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Removal of Gas-Phase Elemental Mercury in Flue Gas by Inorganic Chemically Promoted Natural Mineral Sorbents

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ABSTRACT: A variety of natural mineral sorbents were synthesized and tested on a lab-scale fixed-bed system to evaluate mercury removal efficiencies under a simulated flue gas condition that contains 84% N₂, 4% O₂, and 12% CO₂ in volume fraction. Three types of natural minerals, bentonite (Ben), mordenite (Mor), and attapulgite (Atp), were selected as raw sorbents, and several chemical promoters, such as CuCl₂, NaClO₃, KBr, and KI, were employed to enhance mercury removal abilities of the raw sorbents. The physical-chemical characteristics of these minerals were analyzed by an X-ray diffractometer (XRD), an accelerated surface area and porosimeter (ASAP) using the N₂ isotherm adsorption/desorption method, and X-ray fluorescence (XRF) spectrometry. The mercury concentration was detected continuously using a VM3000 online mercury analyzer. The results showed that CuCl₂-impregnated Atp (Cu-Atp) and CuCl₂-impregnated Ben (Cu-Ben) presented about 90% average Hg⁰ removal efficiencies at 120 °C, respectively. In addition, as the temperature increased, the removal efficiencies decreased. Although NaClO₃-impregnated Atp showed an average Hg⁰ removal efficiency more than 90% at 120 °C, its performance was limited by the testing temperature, and that was probably due to the high iron oxide content in Atp. For the KI-impregnated sorbents, high mercury removal efficiencies could be observed, and the efficiencies increased steadily with the temperature increased from 70 to 150 °C. The three natural minerals presented poor adsorption abilities for bromine, which resulted in the disappointing mercury removal efficiencies. Generally, Cu-Atp, Cu-Ben, and KI-impregnated sorbents were promising cost-effective mercury sorbents.

1. INTRODUCTION

Mercury (Hg) is a toxic heavy metal because of its bioaccumulation as methylmercury in the environment and its neurological health impacts.¹ Meanwhile, it has a long atmospheric residence time in a range 0.5–2 years due to its volatility.² These properties make mercury pollution being a global problem.

Increasing attention has been paid on the mercury pollution problem in China because of the considerable amount of mercury emissions.^{3,4} The studies^{5,6} on mercury emissions and transfer have been carried out to evaluate the effect of mercury pollution on environment and biology in China. The total atmospheric mercury emission amount in China is estimated to be 536 tons, and approximately 38% comes from coal combustion.⁷ Obviously, coal-fired power plants are one of the largest anthropogenic sources of mercury emissions. Moreover, coal is and will be the main energy source in China. Resultant huge amounts of coal consumption will result in serious environmental problems relating to mercury. Therefore, it is necessary to control the mercury emissions from coal-fired power plants. On December 21, 2011, the U.S. Environmental Protection Agency (EPA) issued the national standard *Mercury and Air Toxics Standards* to limit mercury, acid gases, and other toxic pollution from power plants.⁸ The standard will reduce mercury pollution from coal-fired power plants by 90%. The State Environmental Protection Administration of China (SEPA) also published the *Emission Standard of Air Pollutants for Thermal Power Plants* to limit mercury emissions from coal-fired power plants in 2011. The mercury emission limit in that standard was 0.03 mg·m⁻³.⁹

There are three species of mercury existing in the flue gases from coal combustion: elemental mercury (Hg⁰), oxidized mercury (Hg²⁺), and particulate mercury (Hg^p).^{10,11} Hg²⁺ and Hg^p could be effectively removed by existing pollutant control devices such as fabric filters (FF), electrostatic precipitator (ESP), and flue gas desulfurization (FGD). However, it is very difficult to capture Hg⁰ directly from the flue gases due to its higher volatility, and also the insolubility in water.¹² Therefore, the key point of the mercury removal technology is the Hg⁰ emission control.

Sorbent injection is applicable for mercury emission control, and activated carbons (ACs) are available as a kind of sorbent. However, the mercury removal performances for virgin ACs are limited.¹³ To enhance mercury removal ability and reduce the sorbents consumption, various chemical promoters were adopted for ACs modification. Yan et al. evaluated a variety of S-impregnated carbons, and the results showed that S-impregnated carbons performed better than nonimpregnated carbons.¹⁰ Metal oxide-loaded activated carbons were also estimated, which showed a promising performance in mercury removal.¹⁴ It has been reported that chlorine (Cl) treated AC had great ability of capturing Hg in flue gases.^{15,16} Besides chlorine, bromine (Br) and iodine (I) were also demonstrated to enhance Hg⁰ oxidation and capture.^{13,17–19} However, although chemically promoted ACs exhibit significant Hg control potential, their application and development are limited by

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the following two reasons: On one hand, the high price of activated carbons and a huge amount of sorbent demanded by coal-fired power plants result in a huge cost for mercury control. On the other hand, the application of carbon-based sorbents increases the carbon content in fly ash and affects the utilization of fly ash in cement production. The cost of brominated carbon for Hg emission control was estimated at \$6060–17700 per pound of Hg removal with a target of 90% Hg removal efficiency. If the byproduct impact was taken into consideration, the cost would increase by nearly three times.²⁰

Noncarbon sorbents were widely evaluated for mercury emission control,^{21–25} and some of them displayed high mercury removal efficiencies. It is reported that clay sorbents could be much cheaper in comparison to a number of common adsorbents, which include commercial activated carbon.²⁶ A variety of natural mineral sorbents, such as sepiolite,²⁷ mordenite,²⁸ zeolite,^{29,30} bentonite,³⁰ and their chemically promoted sorbents, have been estimated as a comparison reference to activated carbons. The results showed that raw mordenite had an initial adsorption rate of 3900 ng/h at the point of 0.5 h, which was comparable to the property of the activated carbon in removing Hg from flue gases. Sulfur-impregnated sepiolite and zeolite treated with a proprietary agent presented significant performances in mercury capture. In addition, the raw zeolite and bentonite gave a removal efficiency of about 50%, and no visible difference was observed between raw and sulfur-impregnated sorbents. Montmorillonite K 10 clay (MK10) is a nano-adsorbent that is produced from bentonite. CuCl₂-MK10 showed an excellent Hg⁰ oxidation capability,³¹ and sodium polysulfide (Na₂S_n)-doped MK10 presented 93% Hg removal efficiency at 70 °C despite its poor capacity at 140 °C.²¹ A type of novel regenerable mercury sorbents was synthesized using natural chabazite as substrate material, and it presented complete mercury capture ability at temperatures up to 200 °C.^{32–34}

In this study, several cost-effective noncarbon sorbents were synthesized and evaluated under a simulated flue gas condition using a lab-scale fixed-bed system. Three types of natural minerals, bentonite (Ben), mordenite (Mor), and attapulgite (Atp), were selected as raw sorbents. Among the minerals, Atp was first used in mercury emission control because of its considerable surface area and good performance in sewage treatment. Several chemical promoters that have demonstrated good affinities to mercury were employed to enhance mercury removal abilities of sorbents. The primary objective of this study is to make a preliminary evaluation and selection on a wide range of chemically promoted mineral sorbents. Moreover, the effects of temperature on the sorbent properties were also studied.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Three natural minerals were directly exploited from Jinhua (Mor), Yuhang (Ben), and Huaiyuan (Atp). Copper chloride dihydrate (CuCl₂·2H₂O), sodium chlorate (NaClO₃), potassium iodide (KI), potassium bromide (KBr), and acetone used in this study were analytical grade.

The raw sorbents were prepared by milling the natural minerals to less than 300 mesh and subsequently drying in an oven at 100 °C to constant weight. The resultant powders were stored in a desiccator for further chemically promoted sorbent synthesis.

CuCl₂-impregnated sorbents were prepared by a method similar to the method used by Lee et al.³¹ 0.25 g copper chloride dihydrate was dissolved in 50 mL acetone under mechanical stirring at the room temperature, and 2 g raw sorbent was added slowly to the solution with continuous stirring for about 2 h. Then, the solvent was filtered out, and the resultant solid was dried to a constant weight at 100 °C. A mass ratio of 0.5 g chemical promoters to 2 g raw sorbents was applied in other sorbents synthesis, and 20 mL deionized water was used as the solvent. After about 5 h stirring, the solvents were filtered out, and the resultant solids were dried at 70 and 120 °C. All of the sorbents were milled to less than 300 mesh and stored in a desiccator for the adsorption experiment. The sorbent details are given in Table 1.

Table 1. Summarization of Chemically Promoted Sorbents Used in the Study

	sorbent abbreviation	raw sorbent	elemental content, wt %
CuCl ₂ -impregnated sorbents	Cu-Atp	attapulgite	1.71/Cu
	Cu-Ben	bentonite	1.82/Cu
	Cu-Mor	mordenite	0.51/Cu
NaClO ₃ -impregnated sorbents	Cl-Atp	attapulgite	4.28/Cl
	Cl-Ben	bentonite	5.06/Cl
	Cl-Mor	mordenite	2.00/Cl
KI-impregnated sorbents	I-Atp	attapulgite	5.96/I
	I-Ben	bentonite	6.56/I
	I-Mor	mordenite	2.53/I
KBr-impregnated sorbents	Br-Atp	attapulgite	0.23/Br
	Br-Ben	bentonite	0.15/Br
	Br-Mor	mordenite	0.13/Br

2.2. Characterization. The natures of raw sorbents were analyzed by an X-ray diffractometer (XRD) (X'Pert PRO, PANalytical B.V., Holland) using Cu K α radiation as X-ray source and an accelerated surface area and porosimeter (ASAP 2020, Micromeritics Instrument Corporation, U.S.A.) using nitrogen (N₂) adsorption–desorption method at 77 K. The elemental component of the sorbents was determined by X-ray fluorescence (XRF) spectrometry using the fluorimeter (EAGLE III, EDAX Inc., U.S.A.).

2.3. Apparatus and Procedures. A lab-scale fixed-bed system was constructed to test a variety of sorbents under a simulated flue gas condition that contained 84% N₂, 4% O₂, and 12% CO₂ in volume fraction. As shown in Figure 1, elemental mercury was generated from a mercury permeation device (VICI Metronics Inc., Santa Clara, CA) and sealed in an U-type glass tube holder, which was placed in a water bath that can maintain the temperature within ± 0.1 °C. A flow of nitrogen gas was supplied as a carrier gas to take the mercury vapor out and finally afforded a constant mercury concentration of 27 ± 2 $\mu\text{g}\cdot\text{m}^{-3}$. The fixed-bed reactor was a U-type quartz tube holder with an inside diameter of 13 mm. The superficial velocity in the empty reactor was 13 cm·s⁻¹ at 23 °C under a total flow rate of 1 L·min⁻¹ used in this study. The reactor was placed in a temperature-controllable oven that could maintain a constant temperature within ± 2 °C. A fritted quartz disk as adsorption bed was placed inside the reactor to prevent the sample from escaping through the bed. The simulated flue gas was preheated using heating tape that was wrapped around the connecting pipe to attain the expected temperature prior to passing through sorbents column placed in the fixed-bed.

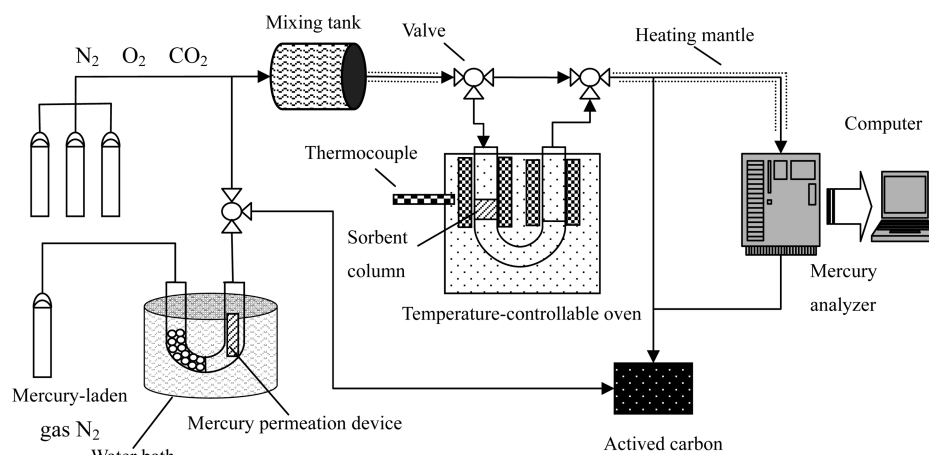


Figure 1. Schematic of a fixed-bed system.

A Teflon-coated thermocouple was inserted into the temperature-controllable oven and contacted with the outside location (sample loading) of reactor to monitor the adsorption temperature. Mercury concentration at the inlet and outlet of the adsorption bed was detected continuously using a VM3000 online mercury analyzer (CEMS, Mercury Instruments Inc., Germany).

In this study, 0.05 g sample was used in each test for Atp, Ben, and their corresponding chemically promoted sorbents, and 0.1 g sample was used for mordenite sorbents to ensure a similar contact time. To examine the effect of temperature, the sorbents were tested at 70 °C, 120 °C, and 150 °C.

During each test, the mercury-laden gas bypassed the empty reactor until the desired mercury concentration was reached. Then, a given mass of sorbent was packed evenly on the bed. After the desired temperature was obtained, the adsorption test began by diverting the simulated flue gas from bypass to the reactor system in downflow mode to avoid fluidization of the sorbent.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Sorbents. Owing to direct exploitation from nature, the three natural mineral sorbents used in this study inevitably contained a small amount of other mineral impurities such as quartz and mica, as shown in Table 2.

Table 2. Components and BET Surface Area of Raw Sorbents

raw sorbents	main component	impurities	BET, m ² ·g ⁻¹
attapulgite	palygorskite	mica, quartz	153.55
bentonite	montmorillonite	cristobalite, quartz	40.89
mordenite	mordenite	clinoptilolite, quartz	6.83

It has been reported that the content of impregnated chemical promoters can affect the mercury removal performance of sorbents.^{16,35} Therefore, it is necessary to evaluate the affinity between the different raw sorbents and the selected chemical promoters used in this study. The adsorption abilities of natural minerals are different and mainly correlate with their structural properties.²⁶ Montmorillonite, as the main component of bentonite, is a layered silicate mineral with expandable layer structure, and a lot of different cations and water molecules exist in the interlayer.²⁶ Similarly, the chemical promoters used in this study may be also adsorbed in the interlayer. Palygorskite is the main component of attapulgite, which

is a type of crystalline hydrated magnesium silicate with the 2:1 layer structure and presents a lath or fibrous morphology. The continuous dimensional tetrahedral sheets alternate with each other. The magnesium containing octahedral layers are discontinuous and sandwiched between tetrahedral sheets to form channels along the fiber axis. These octahedral layers with available charge imbalance are beneficial for the adsorption of various ions.^{36,37} The structure of mordenite is nonswelling. The assemblage of 12-membered rings and 8-membered rings form two different types of pore channels and void systems, respectively. It is used to concentrate the metal ions.³⁸ Therefore, the promoters used in the study could be effectively adsorbed on the mineral surface and maintained under a stable state for a long time.

The typical elemental contents of different sorbents were analyzed by using an X-ray fluorescence, and the results are shown in Table 1. In general, attapulgite and bentonite showed better performance in chemical promoter adsorption among these three raw sorbents, and this may be correlated with their particular layered structure and larger BET surface areas than those of mordenite. In addition, the contents of the chemical promoters in each sorbent also presented a same trend (KI > NaClO₃ > CuCl₂ > KBr).

3.2. Data Processing. It is worth noting that the sorbent residence time after the sorbent is injected into the duct of a coal-fired power plant is just 3–5 s in the electrostatic precipitator and approximately 25 min in the bag filter.³⁹ Therefore, the initial mercury removal performance of sorbent is very important and practically reflects the sorbent application possibility in mercury emission control. In this study, a period of 30 min was selected as a specific time for each test when steady adsorption can be observed. The average Hg⁰ removal efficiency (*q*) in this specific time is defined as a standard to evaluate the mercury removal performance for each sorbent in this study, and the value is calculated using the following equation:

$$q = (1 - Q_t/Q_0) \times 100 \quad (\text{a})$$

where *Q*₀ (ng) and *Q*_{*t*} (ng) are the total amount of mercury in simulated flue gas passing through the inlet and outlet of the reactor in the specific time, respectively. The values of *Q*₀ and *Q*_{*t*} are calculated using the following equations:

$$Q_t = \int_{t_1}^{t_2} C_t F \, dt \quad (\text{b})$$

$$Q_0 = C_0 F (t_2 - t_1) \quad (\text{c})$$

where F ($\text{L}\cdot\text{min}^{-1}$) is volumetric flow rate of the simulated flue gas, C_t and C_0 ($\text{ng}\cdot\text{L}^{-1}$) are the mercury concentrations in simulated flue gas at outlet and inlet of the reactor, respectively, and the difference between t_2 and t_1 is the specific time.

3.3. CuCl_2 -Impregnated Sorbents. Figure 2 displays the comparison of average Hg^0 removal efficiencies between raw

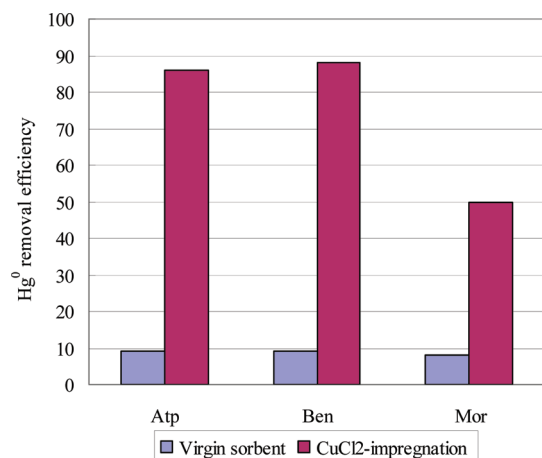
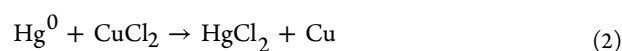
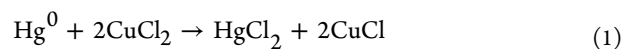


Figure 2. Comparison of average Hg^0 removal efficiency between raw sorbents and CuCl_2 -impregnated sorbents. Experimental temperature is 120 °C.

sorbents and CuCl_2 -impregnated sorbents at 120 °C. The remarkable improvements in average Hg^0 removal efficiencies for the three CuCl_2 -impregnated sorbents were observed, especially for Cu-Ben and Cu-Atp with an increase of approximate 80% over the raw sorbents. Similar results have been reported by Lee et al.^{31,40} In their study, two CuCl_2 -impregnated sorbents (CuCl_2 -clay and CuCl_2 -AC) were examined on a fixed-bed system in comparison to Darco Hg-LH, which is a commercial brominated activated carbon and has demonstrated good performance for mercury removal at full-scale tests. Their results showed that both of the sorbents presented approximate 90% removal efficiency, which was comparable to that of Darco Hg-LH.

Copper chloride was proved to be a promising chemical promoter in terms of mercury emission control. However, Mor had low surface area as compared to Atp and Ben, and it exhibited poor capacity in ionic copper adsorption.⁴¹ Therefore, Cu-Mor had the lowest copper content in the three CuCl_2 -impregnated sorbents under the same synthesis process. The decrease in CuCl_2 loading in sorbent could inhibit Hg^0 removal efficiency.⁴² As a result, Cu-Mor exhibited only 50% Hg^0 removal efficiency. Therefore, the key point of the application of cost-effective CuCl_2 -impregnated sorbents is a proper choice of low-price sorbent material with available CuCl_2 capacity. Obviously, Cu-Atp and Cu-Ben, which were synthesized by natural silicate minerals and have proven significant performances in mercury removal, are potential novel sorbents for mercury emission control.

The possible reaction equations for mercury removal by CuCl_2 -impregnated sorbents are listed as follows:⁴³



The elemental mercury is directly oxidized to gaseous HgCl_2 ,^{31,43} which may be readsorbed by sorbents as a result of their abilities in metal ion adsorption. Even if the resultant HgCl_2 emits to flue gas, it also could be removed simultaneously with SO_2 in a coal-fired power plant equipped with wet scrubbers because of its good water-solubility. In addition, the copper ions in the sorbents tend to migrate and concentrate on the surfaces of sorbents.⁴⁴ This phenomenon may be due to the polarity of aluminosilicates combined with geometrical restrictions of interlayer regions.⁴⁵ The concentration of copper on the surfaces of sorbents might enhance the mercury removal.

The effect of temperature on average Hg^0 removal efficiency for the three CuCl_2 -impregnated sorbents was examined at three different temperatures, and the results are given in Figure 3. It is obvious that the average Hg^0 removal efficiency

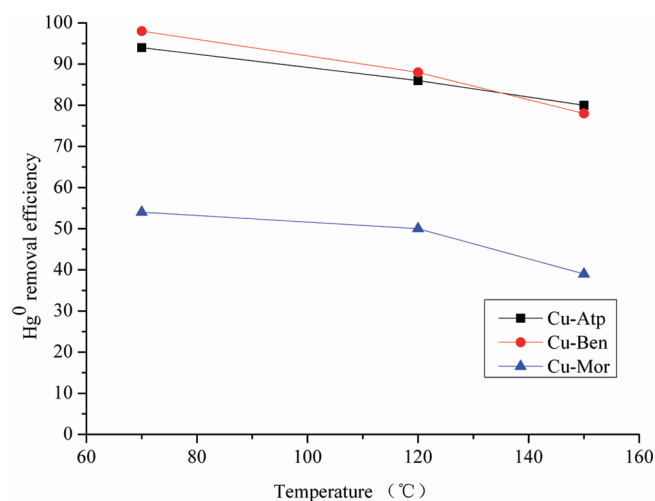


Figure 3. Experimental results of Hg^0 removal efficiency at different temperature for CuCl_2 -impregnated sorbents.

decreased slightly with an increase in temperature. Nevertheless, the average Hg^0 removal efficiencies for Cu-Atp and Cu-Ben also maintained at about 80% at 150 °C, indicating that these two sorbents are still available in the application of mercury emission control.

On the basis of reaction eqs 1 and 2, the basic data of thermodynamic equilibrium calculations were given in the literature by Lee et al.⁴³ According to the change of enthalpy and Gibbs free energy values, these two reactions were both exothermic and irreversible. In addition, the equilibrium constant values decreased with increasing experimental temperature, indicating that less HgCl_2 was created at higher temperatures.⁴⁶ Therefore, it can be concluded that the mercury removal performance for CuCl_2 -impregnated sorbents should decrease with an increase in temperature, which is in good agreement with the experimental results in this study.

3.4. NaClO_3 -Impregnated Sorbents. NaClO_3 is a strong oxidant and has been widely used as the oxygen source for emergency oxygen generation.⁴⁷ It could react with Hg^0 in flue gas and result in the decrease of Hg^0 emission capacity. Therefore, NaClO_3 was employed as a chemical promoter in the synthesis of mercury sorbents in this study.

As shown in Figure 4, the NaClO_3 -impregnated sorbents used in this study presented an enormous difference in mercury removal abilities at 120 °C. The significant average Hg^0 removal efficiency of about 90% for Cl-Atp was observed, whereas Cl-

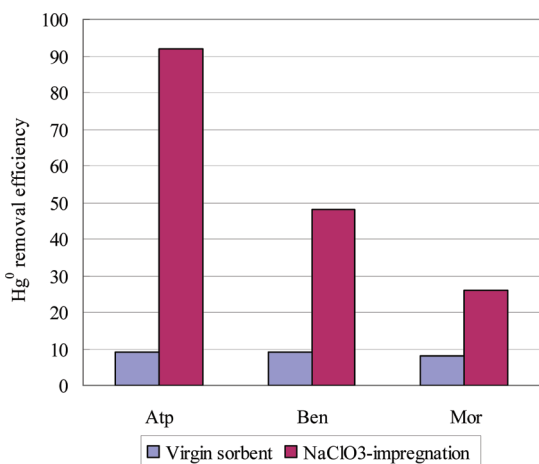


Figure 4. Comparison of average Hg^0 removal efficiency between raw sorbents and NaClO_3 -impregnated sorbents. Experimental temperature is 120 °C.

Mor displayed a disappointing result of just 26%. This phenomenon may be caused by the different contents of NaClO_3 in the sorbents. However, it is noticeable that Cl-Atp and Cl-Ben, with a similar content of chemical promoter, presented much different performances in mercury removal, suggesting that the raw sorbents may have affected the reactions between Hg^0 and NaClO_3 .

It can be seen from Figure 5 that the three NaClO_3 -impregnated sorbents displayed the same trend in average Hg^0

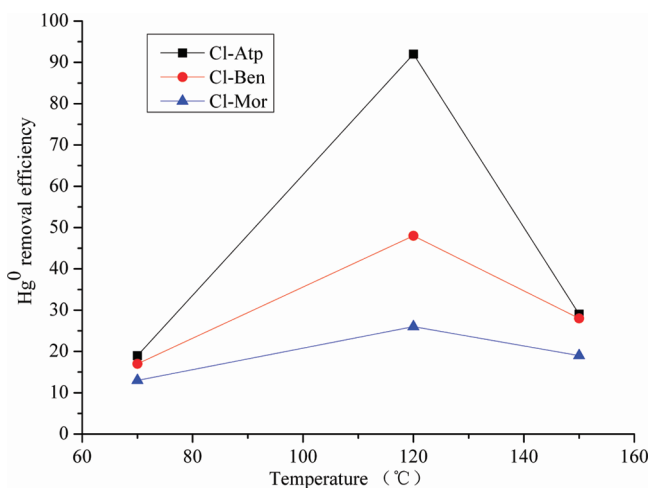
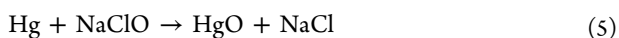
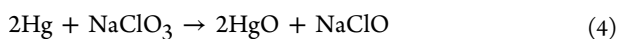
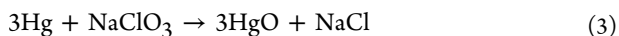


Figure 5. Experimental results of Hg^0 removal efficiency at different temperature for NaClO_3 -impregnated sorbents.

removal efficiency with the temperature varying from 70 to 150 °C. According to the experimental results, it can be assumed that the process of Hg^0 removal by NaClO_3 -impregnated sorbents was based on a chemical adsorption mechanism. The following reaction equations may be applicable for Hg^0 oxidation:



As a chemical process, the reactions required activation energy and proceeded at a limited rate, which increased with increasing temperature.¹³ Therefore, it is reasonable that the three NaClO_3 -impregnated sorbents displayed neglectable performances in mercury removal at 70 °C.

The average Hg^0 removal efficiencies of the three sorbents were different at 120 °C and subsequently were reduced to a similar level when the temperature varied from 120 to 150 °C, as shown in Figure 5. This phenomenon may be correlated with the iron oxide existing in the raw sorbents. The related results are listed in Table 3. Iron oxide has been reported as a quite

Table 3. Results of Element Content and Average Hg^0 Removal Efficiency for NaClO_3 -Impregnated Sorbents

sorbents	avg Hg^0 removal efficiency at 120 °C, %	Cl content, wt %	Fe content, wt %
Cl-Atp	92	4.28	12.10
Cl-Ben	48	5.06	4.79
Cl-Mor	26	2.00	2.62

active catalyst in the decomposition of sodium chlorate. It is confirmed that iron ion can attract an unshared electron pair from an oxygen atom in sodium chlorate molecule and forms a coordination bond ($\text{Fe}^{3+}-\text{O}$). The formation of coordination bond can weaken the $\text{Cl}-\text{O}$ bond in the chlorate and make it to rupture.⁴⁸ This mechanism made the reactions between Hg^0 and NaClO_3 easier to occur. Therefore, the higher iron content for Atp could form more $\text{Fe}^{3+}-\text{O}$ bonds and resulted in the best mercury removal performance at 120 °C among the three sorbents. When the temperature increased to 150 °C, sodium chlorate decomposed to sodium chloride and oxygen, as described in the reaction eq 6.⁴⁸



As reported in ref 49, the decomposition of sodium chlorate began at 420 K (147 °C), and the presence of iron oxide accelerated this process by weakening the $\text{Cl}-\text{O}$ bond. On the other hand, in the presence of alkaline-earth metals, which partly existed in the natural minerals used in this study, iron oxide could be oxidized to ferrate by sodium chlorate. The ferrate contains oxidation state iron ions, Fe^{4+} , which have higher catalytic activity than Fe^{3+} . It has been confirmed that the alkaline-earth metal ferrates are also active catalysts for the decomposition of sodium chlorate.⁴⁸ Therefore, the three NaClO_3 -impregnated sorbents presented a similar poor performance in mercury removal at 150 °C.

Obviously, it is different with CuCl_2 -impregnated sorbents that the temperature is an important factor affecting mercury removal for NaClO_3 -impregnated sorbents. Furthermore, a suitable active catalyst is necessary.

3.5. KI-Impregnated Sorbents. As mentioned, iodine(I) demonstrated good performance in Hg^0 oxidation and capture. Therefore, KI-impregnated mineral sorbents were synthesized and evaluated.

As can be seen in Figure 6, the three raw sorbents presented significant improvements in mercury removal after KI impregnation. The average Hg^0 removal efficiencies above 90% were observed for the I-Atp and I-Ben. This was comparable with the performance of I-impregnated activated carbon reported by Lee et al.¹³

The temperature effect on mercury removal was also investigated, and the results are shown in Figure 7. It is clear that

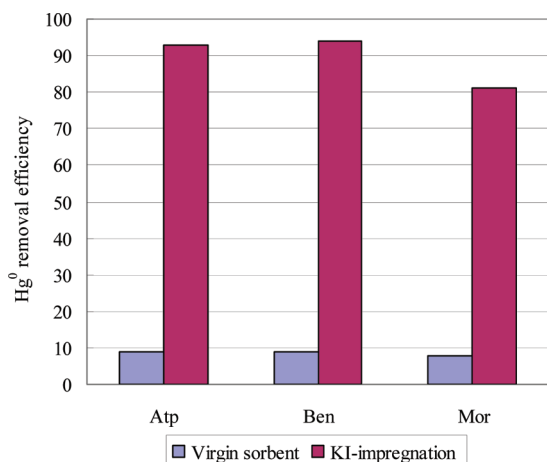


Figure 6. Comparison of average Hg^0 removal efficiency between raw sorbents and KI-impregnated sorbents. Experimental temperature is 120 °C.

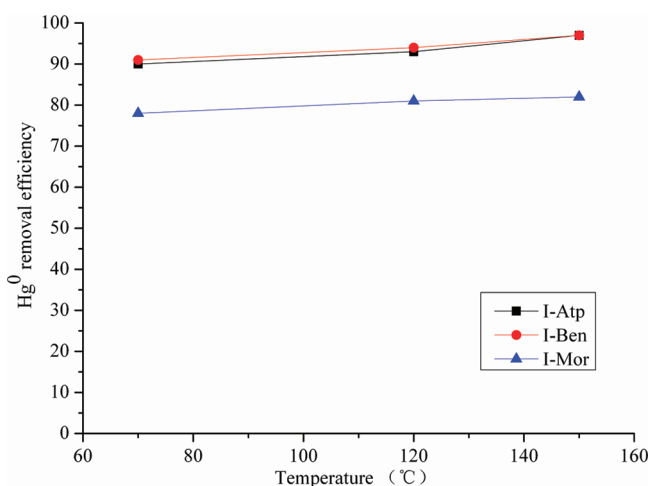
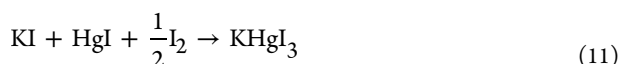
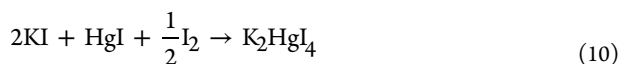


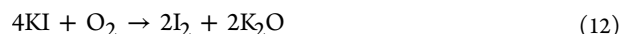
Figure 7. Experimental results of Hg^0 removal efficiency at different temperature for KI-impregnated sorbents.

the average Hg^0 removal efficiencies increased steadily as temperature increased from 70 to 150 °C. This phenomenon is consistent with the result reported by Lee et al.¹³ The process of mercury removal is based on the chemical adsorption mechanism. Relevant studies on iodine and potassium iodide promoted activated carbon sorbents were previously carried out, and several potential mechanisms for mercury removal were suggested.^{50,51} The following reaction equations may be applicable for Hg^0 removal:



The resultant HgI would probably emit to the flue gas, which is similar to the possibility of HgCl_2 emission mentioned above.

It is noticeable that I_2 was an indispensable reactant in the reactions described, indicating that I_2 emerged in the KI-impregnated sorbents. This inference had been confirmed by following starch–iodine test, and the reactant I_2 came from the oxidation of KI by O_2 , as described in the reaction eq 12.¹⁸



Moreover, the resultant K_2O , as an alkaline oxide, may be helpful for acid gas removal from flue gas in coal-fired power plant such as SO_2 and NO_x .

In addition, we can also conclude that the oxidation of KI had already occurred prior to the adsorption experiment. One important reason is because of the fact that the high Hg^0 removal efficiencies for the three sorbents were observed at the beginning of the tests. Moreover, another important reason is due to the fact that the three sorbents used in this study presented excellent mercury removal efficiencies at the testing temperature, but KI showed poor mercury removal performance at the similar temperature.¹⁸ It means that enough I_2 had been produced in the sorbents prior to the adsorption experiments. The oxidation of KI was most likely to occur in the drying process.

To investigate oxidation of KI and volatilization of I_2 in the sorbents, additional tests were conducted as follows.: First, each sample of the three KI-impregnated sorbents was evenly put into a beaker, and the beakers were put into an oven at 120 °C. Then, a portion of sample was taken out over a certain period of time, and the iodine content in it was analyzed. The results are summarized in Figure 8. Obviously, the concentration of I

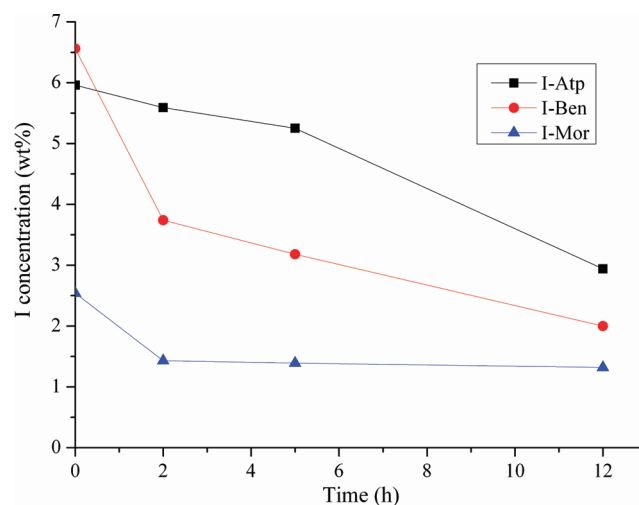


Figure 8. I content in KI-impregnated sorbents at different times at 120 °C.

in the sorbents continuously decreased, indicating that I_2 was produced and emitted to air, as KI was not volatilized at this temperature.¹⁸ In addition, a starch–iodine test was carried out to detect potentially volatilized I_2 , and the results are shown in Figure 9. The reagent was prepared as described by Li et al.¹⁸ The samples of the KI-impregnated sorbents were maintained at a constant temperature of 120 °C, and air was used as carrier gas to carry potentially volatilized I_2 into the reagent. It is clear that I_2 could be generated at 120 °C. The oxidation of KI at 120 °C for KI-impregnated natural mineral sorbents may be due to the smaller KI particles in the sorbents, because smaller

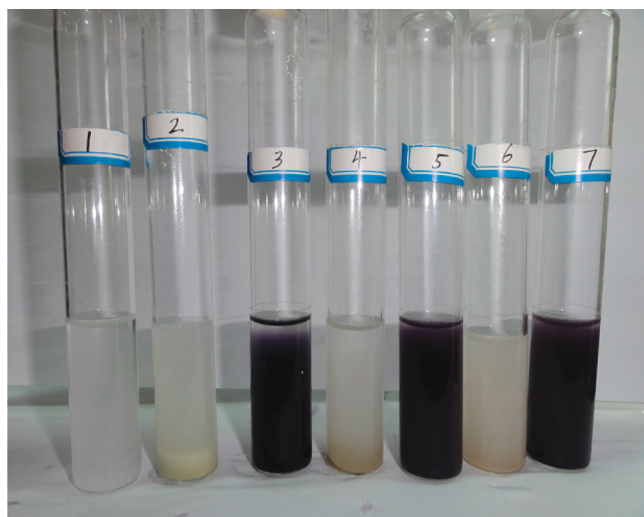


Figure 9. Volatilized I_2 detection by starch–iodine test: (1) blank reagent; (2) (4) (6) reagents added no drying sorbents of I-Ben, I-Atp, and I-Mor, respectively; (3) (5) (7) reagents after flowing I_2 contained carrier gas for I-Ben, I-Atp, and I-Mor, respectively.

particles would usually result in better contact between reactants. However, the I_2 release by KI oxidation from KI-impregnated activated carbons is very rare at such a low temperature. It is clear that I_2 can sublime at 113 °C.¹⁸ The peak desorption temperature of iodine loaded activated carbon was above 200 °C.⁵² Therefore, a possible reason is that the adsorption strength between KI (or I_2) and natural mineral materials' surface is much weaker than those between KI (or I_2) and activated carbons' surface.

The average Hg^0 removal efficiencies for the KI-impregnated sorbents with additional 12 h drying were also examined at 30 °C to verify the presence of I_2 again. As Table 4 displays,

Table 4. Average Hg^0 Removal Efficiency for KI-Impregnated Sorbents with Additional 12 h Drying

sorbents	I content after additional 12 h drying, wt %	avg Hg^0 removal efficiency at 30 °C, %
I-Atp	2.94	81
I-Ben	2.00	82
I-Mor	1.32	54

although the contents of iodine reduced by more than a half for I-Atp and I-Ben, the average Hg^0 removal efficiencies were also above 80%, indicating that there were still enough I_2 left in the sorbents after additional 12 h drying.

Obviously, the three KI-impregnated sorbents performed well in mercury removal. However, the KI or I_2 could probably react with other flue gas components such as SO_2 and H_2O , and the volatilized I_2 would cause corrosion problems in power plants. More attention should be paid on these potential concerns in future studies and applications.

3.6. KBr-Impregnated Sorbents. Bromine has been reported to enhance mercury removal from flue gases in coal-fired power plants. Therefore, KBr was employed as a chemical promoter to enhance mercury removal ability of mineral materials and the results are shown in Figure 10. However, the bromine adsorption abilities of the three natural minerals were too low to result in high mercury removal efficiencies. It may be inferred that the three natural minerals used in this study were

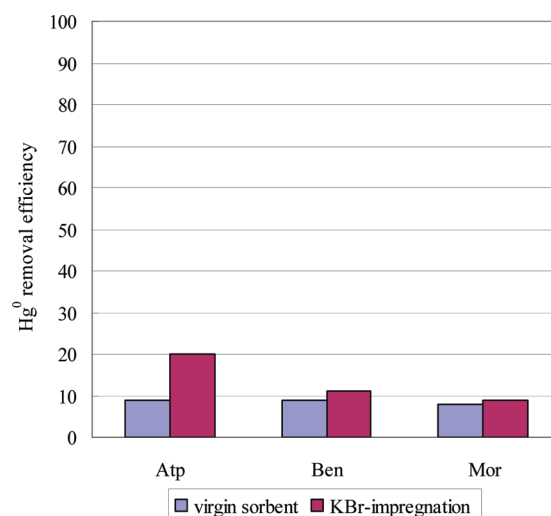


Figure 10. Comparison of average Hg^0 removal efficiency between raw sorbents and KBr-impregnated sorbents. Experimental temperature is 120 °C.

unsuitable for modification by KBr. More attention would be concentrated on the new synthesis method and the selection of proper bromine contained promoters.

4. CONCLUSION

Average Hg^0 removal efficiencies of different sorbents were tested on a lab-scale fixed-bed system. The effects of different chemical promoters and temperature on mercury removal were investigated and the influence of sorbent material was also examined. The conclusions from the results are summarized as follows.

Cu-Atp and Cu-Ben presented significant mercury removal performances and showed about 90% average Hg^0 removal efficiencies at 120 °C. Although the Hg^0 removal abilities decreased with an increase in temperature for them, it was not crucial because the average Hg^0 removal efficiencies also maintained at about 80% at 150 °C. Therefore, they were promising low-cost mercury sorbents for further studies. Cl-Atp showed the best mercury removal performance among the three Cl-impregnated sorbents, and more than 90% average Hg^0 removal efficiency was observed at 120 °C. This result might be correlated with the high iron oxide content in Atp and the formation of a Fe^{3+} –O bond that could weaken the Cl–O bond in the chloride and make the reactions between Hg^0 and $NaClO_3$ occur more easily. In addition, Cl-Atp should be applied at a suitable temperature to prevent $NaClO_3$ decomposition. All the KI-impregnated sorbents showed remarkable performance in mercury removal. In addition, it is confirmed that I_2 as an indispensable reactant came from the oxidation of KI and the oxidation initially occurred in the sorbents drying process.

Although the surface area of mineral materials is poor in comparison to activated carbons, natural mineral materials are cost-effective and possess unique adsorption properties such as cation exchange capacity. Appropriate combination of chemical promoters and mineral materials can produce excellent mercury sorbents. The silicate mineral material is a natural additive in the cement production process. Therefore, the application of mineral sorbents would not affect the utilization of fly ash in cement. Whether the adsorbed mercury affects the quality of cement will be evaluated in our future work.

The experiments were conducted under a simulated flue gas condition consisting of elemental mercury in a carbon dioxide–oxygen–nitrogen mix. However, the composition of coal-derived flue gas is more complicated. A typical untreated flue gas derived from the combustion of an U.S. Low Sulfur Eastern bituminous coal contained: 5–7% H₂O, 3–4% O₂, 15–16% CO₂, 1 ppb total Hg, 20 ppm CO, 10 ppm hydrocarbons, 100 ppm HCl, 800 ppm SO₂, 10 ppm SO₃, 500 ppm NO_x, and balance N₂.^{53–55} The acid gases such as SO₂, SO₃, HCl, and NO may have a potential impact on mercury removal, and other oxidizable species such as carbon monoxide and hydrocarbons may also cause competition with mercury on the sorbents. This will be a fruitful area in our future research.

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Notes

The authors declare no competing financial interest.

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