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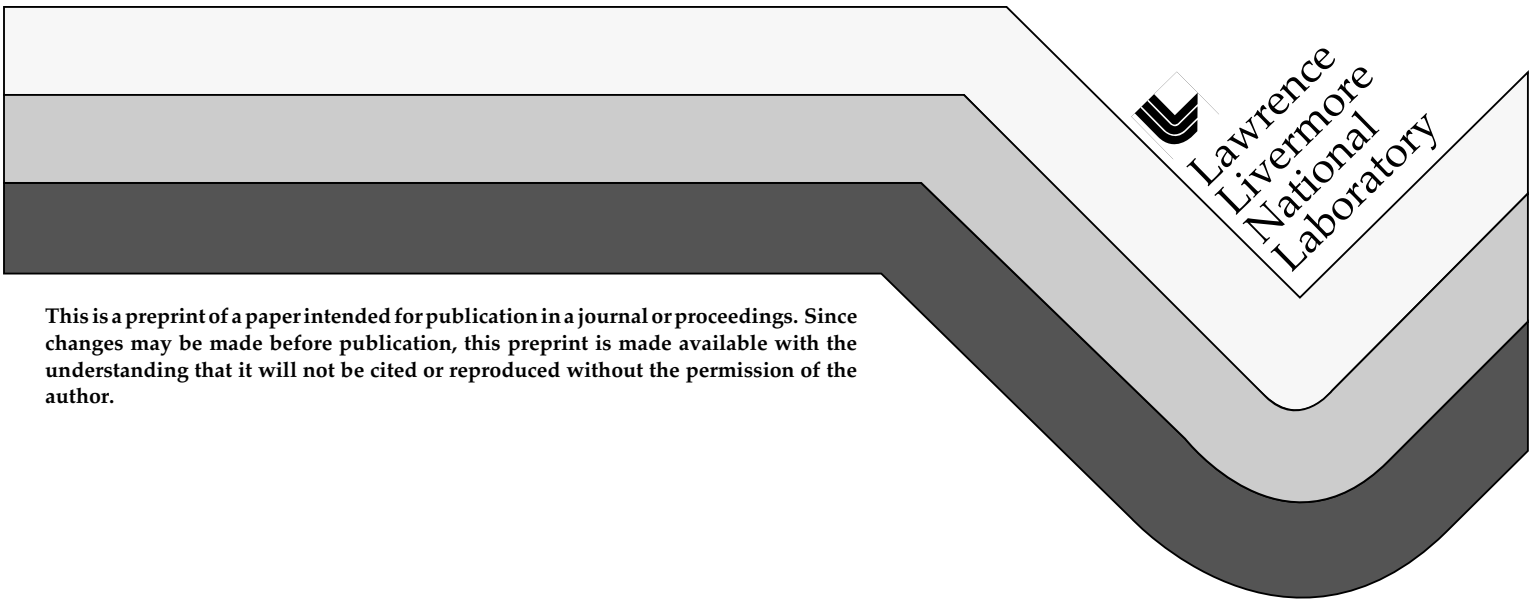

REMOVAL OF NO_X FROM DIESEL GENERATOR EXHAUST BY PULSED ELECTRON BEAMS

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ABSTRACT

The objective of this paper is to determine the effects of electron beam pulse parameters on the utilization of the reactive free radicals for removal of NO_X from diesel generator exhaust. A dose per pulse less than 1 kGy has been determined to be optimum for effective radical utilization. During each post-pulse period, the radicals are utilized in the removal of NO_X in a timescale of around 100 microseconds; thus, with pulse frequencies of around 10 kHz or less, the radical concentrations remain sufficiently low to prevent any significant competition between radical-pollutant and radical-radical reactions. It is shown that a pulsed electron beam reactor, operating with a dose per pulse of less than 1 kGy/pulse and pulse repetition rate of less than 10 kHz, will have the same plasma chemistry efficiency (parts per million of removed NO_X per kGy of electron beam dose) as an electron beam reactor operating with a low dose rate of 50 kGy/s in continuous mode. Ozone accumulation is a limiting factor under high pulse frequency conditions. The total dose requirement determines the optimum combination of dose per pulse and pulse frequency for both radical utilization and prevention of ozone buildup.

INTRODUCTION

Pollution control using high power electron beams is an important new market area for accelerator technology. In order to be cost competitive with conventional scrubber technologies, electron beam generators will have to be developed with high average power capability, smaller size and low cost per beam watt. The use of pulsed electron beams may provide a cost-effective solution to this problem. Compared with conventional electron gun technology, the use of pulsed electron beams may require fewer electron guns and much smaller facility to house the electron guns.

The application of the electron beam method for the treatment of flue gases from coal-fired power plants and municipal waste incinerators has been investigated extensively in both laboratory- and pilot-scale experiments[1-20]. Data in the existing literature is not available for emissions from diesel-powered generators. Diesel generators up to roughly 5,000 horsepower are used extensively as an electrical power source in a variety of industries throughout the world. The abatement of nitrogen oxides (NO_X) emissions from diesel generators has become a very important issue to these industries. There is no theoretical or experimental work evaluating electron beam treatment of NO_X for the particular gas composition found in diesel generator exhaust.

The objective of this paper is to determine the combination of pulse parameters that is optimum for pulsed electron beam treatment of NO_X from diesel generator exhaust. Parametric studies are particularly difficult to do in practical devices. Computer models have been developed to describe the chemistry of the electron beam process[21-24]. These models have been validated by comparison with experiments designed specifically to study the basic reaction kinetics of the process[25]. Once validated under specific sets of gas conditions, these computer models can be used to make predictions for a

wide variety of operating parameters. This paper uses the chemical kinetics code developed by Penetrante[24] to predict the dependence of the NO_x removal efficiency on the electron beam pulse parameters for a gas mixture simulating a diesel exhaust.

KINETIC ANALYSIS

The initial NO_x concentration used in the calculations is 1000 ppm, consisting mainly of nitric oxide (NO). The SO_2 concentration is presumed to be much lower compared to that encountered in coal-fired power plant flue gases. The typical background gas constituents are 72% N_2, 13% O_2, 5% CO_2 and 10% H_2O. With such high O_2 and H_2O concentrations, the removal of NO proceeds predominantly via oxidation to NO_2 and acids. Less than 20% of the NO_x is chemically reduced to N_2 and O_2. In the typical implementation of the electron beam dry scrubbing process, the main objective is to convert NO_x to nitric acid; a stoichiometric amount of ammonia is then used as an additive to transform this acid into particulate ammonium nitrate. The gas temperature is assumed to be 100°C.

In coal-fired power plant flue gases, the concentration of SO_2 could be as much as ten times the concentration of NO_x. The OH radical plays the key role in the simultaneous removal of NO_x and SO_2. The important primary radical-pollutant reactions that consume OH radicals are:

$$OH + SO_2 + M \rightarrow HSO_3 + M$$

followed by the production of the strongly oxidizing radical HO_2:

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$

The reaction of SO_3 with water vapor leads to the formation of sulfuric acid products:

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

The OH radical is regenerated while simultaneously oxidizing NO:

$$HO_2 + NO \rightarrow NO_2 + OH$$

This sequence of reactions simultaneously oxidize NO and SO_2 while regenerating the OH radical. This is the reason why this technique is particularly efficient for off-gases generated by utilities burning high sulfur coal. Another OH radical could induce the formation of nitric acid products:

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

For diesel generator exhausts, the SO_2 concentration is much lower compared to that encountered in coal-fired power plant flue gases. The radical utilization and power requirements for the oxidation for NO_x would therefore be different. The reaction responsible for the primary oxidation of NO is

$$O + NO + M \rightarrow NO_2 + M$$

followed by the conversion of NO_2 by OH radicals to nitric acid.

If the concentration of radicals is too high relative to the concentration of the pollutant molecules, then loss of radicals via radical-radical recombination could become deleterious to the efficiency of the process. Under high dose rate or high dose per pulse conditions, radical-radical reactions could waste the radicals and may even produce NO_x. For example:

$$N + OH \rightarrow NO + H$$

The H would react readily with O_2, which is present in large concentrations, to produce HO_2. Another reaction could then deplete the two important oxidizing radicals OH and HO_2:

$$OH + HO_2 + M \rightarrow H_2O + O_2 + M$$

The dose per pulse is the important parameter that determines the maximum concentration of radicals produced during each pulse. The calculations assume 4 microsecond pulses. The pulse length is usually much shorter compared to the time interval between pulses. Whether the radicals are completely utilized between pulses is determined by the pulse repetition rate.

The radical production rates are determined by a set of electron-impact reactions representing the dissociation and ionization of the background gas molecules by the electron beam. The set of primary electron-impact reactions included in the chemical kinetics calculations are discussed in Ref. 23-24. The radical production is commonly described in terms of the G-values (number of radicals produced per 100 eV of input energy).

RESULTS

Figure 1 shows the concentration of NO as function of the dose delivered to the exhaust gas, under various dose per pulse conditions. The initial NO concentration is 1000 ppm. A dose per pulse less than or equal to 1 kGy/pulse is required for effective radical utilization.

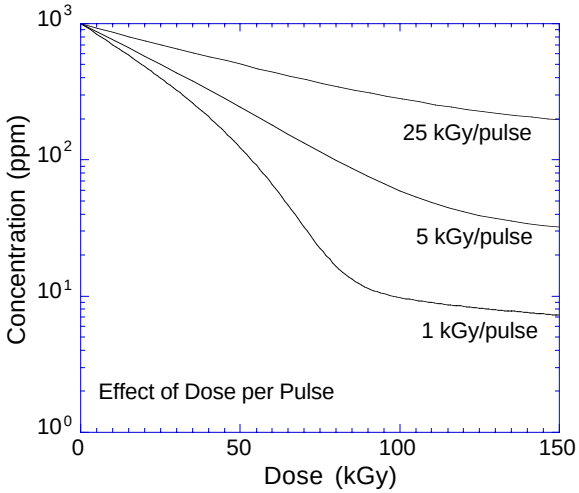

Figure 1. Effect of dose per pulse on the removal of NO.

To first order, the concentration [NO] can be expressed by

$$\log([NO]/[NO]_o) = -\phi/E$$

where $[NO]_o$ is the initial concentration, E is the input dose, and ϕ is the 9-factor. The 9-factor is the dose required to decrease the initial concentration by 90%. At 1 kGy/pulse, the 9-factor is around 58 kGy.

When the dose per pulse is low (less than 1 kGy per pulse), the peak concentrations of radicals are small enough such that the radicals are used effectively for NO removal. Figure 2 shows the radical concentrations for the case of 0.2 kGy/pulse, with a 4 μs square-wave pulse at 250 Hz. The concentrations of the radicals increase during the duration of the electron beam pulse. After the pulse, the radicals are utilized in reactions with NO. The time required to fully utilize the O radicals is

around 100 μs. Thus, with pulse frequencies of around 10 kHz or less, the radical concentrations remain sufficiently low to prevent any significant competition between radical-pollutant and radical-radical reactions.

Some ozone (O_3) is formed from the interaction of O radicals with the background O_2. The ozone formation reaction competes with the NO to NO_2 oxidation reaction. The reaction of O_3 is relatively slow compared to the other radical reactions. It takes more than 2 ms for the O_3 to disappear. The build-up of O_3 could be a limiting factor under high repetition rate conditions. The O_3 build-up could be prevented by using pulse frequencies on the order of 100 Hz. For example, since only 60 kGy is required for 90% NO removal, a 0.5 kGy/pulse electron beam running at 150 Hz would deliver the required dose without encountering O_3 as a byproduct.

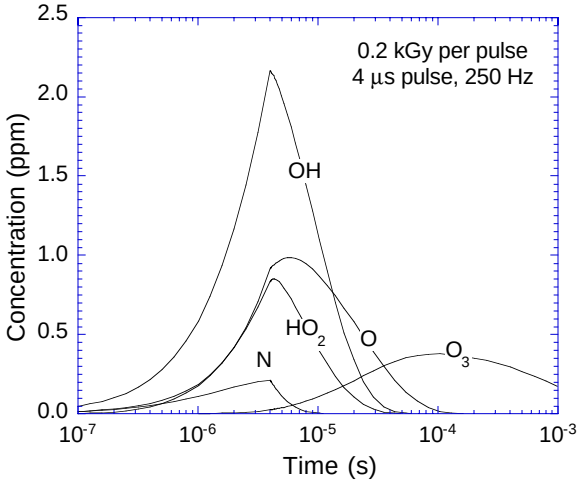

Figure 2. Radical concentrations in the case of a low dose per pulse electron beam source.

Figure 3 shows the radical concentrations for the case of 5 kGy/pulse, with a 4 μs square-wave pulse at 10 Hz. When the dose per pulse is too high, the radicals are wasted in radical-radical reactions because their concentrations are too high. As shown in Figure 1, the efficiency of the process degrades substantially when the dose per pulse is increased from 1 to 5 kGy/pulse.

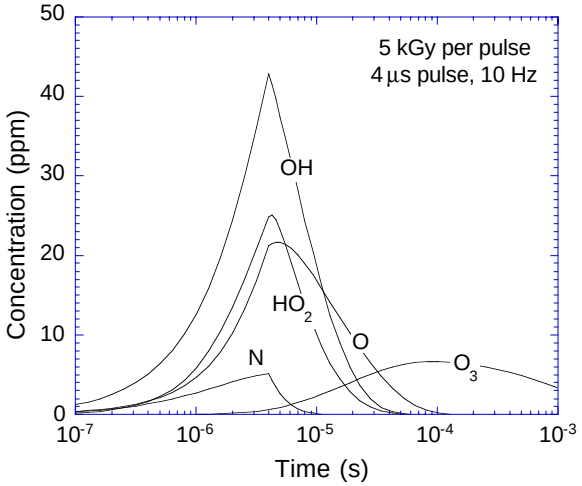

Figure 3. Radical concentrations in the case of a high dose per pulse electron beam source.

Figure 4 shows the effect of dose rate on the removal of NO for a DC electron beam source. For an initial NO concentration of 1000 ppm, and dose rates between 0.5 and 5000 kGy/s, 90% removal can be obtained without any noticeable effect from the dose rate. For more than 90% removal, a dose rate of around 50 kGy/s is optimum. When the NO concentration is already less than 10 ppm, the radical production rate matters on how well the radicals are utilized. When the dose rate is too low, the radical-pollutant reaction rates are too slow for effective radical utilization. When the dose rate is too high, the radical-radical reactions dominate over the radical-pollutant reactions. Figure 5 shows a comparison of a pulsed electron beam reactor operating at a dose per pulse of 1 kGy/pulse, and a DC electron beam reactor operating at a dose rate of 50 kGy/s.

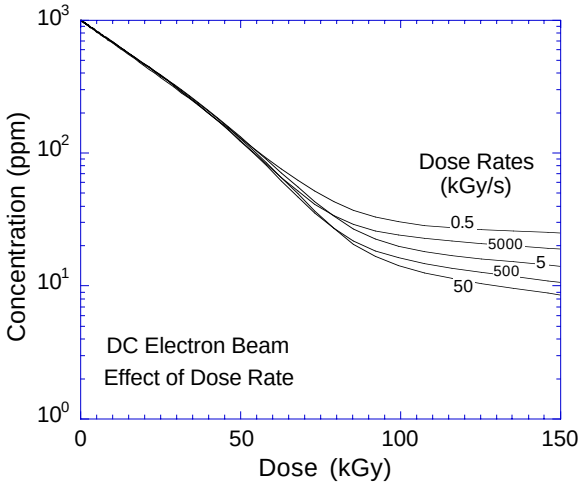

Figure 4. Effect of dose rate on the removal of NO for a DC electron beam source.

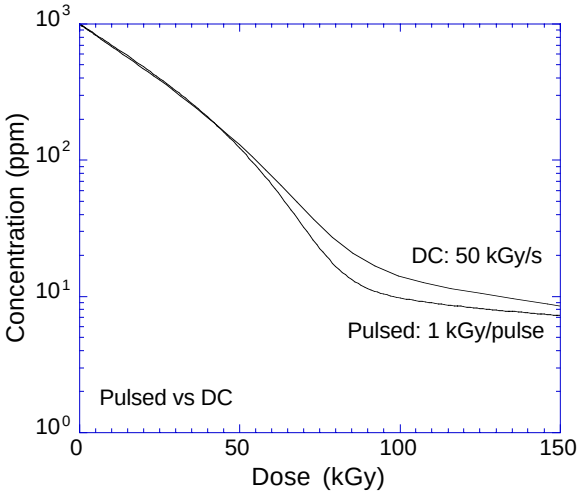

Figure 5. Comparison between DC and pulsed (low dose per pulse) electron beam sources.

CONCLUSIONS

A dose per pulse less than 1 kGy has been determined to be optimum for effective radical utilization. During each post-pulse period, the radicals are utilized in the removal of NO_x in a timescale of around 100 microseconds; thus, with pulse frequencies of around 10 kHz or less, the radical concentrations remain sufficiently low to prevent any significant competition between radical-pollutant and radical-radical reactions. A pulsed electron beam reactor, operating with a dose per

pulse of less than 1 kGy/pulse and pulse repetition rate of less than 10 kHz, will have the same plasma chemistry efficiency (parts per million of removed NO_X per kGy of electron beam dose) as an electron beam reactor operating with a low dose rate of 50 kGy/s in continuous mode. The buildup of ozone is a limiting factor under high pulse frequency conditions. The ozone build-up could be prevented by using pulse frequencies on the order of 100 Hz. For example, since only 60 kGy is required for 90% removal of a 1000 ppm initial NO, a 0.5 kGy/pulse electron beam running at 150 Hz would deliver the required dose without encountering ozone as a byproduct.

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