Comparison of Hg^0 Capture Efficiencies of Three *in situ* Generated Sorbents

Tai Gyu Lee and Pratim Biswas
Aerosol and Air Quality Research Laboratory, Environmental Engineering and Science Division,
University of Cincinnati, Cincinnati, OH 45221

Elizabeth Hedrick
National Exposure Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268

Three different sorbent materials (Ti-, Si-, and Ca-based) were compared for their mercury (Hg^0) capture efficiencies in an entrained flow reactor. Agglomerated particles with a high specific surface area were generated in situ by injecting gas-phase sorbent precursors into a high-temperature furnace reactor. Titania particles in the presence of UV *irradiation were most effective at mercury capture ($> 98\%$). In situ generated CaO particles had a capture efficiency of 33% (without any* UV *irradiation), while SiO_2 was completely ineffective at Hg^0 capture. The efficiency of elemental Hg capture of both CaO and TiO_2 particles decreased with increasing SO_2 concentration. The increase in the feed rate of the Ti sorbent resulted in the recovery of the higher Hg^0 capture efficiency due to the availability of more active sites. The in situ generated titania sorbents were also effective at Hg^0 capture ($> 87\%$) at elevated temperatures (160°C).*

Introduction

Toxic metal emissions control from combustors is currently being stipulated by the U.S. EPA in the form of maximum achievable control technologies (MACT) for 11 metals (As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, and Se) and their compounds under Title III of the 1990 Clean Air Act Amendments. Mercury is receiving significant attention due to its unique characteristics, such as high volatility, tendency to bioaccumulate, and its toxicity. Unlike most other trace metals that are emitted in particulate form, mercury has been reported to be released in the vapor phase in the elemental form. In a recent report (U.S. EPA Report, 1998), the EPA estimated that mercury emissions produced by human activities rival or exceed natural inputs. In the United States alone, the reported total emissions of mercury from all identified and quantified sources for the time period of 1994−1995 was 158 tons (over 12 months). Nriagu and Pacyna (1988) reported that the estimated global anthropogenic emissions of vapor-phase mercury are about 1,000 to 6,000 ton/yr. The major anthropogenic sources of the mercury emissions are coal combustors and municipal waste incinerators. In the U.S., total mercury emissions from all identified coal combustors (utility boilers and commercial/industrial boilers) are 72.3 tons per year, while those from waste incinerators (MWCs) (municipal, medical, and hazardous waste) are 52.7 tons per year, accounting for approximately 80% of the total amount (Biswas, 1999). In coal combustion, mercury is reported to be released primarily in elemental form in most cases (Hall et al., 1990; Meij, 1991; Wu and Biswas, 1993; Morency, 1994; Chu and Porcella, 1995), though recent reports (Fahlke and Bursik, 1995; Evans and Nevitt, 1997; Senior et al., 1997) indicate a higher oxidized fraction. In waste incineration, the elemental mercury fraction ranges from 10% to 90%, depending on the waste composition and operating conditions (Lindqvist, 1986; Bergström, 1986; Reimann, 1986; Hall et al., 1991; Livengood et al., 1994). Elemental mercury vapor is not effectively captured in typical air-pollution control devices. It can remain airborne for about a year and can be transported over thousands of miles before eventually be-

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Correspondence concerning this article should be addressed to P. Biswas at this current address: Environmental Engineering Science, Campus Box 1180, Washington University in St. Louis, St. Louis, MO 63130.

Current address of T. G. Lee: KIST, Seoul 136-650, Korea.

ing deposited to the ground and water, while a fraction of it may be transformed to form more toxic species such as methyl mercury (Hanisch, 1998). It may also bioaccumulate in the food chain, which may result in adverse health effects in human beings and predator animals (Lindqvist, 1986; Hall et al., 1990, 1991; Aizpún et al., 1994; Seigneur et al., 1994). Due to its high toxicity, stringent regulations have been proposed for mercury emissions (CFR, 1992b; U.S. EPA Report, 1998), making effective control of mercury emissions critical.

Currently, the most widely used technique for Hg capture involves the use of activated carbon; and activated carbon impregnated with sulfur, chlorine, or iodine is found to be most effective (Sinha and Walker, 1972; Otani et al., 1986; Krishnan et al., 1994; Livengood et al., 1994; Morency, 1994). Activated carbon injection is particularly effective in MWCs, where the Hg concentration is usually very high. However, its effectiveness on a wide range of power plants is still uncertain, because of their mercury concentrations, which are typically one or two orders of magnitude lower than those in MWCs (Lausman and Lavely, 1997). Also, the use of activated carbon is limited because of its very high cost, poor capacity, low applicable temperature range, and its slow re-

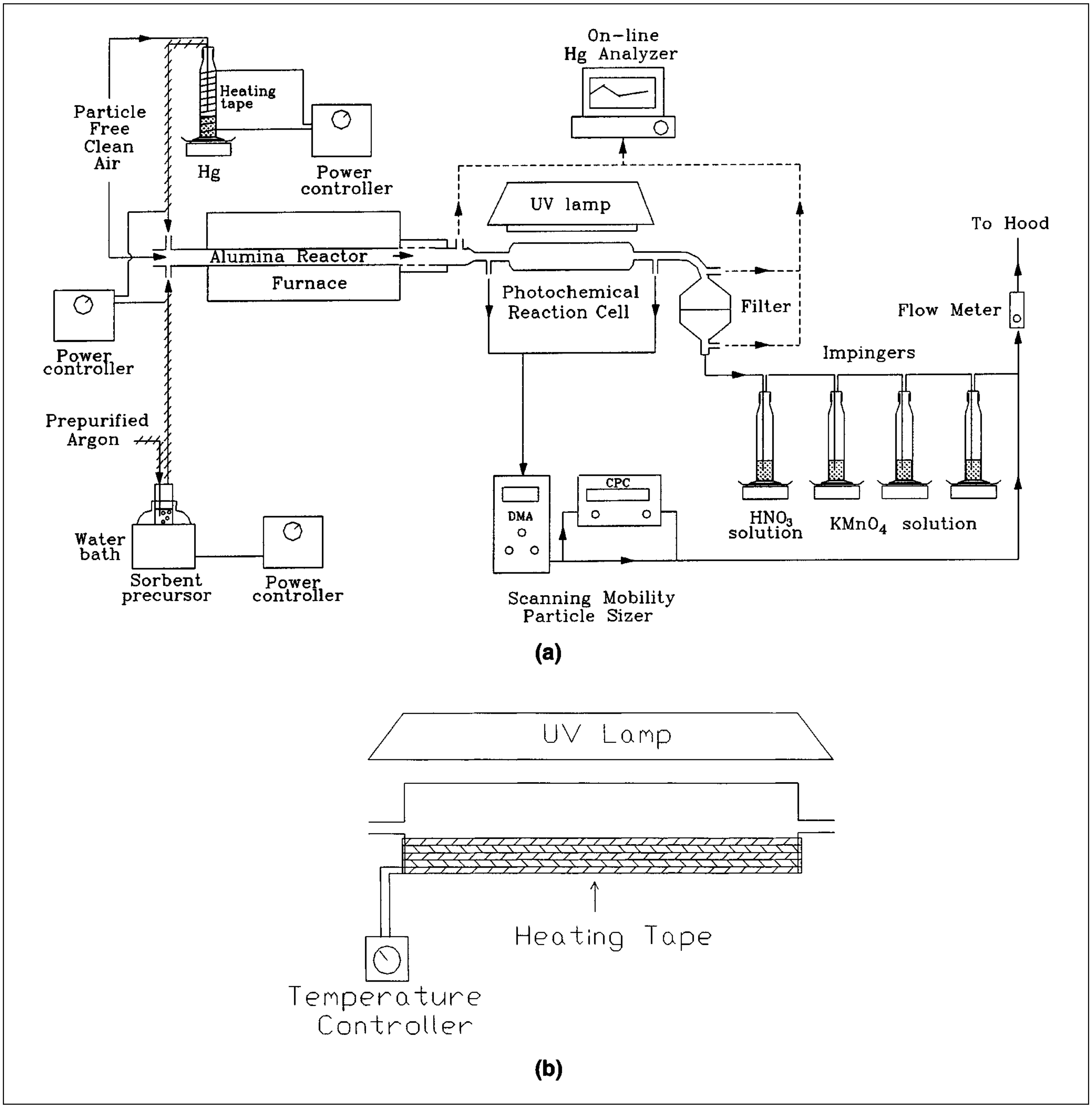

Figure 1. Experimental setup: (a) flow reactor system; (b) modified photochemical reaction cell.

generation and adsorption rates (Otani et al., 1986; Quimby, 1993). In a recent study, the effectiveness of an activated-carbon fiber filter for mercury removal from an air stream with much improved properties, such as regeneration and adsorption rates, was demonstrated (Hayashi et al., 2000). A novel low-cost methodology for capture of mercury using Ti sorbents and UV light has also been developed (Wu et al., 1998).

Sorbent particles have been demonstrated to be effective for the capture of certain toxic metals in combustion environments (Uberoi and Shadman, 1990, 1992; Ho et al., 1992; Gullet and Ragnunathan, 1994; Biswas and Wu, 1998). Compared to traditional bulk sorbent particles used in a fixed bed or fluidized bed, *in situ* generated agglomerates by injecting a gas-phase sorbent precursor have been shown to possess higher capture efficiency (Owens and Biswas, 1996a,b; Biswas and Zachariah, 1997) as well as to suppress the formation of submicrometer particles (Owens and Biswas, 1996a), and thus result in lower emissions without any increase in a pressure drop. This is due to the higher surface area provided by the larger number of agglomerated particles. The resultant sorbent particle characteristics would be controlled to obtain agglomerates that are readily captured in existing particulate control devices.

In this study, three different sorbent materials (Ti-, Si- and Ca-based) were tested for their ability to capture elemental mercury in a high-temperature environment using the novel *in situ* vapor-phase sorbent precursor injection technique. Based on the previously reported studies (Wu et al., 1996, 1998), TiO_2 was demonstrated to be very effective for mercury capture in the presence of UV irradiation. SiO_2 was selected due to its proven effectiveness in capture of lead, resulting in formation of environmentally benign (low leachability) lead silicate (Owens and Biswas, 1996a, 1996b). CaO was chosen, as it is currently being used for the control of sulfur compounds in the flue gases. Also, the role of SO_2 on the effectiveness of mercury capture by the three different sorbent materials (Ti-, Si- and Ca-based) was established.

Apparatus and Materials

A flow reactor with real-time measurement of particle-size distribution and composition analysis was used to study the capture of mercury by *in situ* generated sorbent particles with and without UV irradiation. Figure 1a shows the experimental system.

The alumina reactor tube was 91.44 cm long with an inner diameter of 2.54 cm.

Compressed air was used as the carrier gas and was passed through a HEPA filter (75-62 FT-IR purge gas generator, Balston Filter Products) to assure it was particle free. Mercury vapor was introduced into the system by passing particle-free air at a precisely controlled flow rate (MKS Mass-Flo Controller, MKS Instruments, Inc.) above liquid mercury contained in a gas washing bottle. The Hg feed bottle was placed in a beaker filled with water and the temperature was controlled with a constant temperature controller (Temp-Cal-Beak, Model EFC200, PDI Inc.). To minimize mercury condensation, a heating tape (Thermolyne) was used for the Teflon tubing (which connected the exit of the bottle to the entrance of the furnace), and the temperature was controlled with a power controller (Type 45500, Thermolyne). The sorbent precursor was introduced into the system by bubbling argon (prepurified, 99.99%, Wright Brothers) through the precursor solution (calcium precursor in solid phase) contained in a bubbler (Midget, 30 mL, Ace Glass). The bubbler was placed in a water bath (No. 5160 wide-neck flask, 500 mL, Pyrex; TM106 heating mantle, 500 mL, Glas-Col), the temperature of which was controlled by a power controller. The tubing before (connected to the argon source) and after (connected to the furnace entrance) the bubbler was wrapped by heating tape to prevent any losses due to condensations. An additional inlet was connected to the reactor for the purpose of feeding the SO_2 gas (3,000 ppm, Wright Brothers) into the system.

A photochemical reaction cell was placed at the exit of the reactor tube, which was irradiated with UV light. The cell was 60 cm in length and 5 cm in diameter, and was made of borosilicate glass (No. 7740, Pyrex). The transmittance of the glass is 94% for 360 nm, 72% for 320 nm, and 30% for 300-nm UV irradiation. The UV lamp (Type XX-40, 80 W, Spectronics) was 120 cm long, and the intensity at 365 nm was 1850 $\mu W/cm^2$ at a distance of 25 cm. A glass fiber filter (No. 61663. Gelman Science) was used downstream to collect particles for XRD analyses. The gas stream was then sent to the on-line mercury analyzer (UV-1201 Mercury Analysis Unit, Shimadzu) for real-time monitoring of relative mercury (Hg^0) concentration in the gas stream. When necessary, after the on-line mercury analyzer, a series of sampling impingers was used to capture the total mercury in the gas phase using a procedure similar to Wu et al. (1998). To measure particle-size distribution in real time, tubings were connected to the system before and after the photochemical reaction cell to direct the sample particles to a Scanning Mobility Particle Sizer (Model 3934 DMPS, TSI Inc.).

The precursor used for titania was titanium(IV) isopropoxide, 97% ($Ti[OCH(CH_3)_2]_4$, Aldrich). For silica and calcium, hexamethyldisiloxane, 98+% ($[CH_3]_3SiOSi[CH_3][CH_3]_3$, Aldrich, and calcium 2,2,6,6-tetramethyl-3,5-heptanedionate ($C_{22}H_{38}O_4Ca$, Gelest), respectively, were used.

A modified photochemical reaction cell was used (Figure 1b) to investigate the effectiveness of TiO_2 on mercury capture in the presence of UV irradiation at various temperatures. The bottom half of the glass column was covered with heating tape so that the temperature inside the photochemical reaction cell could be varied from in the range of 24 to 160°C. Only the bottom half of the column was covered to allow UV light to penetrate through the top half of the glass column.

Procedures and Measurement

A series of experiments were conducted to compare the effectiveness of the three different sorbent materials (Ti, Si, and Ca) on Hg^0 capture in simulated flue gas system (Table 1). The flow rates of argon through the precursor bubblers was controlled to obtain similar feed rates of the sorbent oxide into the reactor. Set IA, IB, and IC were carried out to characterize the *in situ* generated sorbent particles (TiO_2, SiO_2, and CaO). Set IIA, IIB, and IIC were to establish the

Table 1. Experimental Conditions for Comparison of Sorbent Materials for Hg Capture Efficiencies

Set No.	Hg Feed Bottle Temp. (°C)	Air Flow Rate through Hg Feed Bottle (cm^3/min)	Precursor Inlet Bubbler Temp. (°C)	Air Flow Rate through precursor Bubbler (cm^3/min)	SO_2 Inlet Conc. (ppm)	Photochemical Cell Temp. (°C)
IA. TiO_2 only	—	—	75	100	—	24
IB. SiO_2 only	—	—	25	5	—	24
IC. CaO only	—	—	100	150	—	24
IIA. $Hg + TiO_2 \pm UV$	30	20	75	100	—	24
IIB. $Hg + SiO_2 \pm UV$	30	20	25	5	—	24
IIC. $Hg + CaO \pm UV$	30	20	100	100	—	24
IIIA. $Hg + TiO_2 + SO_2 \pm UV$	30 (24)	20	75	100, 150 (100, 200)	300, 600 (0, 600, 1,200 1,800, 2,400, 3,000)	24
IIIB. $Hg + SiO_2 + SO_2 \pm UV$	30	20	25	5	300, 600	24
IIIC. $Hg + CaO + SO_2 \pm UV$	30	20	100	100	300, 600	24
IV. $Hg + TiO_2 + UV$	24	20	80	300	0	24, 54, 68, 85, 100, 116, 160

Note: Furnace temperature: 1,000°C; total flow rate in reactor: 1 Lpm.

effectiveness of the *in situ* generated sorbent particles for Hg capture with and without UV irradiation. Set IIIA, IIIB, and IIIC were performed to investigate the effect of sulfur (SO_2) on the Hg^0 capture. Except for the addition of SO_2 gas, conditions for Set III were similar to that of Set II. The feed rate of Ti was increased to examine the effect on the capture efficiency.

The total flow rate in the reactor was maintained at 1 Lpm in all experiments. Mercury vapor was entrained in a 20 cm^3/min air stream at 30°C. The corresponding residence time in the furnace reactor was approximately 3 s at a set temperature of 1,000°C. Though combustion systems have a range of temperatures, we selected this value and compared the performance of the different sorbents under this condition. The temperature in the entire photochemical reaction cell was 24°C, and the residence time was 70 s. This is a long residence time relative to that observed in practical systems, and other experiments have been conducted to explore the kinetics of the sorbent−mercury reactions under varying residence times (Lee, 1999). The experiments were conducted after both the system and the on-line analyzer readings had stabilized. Inlet mercury (Hg^0) concentrations in the system were measured to be in the range of 5.5−6.5 $\mu g/m^3$.

In Set IV, the photochemical reaction cell was modified so that the reaction temperature in the cell could be controlled. This was to validate the effectiveness of mercury removal by TiO_2 at elevated temperatures (Table 1). Cell temperatures up to 160°C were used to simulate the combustion flue gas temperature before it enters an electrostatic precipitator (ESP). This was important in the following aspect: the corona of the ESPs, which can be found in most air cleaning devices of coal combustors, can also be utilized as the potential source of UV irradiation (the flue gas temperature when it enters the ESP ranges from 150°C to 200°C). Therefore, the validation of TiO_2's effectiveness on mercury (Hg^0) capture with UV irradiation at this temperature range is important.

The objective of this study was to establish the fraction of mercury collected on the filter (or the partitioning between the particulate and gaseous phases, also defined as the capture efficiency). This was done by measuring the Hg^0 concentration with an on-line mercury analyzer before and after the injection of sorbent precursors. The on-line mercury analyzer was calibrated by using a procedure similar to U.S. EPA Method 29 and Cold Vapor Atomic Adsorption (CVAA) analyzer (mercuryModule, Thermo Separation Products). The first sampling impinger contained a 0.1-M HNO_3 solution and was used to trap the oxidized forms of Hg (HgO in our experiments) (Wu et al., 1998). In this study, no mercury was trapped in the first impinger solution, indicating the absence of oxidized forms of mercury. Subsequent impingers containing 0.4% $KMnO_4/10\% H_2SO_4$ were used to trap elemental Hg in the gas phase (CFR, 1992a). The concentration of $KMnO_4$ was selected to minimize any interferences in the Hg measurement. For all experiments, it was determined that the last permanganate impinger captured less than 1.0% of the total measured mercury, providing assurance that all the Hg was being trapped in the impingers. The impinger solutions were analyzed to determine the elemental Hg concentration and oxidized Hg species concentration in the gas phase (no oxidized forms of mercury were found in this study). Dilutions were usually required due to high concentrations of Hg in the impinger solutions. Just before the analysis by CVAA, for impingers with low Hg concentration, microliter volumes of a 50% hydroxylamine solution were added until the purple color of the $KMnO_4$ disappeared.

Due to the nature of Hg and the various reports in the literature on the difficulty in performing reliable experiments, extra precaution was exercised. Before every experiment, the reactor was scrubbed clean at a high temperature (1,200°C) and blank measurements were carried out to ensure there was no residual mercury in the system. The Teflon tubing was also changed prior to each experiment or acid cleaned. Also, the on-line Hg analyzer was acid cleaned before every experiment.

Particle-size distribution is also an important factor that affects the capture efficiency. The distribution was determined by the Scanning Mobility Particle Sizer (SMPS), which provided information about the mean particle size, number concentration, volume concentration, and standard deviation. Measurements were made after the system had stabilized, and

Table 2. Structural Characteristics of *in situ* Generated Sorbent Particles (TiO_2, SiO_2, CaO)

Sorbent Type	TiO_2	SiO_2	CaO
Density [g/cm^3]	3.9	2.334	3.34
Geometric mean dia. (nm)	227.8	127.7	161.6
Total no. conc. ($no./cm^3$)	9.08×10^6	1.76×10^6	4.40×10^5
Total surface-area conc. ($nm^2/cm^3{}_{air}$)	2.25×10^{12}	3.39×10^{11}	5.26×10^{10}
Total volume conc. ($nm^3/cm^3{}_{air}$)	1.32×10^{14}	1.09×10^{13}	2.35×10^{12}
Spec. surface area by SMPS (m^2/g)*	4.36	14.25	6.69
Spec. surface area by BET (mg^2/g)	50.4	247.7	41.4
Crystalline structure	Anatase	Amorphous	Amorphous

Note: Experimental conditions (IA, IB, and IC) are described in Table 1.
*Based on the assumption of spherical shape for the measuring particles.

at least three measurements were averaged for each run. The morphology of the particles was examined by Transmission Electron Microscopy (CM 20, Philips). The surface areas of the sorbent particles were measured using a BET analyzer.

Results and Discussion

Several experiments were conducted (Table 1) to understand the mechanism and determine the effectiveness of the capture process. The previous analyses (Wu et al., 1997, 1998) and the measurement by SMPS and the on-line mercury analyzer both indicated that no detectable transformation to the aerosol phase and no oxidation of Hg was taking place at combustion temperatures (1,000°C) under various residence times with and without UV irradiation. The first set of experiments was aimed at characterizing the *in situ* generated sorbent particles. These were followed by experiments designed to investigate the effectiveness of Hg^0 capture by the three sorbent materials under various conditions (UV and SO_2). The concentration of SO_2 was varied to further elucidate its effect on the Hg capture by TiO_2 in the presence of UV (Table 2). Finally, the effectiveness of the UV-irradiated titania on mercury capture was investigated by varying the photochemical reaction cell temperature from 24°C to 160°C (Table 2). The results are discussed in the following sections.

Characterization of in situ generated sorbent particles (Set I)

The objective was to examine the structural characteristics of *in situ* generated sorbent particles (Ti, Si, and Ca based) by the gas-phase sorbent precursor injection method using different sorbent materials. The engineering of the sorbent particle formation process is critical to the effectiveness of the capture of metals. First, a high surface area/mass ratio should be obtained for the resulting sorbent oxide. For the high-temperature sorbent generation, extensive sintering should therefore be avoided to prevent a reduction in the surface area. The formation of an agglomerate structure with small primary particles is preferred. The *in situ* sorbent formation methodology allows the characteristics just listed to be controlled (Biswas and Wu, 1998). The gas-phase sorbent precursor enters the reactor and is readily oxidized to form sorbent particles. These particles then grow by coagulation and sintering mechanisms that result in a highly agglomerated structure (Yang et al., 1996; Yang and Biswas, 1997). The size distributions of the high-temperature oxidation-generated agglomerate particles (TiO_2, SiO_2, and CaO) are shown in Figure 2 and representative TEM pictures in Figure 3. The structural characteristics of the sorbent particles are listed in Table 2. The calculated specific surface areas from the SMPS measurements are 4.36, 14.25, and 6.69 m^2/g for TiO_2, SiO_2, and CaO, respectively. The specific surface areas of TiO_2, SiO_2, and CaO by BET analyses are 50.4, 247.7 and 41.4 m^2/g, respectively. BET surface areas are much higher than the calculated values from SMPS measurements. This is because the SMPS inversion routine assumes a spherical shape, whereas the *in situ* generated sorbent particles (TiO_2, SiO_2, and CaO) are highly agglomerated (Figure 3), and therefore underestimates the total surface area (Lee, 1999). The agglomerated structures provide for an open surface for transfer of the Hg species to the sorbent particle.

X-ray diffraction patterns indicated that the titania particles were primarily the anatase phase (the desired TiO_2 phase for the subsequent photooxidation of mercury), while calcium oxide and silica particles were amorphous.

Although not investigated, it should be noted that the characteristics of the resultant sorbent could be readily varied by altering the precursor injection rate, residence time, and temperatures. In a full-scale system, an appropriate injection strategy would have to be used to assure the desired structural characteristics of the sorbent.

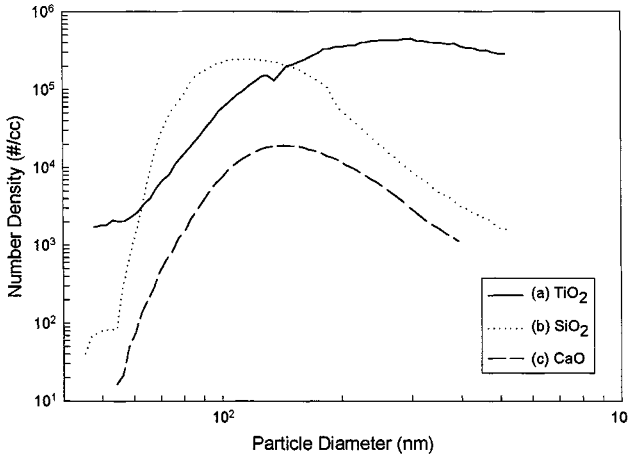

Figure 2. Size distributions of *in situ* generated sorbent particles: (a) TiO_2; (b) SiO_2; and (c) CaO.

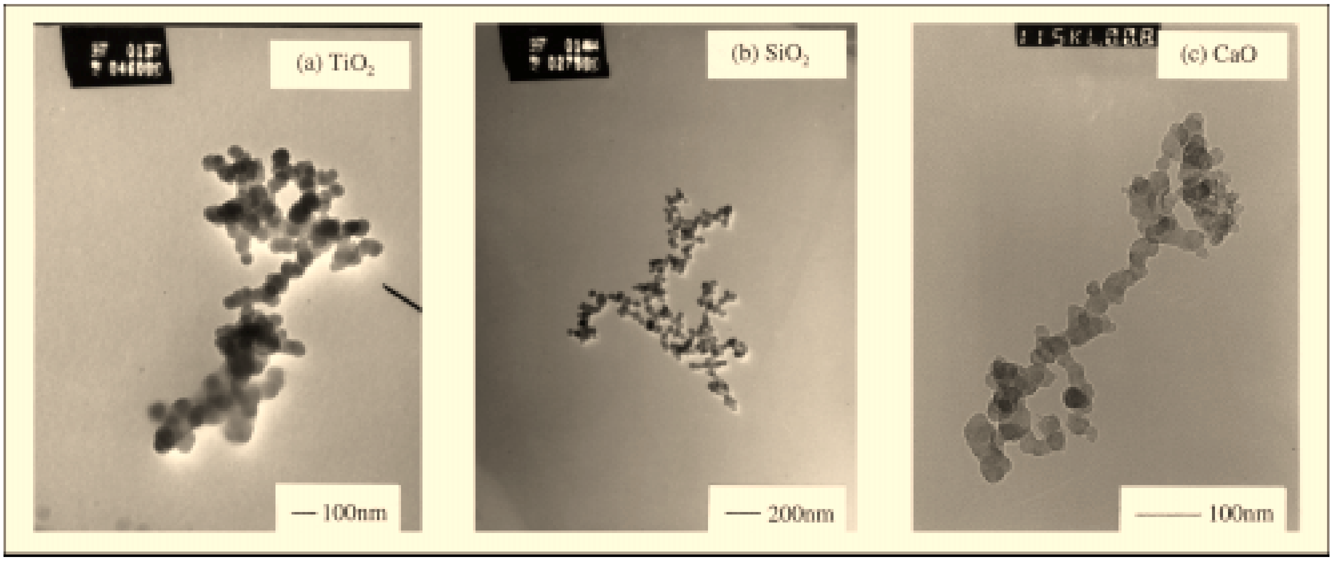

Figure 3. TEM micrographs of *in situ* generated sorbent particles: (a) TiO_2; (b) SiO_2; and (c) CaO.

Effectiveness of mercury (Hg^0) capture by in situ generated sorbent particles (Set II)

A series of experiments were performed to compare various sorbent materials for their mercury capture efficiencies, with and without UV irradiation.

A detailed study of the reaction of *in situ* generated titania sorbents with elemental mercury has been reported by Wu et al. (1998) and the pertinent results are listed in Table 3 for comparison purposes. In the absence of UV irradiation, no mercury is captured by the titania particles. Although the specific surface area is quite high, the intraparticle porosity is low and the elemental mercury associated with the titania particle is readily reentrained. On irradiation with UV light, the titania is activated and electron−hole pairs are generated on the particle surface. The positive holes may result in OH radicals formation, which then oxidize the mercury, thus creating a lower volatile form (HgO) that is retained on titania particle surface (capture efficiency $> 98\%$, Table 3).

An objective of the study was to compare the performance of the titania sorbents to other sorbents. Silica was selected as the *in situ* form was proven to be very effective for capture of heavy metals such as lead (Owens and Biswas, 1996b). However, silica was totally ineffective in mercury capture, though the specific surface area was the largest (Table 2). The irradiation with UV light had no effect, as the amorphous silica produced is not a semiconducting oxide.

The next sorbent tested was an *in situ* generated CaO material (Table 2). The sorbent particles captured approximately 33% of the Hg (Table 3), much higher than titania (in the absence of UV irradiation) and silica. This is probably due to the presence of active sites on the *in situ* generated CaO. Ghorishi and Sedman (1998) have examined the capture of mercury by calcium-based sorbents in a packed bed and observed that the elemental mercury capture efficiency was approximately 5%. The higher capture efficiencies ($\sim$ 33%) of our *in situ* generated CaO sorbents was due to the structural characteristics, better mass transfer (entrained state compared to use of a packed bed), and higher specific surface areas with more active sites.

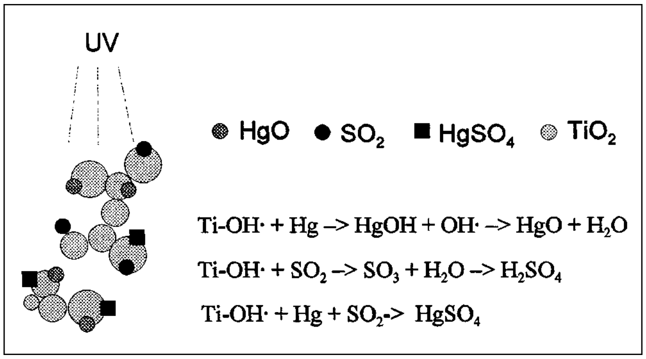

Figure 4. Mechanistic description of Hg capture by UV irradiated TiO_2 in the presence of SO_2.

Effect of SO_2 on the mercury (Hg^0) capture by in situ generated sorbents (Set III)

Silica particles were ineffective in the capture of elemental mercury, even in the presence of SO_2. For both Ca- and Ti-based sorbents, however, there was a decrease in the mercury capture efficiency (Table 3) due to a reduction in the active sites. In the case of titania, the active sites are the ones that are photoactivated and are potential oxidants. Some of these sites are occupied by sulfur dioxide (Figure 4), and are thus not available to oxidize and trap the mercury species, resulting in a decreasing capture efficiency. The Hg capture efficiency decreases with increasing sulfur dioxide concentration. On increasing the titanium precursor feed rate, a higher number concentration of titania particles are formed, and as more active sites are available, this results in an increase in the Hg capture efficiency ($> 80\%$).

In the case of our CaO sorbent particles, the active sites may have a chemical affinity for sulfur dioxide, resulting in a

Table 3. Mercury Capture Efficiencies of Sorbent Materials (Ti-, Si-, and Ca-Based)

Set	Argon Flow Rate through Precursor Bubbler (cm^3/min)	SO_2 Inlet Conc. (ppm)	η^{**}
Ti Precursor: Titanium (IV) Isopropoxide, 97%, $Ti[OCH(CH_3)_2]_4$			
Air + Hg + Ti	100	0	0
Air + Hg + Ti + *UV*	100	0	0.986
Air + Hg + Ti + SO_2	100	300	0
Air + Hg + Ti + SO_2	100	600	0
Air + Hg + Ti + SO_2 + *UV*	100	0	0.986
		300*	0.64
		600*, 600	0.56*, 0.78
		1,200	0.72
		1,800	0.75
		2,400	0.74
		3,000	0.69
	150	300	0.82
		600	0.82
	200	0	0.999
		600	0.93
		1,200	0.99
		1,800	0.92
		2,400	0.95
		3,000	0.94
Si Precursor: Hexamethyldisiloxane, 98 + %, $[CH_3]_3SiOSi[CH_3]_3$			
Air + Hg + Si ± *UV*	5	0	0
Air + Hg + Si + SO_2	5	300	0
		600	0
Ca Precursor: Calcium 2,2,6,6-Tetramethyl-3,5-Heptanedionate, $C_{22}H_{38}O_4Ca$			
Air + Hg + Ca	100	0	0.33
Air + Hg + Ca + *UV*	100	0	0.33
Air + Hg + Ca + SO_2	100	300	0.24
		600	0.18
Air + Hg + Ca + SO_2 + *UV*	100	300	0.24
		600	0.18

Note: Concentration of Hg^0 measured as shown in Figure 1.
*Hg feed bottle temperature = 30°C.

$$^{**}\eta = \frac{(C_{Hg}\text{ before sorbent precursor injection}) - (C_{Hg}\text{ after sorbent precursor injection})}{(C_{Hg}\text{ before sorbent precursor injection})}.$$

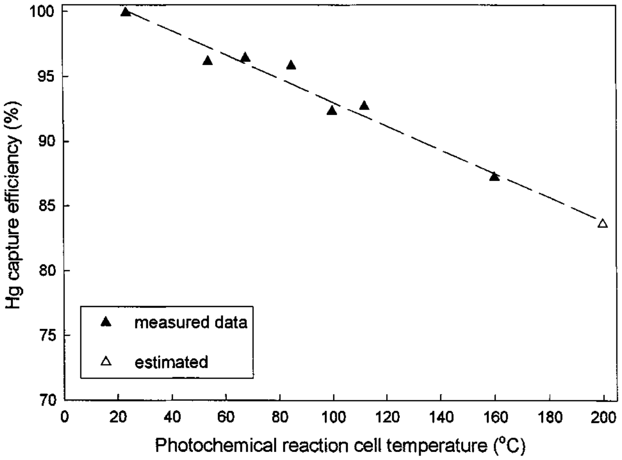

Figure 5. Hg capture efficiency by TiO_2 + UV vs. photochemical reaction cell temperature.

decreased capture efficiency (24.4% for 300 ppm SO_2, 18.1% for 600 ppm SO_2). This is in contrast to the report by Ghorishi and Sedman (1998), who observed that the efficiency of the capture of mercury by various lime sorbents increased with increasing SO_2 concentration. They attributed this to reaction of Ca sorbents with SO_2 to create active sulfur sites for adsorption of Hg^0, probably by chemisorption. This further indicates the importance of the structure of the sorbent material in establishing Hg capture. In case of our *in situ* generated Ca sorbents, sufficient sites were present to capture Hg (~ 33% compared to less than 5% as demonstrated by Ghorishi and Sedman, 1998). However, the presence of SO_2 resulted in a decrease in the active sites of the *in situ* generated Ca particles, whereas it created chemisorption-type sites for the Ca-based sorbents of Ghorishi and Sedman (1998). It should be noted that the same Ca-based sorbents used by Ghorishi and Sedman (1998) showed a contrary effect for $HgCl_2$ capture-decreased efficiency in the presence of sulfur dioxide, similar to what we observed for the capture of elemental mercury with our Ca-based sorbents.

Effectiveness of TiO_2 on Hg^0 capture at various photoreaction temperatures (Set IV)

Because titania was shown to be the most effective among the three sorbents tested for Hg capture (efficiency > 98% in the presence of UV irradiation), another objective of this work was to examine the effectiveness of TiO_2 in the presence of UV irradiation for its mercury capture at elevated photochemical reaction cell temperatures (analogous to temperatures experienced in an ESP). The photochemical reaction cell temperatures were elevated to 160°C, the typical temperature range (150 ~ 200°C) of the flue gases entering the electrostatic precipitator (ESP) in coal combustors. Another reason for testing it under ESP conditions is due to the fact that the corona may be a potential source of UV light. Experiments with titania and mercury in the presence of UV irradiation were carried out at seven different photochemical reaction cell temperatures (Table 1, Set IV). Figure 5 shows that the Hg capture efficiency in the range of 87.2% (160°C) to 99.9% (24°C), indicating TiO_2 in the presence of UV irradiation, can be effective even at the flue gas temperature entering the ESP. It can be concluded from the preceding results that the gas-phase sorbent precursor injection method using titania precursor can be highly effective in controlling vapor-phase elemental mercury emissions from coal combustors at typical flue-gas temperatures.

Conclusions

A gas-phase sorbent precusor injection method was used to generate different sorent materials (Ti, Si, and Ca based), and their mercury (Hg^0) capture efficiencies were determined under a variety of conditions. Titania particles in conjunction with UV irradiation were the most effective (> 98%) for elemental Hg^0 capture, followed by CaO (~ 33%) particles. SiO_2 showed no effectiveness for Hg^0 capture under the different conditions tested. Addition of SO_2 gas resulted in a decrease in Hg^0 capture efficiencies for both TiO_2 and CaO particles due to the occupation of some active sites by the SO_2 gas molecules (which otherwise might have been available for Hg^0 capture). The higher capture efficiencies ($\sim$ 95%) could be obtained by increasing the titania particle feed rates, as sufficient sites were then available for Hg^0 capture. Although the efficiency of capture decreased slightly at elevated temperatures (160°C), it was still high ($\sim 85\%$) at typical flue gas temperatures.

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