

Photochemical Removal of Mercury from Flue Gas

Evan J. Granite* and Henry W. Pennline

National Energy Technology Laboratory, United States Department of Energy, P.O. Box 10940, Pittsburgh, Pennsylvania 15236-0940

Photochemical reactions of mercury with various constituents in flue gas produced by burning coal could be an attractive alternative to dry sorbent- or wet scrubber-based processes for mercury control. The sensitized oxidation of elemental mercury using 253.7-nm ultraviolet radiation has been extensively studied. The photochemistry of elemental mercury in simulated flue gases was examined using quartz flow reactors. Mercury-containing simulated flue gases at temperatures between 80 and 350 °F were irradiated with 253.7-nm ultraviolet light. Results are presented for the photochemical removal of elemental mercury from simulated flue gases, as well as from nitrogen mixtures that contain oxygen, water vapor, or nitrogen oxide. Optimization of the process parameters, including light intensity, is discussed. The implications of photochemical oxidation of mercury with respect to direct ultraviolet irradiation of flue gas for mercury control, analysis of gases for mercury content, and atmospheric reactions are discussed.

Introduction

Photochemical reactions of mercury with various constituents in flue gas could be an attractive alternative to sorbent-¹⁻⁸ or scrubber-based⁹ processes for mercury capture. The photochemical oxidation of mercury using 253.7-nm ultraviolet radiation has been extensively studied.¹⁰⁻³⁶ Using oxygen/mercury mixtures, Dickinson and Sherrill demonstrated the photochemical formation of mercuric oxide via the sensitized formation of ozone in 1926,^{10,11} and these experiments were reproduced in our laboratory.¹¹ The overall reaction between mercury and oxygen in the presence of 253.7-nm light is given by eq 1



In the reaction mechanism, elemental mercury serves as a sensitizer for the formation of ozone, and ozone oxidizes mercury to form mercuric oxide.^{10,11} Sensitized oxidation is a potential method for mercury removal from flue gases.¹²⁻¹⁵ The photochemical formation of mercuric oxide can also have a significant impact on on-line ultraviolet-based methods for the measurement of mercury in flue gas, as well as potential environmental consequences.¹¹⁻¹³

The quenching of fluorescent emission by mercury in the 6(³P₁) state is due to collisions with other gas atoms or molecules. There must be a transfer of energy from the photoexcited mercury to the other gas species. Mercury can return to the ground state after a quenching collision. Quenching efficiency or cross-sectional area is a function of the size, shape, and reactivity of the molecule.¹⁶⁻²⁵ Transition state theory proposes that, for a reaction to occur, species must collide and form an activated complex. The cross-sectional area for the quenching of 6(³P₁) Hg, already known for many atoms and molecules, suggests reactivity.²⁴ The quenching cross sections for several constituents of flue gas are given in Table 1,¹⁶⁻²⁵ with the larger quenching cross-

Table 1. Quenching Cross Sections for Hg 6(³P₁) → Hg 6(¹S₀)

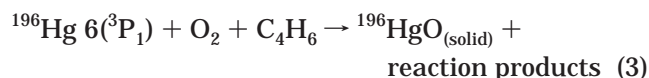
species	cross section (cm ²)
HCl	37.0 × 10 ⁻¹⁶
NO	24.7 × 10 ⁻¹⁶
O ₂	13.9 × 10 ⁻¹⁶
CO	4.1 × 10 ⁻¹⁶
CO ₂	2.5 × 10 ⁻¹⁶
H ₂ O	1.0 × 10 ⁻¹⁶
N ₂	0.4 × 10 ⁻¹⁶
Ar	0.04 × 10 ⁻¹⁶

sectional areas implying greater quenching efficiencies.

Gunning demonstrated the photochemical oxidation of mercury by water or hydrogen chloride at room temperature using a mercury lamp.²⁶⁻²⁸ Mercuric oxide and mercurous chloride were the main reaction products. Gunning also demonstrated the photochemical oxidation of mercury by N₂O to form mercuric oxide.

Burton determined the tendency of mercury in the 6(³P₁) state to form complexes with various gases, such as ammonia, methanol, ethanol, and *n*-propanol.²⁹ These complexes decompose and emit characteristic radiation, allowing for the detection of many different contaminant gases at trace levels.

Mercury-196 is used in fluorescent lamps to increase light efficiency.³⁰⁻³² At the Kurchatov Institute in Moscow, Russia, the photochemical separation of mercury is performed by isotopically selective photooxidation of mercury atoms in the presence of butadiene, as shown by reactions 2 and 3



McGilvery³³ suggested that the decomposition of NO, represented by



is photosensitized by Hg 6(¹P₁) atoms, whereas Noyes determined the reaction to be photosensitized by Hg

* To whom correspondence should be addressed. Tel.: (412) 386-4607. Fax: (412) 386-6004. E-mail: evan.granite@netl.doe.gov.

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Table 2. Typical Untreated Flue Gas Composition from a Power Plant Burning Low Sulfur Eastern Bituminous Coal

species	concentration (by volume)
H ₂ O	5–7%
O ₂	3–4%
CO ₂	15–16%
total Hg	1 ppb
CO	20 ppm
hydrocarbons	10 ppm
HCl	100 ppm
SO ₂	800 ppm
SO ₃	10 ppm
NO _x	500 ppm
N ₂	balance

6(³P₁) atoms.³⁴ Noyes^{35,36} also studied the photochemical oxidation of mercury by NO₂ using 253.7-nm radiation. Mercuric oxide was assumed to be the reaction product.^{35,36}

Biswas^{37,38} found that the longer 360-nm ultraviolet light alone is ineffective at oxidizing mercury in air. The 360-nm wavelength was highly effective when used with a titanium oxide photooxidation catalyst, capturing mercury as mercuric oxide in a heterogeneous oxidation reaction.^{37,38} The experiments described in our research effort involve gas-phase oxidation using 253.7-nm light, with subsequent deposition of oxidized mercury on a quartz substrate.

Caren^{39,40} discovered that reactive hydroxyl radicals form when automobile exhaust is irradiated with 253.7-nm light. Hydroxyl radicals, obtained from moisture in the exhaust, were demonstrated to be effective oxidizing agents for carbon monoxide and unburned hydrocarbons. Tabatabaie-Raissi^{41,42} found that hydroxyl radicals are produced when flue gas is exposed to 253.7-nm radiation, causing the oxidation of sulfur dioxide to sulfur trioxide. The sulfur trioxide formed can condition the fly ash particles entering an electrostatic precipitator.

A typical untreated flue gas composition from a coal-fired utility burning a low-sulfur eastern bituminous coal is shown in Table 2. It is noted that many reactive quenching agents are present in flue gas, such as O₂, H₂O, HCl, NO, and SO₂. These compounds are prime candidates for oxidizing mercury under the influence of 253.7-nm radiation (sensitized oxidation).

Experimental Section

The assembly used for studying the photochemical oxidation of mercury is an improved version of an apparatus described earlier.¹¹ It consists of an elemental mercury permeation tube, a heated quartz photoreactor with an ultraviolet lamp, and a flue gas blending system. The reactor scheme is shown in Figure 1. The flow photoreactor is a 20-in.-long by 1/4-in.-outer-diameter (1/6-in.-inner-diameter) cylindrical quartz tube. Once at thermal equilibrium, simulated flue gases flow through a quartz photoreactor that is irradiated with 253.7-nm light for 350 min—the time length of an experiment. Quartz is used for the photoreactor because it is transparent to 253.7-nm light. A large half-clam-shell furnace is used to heat the quartz photoreactor. The temperature profile is nearly isothermal within the section of tube that is being irradiated. An 8-in.-long, 6-W ultraviolet lamp from Spectrolite (Spectronics BLE-6254S) is used as the source of the 253.7-nm light. A 6-in.-long filter is used to remove other wavelengths of

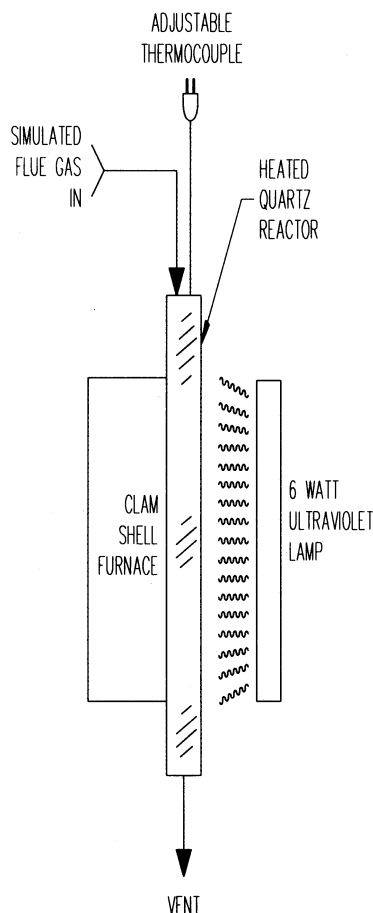


Figure 1. Photoreactor for mercury removal from flue gas.

light emanating from the mercury bulb. The quartz tubes are initially cleaned by rinsing first with trace-metals-grade 37% hydrochloric acid, then with distilled water, and last with analytical-reagent-grade acetone. The permeation tube, located in a heated bath, is held at 212 °F in a nitrogen stream at all times and releases 159 ng of elemental Hg/min. The permeation tube releases $55.7 \pm 3.3 \mu\text{g}$ of mercury during the 350-min irradiation of the flue gases.

The distance of the quartz photoreactor from the ultraviolet lamp was fixed at 1.75 in. The intensity of 253.7-nm light at this distance from the lamp is $1.4 \pm 0.07 \text{ mW/cm}^2$, as measured by a VLX-3W radiometer. The gas mixtures entered and exited the photoreactor at near ambient pressure. The simulated flue gases were heated to either 280 or 350 °F (typical temperatures found near a particulate collection device in a coal-fired power plant), and the flow rate was 60 mL/min. A portion of the flow photoreactor is illuminated by the ultraviolet lamp. The gas residence time (irradiated reactor volume divided by the gas flow rate) is approximately 2 s, which is near the residence time of flue gas found in a power generation facility's ductwork before the particulate collection device. The composition of the simulated flue gases was either (A) 16% CO₂, 5% O₂, 2000 ppm SO₂, 300 ppb Hg, balance N₂ or (B) 16% CO₂, 5% O₂, 2000 ppm SO₂, 500 ppm NO, 300 ppb Hg, balance N₂. Certified gases from Matheson were blended to make the simulated flue gases. Other gas compositions examined included an oxygen–nitrogen mixture (13.9% O₂, 300 ppb Hg, balance N₂), a water vapor

Table 3. Photochemical Removal of Mercury from Flue Gases^a

gas ^b	temperature (°F)	replicates	mercury capture (%)
A ^c	350	1	0.0
A ^c	280	1	2.5
A ^c	80	1	0.5
A	350	8	2.3 ± 2.0
A	320	1	3.5
A	311	1	1.9
A	302	1	1.1
A	280	5	71.6 ± 30.1
A	80	6	67.8 ± 28.8
B	280	8	26.8 ± 11.7
C	280	1	0.8

^a Flow rate = 60 mL/min. Intensity = 1.4 mW/cm² ^b Gas compositions: (A) 16% CO₂, 5% O₂, 2000 ppm SO₂, 300 ppb Hg, balance N₂; (B) 16% CO₂, 5% O₂, 2000 ppm SO₂, 500 ppm NO, 300 ppb Hg, balance N₂; (C) 1000 ppm NO, 300 ppb Hg, balance N₂. ^c Blank, no UV.

mixture (2% H₂O, 300 ppb Hg, balance N₂), and a nitrogen oxide (1000 ppm NO, 300 ppb Hg, balance N₂) blend.

Cold vapor atomic absorption spectrophotometry (CVAAS) was used to determine the mass of mercury contained in the white-colored stains that formed near the bottom of the quartz photoreactor. Both 8 N HCl and acidic permanganate were used to dissolve the stains; the resulting solutions were analyzed by CVAAS. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy-dispersive X-ray methods (SEM-EDX) were utilized to confirm the formation of mercury compounds on the walls of the quartz tubes. Ion chromatography (IC) was used to determine the mass of sulfate ion within some of the stains. Inductively coupled argon plasma atomic emission spectrometry (ICP-AES) was employed to determine the amount of sulfur within the stains.

Experimental Results

Parametric studies within the reactor system were conducted. The impacts of gas composition, radiation intensity, and temperature on mercury removal were determined. Analysis of the solid formations contributed to an explanation of the results.

Cleaning Procedure. Analysis of the acidic washings from the empty quartz tubes showed extremely low to nondetectable amounts of mercury (average 0.015 μg), indicating that the cleaning procedure is adequate. The mass of mercury in the clean tubes is insignificant relative to the 55.7 μg of mercury that passes through the tubes during a photooxidation experiment. The levels of sulfate in the clean tubes were nondetectable via ion chromatography.

Simulated Flue Gases. The results for the photochemical reaction of elemental mercury with components of simulated flue gases are presented in Table 3. Depending on the conditions, white stains formed within the quartz tubes. A variable but significant level of mercury was removed from the gases by irradiation with the ultraviolet light, especially at temperatures below 300 °F. Mercury capture is defined as the mass of mercury contained in the quartz photoreactor divided by the 55.7 μg of mercury that passes through the tube in 350 min.

Blank runs, where simulated flue gases that were not spiked with mercury were flowed through the irradiated

Table 4. Photosensitized Oxidation in Oxygen–Nitrogen Mixtures^a

temperature (°F)	intensity (mW/cm ²)	replicates	mercury capture (%)
80	1.0	1	81.5
280	1.0	2	65.0 ± 5.6
302	0.9	1	38.2
320	0.9	1	23.2
350	1.0	1	2.7

^a Gas composition: 13.9% O₂, 300 ppb Hg, balance N₂. Flow rate = 60 mL/min.

Table 5. Photochemical Removal of Mercury from Water Vapor^a

temperature (°F)	intensity (mW/cm ²)	water (%)	mercury capture (%)
280	1.1	2.03	19.7
280	1.0	2.08	31.1
average stain capture			25.4 ± 5.7

^a Gas composition: 2% H₂O, 300 ppb Hg, balance N₂. Flow rate = 60 mL/min.

reactor, revealed negligible mercury deposits and indicated that the flow system was not contaminated.

As can be seen in Table 6 below, the impact of intensity on mercury removal was investigated. The intensity of the light was varied by changing the distance between the lamp and the quartz photoreactor. Removals of mercury were insignificant at the lower radiation intensities.

Other Gas Compositions. Table 4 shows the results for the sensitized oxidation of mercury in an oxygen–nitrogen mixture at temperatures ranging from 80 to 350 °F. Reddish-brown stains formed within the quartz tubes. Dickinson and Sherill discovered this reaction at ambient temperature.¹⁰ The photochemical oxidation of mercury at 280 °F in a water vapor mix is presented in Table 5. Gunning had earlier demonstrated the sensitized oxidation of mercury in water vapor at room temperature.²⁶

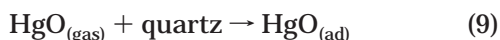
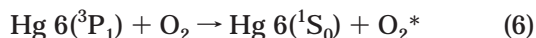
In Table 3, the blank runs at various temperatures without ultraviolet light showed an extremely low mass of mercury, indicating that irradiation is critical in the mercury reaction. There is scatter in the mercury removals obtained by irradiation of flue gas A at both 280 and 80 °F, as shown by the standard deviations of 30 and 29%, respectively, in Table 3. Several factors impact the uncertainties in the mercury removals. In earlier tests, it was noted that the visible-range brightness of the lamp had significant daily variations; concurrent variations in intensity of the 253.7-nm light could have an impact on mercury removal. The intensity of 253.7-nm light will vary by at least 5% over a 350-min test, as determined in recent tests with the radiometer. Also, the intensity of light diminishes with the square of the distance from the source. The uncertainty in the distance between the lamp and the quartz photoreactor was ±¹/₁₆ in., introducing an uncertainty in the intensity of 15%. Additionally, an uncertainty in the mercury capture is introduced by the CVAAS analysis. The uncertainty associated with the recovery and CVAAS measurement of mercury is at least ±10%. The mercury output from the permeation tube has an uncertainty level of at least ±6%. Therefore, the scatter in the mercury removals is not surprising. Nevertheless, analyses with CVAAS, XPS, and SEM-EDX showed that mercury in the simulated flue gases is photochemically oxidized by 253.7-nm light. From testing with simulated

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flue gas B, XPS analysis of the white stains suggests the formation of mercurous sulfate and mercuric oxide.

Discussion

The mechanism for the removal of mercury from oxygen as mercuric oxide was deduced by Dickinson and Sherrill¹⁰ and is shown below.



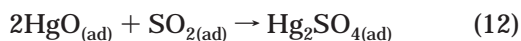
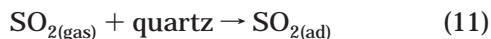
It is likely that this also represents the mechanism of mercury capture from flue gas that is irradiated by 253.7-nm light.

Reaction 5 is the excitation of elemental mercury by 253.7-nm UV radiation. Reaction 6 is the quenching of the excited mercury atom by oxygen, with the formation of an excited oxygen molecule. Step 7 is the quenching of an excited oxygen molecule, with the formation of ozone and an oxygen atom. Reaction step 8 is the thermal reaction of elemental mercury and ozone, with the formation of mercuric oxide and oxygen. Step 9 is the physical adsorption or condensation of mercuric oxide on quartz. Reaction 10 is the combination of an oxygen molecule with a reactive oxygen atom to form ozone.

The overall reaction is the sum of reaction steps 5–10



In flue gas, a secondary reaction between sulfur dioxide and mercuric oxide can occur



Step 11 is the adsorption of sulfur dioxide on the quartz wall. Reaction 12 is the thermal reaction between the mercuric oxide film and adsorbed sulfur dioxide to form adsorbed mercurous sulfate.

Steps 5–12 can explain the observed formation of mercuric oxide and mercurous sulfate films when simulated flue gases are irradiated with 253.7-nm light. The mass of sulfur within the stain, as determined by ICP-AES, is consistent with the formation of mercurous sulfate within the uncertainty associated with the detection method. The mass of sulfur found also indicates that little removal of sulfur dioxide occurs at 280 °F other than its reaction with mercury to form mercurous sulfate. It is noted that ICP-AES is not the preferred method for the detection of trace levels of sulfur because other elements share the same emission line as sulfur. It is noted that mercurous sulfate is speculated to form on the surface of activated carbons used for mercury control in municipal waste incinerators^{43–45} and on the surface of gold amalgam

electrodes exposed to sulfuric acid.⁴⁶ In addition, from the results presented in Table 5, it is speculated that the hydroxyl radical can also oxidize mercury at 280 °F.

From Tables 3 and 4, it appears that larger removals of mercury from flue gas and oxygen–nitrogen mixtures are obtained at 80 and 280 °F as compared to 350 °F. The rate of thermal decomposition of ozone becomes appreciable at temperatures above 212 °F.^{20,47–50} The thermal decomposition of ozone is known to proceed rapidly within the temperature range of 298–354 °F.^{48–50} The experimentally determined rates of thermal ozone decomposition increase by a factor of 13 over this temperature range.^{48–50} The thermal decomposition of ozone is the simplest explanation for the observed drop in mercury removal from both simulated flue gas and oxygen–nitrogen mixtures as the temperature increases from 280 to 350 °F and is consistent with the mechanism outlined by steps 5–12.

In addition, the effect of temperature on photochemical reactions is quite different from that on thermal reactions.¹⁹ Activation energy is acquired through the absorption of ultraviolet radiation rather than only through thermal energy. A decrease in rate with increasing temperature has been previously observed for many photochemical reactions.¹⁹ Higher temperatures will result in a larger number of collisions between the photoexcited mercury and the quartz walls, with a possible reduction in both the population of Hg 6(^3P₁) and the reaction rate. Also, other reactions within the flue gas could predominate at elevated temperatures, such as the oxidation of sulfur dioxide by ozone, viz.



Furthermore, the deposition and stability of solid mercury compounds and the deposition of sulfur dioxide on the quartz surface will be enhanced by lower temperatures. The ability of mercuric oxide to condense on surfaces is considerable and associated with its low vapor pressure at ambient temperature.^{51,52} Physical adsorption of mercury compounds on quartz (such as in step 9) is expected to decrease with increasing temperature. Physical adsorption of sulfur dioxide (step 11) on quartz will also diminish as the temperature increases. When the temperature of the irradiated section of the photoreactor is 350, 280, and 80 °F, the corresponding quartz tube temperature 3 in. beyond the furnace is 223, 180, and 80 °F, respectively. The high levels of mercury capture obtained when gases A and B were irradiated at 280 °F suggest that the warm surfaces near the bottom of the photoreactor are not inhibiting the deposition of mercury compounds. Gas A was irradiated at 350 °F using a longer quartz tube to provide more cold surface area for the condensation of oxidized mercury. No significant increase in mercury capture was found.

Finally, the intensity of 253.7-nm light emanating from the mercury lamp is expected to decrease with increasing temperature. At elevated temperatures, mercury within the germicidal bulbs can vaporize. Vapor-phase mercury can absorb some of the 253.7-nm radiation. Light intensities were measured when the lamp was cool, before and after the experiments, and the intensities were unchanged. The lamp face reached a temperature of 106 °F when the photoreactor was held at 350 °F. Previous researchers have suggested that a mercury emission device be cooled to minimize self-absorption of ultraviolet light. In addition, Doppler

Table 6. Effect of Radiation Intensity on Mercury Removal^a

temperature (°F)	replicates	intensity (mW/cm ²)	mercury capture (%)
280	5	1.4	71.6 ± 30.1
280	4	0.5	0.2 ± 0.1
350	8	1.4	2.3 ± 2.0
350	1	0.5	0.1

^a Gas composition A: 16% CO₂, 5% O₂, 2000 ppm SO₂, 300 ppb Hg, balance N₂. Flow rate = 60 mL/min.

broadening of the 253.7-nm emission line will also occur at elevated temperatures.⁵³

The presence of NO in a simulated flue gas matrix seems to decrease the removal of mercury, as shown in Table 3. The decrease in mercury removal in the presence of NO could be due to ozone loss by the reaction



The quenching cross section for NO shown in Table 1 is relatively large, suggesting high reactivity with mercury. However, Noyes determined that mercury photosensitizes the conversion of NO to N₂O₃.³⁴ The irradiation of gas C (NO and Hg in N₂) at 280 °F resulted in little mercury removal, suggesting that NO does not react appreciably with mercury by itself. XPS analysis from the treatment of flue gas B (which contains NO) indicated the formation of mercurous sulfate or mercuric oxide, consistent with photochemical oxidation of mercury with SO₂ and/or O₂. The works by Gunning,^{26–28} Caren,^{39,40} Tabatabaie-Raissi,^{41,42} and Stromberg^{51,52} suggest that H₂O and HCl might be important components of flue gas as the precursors to reactive hydroxyl and chlorine radicals.

A dramatic impact of radiation intensity on mercury removal is shown in Table 6. A decrease in radiation intensity by a factor of about 3 causes a much larger decrease in mercury capture. This suggests parasitic absorption of 253.7-nm light by sulfur dioxide. Sulfur dioxide absorbs 253.7-nm UV and is present in simulated flue gas A at a concentration (2000 ppm) that is almost 4 orders of magnitude greater than the mercury concentration (300 ppb). Sulfur dioxide could be screening out the UV from mercury until a saturation intensity level is reached. It is noted that, in a typical untreated flue gas from a coal-fired utility (Table 2), sulfur dioxide is present at a concentration that is 6 orders of magnitude greater than the concentration of mercury.

A possible commercial application of the photochemical removal of mercury from flue gas is described in a recent patent application on the GP-254 process.¹⁴ Sorbents and fly ashes tend to exhibit greater capacities for oxidized mercury in comparison to elemental mercury.^{2,7,8} Oxidized mercury is highly soluble in water, whereas elemental mercury is insoluble. Depending on where the ultraviolet radiation is applied, sensitized oxidation can enhance the removal of mercury within the particulate collection device or wet scrubber of a coal-fired power plant. An advantage of the GP-254 Process is that simple equipment, similar to that used in water treatment plants for the eradication of microbes, is employed. Ozone is generated in situ via reactions 5–8 and 10, avoiding the need for direct handling of this toxic and corrosive compound.

The direct photochemical oxidation of mercury in various gas matrices with 253.7-nm light has several additional consequences. Many of the prototype on-line

continuous emissions monitors for mercury in flue gas are based on atomic absorption spectrophotometry (AAS) or atomic fluorescence spectrophotometry (AFS). These techniques utilize 253.7-nm radiation to determine mercury concentration. Unless precautions, such as preconditioning of the flue gas, are taken, photochemical oxidation will interfere with the determination of mercury.^{11–13} The photosensitized formation of ozone by Hg 6(³P₁) can interfere with the ultraviolet measurement of elemental mercury in several ways: absorption of ultraviolet radiation by ozone, decrease in the population of mercury atoms by the formation of mercuric oxide, and attenuation in the intensity of the absorbed (AAS) or emitted (AFS) 253.7-nm radiation by elemental mercury because of the deposition of mercuric oxide on the quartz detector cell walls. Mercury can also photochemically react or sensitize reactions with SO_x, HCl, H₂O, and NO_x. Other compounds, such as mercurous sulfate and mercurous chloride, could also form on the quartz walls, attenuating the intensity of absorbed or emitted ultraviolet light. Additionally, a reduction of the population of excited mercury atoms by energy transfer to oxygen, carbon dioxide, water, etc. (quenching) can influence the ultraviolet measurement of elemental mercury. However, the formation and deposition of mercuric oxide, sulfate, and chloride can be inhibited by heating the quartz photocell used for mercury detection, although heating will not stop the quenching of excited mercury atoms. It is noted that several prototype continuous emissions monitors for mercury in flue gas, based on absorption of 253.7-nm light, use quartz cells that are heated to over 500 °C, above the decomposition temperatures of mercuric oxide and ozone.⁵⁴

Photochemical oxidation can affect the fate of mercury in the atmosphere, especially in the upper atmosphere where short-wave ultraviolet radiation is more prevalent. Mercuric oxide, associated with fine particulates, has been detected recently in the tropopause and is speculated to form by oxidation of elemental mercury by ozone.^{55,56} Ground-level mercury concentrations in the Arctic have also been found to vary with seasonal changes in sunlight, temperature, and upper-atmosphere ozone level.^{57,58} Because of the absence of short-wave ultraviolet radiation in the lower atmosphere, ground-level mercury is unlikely to impact the level of ground-level ozone, where ozone is a prime constituent of smog.⁵⁹ Elemental mercury has a half-life of approximately 1 year in the upper atmosphere, possibly because of the small concentration of ozone (30 ppb) available for reaction.⁶⁰ The hydroxyl radical might also be an important photochemical oxidant of elemental mercury in the troposphere.⁵²

Conclusions

Photochemical oxidation of mercury with 253.7-nm radiation is a potential means of mercury removal from flue gases. Ultraviolet irradiation with 253.7-nm light will induce many components of flue gas to react with elemental mercury. The experiments conducted with simulated flue gases suggest a high level of mercury removal as mercurous sulfate and mercuric oxide. The removal of elemental mercury is facilitated by irradiation at temperatures below 300 °F. Sensitized oxidation can have a deleterious effect on detectors for mercury based on absorption or emission of 253.7-nm radiation. Photochemical oxidation might also impact the global

transport of elemental mercury emanating from flue gases.

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