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Project title

**A Novel Method for the Removal of Trace Concentration of
Elemental Mercury from Utility Emissions**

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Abstract:

A new technique for removal of elemental mercury from emissions of coal-fired utilities was investigated. The key idea is to selectively photo ionize the mercury atoms. A strong electric field gradient then drags them to the negative plate where they can be collected and removed.

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Introduction

The minimization of mercury emissions from coal-fired power plants is of great interest since mercury is a potential human health hazard, even at very low concentrations. A very recent EPA notice of regulatory finding¹ states (on page 79,827, in the first paragraph, first sentence), "Based on the assessment of hazards and risks due to emissions of HAP (Hazardous Air Pollutants) from electric utility steam generating units, mercury is the HAP of greatest concern." Coal-fired utilities are currently the source of approximately one third of the mercury deposited across the U.S.² Much of this mercury is in elemental form, a form that can remain in the atmosphere for long periods of time². Some of this mercury lands in lakes where it is readily converted into methyl mercury, a bioaccumulation neurotoxin.^{1,c}

The EPA notice of regulatory finding¹ goes on to explain that mercury in the flue gas from coal combustion may be present in three different forms. The forms, called species, include elemental mercury, divalent oxidized forms, and mercury adsorbed onto the surface of fly ash or other particles. Adsorbed mercury onto particles is removable using conventional devices such as electrostatic precipitators (ESP). The divalent forms of mercury are generally water soluble and removable in wet scrubbers or in flue gas desulphurization (FGD) systems^{1,3}. However, "elemental mercury is insoluble in water, does not react with alkaline reagents used in FGD systems, and cannot be captured in wet scrubbers,"¹ consequently elemental mercury remains mostly unresolved from flue gas.

Even when equipped with a dry ESP and a FGD, coal-fired utilities fail to remove about a third of the mercury from burnt coal³. Almost all of this mercury is in elemental form. In a dry ESP much of the elemental mercury either does not become ionized or is re-entrained in the gas during the rapping cycle of the ESP⁴. Since mercury is not soluble in water and does not react with alkaline agents, FGD systems and wet scrubbers also fail to remove the elemental mercury. Even when fully equipped, the atomic mercury concentration^{2,3} in a typical coal-fired utility's exhaust is 1 to 10 : g per cubic meter (90 to 900 parts per trillion).

It would be of great benefit to have available methodology designed to remove elemental mercury from such sources and to preclude its deposition into the environment.

Removal by Electric Field Gradients

Charged particles will migrate towards an oppositely charged surface. Their migration velocity is dependent on the size of the particle. As particle size decreases the migration velocity increases^{5,6}. This phenomenon makes electrostatic precipitation very effective at capturing charged particles in the 40 nm to 1000 nm size range since they will quickly move towards an oppositely charged surface. The lower limit arises because the effectiveness of electrostatic precipitators decreases with decreasing particle size due to the decreasing likelihood of the particle colliding with an electron or a charged gas molecule⁴. Another method of associating charge and mercury atoms therefore is needed. *If* the mercury atoms themselves could be charged, then a strong electric field gradient could be used to pull them to a collection surface. The collection surface can be coated with a material with either oxidizes or forms an amalgam with the mercury thus preventing its revaporization.

Executive Summary

A new technique for removal of elemental mercury from emissions of coal-fired utilities was investigated. The key idea is to selectively photo ionize the mercury atoms. A strong electric field gradient then drags them to the negative plate where they can be collected and removed.

Then it was shown that very selective photoionization of mercury atoms is possible by irradiation the XXX exhaust with 253.65nm photons and simultaneously (or within 100 ms) with 435.83nm photons, or by 626.36 nm photons some of which have been frequency doubled to 313.18 nm. Detailed calculations of the probability of such ionization as a function of photon density (i.e. laser light brightness) were made. They show that a 90 percent removal is possible with currently available lasers. The some equations can be used to calculate 99 percent removal.

Selective Ionization of Mercury Atoms

One method of causing the atoms of mercury to become charged is by *photoionization*^{7,8,9}. To effectively use photo ionization to remove extremely small concentrations of atomic mercury from a gas requires efficient use of the photons. The key to removal of atomic mercury using photo ionization is the great selectivity provided by using a 253.65 nm photon. The excited state (6s6p ³P₁) thus produced has a relatively long lifetime⁸ (118 ns) and a very large cross section for the absorption of additional photons. The subsequent absorption of additional photons, whose combined energy is more than 5.68 eV, causes ionization, thus converting the mercury atoms into positively charged mercury ions. On absorbing a 435.83 nm photon a mercury atom is excited to an even higher state (6s7s ³S₁) with a lifetime⁸ which is long (8 ns) when compared to the duration of a laser pulse (~1 ns). Mercury atom ionization also can be accomplished⁹ by following the absorption of a 253.65 nm photon with the resonant absorption of a 313.18 nm photon obtained from a frequency doubled 626 nm tunable lasers. Ionization then is caused by the absorption of a 626.36 nm photon (i.e. both wavelengths are in the laser beam which exits the doubler).

Model of Photon Absorption by Elemental Mercury at 253.65 nm

To determine the amount of energy required to excite a concentration of mercury atoms in a volume of gas into the sp³ excited state one uses the following: First one calculates the absorbance of the exhaust gas to determine the amount of light that will be absorbed. Since the mercury concentration is very small (exhaust gas typically has between 90 ppt and 900 ppt of mercury^{2,3}), unless the path length is extremely long the absorbance will be small. The absorbance of a gas containing mercury can be calculated using Beer's law.

$$A = -\ln(I/I_0) = FLC \quad (1)$$

where A is the absorbance, I is the transmitted intensity, I_0 is entering intensity, F is the extinction coefficient (i.e. absorbance cross section) at the appropriate wavelength, L is the path length, and C is the concentration of mercury. The extinction coefficient, F , of mercury¹⁰ at 253.65 nm is $3.3 \times 10^{-18} \text{ m}^2$. Note that the transmittance, T , is *defined* by $T = I/I_0$, thus equation (1) can be rewritten as

$$T = e^{-FLC} \quad (2)$$

When scattering is negligible, the fraction of light absorbed, F , is

$$F = (1-T) = 1 - e^{-FLC} \quad (3)$$

The number of laser pulses, n , that the mercury atoms in the flowing gas are exposed to (in a flow path of length L) is

$$n = fL/u \quad (4)$$

Where f is the frequency of the light pulses and u is the linear gas flow rate. One can think of the gas flow path as divided into a number of segments equal in number to the number of pulses that each volume of gas is exposed to before exiting the light path. Thus, the thickness of a segment, L/n , is related to the linear gas flow velocity by

$$L/n = u/f \quad (5)$$

For mercury concentration $\times$ path length products (i.e. CHL) which are small, the intensity of light entering each segment is approximately the same. The fraction of light absorbed by a segment, F , then is

$$F = 1 - e^{-FCL/n} \quad (6)$$

The number of photons in a laser pulse, L , is the pulse energy divided by the energy per photon, i.e.

$$L = E/(hc/\lambda) \quad (7)$$

Where E is the energy per pulse and $hc/8$ is the energy per photon. Since the laser pulse duration is extremely short compared to a mercury atom's excited state lifetime and there be no excited state at twice the energy of a 253.65 nm photon (thus no resonant absorption) a mercury atom can only absorb one 253.65 nm photon. Thus,

$$\# \text{ of excited Hg atoms in a segment} = LHF \quad (8)$$

The volume of a segment, V , is the segment cross sectional area, A , times the segment thickness.

$$V = AL/n \quad (9)$$

The concentration of mercury excited by a pulse is thus:

$$\text{Conc. of Hg excited/pulse} = (LHF)/V \quad (10)$$

Substituting in for LHF from equations (7) and (8) and for V from equation (9)

$$\text{Conc. of Hg excited/pulse} = (nE/AL)(8/hc)(1 - e^{-FCL/n}) \quad (11)$$

After a segment receives one pulse, the *unexcited* mercury concentration, C_1 , is

$$C_1 = C_0 - (E/AL)(8/hc)(1 - e^{-FCL/n}) \quad (12)$$

After two pulses

$$C_2 = C_1 - (2E/AL)(8/hc)(1 - e^{-FCL/2n}) \quad (13)$$

After j pulses

$$C_j = C_{j-1} - (jE/AL)(8/hc)(1 - e^{-F(C_{j-1})L/n})$$

(14)

For weak absorption, i.e. small FHLHC, the exponential can be linearized, i.e. $e^{-FCL} \approx 1 - FCL$ and upon substitution into equation (14) one obtains

$$\begin{aligned} C_j &= C_{j-1} - (nE/AL)(8/hc)(FC_{j-1}L/n) \\ &= C_{j-1}[1 - (nE/AL)(8/hc)(FL/n)] \\ &= C_{j-1}[1 - (EF/A)(8/hc)] \end{aligned} \quad (15)$$

This linearized form is useful when one exposes each mercury atom to a large number of pulses. One can repeatedly solve for C and substitute in and thus obtain

$$C_n = C_0[1 - (EF/A)(8/hc)]^n \quad (16)$$

Let P/ Average Power = energy from the laser per unit time (choose one second).

$$P = EHf = nuE/L \quad (17)$$

For very large n (i.e. a quasicontinuous light source) equation (16) becomes

$$C_n = C_0 e^{-(PLF/uA)(8/hc)} \quad (18)$$

Example calculations

Calculations were made using a volumetric gas flow rate of 472 m³/s (i.e. one typical of a 250 MW_E power plant³). For other flow rates these numbers will scale linearly. If one uses 1.23m as the radius for a typical cylindrical stack (i.e. A = 4.72 m²), then this volumetric flow rate corresponds to a linear flow rate of 100 m/s. The required pulse energy and average power for a given path length and laser frequency for a mercury concentration³ of 1: g/m³ (i.e. C = 90 ppt = 3H10¹⁵ Hg atoms/m³) with an extinction coefficient¹⁰ at 253.65 nm of 3.3*10⁻¹⁸ m² were calculated. Using a path length of 10 m and laser pulse rate of 10 pps (i.e. f = 10 Hz) provides one light pulse to each mercury atom before the atom leaves the light path. For a single pulse to provide an excitation of 99% of the mercury (i.e. C/C₀=0.01), one can solve equation (16) for E and substitute in the above values to obtain the energy per pulse requirements.

	$E = (1 - C/C_0)(A/F)(hc/8)$
Average Power	$E = 1.11 \text{ J}$ $P = Ef = (EQ)/(AL)$
Laser frequency	$P = 11.1 \text{ W}$ $f = nu/L$ $f = 10 \text{ s}^{-1}$

Similarly for a quasicontinuous light source equation (18) results in an average power requirement of 51.6 W for 99% excitation. Repeating the above calculations for 99% excitation and a mercury concentration of $3 \times 10^{16} \text{ Hg atoms/m}^3$ results in no change in the energy or power requirements. This occurs when the mercury concentration is low because a linear approximation of the exponential in equation (14) can be made so that the amount of light absorbed increases linearly with the concentration. At higher mercury concentrations the linear approximation is no longer valid and equation (14) should be used when calculation power requirements.

For a desired removal of 90% at a laser frequency of 10 Hz using the same flow rates and dimensions as in the above example with a concentration of $3 \times 10^{15} \text{ Hg atoms/m}^3$, using equation (12) we find that for a single pulse traveling through a 10 m path length the energy is given by

$$C_1 = C_0 - (E/AL)(8/hc)(1 - e^{-FC_0L})$$

$$C_1/C_0 = 1 - (E/AL)(8/hc)(1 - e^{-FC_0L})/C_0$$

After solving for E one obtains

$$E = (1 - C_1/C_0)[(1/AL)(8/hc)(1 - e^{-FC_0L})/C_0]^{-1} \quad (19)$$

For $C_1/C_0=0.1$ one obtains

$$E = 1.059 \text{ J}$$

The number of photons used for the excitation is

$$\text{\#photons used} = (C_0 - C_1)AL = 1.274 \times 10^{17} \text{ photons}$$

The energy left in the pulse after traveling through 10 m of gas is

$$E_1 = E_0 - \text{\#photons used}(hc/8) = 0.959 \text{ J}$$

We now calculate what happens when the light is co current to the gas flow, for the same gas flow but for a path length which is twice as long (i.e. $L = 20 \text{ m}$). For this case, the energy E_1 will enter 10 m of gas that has already been reduced in concentration by 90% to the concentration C_1 . The new mercury concentration due to E_1 will be

$$C_2 = C_1 - (E_1/AL)(8/hc)(1 - e^{-FC_1L})$$

$$C_2 = 4.44 \times 10^{13}$$

By doubling the path length to 20 m so that two pulses enter the system before the gas leaves the removal rate is 98.5% instead of 90%. If instead we only wanted 90% removal for the 20 m length then we can calculate a new pulse energy by solving equation (16) for E with $n=2$.

$$C_2 = C_0[1 - (EF/A)(8/hc)]^2$$

$$E = [1 - (C_2/C_0)^{1/2}](Ahc/F8)$$

$$E = 0.77 \text{ J}$$

This calculation shows that by doubling the path length the required pulse energy to remove 90% of the mercury is reduced by 27.3% and the average power is 7.7 W. If we once again double the path length to 40 m and calculate the pulse energy using equation (16) with $n=4$ we obtain $E=0.49 \text{ J}$ which is 36% less than the pulse energy for the 20 m case. Let us also calculate the energy for a single pulse to remove 90% of the mercury if the path length is 20 m (i.e. for a laser frequency of 5 Hz instead of 10 Hz). Using equation (19) we find that the energy for a single pulse is 1.11 J with an average power of 5.55 W. This indicates that by exposing each mercury to multiple pulses one can lower the energy needed per pulse, but by exposing each mercury atom to only one pulse of sufficient intensity one can use the least average power.

Mass of Mercury Removed

Once the mercury has impacted on the collection surface it is necessary to prevent the mercury from revaporizing. This can be accomplished by making the collection surface out of a substance which can either oxidize or form an amalgam with the mercury (e.g. silver, zinc, etc.). It is therefore of interest to calculate how fast mercury will accumulate on the surface.

$$m = 200.59 \text{ [g/mol]} / 6.023 \times 10^{23} \text{ [Hg atoms/mol]}$$

$$m = 3.343 \times 10^{-22} \text{ [g/Hg atom]}$$

Fraction of unremoved mercury, $g = 0.01$

$$C = 3 * 10^{15} \text{ [Hg atom/m}^3\text{]}$$

$$M = m(1-g)CQ$$

For a 250 MW_e Power Plant

$$Q = 472 \text{ m}^3/\text{s}$$

Time	M [g]	V _{Hg} [cm ³]
second	$5.2*10^{-5}$	$3.8*10^{-6}$
hour	0.187	$1.37*10^{-2}$
day	4.49	0.329
year	1640	120

For 99% removal of mercury

Assuming that the mercury collection surface is one large tube with a radius of 1.23 m and length of 10 m gives a surface area of approximately 70 m². The mercury film thickness that will build up on the surface is given by

$$\text{film thickness} = V_{\text{hg}}/A_s$$

At a collection rate of $1.2*10^{-4} \text{ m}^3$ per year results the production of a mercury film at a rate of 1.7 : m per year. Even at a mercury concentration of 900 ppt the mercury film will still only be produced at a rate of 17 : m per year. This example calculation shows that the collection surface will *not* need to be replaced often due to mercury buildup.

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