

## Mercury Removal in Flue Gases by Dielectric Barrier Discharge Technique

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The pronounced volatility of elemental mercury ( $\text{Hg}^0$ ) and some of its compounds, coupled with their extreme toxicity, makes these substances extremely hazardous. The concern over mercury pollution grows as coal in large amounts is being used in power generation. It is proposed to establish sixty-five new coal-fired power plants in the United States in the next five years to meet the increasing energy demands. The major emitters of mercury to the air include coal-fired electric utilities, municipal waste combustors (MWCs), medical waste incinerators (MWIs), and chemical industry such as chlor-alkali and cement plants. The first three major emitters account for about 75% of the U.S. total annual Hg emission of 158 tons. Three main forms of mercury emissions are particle-associated mercury, gaseous divalent mercury ( $\text{Hg}^{2+}$ ), and elemental mercury vapor ( $\text{Hg}^0$ ). Studies have shown that mercury emission from a combustion process is mostly in the state of elemental mercury vapor ( $\text{Hg}^0$ ). There are two major differences in flue gases from coal-fired electric utilities and MWIs/MWCs, namely, mercury concentration and flue gas flow rate. The concentration of total mercury in the flue gas from typical coal-fired electric utilities ranges from less than 10 to more than  $50 \mu\text{g}/\text{Nm}^3$  (1-5 ppbv) while it is usually several orders of magnitude higher in flue gases from MWIs/MWCs.

Consequently, better pollution control techniques are essential. Of all the developing pollution control techniques, electrical techniques are the most favorable over the others due to their inherent advantage as multi-pollutant control processes. Although adsorption techniques are in development, all control strategies are complicated by the speciation ( $\text{Hg}^0$  and  $\text{Hg}^{2+}$ ) of mercury. Conversion of  $\text{Hg}^0$  to  $\text{HgO}$  would significantly enhance mercury removal from flue gases. The basic premise of this approach is that  $\text{Hg}^0$  in vapor form cannot be easily removed in an absorption tower whereas  $\text{HgO}$  as a particulate is amiable to water scrubbing. In our approach, a dielectric is placed between two electrodes allowing dielectric barrier discharge (DBD) plasma to occur through which the gases containing  $\text{Hg}^0$  are made to flow. In the DBD plasma, energetic electrons cause excitation, ionization, electron multiplication and formation of atoms and compounds, forming a very strong oxidizing environment especially for the oxidation of  $\text{Hg}^0$ . We have conducted studies since the late 1980's on the use of DBD for air pollution control. These studies have shown that  $\text{NO}_x$ ,  $\text{SO}_2$  and hydrocarbons can be oxidized successfully in the highly oxidizing plasma environment.

The proof of concept of mercury oxidation under plasma conditions has been established by our experimental studies (1,2). To the best of our knowledge, no similar work has been reported in the literature. Our investigation focuses on effects of some of the constituents such as  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{NO}_x$  present in flue gases on elemental mercury oxidation in the DBD reactor. Fig. 1 shows the schematic of benchtop DBD system. The results show that Hg vapors (concentration  $61 \mu\text{g}/\text{m}^3$  or 6 ppbv) in a stream of 0.1%  $\text{O}_2$  and  $\text{N}_2$

can be effectively oxidized at the energy density of up to 114 J/L (Fig. 2). It is found that 0.1% O<sub>2</sub> in the inlet N<sub>2</sub> gas stream through the plasma is adequate to oxidize almost all mercury vapors.

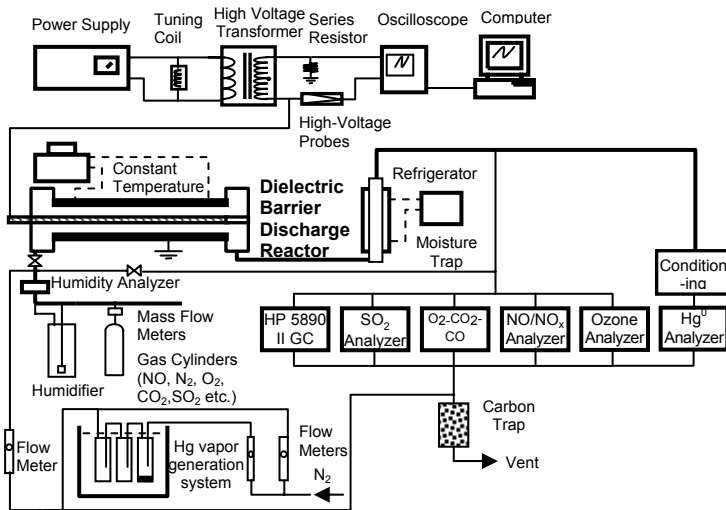


Fig. 1 Schematic of DBD System

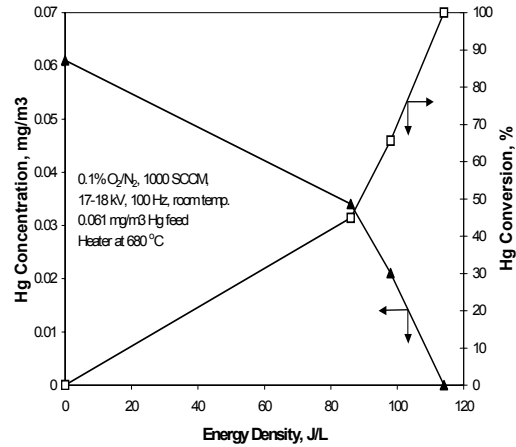
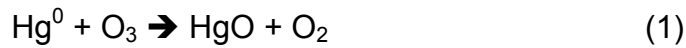


Fig. 2 Effect of Energy Density on Hg Conversion

The following is proposed to be the main oxidation reactions in the plasma reactor:



Effect of O<sub>2</sub> on mercury oxidation is further investigated by increasing O<sub>2</sub> concentration from less than 1 ppm to 0.1%. Shown in Figure 3 are the outlet Hg concentrations and conversions as a function of input O<sub>2</sub> concentration. Hg conversion is about 80% at O<sub>2</sub> concentration of 0.03-0.04%. As O<sub>2</sub> concentration is increased to 0.06%, Hg conversion reaches about 100%.

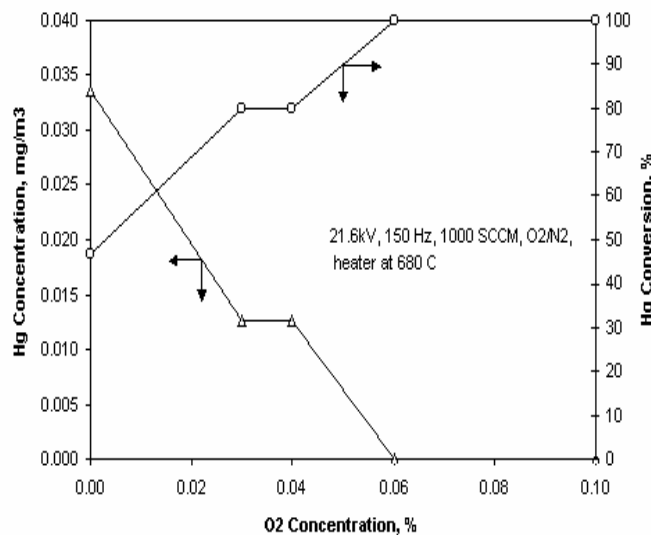
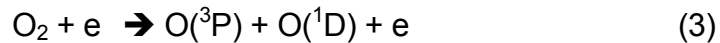


Fig. 3 Effect of O<sub>2</sub> Concentration on Hg Conversion

The experimental results show that H<sub>2</sub>O vapors have an effect on mercury oxidation due to the formation of OH<sup>•</sup> radicals. These radicals react with mercury to form mercury(I) hydroxide (Hg<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub> and mercury(II) hydroxide Hg(OH)<sub>2</sub>. CO<sub>2</sub>, however, helps convert Hg into HgO. Hg conversion of over 80% can be achieved when present in a gas mixture of 8% O<sub>2</sub>, 2% H<sub>2</sub>O and 10% CO<sub>2</sub> in N<sub>2</sub>. The presence of NO<sub>x</sub> enhances mercury oxidation in the DBD reactor.

A preliminary effort has also been made to study kinetics and global model for Hg oxidation under DBD conditions. Hg oxidation chemistry under barrier discharge plasma is very different from oxidation in a combustion process or under atmospheric conditions. The gaseous reactions in plasma can be very complex involving energetic electrons, ions, metastable neutral compounds, etc. resulting in tens of reactions. The main reactions for Hg oxidation proposed earlier in this study can be explained as follows:



Rate equation for reaction (7) can be expressed as follows:

$$-d[\text{Hg}]/dt = k_p [\text{Hg}]^\alpha [\text{O}_2]^\beta \quad (8)$$

where [Hg] and [O<sub>2</sub>] represent concentrations of Hg and O<sub>2</sub>, respectively in the plasma reactor and  $k_p$  is specific reaction rate. In addition to the effect of concentrations, the impact of all other variables such as electrical, chemical and hydrodynamic on reaction rate is accounted for by the rate constant  $k_p$ . In a non-thermal plasma condition in which reactions are mostly conducted at ambient temperature, the effect of temperature on reaction is negligible compared with discharge energy input. It is expected that higher discharge energy input will result in higher reaction rate.

We proposed a Arrhenius-type correlation for the specific reaction rate and successfully applied it to the expression of oxidation of NO in a non-thermal plasma condition. Accordingly, the same type of correlation can be used for the oxidation of elemental mercury. The correlation is

$$k_p = A_p e^{-E_a/E_d} \quad (9)$$

where  $A_p$  is frequency factor,  $E_a$  is effective activation energy and  $E_d$  is energy density (discharge power divided by gas flow rate). It should be noted that the item RT in regular Arrhenius-type equations is replaced with  $E_d$  in this new correlation. The effect of temperature is negligible compared to that of electric discharge. The activation energy and the frequency factor in the modified Arrhenius equation are found to be  $E_a = 10,034$  J/mole and  $A_p = 84,373$ ,

respectively. An elementary reaction between mercury and oxygen is assumed, i.e.,  $\alpha = 1$ ,  $\beta = 0.5$ .

The establishment of rate equation and the Arrhenius-type correlation will provide effective guidance in laboratory experiments and non-thermal plasma reactor design. It is expected that non-thermal plasma can lower activation energy for reactions such as  $\text{Hg} + \frac{1}{2}\text{O}_2 \rightarrow \text{HgO}$  and  $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$ . Comparison of the effective activation energies under plasma reaction conditions and under conventional reaction conditions would provide a quantitative interpretation of the “electro-catalytic” effect of non-thermal plasma. This will lead to a better understanding of Hg oxidation under non-thermal plasma conditions.

## Conclusions

The present study shows that Hg can be simultaneously removed together with the other two pollutants, namely,  $\text{NO}_x$  and  $\text{SO}_2$  in one barrier discharge reactor followed by a wet scrubber system. This avoids the need of three techniques for the removal of major gaseous pollutants from coal-fired power plants.

## Acknowledgement

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## References

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