

RESEARCH NOTES

Sorbents for Mercury Capture from Fuel Gas with Application to Gasification Systems[†]

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In regard to gasification for power generation, the removal of mercury by sorbents at elevated temperatures preserves the higher thermal efficiency of the integrated gasification combined cycle system. Unfortunately, most sorbents display poor capacity for elemental mercury at elevated temperatures. Previous experience with sorbents in flue gas has allowed for judicious selection of potential high-temperature candidate sorbents. The capacities of many sorbents for elemental mercury from nitrogen, as well as from four different simulated fuel gases at temperatures of 204–371 °C, have been determined. The simulated fuel gas compositions contain varying concentrations of carbon monoxide, hydrogen, carbon dioxide, moisture, and hydrogen sulfide. Promising high-temperature sorbent candidates have been identified. Palladium sorbents seem to be the most promising for high-temperature capture of mercury and other trace elements from fuel gases. A collaborative research and development agreement has been initiated between the Department of Energy's National Energy Technology Laboratory (NETL) and Johnson Matthey for optimization of the sorbents for trace element capture from high-temperature fuel gas. Future directions for mercury sorbent development for fuel gas application will be discussed.

Introduction

There are increasing concerns over mercury pollution in the environment. Mercury is a powerful neurotoxin and can bioaccumulate up the food chain. The United States Environmental Protection Agency (USEPA) announced, on December 14, 2000, its intention to regulate coal-utilizing facilities such as traditional pulverized coal-fired combustors and more-advanced power generation gasification units for mercury emissions. The USEPA issued the regulation in March 2005.¹ With the USEPA's Clean Air Mercury Rule, and several states promulgating their own regulations, the need exists for a low-cost mercury removal technique that can be applied to integrated gasification combined cycle (IGCC) and coal-burning power plants.

Gasification is an important strategy for increasing the utilization of abundant domestic coal reserves. The Department of Energy (DOE) envisions increased use of gasification in the United States during the next 20 years. As such, the DOE Gasification Technologies Program, including the FutureGen initiative, will strive to approach a near-zero emissions goal, with respect to pollutants such as mercury.

Many sorbents such as activated carbons can remove mercury at near-ambient temperatures.^{2–11} In regard to gasification for power generation, the removal of mercury by sorbents at elevated temperatures preserves the high thermal efficiency of

the integrated gasification combined cycle system. In addition, "humid" gas cleaning at elevated temperature represents a location where all of the mercury can be captured, unlike cold gas mercury cleanup, where some could possibly deposit in other contaminant cleaning steps. Unfortunately, most sorbents such as activated carbons, metal oxides, metal sulfides, and metals will display poor capacity for elemental mercury at elevated temperatures.^{2–11} Carbon has been shown to exhibit poor capacities for mercury in syngas at elevated temperatures at both laboratory and pilot-scales.^{8–11} Mercury is expected to exist in the difficult-to-capture elemental form under the reducing conditions of coal gasification.^{12,13}

Previous experience with sorbents in flue gas has allowed for judicious selection of potential high-temperature candidate sorbents.^{2–7} In addition, other fuel gas compounds such as carbon monoxide, hydrogen sulfide, water, and hydrogen may also interfere with the adsorption of mercury.

The capacities of many sorbents for elemental mercury from nitrogen, as well as from four different simulated fuel gases in the temperature range of 204–371 °C, were determined. The simulated fuel gas compositions contain varying concentrations of carbon monoxide, hydrogen, carbon dioxide, moisture, and hydrogen sulfide. Promising high-temperature sorbent candidates have been identified. Early results for the metal sorbents are presented. Palladium sorbents show promise for the high-temperature removal of mercury from fuel gas.

Experimental Section

The assembly used to study the capture of mercury from simulated fuel gases is a modified version of an apparatus that has been described earlier.^{2–7} It consists of an elemental mercury

[†] Disclaimer: Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement by the United States Department of Energy. This early work on the metal sorbents was originally presented at the 20th and 22nd Annual International Pittsburgh Coal Conferences, Pittsburgh, PA, in September 2003 and September 2005, respectively.

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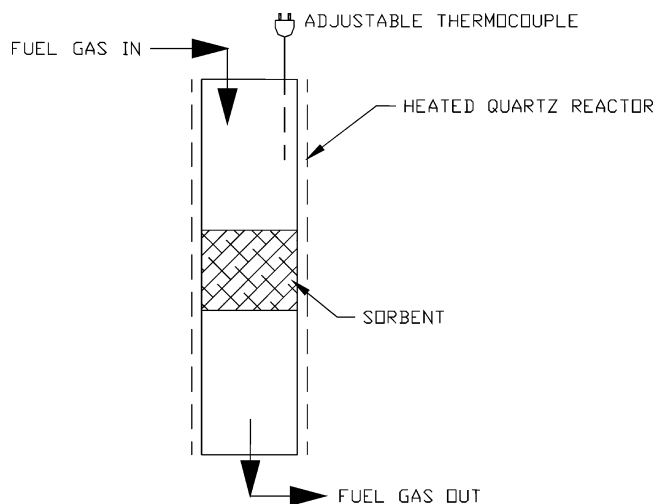


Figure 1. Laboratory-scale packed-bed reactor.

permeation tube, a heated quartz packed-bed reactor, and a fuel gas blending system. The reactor scheme is shown in Figure 1.

The vertical-flow packed-bed reactor is a 20-in.-long by 1/4-in.-outer diameter (1/6-in.-inner-diameter) cylindrical quartz tube. Ten milligrams of sorbent are placed upon a quartz wool support. Gas flows down through the bed at a flow rate of 60 or 80 mL/min.

All of the plumbing and valves that come into contact with mercury are constructed from either stainless steel or Teflon. These materials have been demonstrated to have good chemical resistance and inertness to mercury. The packed bed of sorbent is surrounded by a large clam-shell furnace. A Self-tune Plus 300 PID controller is used to maintain the bed at the desired temperature. The temperature at the top of the bed has been determined to be within 1.0 °C of the temperature at the bottom of the bed.

A certified Dynacal permeation tube (from VICI Metronics) is used as the source of elemental mercury for the sorbent experiments. The permeation tube is certified by the manufacturer to release 130 ng of mercury/min at 100 °C. The permeation tube is located at the bottom of a Dynacal glass U-tube, which is maintained at a temperature of 100 ± 1.0 °C at all times by immersing it in a Hacke L oil bath. A flow of ultrahigh-purity carrier-grade nitrogen passes over the permeation tube and is maintained at all times by a thermal conductivity mass-flow controller.

The detector for elemental mercury is a Brooks Rand CVAFS-2 cold vapor atomic fluorescence spectrophotometer (AFS). When used as a continuous on-line monitor for elemental mercury in nitrogen, the detection limit is ~ 1 ppb. The AFS is an ultraviolet (UV) detector for elemental mercury; Hg atoms absorb 253.7-nm light and re-emit (fluoresce) this wavelength. A mercury bulb serves as the UV source, and a photomultiplier tube serves as the UV fluorescence detector. The AFS was used as the on-line detector of elemental mercury when mercury-in-nitrogen experiments were performed. For more-complex simulated fuel gases, the sorbent capacity was determined off-line by analyzing the spent sorbent with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or cold vapor atomic absorption spectrometry (CVAAS). The ICP-AES system is a Perkin-Elmer model Optima 3000 radial view spectrometer. The CVAAS system is a CETAC model M-6000A unit that has been dedicated for the analysis of elemental mercury.

The appropriate precautions for handling and transporting fuel gas compounds are followed.¹⁴⁻¹⁷ Because carbon monoxide

Table 1. Mercury Removals in Nitrogen^a

metal	Mercury Removal (%)		
	204 °C	288 °C	371 °C
iridium	38	93	40
platinum	58	100	26
silver	17	8	
palladium	14	65	
rhodium	0	1	0.5
titanium	11	20	
ruthenium	60	65	36

^a Gas composition: 240 ppb of mercury in nitrogen gas (N₂). Flow rate = 60 mL/min. Time of exposure: 350 min. Sorbent composition: 100% of metal indicated in either powder or black form.

is known to readily react with certain steels to form iron and nickel carbonyls, aluminum cylinders are used for carbon monoxide. Any traces of iron or nickel carbonyls are removed by a large carbon trap that is located upstream of the packed-bed reactor. The reactor system is located in a ventilation hood, and a bank of six MSA Ultima gas detectors and alarms for CO, H₂, and H₂S are used to monitor for unlikely gas leaks.

Oxygen can permeate through Teflon gas lines. Stainless steel gas lines are used for fuel gas components, and two large oxygen traps are placed in series upstream of the packed-bed reactor to avoid contamination of the simulated fuel gases with trace oxygen. The first trap is an Alltech Oxy-Trap, and the second oxygen removal bed is the Alltech Big Oxygen Trap. The Alltech Big Oxygen Trap has a capacity of 3200 mg of O₂, and it can reduce O₂ levels to <1 ppb.

The following five simulated fuel gas (SFG) compositions were used to expose the sorbents to mercury:

- (1) 240 ppb of mercury in nitrogen gas;
- (2) SFG-1, which has a composition of 27% H₂, 36% CO, 4% CO₂, and 240 ppb of mercury, with the balance being nitrogen gas;
- (3) SFG-2, which has a composition of 14% H₂, 18% CO, 2% CO₂, 0.3% H₂S, and 240 ppb of mercury, with the balance being nitrogen gas;
- (4) SFG-3, which has a composition of 10% H₂, 14% CO, 2% CO₂, 0.2% H₂S, 1% H₂O, 180 ppb of mercury, with the balance being nitrogen gas; and
- (5) SFG-4, which has a composition of 14% H₂, 18% CO, 2% CO₂, 1% H₂O, 240 ppb of mercury, with the balance being nitrogen gas.

The flow rate of gas through the packed bed is 60 mL/min, except for SFG-3, where it is 80 mL/min. The used sorbent is removed from the packed-bed reactor after 350 min of exposure to the simulated fuel gas, and it is analyzed for mercury content using CVAAS or ICP-AES. Palladium is known to interfere with CVAAS analysis for mercury, so all palladium sorbents were analyzed by ICP-AES.¹⁸ An on-line mass spectrometer was used to verify that the sorbent candidates are not converting the fuel gas components to other compounds (for example, through Fischer-Tropsch synthesis reactions).

Experimental Results

Metal sorbents were initially screened for mercury capacity in a simple mercury-nitrogen mixture. Many base metals such as copper, zinc, and cobalt were previously examined, and most displayed poor capacity for mercury over the 350-min test. Some of these early results are shown in Table 1. In the discussion, the percentage of mercury removed is defined by the mass of mercury captured by the sorbent divided by the mass of mercury emanating from the permeation tube over the 350-min experiment. Sorbent capacity is defined as the mass of mercury

Table 2. Mercury Removals in SFG-1^a

metal	Mercury Removal (%)		
	204 °C	288 °C	371 °C
iridium	10	3	0.4
silver	1		
ruthenium		1	
platinum	45	100	10
palladium	34	54	38

^a Gas composition of SFG-1: 27% H₂, 36% CO, 4% CO₂, 240 ppb mercury, balance N₂. Flow rate = 60 mL/min. Time of exposure = 350 min. Sorbent composition = 100% of metal indicated in either powder or black form.

Table 3. Palladium Capacity in Simulated Fuel Gases: 1% Palladium on Alumina^a

gas	temperature (°C)	number of runs	mean capacity or loading (μg/g)
SFG-1	204	7	460
SFG-3	204	1	225
SFG-4	204	3	550
SFG-1	288	6	280
SFG-3	288	5	260
SFG-4	288	3	240

^a Sorbent: 1% palladium on alumina. Flow rate = 60 mL/min for each gas, except for SFG-3, where it is 80 mL/min. Time of exposure = 350 min.

Table 4. Palladium Capacity in Simulated Fuel Gases: 5% Palladium on Alumina^a

gas	temperature (°C)	number of runs	mean capacity or loading (μg/g)
SFG-1	204	3	425
SFG-3	204	1	550
SFG-4	204	3	520
SFG-1	288	6	900
SFG-3	288	3	430
SFG-4	288	1	870

^a Sorbent: 5% palladium on alumina. Flow rate = 60 mL/min for each gas, except for SFG-3, where it is 80 mL/min. Time of exposure = 350 min.

captured by the sorbent divided by the 10 mg mass of sorbent, and is reported as milligrams or micrograms of mercury per gram of sorbent.

It was found that iridium displayed a high capacity for elemental mercury at elevated temperatures. Later, it was found that platinum and palladium also display high capacities for mercury at elevated temperatures. Many other sorbent candidates such as carbons, oxides, halides, sulfides, and selenides were also examined in the simple mercury–nitrogen gas mixture at elevated temperatures. Most of these materials displayed poor capacities for mercury at elevated temperatures. The promising capacities shown by the precious metals iridium, palladium, and platinum prompted further testing in more-complex gas mixtures.

The mercury removals by the metal sorbents in SFG-1 over the 350-min test are shown in Table 2. The metal sorbents exhibit reduced capacity in SFG-1, as compared to nitrogen. However, platinum and palladium retain high capacities for mercury in the simple simulated fuel gas mixture SFG-1.

Two commercially available supported palladium catalysts were examined in several simulated fuel gases. These sorbents were 1% and 5% palladium on alumina. The effect of the palladium loading is shown by comparing the capacities in Tables 3 and 4.

Discussion

Metals can form amalgams with mercury.^{2–7,19,20} Many base metals were examined for mercury capture at elevated temperatures, and these exhibited poor capacities. Iridium, platinum, and palladium display high capacities for mercury at elevated temperatures in a nitrogen gas stream. Mercury removals decrease in going from 288 °C to 371 °C, possibly because of dealumination at elevated temperatures. However, iridium's capacity for mercury dramatically decreases in a simulated fuel gas matrix, suggesting that fuel gas species impact the adsorption of mercury. Palladium and platinum still retain significant capacity for mercury in a fuel gas matrix containing carbon monoxide, carbon dioxide, and hydrogen, as shown in Table 2.

An effort was made to examine the capability of palladium sorbents for mercury capture from more-complex fuel gases. The effect of loading was determined by testing both 1% and 5% palladium on alumina. Comparison of the mercury capacities shown in Tables 3 and 4 indicates that increased palladium loading increases capacity in most cases. The early data do not allow us to determine whether the maximum adsorption of mercury occurs at 204 °C or at 288 °C.

The metal sorbents examined were either metal powders or blacks or palladium on alumina. In all cases, the Brunauer–Emmett–Teller (BET) surface areas are relatively low, ranging from 1 m²/g to 30 m²/g. It is expected that larger capacities can be obtained through the use of well-dispersed palladium on higher surface area supports. The effects of both surface area and loading upon palladium capacity for mercury will be examined in future work with Johnson Matthey.

Noble metals such as palladium, platinum, iridium, rhodium, and gold have been used as modifiers for graphite tube atomic absorption or emission (GTAA) analysis of solid and liquid samples.^{21–32} The extensive literature that is available suggests that palladium is the best modifier for GTAA analysis.^{21–32} As a modifier for GTAA, palladium adsorbs the semivolatile elements mercury, arsenic, selenium, and cadmium at elevated temperatures during the drying and pyrolysis stages of the thermal treatment of the solid and liquid samples. These temperatures can go as high as 400 °C. Several mechanisms for the high-temperature retention of mercury, arsenic, and selenium by palladium during GTAA are proposed by Matousek et al.,²⁹ Styris and co-workers,^{30,31} and Docekal et al.³² The mechanisms for trace metal capture include the formation of palladium–mercury, palladium–arsenic, and palladium–selenium alloys.^{29–32} Palladium's high-temperature retention of the semivolatile elements mercury, arsenic, selenium, and cadmium in GTAA also suggests that it merits examination as a high-temperature flue gas sorbent for the semivolatile trace elements.

Palladium also can form selenides that have high-temperature stability.³³ From the literature, a brief list of potential species that can form on the surface of a palladium sorbent in fuel or flue gas is given in Table 5. It can be seen that a myriad of compounds can form between the trace elements in fuel or flue gas and palladium. The oxygen-containing species are unlikely to form in the reducing fuel gas environment but could form in flue gases. The mechanism of high-temperature mercury capture by palladium will be further examined through extensive surface analysis of used sorbents. It is also suggested that the palladium membranes proposed for high-temperature separation of hydrogen from fuel gas can potentially form sulfur, chlorine, selenium, arsenic, and mercury surface species. Great progress has recently been made in formulating palladium alloy compositions that have sulfur resistance.^{34,35}

Table 5. Potential Surface Species Present on Palladium Exposed to Fuel or Flue Gases^{29–33}

species	comment
PdO	melting point: 870 °C
PdSe	melting point: <960 °C
PdSe ₂	melting point: <1000 °C
PdCl ₂	decomposes at 500 °C
PdS	decomposes at 950 °C
Pd–Hg alloy	found in GTAA studies
HgO	decomposes at 500 °C
As ₂ O ₃	melting point: 312 °C
PdO–As ₂ O ₃	found in GTAA studies
Pd–As alloy	found in GTAA studies
Pd–Se alloy	found in GTAA studies

The regeneration of the palladium sorbents is of significant interest. Regeneration of the used palladium sorbent could be achieved through either chemical or heat treatments. Heat can be used to drive off the trace elements from a palladium surface, as evidenced by the GTAA analytical technique.^{21–32} Chemical treatments for regeneration can include various acid digestions for the removal of the trace metals from the used sorbents.⁵ Preliminary tests suggest that a mild heating to 430 °C in a nitrogen stream can remove some of the mercury from the used sorbent and allow it to be reused for several cycles. Further investigations will focus on the optimum method for regeneration of the used palladium sorbents.

Conclusions

A packed-bed reactor system was used to screen sorbents for the removal of mercury from simulated fuel gases. An on-line atomic fluorescence spectrophotometer was used to measure elemental mercury in nitrogen on a continuous basis. For the simulated fuel gas mixtures, sorbent capacities were determined off-line via cold vapor atomic absorption spectrometry (CVAAS) or inductively coupled plasma–atomic emission spectroscopy (ICP–AES), with ICP–AES being applied for the palladium sorbents. Most sorbent candidates exhibit poor capacities for mercury from fuel gases at temperatures of >204 °C. Fuel gas species such as moisture, hydrogen sulfide, carbon monoxide, and hydrogen impact the adsorption of mercury. Palladium is an attractive sorbent candidate for the removal of mercury from fuel gases at elevated temperatures. Increasing the palladium loading typically increases the sorbent capacity.

A collaborative research and development agreement has been initiated between the Department of Energy's National Energy Technology Laboratory and Johnson Matthey for optimization of the sorbents for trace element capture from high-temperature fuel gas. The effects of both surface area and loading upon palladium capacity for mercury will be examined in future work with Johnson Matthey. Future work will involve larger-scale testing of the palladium sorbent at a gasification facility. In addition to mercury, palladium has potential to serve as a high-temperature sorbent for the removal of other trace elements such as arsenic and selenium from fuel gas.

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