (WFGD) facilities and activated carbon injection [4]. By way of these removal technologies can effectively remove Hg²⁺ or Hg_p in flue gas but ineffective in capturing Hg⁰ [5]. For this reason in the mercury removal studies, there have been lots of discuss on the elementary mercury removal.

Activated carbon is commercially available for industrial desulfurization, and it has been reported to be effective for removal of Hg⁰ from flue gas at temperatures below 200 °C. However, the major drawbacks of activated carbons are high costs and narrow operation temperature range [6]. To overcome these shortcomings, it has been reported that activated carbon impregnated with some metal oxides and some novel metal or metal oxides was effective for Hg⁰ removal [7].

Many precious metal and metal oxides had been used to capture mercury such as Au, Ag, V₂O₅, MnO₂, etc. They could serve as the oxidant of mercury to oxidize elemental mercury, thereby affecting the mercury removal amount. A comparison of cost and removal capacity of potential sorbents is given in Table I [8].

Therefore manganese oxides as well as ceria have been studied extensively and proven to be good catalysts for Hg⁰ catalytic oxidation and there are limitations on the use of temperature [9], [10]. A novel material layered double hydroxides (LDHs) are a class of synthetic anionic clays which were containing layer-like structure there some of the divalent cations have been replaced by trivalent ions, giving positively charged plates [11]. The manganese aluminum layered hydrates are often used as adsorbents for heavy metals in wastewater due to their excellent ion exchange properties in the study of pollutants removal [12], but they are rarely mentioned in the removal of mercury. This study will introduce novel layer manganese aluminium mercury sorbent with developed and testing process in a lab-scale fixed-bed system.

TABLE I: SORBENT COST

Sorbent	Cost, \$ per ton	Capacity (10 ⁻⁶ g Hg/g)
Au	10,000,000	1 - 10 (on thin films)
Ag	145,000	1 (on thin films)
V ₂ O ₅	12,000	
PAC	3,000	50 - 17,000
AC	1,000	1 - 50
MnO ₂	250	200

II. EXPERIMENTAL

A. Sorbent Synthesis

LDH materials are traditionally synthesized by co-precipitation reactions from aqueous solution. The commercial guarantee reagent Mn(NO₃)₂·4H₂O,

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$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaOH and Na_2CO_3 was purchased from Merck Chemical Co. LTD. The Mn–Al powder was prepared by co-precipitating method with $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in an alkaline NaOH/ Na_2CO_3 solution that contains 0.3 mole Mn^{2+} and 0.1 mole Al^{3+} in deionized H_2O treated with 0.2 mole NaOH and 0.05 mole Na_2CO_3 . 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, CO_2 , CH_4 and H_2 . Mercury was introduced using permeation tubes (VICI Inc., CA) by blending trace amounts of mercury into the synthetic flue gas. Hg^0 is immersed in a temperatures-controlled permeation oven and the inlet Hg^0 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 Hg^0 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.

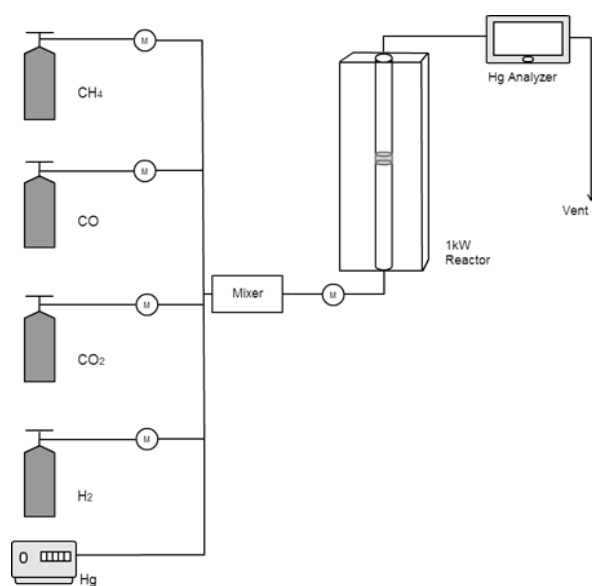


Fig. 1. Schematic of the experimental apparatus.

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

$$\text{Hg capacity (E)} = (C_0 - C_i) / C_0 \times 100\% \quad (1)$$

$$W_{\text{Hg}} = \int_0^t (C_0 - C_i) \times V \times t \quad (2)$$

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 (MESA-50, Horiba, Japan) and the surface property was analyzed by scanning electron microscope (SEM, S-4800, Hitachi, Japan). The pore size distribution and Brunauer-Emmett-Teller (BET) surface area were determined using a Micromeritics ASAP 2020 N_2 adsorption apparatus.

III. RESULTS

A. Characterization of Sorbents

The XRD pattern is shown in Fig. 2 below. There are both Mn_3O_4 and Mn_2O_3 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 Mn_2O_3 . The concentration of Mn, Al was measured by XRF in Table III.

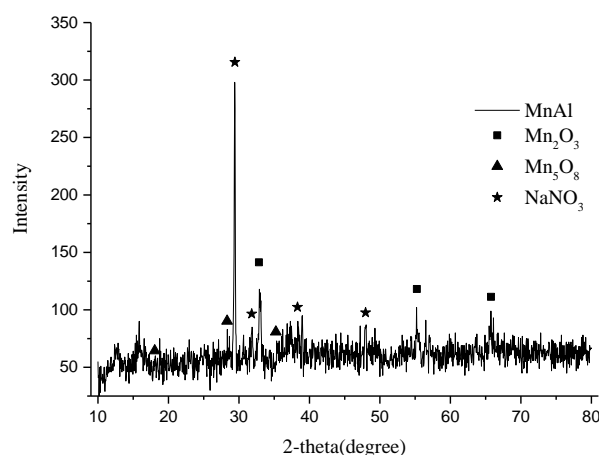


Fig. 2. XRD patterns of the samples.

TABLE II: BET ANALYSIS OF SORBENTS

Sorbents	Surface area (m^2/g) (Multi-BET)	Pore volume (c.c/g) (BJH)	Pore radius Dv(r) (BJH)
Mn_2O_3	6.05	0.008	15.523 Å
Mn-Al	24.86	0.039	19.235 Å

TABLE III: XRF ANALYSIS OF SORBENTS

Sorbents	Mn_2O_3 (%)	Al_2O_3 (%)
Mn_2O_3	99.98	0.008
Mn-Al	85.10	14.89

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.

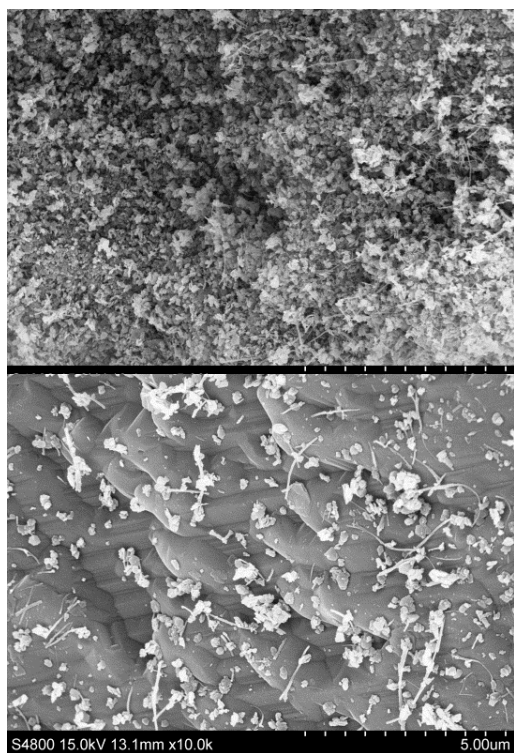


Fig. 3 SEM images of the sorbents.

Equilibrium mercury adsorption equivalent ($\mu\text{g Hg}$ 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.

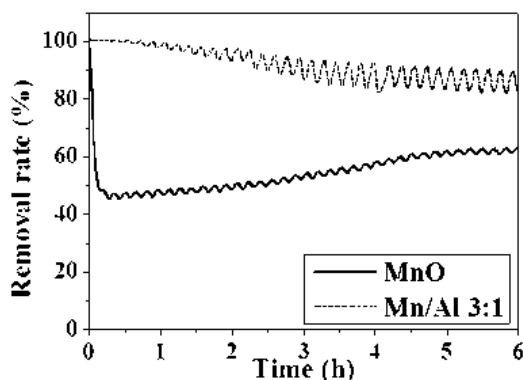


Fig. 4 Mercury adsorption by MnO and Mn-Al at 200°C.

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 247 $\mu\text{g/g}$ in 300 °C .

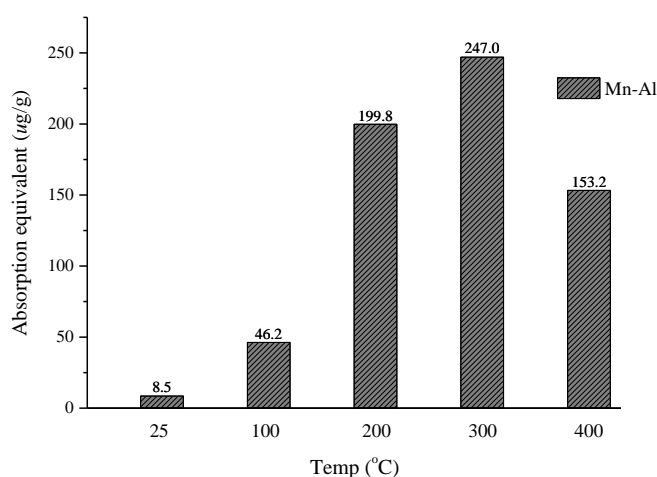


Fig. 5 Mercury adsorption equivalent at 25-400°C.

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.

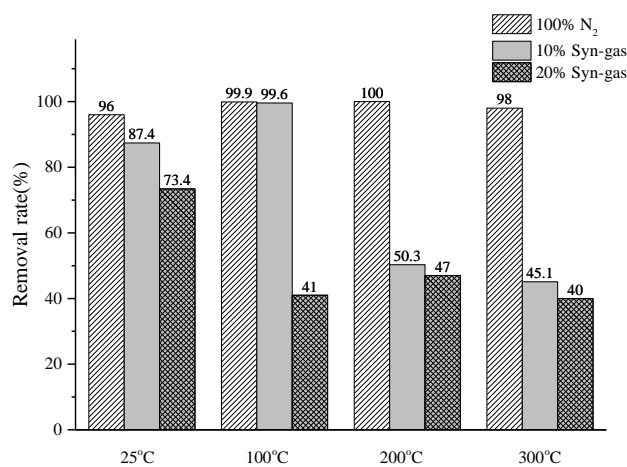


Fig. 6. Mercury removal rate at 25-300°C and 0-20% syn-gas.

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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