

**Proceedings of the 22<sup>nd</sup> Annual International Pittsburgh Coal Conference**  
**Paper 5-1**  
**Pittsburgh, PA**  
**September 12-15, 2005**

# The PCO Process for Photochemical Removal of Mercury from Flue Gas

**Christopher R. McLarnon, Ph.D.**

Powerspan Corp., P.O. Box 219, 54 Old Bay Road, New Durham, NH 03855

**Evan J. Granite\* and Henry W. Pennline**

National Energy Technology Laboratory, United States Department of Energy,  
P.O. Box 10940, MS 58-106, Pittsburgh, PA 15236-0940

\*Corresponding author. Tel.: +1412-386-4607; fax: +1412-386-6004

E-mail address: [evan.granite@netl.doe.gov](mailto:evan.granite@netl.doe.gov)

## Abstract

A promising technology has been developed to capture and remove elemental mercury species from coal-fired power plants. Powerspan Corp. has licensed the technology and initiated a bench and pilot test program to develop the Photochemical Oxidation, or PCO™, process for commercial application with subbituminous and lignite fuels.

The process has the potential to serve as a low cost mercury oxidation technology that will facilitate elemental mercury removal in a downstream SO<sub>2</sub> scrubber, wet electrostatic precipitator (WESP), or baghouse. It uses 254-nanometer (nm) ultraviolet light from a mercury lamp to produce an excited state mercury species in the flue gas, leading to oxidation of elemental mercury. This paper presents results of Powerspan's initial bench-scale testing on a simulated flue gas stream. Preliminary testing conducted in Powerspan's bench-scale facility showed greater than 90% oxidation and removal of elemental mercury. The process also has potential to serve as a low cost method for the removal of mercury from waste incinerator flue gases.

*Keywords:* Mercury; flue gas; sensitized oxidation; ultraviolet; photochemical

## 1. Introduction

Data collected on mercury emissions from coal-fired power plants indicate that oxidized mercury species, the predominant species present in the flue gas when burning bituminous coals, are readily collected in air pollution control devices such as SO<sub>2</sub> scrubbers. Elemental mercury species, the predominant species present in flue gas when burning subbituminous or lignite coals, are not efficiently removed by existing air pollution control devices. With EPA's Clean Air Mercury Rule, and several states promulgating their own mercury emission limits, the need exists for a low cost mercury oxidation process that can be applied to flue gas treatment systems of coal-based power plants.

The U.S. Department of Energy has developed and patented a method to oxidize elemental mercury (Hg<sup>0</sup>) in the flue gas of fossil fuel-fired power plants [1, 2]. The Photochemical Oxidation, or PCO, method introduces ultraviolet (UV) light at a wavelength of 254 nm into the

flue gas, resulting in the conversion of  $\text{Hg}^0$  to an oxidized form ( $\text{Hg}^{+2}$ ,  $\text{Hg}_2^{+2}$ ). Oxidized mercury is subsequently captured in a downstream collection device such as a scrubber, ESP, or baghouse (fabric filter). UV light is used commercially in water treatment plants to eradicate microbes and oxidize organic contaminants. The UV light employed in the PCO process is similar.

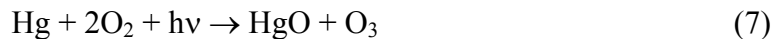
Powerspan has conducted preliminary tests of UV-initiated oxidation of mercury in its bench-scale test facility, with promising results. Greater than 90% oxidation and capture was achieved in a simulated flue gas stream containing 12 to 15  $\mu\text{g}/\text{Nm}^3$  of elemental mercury.

## 2. Principle of mercury oxidation

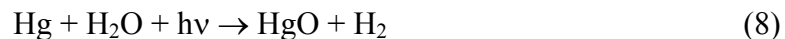
The proposed mechanism for oxidation of mercury with ultraviolet light is shown below [1-3]:



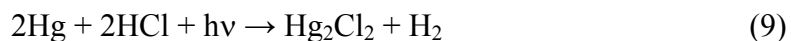
A low-pressure mercury lamp produces 254 nm light, which excites elemental mercury in (1). Quenching of the excited state mercury with oxygen ( $\text{O}_2$ ) in (2) returns the excited state mercury ( $\text{Hg}^*$ ) to its ground state ( $\text{Hg}$ ) and produces excited state oxygen ( $\text{O}_2^*$ ). The species responsible for oxidation of elemental mercury are formed in (3) and (4) through quenching of excited state oxygen with oxygen forming ozone ( $\text{O}_3$ ) and an oxygen radical ( $\text{O}$ ), and the reaction of an oxygen radical with oxygen. Both ozone and oxygen radicals react with elemental mercury to form mercuric oxide ( $\text{HgO}$ ) as shown in (5) and (6). Most of the mercuric oxide is formed through the thermal reaction with ozone so that the overall reaction is obtained by adding reaction steps (1) through (5):



Other compounds present in flue gas may also oxidize mercury under the influence of 254-nm light [1, 2, 4-9]. For example, elemental mercury can react with moisture present in flue gas to form mercuric oxide:



Mercury will be oxidized by hydrogen chloride under the influence of 254-nm light, forming mercurous chloride:



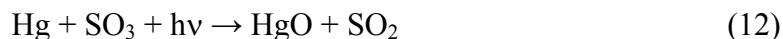
Any hydrogen formed through reactions (8) and (9) will be subsequently oxidized by various flue gas compounds. The photochemical oxidation of mercury by nitrogen dioxide will result in formation of mercuric oxide and can be represented as:



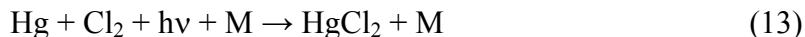
The slow sensitized oxidation of mercury by carbon dioxide has also been reported, and can be crudely depicted as:



It is speculated that elemental mercury will react with sulfur trioxide under the influence of 254-nm light, viz:



Miller [10] suggests that elemental mercury will react with chlorine under the influence of 254-nm light, viz:



M represents a surface or third atom or molecule.

As can be seen by examination of reactions (7) through (13), there are many potential compounds in flue gas that can oxidize mercury under the influence of 254-nm light.

### 3. Testing of mercury oxidation

Testing of elemental Hg oxidation in a flue gas environment at laboratory-scale was initially done by Granite and Pennline at the U.S. Department of Energy National Energy Technology Laboratory using a simulated flue gas containing 16% CO<sub>2</sub>, 5% O<sub>2</sub>, 2000 ppm SO<sub>2</sub>, 0 or 500 ppm NO, 300 ppb Hg(0), and balance N<sub>2</sub> [2]. The apparatus for testing shown in Figure 1 consisted of (i) mercury addition, (ii) quartz reactor, (iii) UV lamp, and (iv) a flue gas mixing system. The results show up to 72% oxidation of Hg(0) under these conditions with an intensity of 1.4 mW/cm<sup>2</sup>. The high mercury concentration (300 ppb) used in these experiments is representative of the levels found in some waste incinerator flue gases. Further testing, discussed below, was performed at Powerspan Corp. to determine the effectiveness of the UV oxidation of elemental Hg at a larger scale and with a mercury concentration representative of flue gas from coal-fired power plants.

### 4. Experimental apparatus

A UV reactor was constructed and installed in Powerspan's bench-scale test system as shown in Figure 2. Powerspan's test system delivers up to 25 scfm of simulated flue gas using a propane burner and cylinder gases. Oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), and hydrochloric acid (HCl) cylinders

are routinely added to the combustor exhaust gas using compressed gas cylinders to create the desired mixture. In addition, moisture (steam) and elemental mercury vapor are added in order to closely simulate the flue gas composition of interest. The flue gas composition used for the preliminary tests discussed in this report consisted of: 5.6% O<sub>2</sub>, 13% CO<sub>2</sub>, 8% H<sub>2</sub>O, 1300 ppm SO<sub>2</sub>, 220 ppm NO, 20 ppm CO, up to 15 µg/Nm<sup>3</sup> Hg and the balance N<sub>2</sub>. The gas flowrate used for testing was 24 scfm and temperature of the gas in the UV reactor was 120 - 140 °F. In addition to the UV reactor, the test system consists of a spray chamber that cools and saturates the flue gas with moisture, a packed column scrubber for removal of NO<sub>x</sub> and SO<sub>2</sub>, a packed column absorber for ammonia vapor capture and a tubular wet electrostatic precipitator (WESP) for capture of aerosols. Figures 3 (a) and (b) show the continuous emissions monitoring, acid gas, and Hg addition systems.

Figure 4 shows a tubular reactor constructed to hold a low-pressure mercury amalgam lamp in a quartz sleeve centered along the axis of the reactor for oxidizing Hg. Flue gas travels through the annulus bounded by the quartz sleeve and the outer walls of the reactor.

The lamp has an active length of approximately 22" with an outer diameter of the quartz sleeve of 1.2". The ID of the reactor is 5.7". Energy output of the lamp at 254 nm was not measured but is reported by the manufacturer to be 36 watts, resulting in a watt density of approximately 13.8 W/cm<sup>2</sup> at the reactor's outer wall. The power output of the lamp was not varied for the testing described in this paper. The reactor was installed in the lab test system, downstream of the spray chamber, where gas temperature ranges from 120 to 140 °F and immediately upstream of the packed column scrubber.

Measurement of mercury in the flue gas was accomplished using impinger solutions and cold vapor atomic absorption (CVAA) spectroscopy. Three sample streams were configured for the testing. Two of the streams were configured to measure elemental Hg at the system inlet and outlet, respectively, and one stream configured for total Hg measurement at the system outlet. Each sample stream consisted of (i) two 25 mL midget impingers filled with appropriate solutions, (ii) a condensing bottle to remove moisture, (iii) a mass flow controller, (iv) a gold trap, and (v) a pump. The solutions used for elemental Hg measurement consisted of 10% potassium chloride (KCl) in the first impinger and 10% sodium hydroxide (NaOH) in the second impinger. The KCl solution captures oxidized Hg, allowing elemental Hg to pass through for adsorption onto the gold trap, while the NaOH solution captures acid gases such as SO<sub>2</sub>, to prevent poisoning of the trap. Total Hg measurement was accomplished using an acidic 10% stannous chloride (SnCl<sub>2</sub>) solution in the first impinger. The SnCl<sub>2</sub> solution reduces oxidized Hg to elemental Hg, while the NaOH solution in the second impinger performs the same function as in the elemental Hg measurement train.

Mercury collected on the gold trap was released by heating the trap to 600°C. The mass of released mercury was then measured using a Buck CVAA spectrometer. Sample collection time varied from 3 to 5 minutes, depending on expected Hg concentration, with a sample flow of 500 mL/min through the trap. Figure 5 shows the sample train and instrumentation used for the mercury measurements.

## 5. Experimental results & discussion

Figure 6 shows the measured concentrations of elemental mercury at the inlet, upstream of the spray chamber, and outlet, downstream of the WESP, of the test system. The testing was conducted by alternately energizing and de-energizing the UV lamp. During this set of tests only elemental mercury measurements were made.

The average inlet Hg concentration for the test shown in Figure 6 is  $13.4 \mu\text{g}/\text{Nm}^3$  and the average outlet concentration with the UV lamp energized is  $1.9 \mu\text{g}/\text{Nm}^3$ , resulting in an oxidation efficiency of 86%. Mercury oxidation is also seen during the periods without the lamp energized. It averaged 18% and is likely due to oxidation by the corona discharge in the WESP, or is an artifact of the sampling method.

A second set of tests was performed during which elemental, Hg(0), and total Hg measurements, Hg(T), were made at the outlet of the test system in order to show Hg oxidation by the UV lamp and capture in the scrubber and WESP. The average inlet elemental Hg concentration was measured to be  $12.7 \mu\text{g}/\text{Nm}^3$  and the average oxidation and capture was 91% over the period of the test. Figure 7 presents these results.

As seen in the previous test, oxidation of a portion of the elemental Hg occurred without the lamp energized, though its capture in the WESP does not appear to be taking place. It is considered that the gas residence time in the WESP is insufficient for both oxidation and capture.

Measurements of mercury in the scrubbing and WESP wash liquids were made for both sets of tests. An increase in Hg was measured in the liquids. However, only a portion of the Hg thought to be oxidized and captured, based on gas phase measurements, could be accounted for by the liquid Hg content. Swabs of the UV reactor and piping between the reactor and scrubber showed significant Hg deposition on the UV reactor and piping surfaces. Complete recovery of the deposited Hg was not attempted but it may account for the apparent Hg deficiency in the scrubbing liquids. Similar types of deposits were found in previous testing [1, 2].

Total power consumed by the UV lamp was not measured during Powerspan's testing. The lamp manufacturer specifies that the lamp consumes 105 watts, with a UV output of 36 watts, though a spectral energy distribution for the lamp was not available at the writing of this report. At 105 watts and 24 scfm of flue gas, the energy consumption of the oxidation process is 4.4 W/scfm. No attempt was made during these preliminary tests to reduce the energy consumption. In addition, the UV reactor was not optimized for efficient utilization of the light or for uniform gas flow distribution. Testing of the Hg oxidation and capture performance is continuing at Powerspan to explore reactor optimization and scale up.

The deposited film of solid mercury compounds can absorb the 254-nm light, thereby reducing the rate of mercuric oxide formation [11]. Many mercury compounds are light sensitive, and will decompose upon exposure to visible or ultraviolet light [11, 12]. For example, mercuric oxide will decompose under exposure to ultraviolet light [11]. These factors can slightly suppress the rate of mercuric oxide formation [11], and are being examined in our laboratories.

It is also noted that the UV oxidation experiments were carried out at 120 - 140°F, far below the thermal decomposition temperature (932°F) of mercuric oxide.

## 6. Conclusions

The preliminary tests conducted to date clearly show the ability of the PCO process to oxidize elemental mercury and the ability to capture oxidized Hg in a scrubber and/or WESP. The high level of Hg oxidation and capture, along with relatively low power requirements, indicate that the PCO process has commercial promise and that further work toward commercialization is warranted.

## Acknowledgements

The authors thank their colleagues at Powerspan and the National Energy Technology Laboratory for helpful comments and suggestions. Rich Hargis of the National Energy Technology Laboratory provided excellent help in reviewing the manuscript.

## Disclaimer

Reference in this report to any specific commercial process, product or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

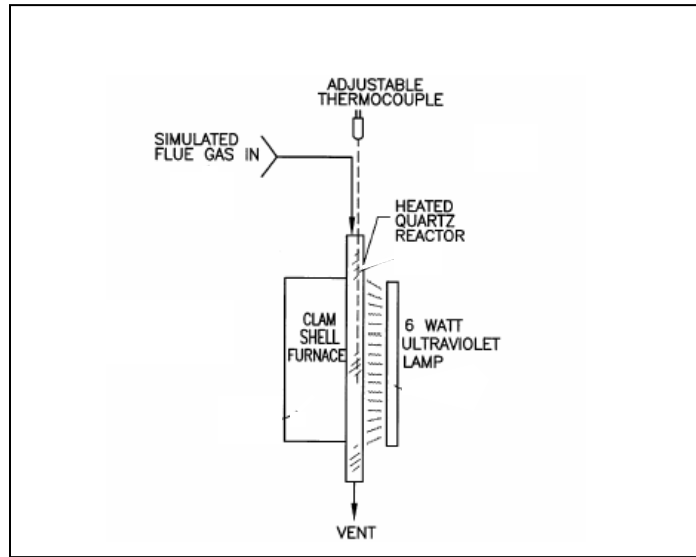
## References

- [1] Granite, E.J.; Pennline, H.W. "Method for Removal of Mercury from Various Gas Streams," US Patent 6,576,092, June 10, 2003.
- [2] Granite, E.J.; Pennline, H.W. Photochemical Removal of Mercury from Flue Gas, *Ind. Eng. Chem. Res.*, 2002, 41, 5470 .
- [3] Dickinson, R.G.; Sherrill, M.S. Formation of Ozone by Optically Excited Mercury Vapor, *Proc. Natl. Acad. Sci.* 1926, 12, 175.
- [4] Gunning, H.E. Primary Processes in Reactions Initiated by Photoexcited Mercury Isotopes, *Can. J. Chem.* 1958, 36, 89.
- [5] Pertel, R.; Gunning, H.E. Photochemical Separation of Mercury Isotopes, *Can. J. Chem.* 1959, 37, 35.
- [6] McDonald, C.C.; McDowell, J.R.; Gunning, H.E. Photochemical Separation of Mercury Isotopes: The Reaction of  $\text{Hg}^{202} 6(^3\text{P}_1)$  Atoms, Photoexcited in Natural Mercury Vapor, with Hydrogen Chloride, *Can. J. Chem.*, 1959, 37, 930.
- [7] Moore, H.R.; Noyes, W.A. Photochemical Studies. II. The Activation of a Mercury Surface by Light, *J. Am. Chem. Soc.* 1924, 46, 1367.
- [8] Pierce, W.C.; Noyes, W.A. A Further Study of the Reaction Between Nitrogen Dioxide and Liquid Mercury, *J. Am. Chem. Soc.*, 1928, 50, 2179.
- [9] Strauss, O.P.; Gunning, H.E. The Decomposition of Carbon Dioxide by  $\text{Hg } 6(^3\text{P}_1)$  and  $\text{Hg } 6(^3\text{P}_0)$  Atoms, *Can. J. Chem.*, 1961, 39, 2244.

- [10] Yan, N-Q; Liu, S-H; Chang, S-G; Miller, C. Method for the Study of Gaseous Oxidants for the Oxidation of Mercury Gas, *Ind. Eng. Chem. Res.*, 2005, ASAP, June 23.
- [11] Cline, J.E.; Forbes, G.S. Rates of Reaction of Excited Mercury with Oxygen, Hydrogen Sulfide and Nitrous Oxide, and their Relation to Effective Collision Diameters, *J. Am. Chem. Soc.* 1941, 63, 2152.
- [12] Kunkley, H.; Horvath, O.; Vogler, A. Photophysics and photochemistry of mercury complexes, *Coordination Chemistry Reviews*, 1997, 159, 85.



**Figure 1: Laboratory-Scale Reactor Used to Test UV oxidation of Hg(0)**



**Figure 2: Powerspan's Bench-Scale Test System (a) First Story, (b) Second Story**



(a)



(b)

**Figure 3: (a) CEMS and Acid Gas Addition System for Powerspan Bench Test Unit;  
(b) Hg(0) Addition System for Powerspan Bench Test Unit**



(a)

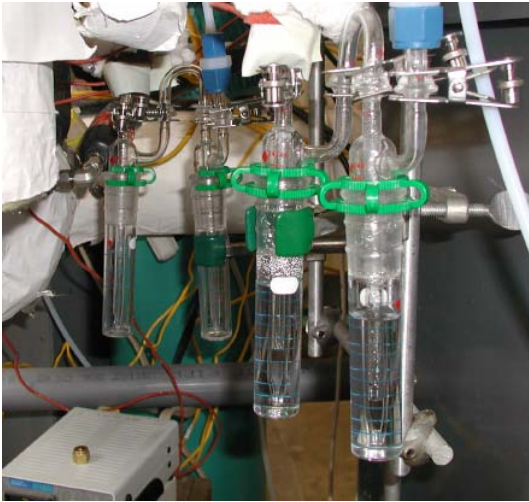


(b)

**Figure 4: Powerspan's Bench-Scale UV Reactor**



**Figure 5: (a) Hg Sampling Impingers; (b) Buck CVAA Analyzer**

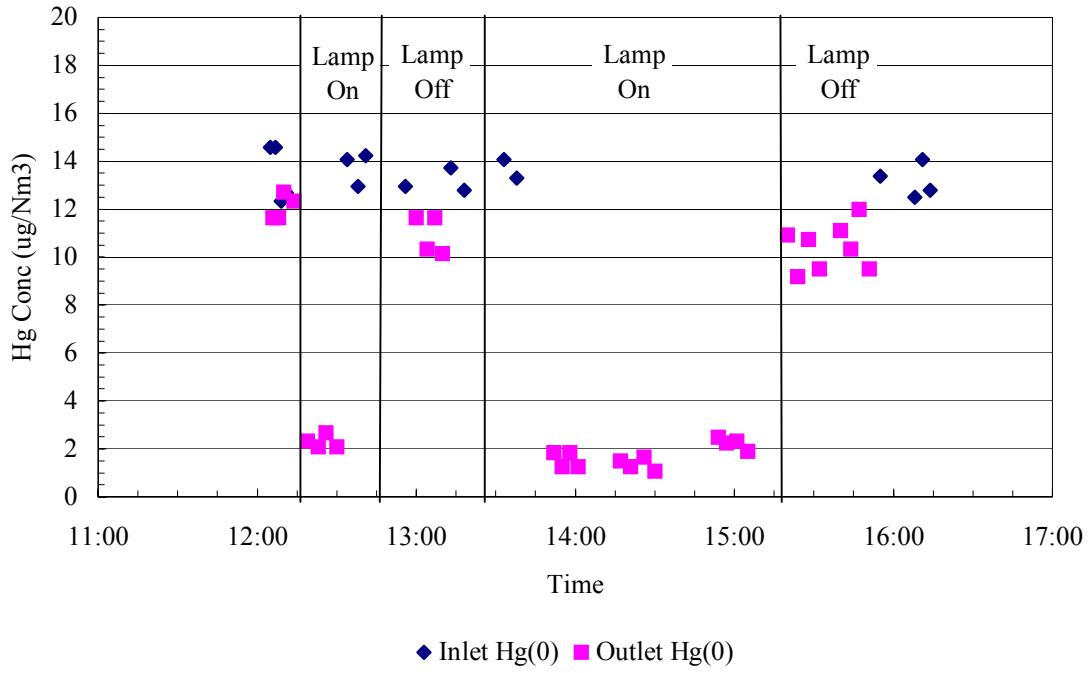


(a)



(b)

**Figure 6: Oxidation of Hg(0) with UV light**



**Figure 7: Oxidation of Hg(0) with Light**

