

Evaluation of Nanocrystalline Sorbents for Mercury Removal from Coal Gasifier Fuel Gas

Raja A. Jadhav^{*1}, Howard S. Meyer¹, Slawomir Winecki², and Ronald W. Breault³

¹Gas Technology Institute, 1700 S. Mount Prospect Road, Des Plaines, IL 60018

Tel: (847) 768-0807, E-mail: raja.jadhav@gastechnology.org

²NanoScale Materials, Inc., 1310 Research Park Dr., Manhattan, KS 66502

³National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26507

ABSTRACT

Gasification-based energy conversion systems, such as IGCC, have the potential to provide energy with higher efficiency and superior environmental performance. The mercury regulations currently proposed for coal-combustion systems will most likely be extended to the next-generation gasification-based systems. Therefore, a significant amount of research work is currently being carried out to address the concern of mercury release from coal-fired gasifiers. A majority of this research is focused on development of sorbents for mercury capture from “warm” fuel gas.

Gas Technology Institute (GTI), in collaboration with NanoScale Materials, Inc. (NanoScale), is evaluating highly reactive nanocrystalline metal oxides/sulfides for capture of mercury from high-temperature (150–370°C) fuel gas. This paper discusses unique properties of nanoscale sorbents and gives preliminary results of mercury capture by these sorbents in nitrogen atmosphere.

INTRODUCTION

Coal-fired utilities are the single largest source of anthropogenic mercury emissions in the U.S. Because of its high volatility, almost all the mercury present in coal is transformed into gas phase during combustion or gasification of coal. Control of mercury emissions from coal-fired power plants is a difficult task, in part due to its high volatility and its much lower concentration (5–20 $\mu\text{g}/\text{m}^3$) in a large volume of flue gas. In addition, depending on the type of coal and combustion conditions, a majority of mercury in the flue gas can exist in the elemental form (Hg^0), which is more difficult to capture than its oxidized (Hg^{2+}) or particulate (Hg^p) forms. The oxidized form of mercury can interact with fly ash and can be captured in conventional flue gas desulfurization (FGD) systems (such as wet FGD systems), whereas, the particulate form can be captured in the particulate control devices (PCDs). However, the elemental form is insoluble in water and does not have much affinity for fly ash. Therefore, almost all of the elemental mercury in the flue gas escapes to the atmosphere.

Due to the reducing nature of coal gasifier fuel gas, mercury exists predominantly in the elemental form.¹ The lack of oxidized mercury in fuel gas is the result of higher concentrations of CO and H_2S , which inhibit mercury oxidation by scavenging the chlorine and other radicals necessary for mercury oxidation.² Activated carbon-based technology currently proposed for flue gas mercury control has limited application in fuel gas because of the lower sorption capacity of the activated carbon at elevated temperatures. The presence of reducing components in the fuel gas provides additional challenge for development of high capacity mercury sorbents for coal-gasifier applications.

In collaboration with NanoScale, GTI is evaluating nanocrystalline sorbents for mercury removal from warm fuel gas (150–370°C). Nanocrystalline materials exhibit a wide array of remarkable chemical and physical properties, and they can be considered as new materials that bridge molecular and condensed matter. One of their remarkable properties is enhanced surface chemical reactivity (normalized for surface area) toward incoming adsorbates, which is attributed to extremely large surface areas, small crystallite size, unique morphology and porous nature of the nanomaterials. Nanocrystalline materials often show reactivity that is not observed in bulk materials. It is expected that such unusual properties of these materials will make them effective sorbents for mercury removal from warm fuel gas.

EXPERIMENTAL

Experimental Setup

The sorbents are evaluated in a lab-scale, fixed bed reactor with the outlet mercury concentration monitored by a semi-continuous mercury analyzer. As shown in Figure 1, the mercury sorbent testing unit essentially consists of a quartz reactor shell and a quartz reactor insert that are externally heated by a three-zone electric furnace. The setup is complete with equipment for feeding and measuring the flow rate of the gases, measuring and controlling the bed temperature, monitoring the reactor pressure and the pressure drop across the bed, off-gas sampling and analysis, and an automated data acquisition system. The reactor system is configured for upward gas flow, and the three-zone furnace is positioned with respect to the sorbent bed to accomplish feed gas preheating. Certified elemental mercury (Hg^0) permeation tube from VICI Metronics is used to generate the Hg^0 vapor. The permeation tube is housed in a VICI Metronics U-tube, heated in a constant temperature water bath. The reactor insert has a 2.3 cm O.D. and a 1.8 cm I.D. sorbent bed cage of a 1 cm height. The top of the cage is a fixed porous frit, while the bottom consists of a similar, but removable porous frit to allow for placement of the sorbent. The height of the sorbent bed is maintained around 0.5 cm, with the bed sandwiched between quartz wool packing. A “semi-continuous” gas-phase mercury analyzer (PSA Sir Galahad II) is used to monitor the concentration and speciation of mercury in the gas stream.

Experimental Procedure

Approximately 0.2 g of the sorbent (size range 180–250 μm) is mixed with 1.8 g of inert alumina (size range 250–425 μm) to prevent channeling of mercury within the sorbent bed. The sorbent is loaded in the quartz reactor insert and the sorbent bed is supported by quartz wool and porous frit on both sides. Next, the reactor is inserted in the shell and preheated to the desired temperature in flowing 2.6 lpm of N_2 stream. A mercury permeation tube is used as a source of mercury with 0.4 lpm N_2 used as a mercury carrier stream. When the temperatures, flow rates, and bypass mercury concentration values are stabilized, the mercury is sent to the sorbent, and the outlet concentration (including mercury speciation) is monitored and recorded by the PSA analyzer. The mercury loading on the sorbent is calculated based on the area above the breakthrough curve. For selected experiments, this result is confirmed using a DMA-80 Direct Mercury Analyzer from Milestone, Inc., which measures total mercury loaded on the sorbent.

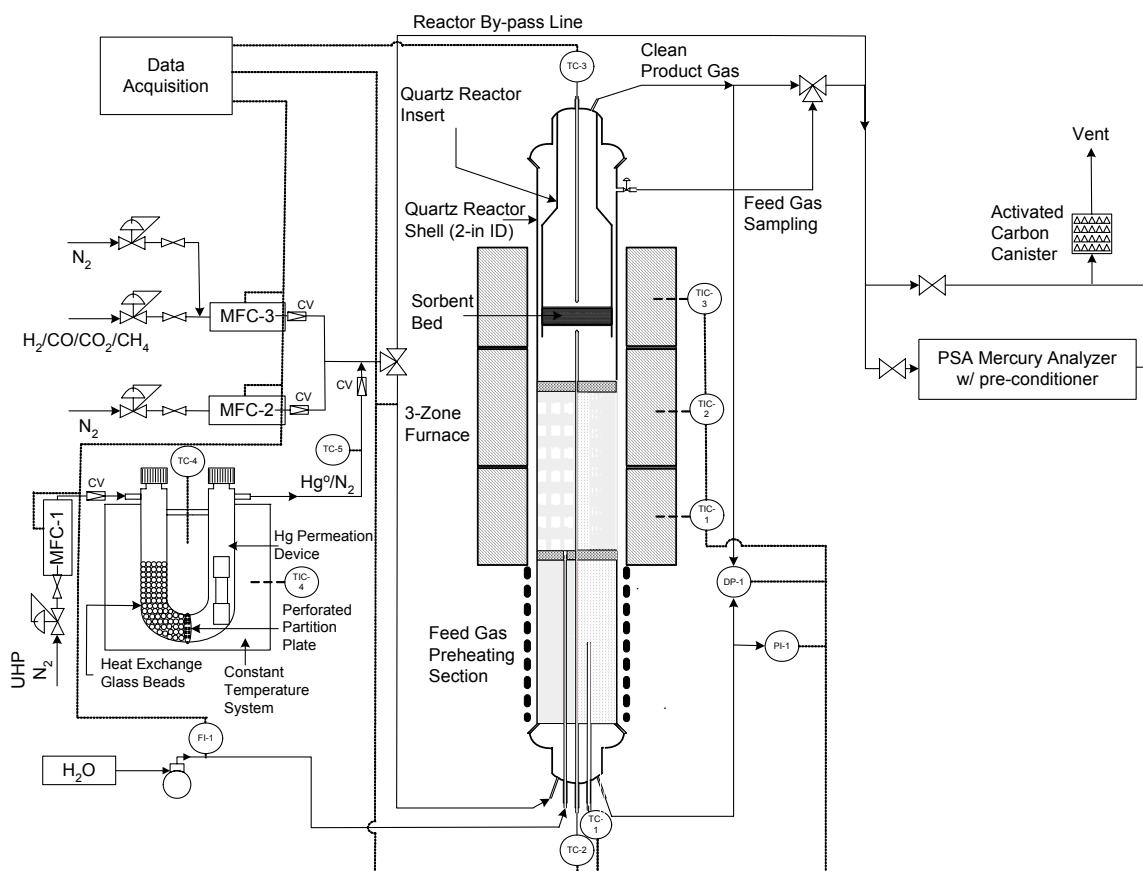


Figure 1 – Schematic of GTI's experimental setup for mercury sorbent testing

Sorbent Synthesis and Characterization

Eight different nanocrystalline metal oxides (viz., NanoActive® TiO₂, CeO₂, ZnO, CuO and NanoActive®-D MoO₃, Cr₂O₃, MnO₂, and MnO₂/alumina) were synthesized by NanoScale using their proprietary techniques. The NanoActive-D MnO₂/alumina is a supported sorbent with about 30 wt.% MnO₂ on a high surface area alumina support. The nanomaterials were pelletized by pressure-compaction method and ground to the desired size range (180–250 μm). Sorbents were characterized for surface area, chemical composition, crystallite size, and mechanical strength.

Specific surface areas were determined using a *Quantachrome* Nova 2200 BET instrument. Chemical composition and crystallite size of metal oxide samples were determined using powder X-ray diffraction (XRD, *Kratos XDS-6000*). To determine the crystallite size, the Scherrer equation was used:

$$\beta = K\lambda / L \cos\theta$$

where: β is the “physical half-value width” (in degrees 2θ), L is the crystallite size (dimension of the crystallite perpendicular to the diffracting net planes), K is a constant (often taken as 0.9) and λ is the wavelength of the radiation employed.

Mechanical strength of the sorbents was evaluated using the ball pan hardness method, as defined in the ASTM D3802 standard. In this test, granulated material is placed on vibrating metal sieves for fixed amount of time (30 min). Fraction of granules that remains on a metal sieve and does not break into smaller particles or powder defines the ball pan hardness.

RESULTS AND DISCUSSION

Characterization of Nanocrystalline Sorbents

Table 1 gives various properties of the eight nanocrystalline metal oxide sorbents synthesized and characterized by NanoScale.

Table 1 – Properties of NanoActive® metal oxide sorbents

Sorbent	Appearance	Specific Surface Area (m ² /g)	XRD Crystallite Size (nm)	Ball-Pan Hardness (%)
NanoActive TiO ₂	White	470	Amorphous	81
NanoActive CeO ₂	Yellow	125	7	31
NanoActive ZnO	Off-white	85	10	38
NanoActive CuO	Black	45	8.1	N/A
NanoActive-D MoO ₃	Grey	40	19	N/A
NanoActive-D Cr ₂ O ₃	Green	103	20.7	N/A
NanoActive-D MnO ₂	Black	38	8.6	N/A
NanoActive-D MnO ₂ /alumina	Brown	240	11	N/A

N/A – not available.

The materials prepared by NanoScale have crystallite sizes below 21 nm; therefore, can be classified as nanocrystalline.

Evaluation of NanoActive Sorbents for Mercury Capture

Mercury sorption capacities of the eight NanoActive metal oxides were determined by following the procedure given earlier. The sorption studies were carried out at two different temperatures of 150 and 260°C with 3 slpm of Hg-laden N₂ stream. The inlet mercury concentration varied over the range of 125–140 µg/m³ for these experiments, believed to be due to the day-to-day variation of the analyzer calibration.

NanoActive TiO₂, CeO₂, ZnO and MoO₃ sorbents were ineffective in capturing mercury, and their Hg-sorption capacities were negligible at both the temperatures. Table 2 gives a summary of the results for the NanoActive CuO, MnO₂, MnO₂/alumina, and Cr₂O₃ sorbents. It should be noted that the Hg-sorption capacity given in the table represents the sorbent capacity for the duration for which the sorbent was exposed to mercury, and does not represent saturation sorption capacity. In this table, the total mercury captured as a percentage is calculated by dividing the total mercury captured by the sorbent by the total mercury exposed to the sorbent.

Table 2 – Comparison of Hg-sorption capacities of NanoActive® sorbents

	150°C				260°C			
	CuO	MnO ₂	MnO ₂ /alumina	Cr ₂ O ₃	CuO	MnO ₂	MnO ₂ /alumina	Cr ₂ O ₃
Inlet Hg conc., µg/m ³	130	125	138	130	140	132	135	133
Final outlet Hg conc., µg/m ³	97	45	10	4	140	106	75	56
Sorption time, hr	6	6	4	6	2.5	5	6	6
Hg-sorption capacity, µg/g	250	490	480	720	74	230	500	530
Total Hg captured, %	36	73	97	~100	21	32	70	73

Of the eight-nanocrystalline sorbents evaluated so far in this work, NanoActive-D Cr₂O₃ was the most effective at both the temperatures. Figure 2 shows a typical mercury breakthrough plot for NanoActive-D MnO₂/alumina sorbent at 150°C.

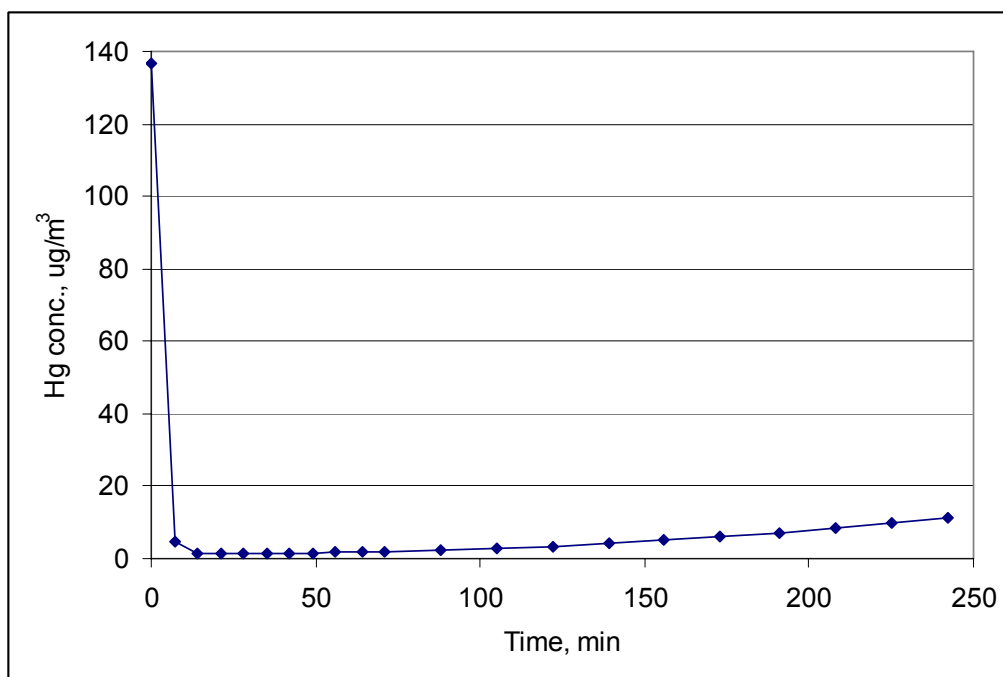


Figure 2 – Mercury breakthrough plot for NanoActive-D MnO₂/alumina sorbent at 150°C

Results in Table 2 indicate that mercury-sorption capacity of the sorbents decrease at higher temperature, suggesting that physical adsorption is the controlling mechanism of mercury capture. Analysis of the mercury speciation data given by the PSA mercury analyzer also suggests that the metal oxides evaluated did not have any potential to oxidize mercury in the inert nitrogen stream (the speciation data are not shown here for clarity).

CONCLUSION

Eight different types of nanocrystalline metal oxide sorbents were synthesized, characterized, and evaluated for their effectiveness in capturing mercury. Screening tests carried out in nitrogen stream indicated that NanoActive-D Cr₂O₃ was the most active of these sorbents in capturing mercury. Physical adsorption was found to be the dominating mechanism of mercury capture. Additionally, it was concluded that the metal oxides did not have any potential to oxidize mercury in the inert nitrogen atmosphere. Future work includes evaluating these sorbents in simulated fuel gas conditions.

ACKNOWLEDGMENT

The funding for the research work is being provided by U.S. Department of Energy's National Energy Technology Laboratory under research Contract No. DE-FC26-04NT42312.

REFERENCES

-
- (1) Reed, G.P., A. Ergudenler, J.R. Grace, A.P. Watkinson, A.A. Herod, D. Dugwell, and R. Kandiyoti, Control of gasifier mercury emissions in a hot gas filter: the effect of temperature, *Fuel*, **80**, 623-634, 2001.
 - (2) Lu, D.Y., D.L. Granatstein, and D.J. Rose, A study of mercury speciation from simulated coal gasification, in Proceedings of Combustion Canada '03 Conference, Vancouver, BC, 2003.