APPLICATIONS OF PULSED POWER IN ADVANCED OXIDATION AND REDUCTION PROCESSES FOR POLLUTION CONTROL

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Abstract

Pulsed power shows strong promise in developing innovative technologies aimed at pollution control. At Los Alamos we are applying pulsed power technology to the environment through the use of relativistic electron beams and nonequilibrium plasmas for the destruction of hazardous organic compounds in aqueous-based and gaseous-based media, respectively. These two techniques have also been applied to the treatment of flue gases such as SO_x and NO_x by other researchers. In this paper, we will describe our electron-beam and plasma experiments carried out on hazardous waste destruction. Additionally, we will describe the scaling of electron-beam and nonequilibrium plasma systems to industrial sizes, including discussions of electron accelerator architecture, comparison of continuous-duty versus repetitively pulsed accelerators, plasma-discharge modulators, and needed pulsed power technology development.

Introduction

A growing social awareness of the adverse impact of pollutants on our environment and the promulgation of environmental laws and regulations has recently stimulated the development of technologies for pollution abatement and hazardous waste destruction. We are working on a promising class of nonthermal methods, advanced oxidation and reduction processes (AOPs and ARPs), in which we employ electrical energy, rather than thermal energy, to create large quantities of highly reactive (oxidative and/or reductive) free radicals. These radicals subsequently react with hazardous organic chemicals, converting them to nonhazardous substances (CO_2, H_2O, and mineralized compounds). Nonthermal processes allow for the promotion of desired chemistry without the large enthalpy losses and potential augmentation of waste streams (e.g., with greenhouse gases) characteristic of thermal processes. Our AOPs/ARPs apply relativistic electron beams and nonequilibrium plasmas to the destruction of aqueous-based and gaseous-based hazardous organic compounds, respectively. We are focusing on the optimization of each technology for a particular waste stream, but because each shares common chemistry and pulsed power, developing one method often aids development of another. We are exploring the connection between the optimal formation of free radicals and the properties of the electrical driver for electron beams and nonequilibrium plasmas.

Electron-Beam Treatment of Aqueous-Based Hazardous Wastes

Background and General Results

High energy electron beams have been shown to be effective for the removal of hazardous organic contaminants in aqueous media and show great potential as a generally applicable technology for disinfection and sterilization [1,2]. The process of electron-beam irradiation is best understood in aqueous solutions in which sizable quantities of free radicals e_{aq}^-, H, and OH, as well as the more stable oxidant H_2O_2 are produced. These highly reactive species react with organic contaminants to produce substances that are not hazardous (CO_2, H_2O, and mineral salts or acids). E-beam technology also appears to be economically competitive with existing methods [3].

We have configured an electron accelerator for technology evaluation studies and demonstrated the destruction of two characteristic hazardous organic compounds. The test bed (see Fig. 1) operates in single-pulse mode (65-ns pulse width), typically producing beam voltages of 1.5-2.0 MeV and doses in the range 4-7 Mrad (40 x 10^3-70 x 10^3 Gy). To better understand the waste removal process and explore e-beam treatment scaling issues, we have employed a computer-based chemical kinetics model to predict the expected removal efficiency and to compare standard electrostatic accelerators to pulsed accelerators in terms of reactive free radical production [4]. Typical measured single-pulse destructions for trichloroethylene (TCE) are in the range 90-95%, in good agreement with our model. It should be pointed out that this short, single-pulse destruction is much less efficient than other dose profiles (e.g., continuous-duty profile) because of the radical-radical recombination phenomenon discussed further below. In addition, we have implemented a laser absorption system for measuring aqueous electron concentrations produced by the electron beam.

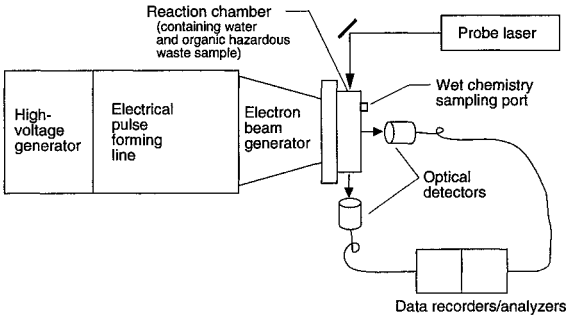

Fig. 1. Schematic diagram of the Los Alamos electron-beam test bed for hazardous waste treatment.

Scaling Studies & Accelerator Architectures

Conventional electrostatic electron accelerator equipment has generally been employed for high average power irradiation applications, while single-pulse accelerators have been utilized for high dose rate research. Recent technology developments [5,6] have lead to a new generation of pulsed linear induction accelerators driven by solid-state electrical power conditioning elements (see Fig. 2). These are considered to be less expensive per unit delivered e-beam dose, physically smaller, modular, and more reliable than conventional electrostatic accelerators. Once demonstrated, these new accelerators will allow a considerable simplification in treatment plant architecture.

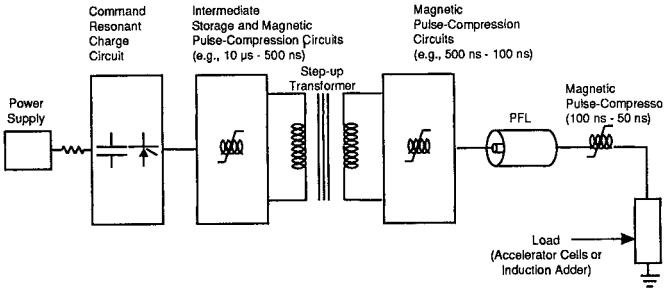

Fig. 2. Schematic diagram of compact high average power solid-state modulator for driving advanced pulsed linear induction accelerators.

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14. ABSTRACT
Pulsed power shows strong promise in developing innovative technologies aimed at pollution control. At Los Alamos we are applying pulsed power technology to the environment through the use of relativistic electron beams and nonequilibrium plasmas for the destruction of hazardous organic compounds in aqueous-based and gaseous-based media, respectively. These two techniques have also been applied to the treatment of flue gases such as SOx and NOx by other researchers. In this paper, we will describe our electron-beam and plasma experiments carried out on hazardous waste destruction. Additionally, we will describe the scaling of electron-beam and nonequilibrium plasma systems to industrial sizes, including discussions of electron accelerator architecture, comparison of continuous- duty versus repetitively pulsed accelerators, plasma-discharge modulators, and needed pulsed power technology development

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Resolving questions about how one chooses a particular accelerator system architecture for overall maximum effectiveness requires an understanding of the basic removal processes. To better understand the waste removal process and e-beam machine scaling, we have also employed a computer-based chemical kinetics model to relate destruction effectiveness to electron-beam dose profiles and electron-beam machine parameters, and to make comparisons with experimental data.

The first of these studies examined radical production with very short (< 100 ns), high dose-rate pulses in pure water. We examined the production and recombination of these transient species as a function of dose parameters. Our goal was to maximize the average free radical concentrations over a given period of time, for a given dose, by varying dose rate, pulse duration, and pulse repetition rate, thus providing greatest destruction potential. Our preliminary simulation results show that low dose rates have advantages over higher dose rates for the efficient production of radicals. This is apparently due to nonlinearities within the water model that favor radical recombination over radical production at higher dose rates. With TCE or other pollutants present, it has been postulated (although not demonstrated) that the formation of radical adducts and their subsequent reactions will produce favorable nonlinear effects that possibly make the pulsed case more advantageous in terms of chemical efficiency.

Our scaling studies have also explored the optimal dose profiles for free radical production and waste destruction using both conventional continuous-duty accelerators and repetitively pulsed accelerators. Although the computer modeling shows that a continuously applied dosage is more efficient in destroying waste than the same amount of single-pulse dosage, the modeling does show that a repetitively pulsed machine can produce similar radical concentrations to those of a DC machine when pulsed at high pulsed repetition rates (e.g., 10 kHz). This is shown in Fig. 3, which gives running averages of radical concentrations for both DC and repetitively pulsed dose profiles.

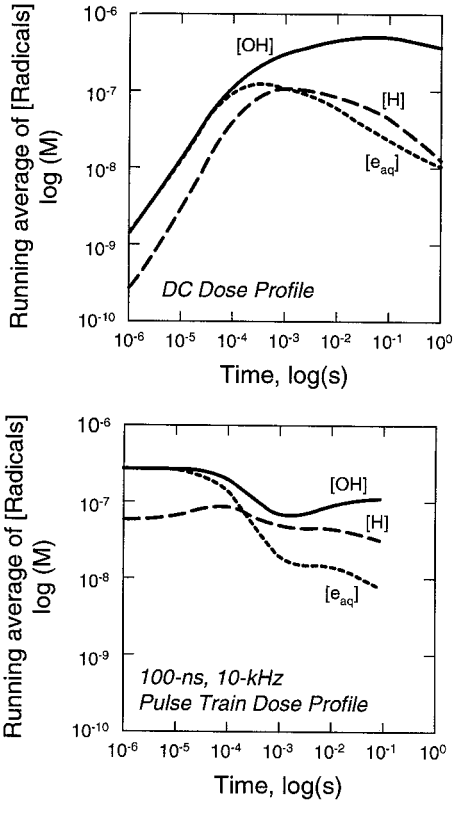

Fig. 3. Plots of running averages of free radical concentrations for DC and repetitive short pulse dose profiles.

Tables 1 and 2 give TCE and CCl_4 destruction Vs dose for four different methods of dose application. The initial concentrations and applied doses are chosen in an attempt to reproduce results from another facility.

Table 1. TCE Destruction Calculated for Different Doses and Methods of Application

Dose Method	Fractional Destruction (%)	
	100-krad	150-krad
100-ns pulse	37.5	46.1
1-kHz pulse train	68.0	92.2
10-kHz pulse train	68.8	95.9
DC	69.4	96.8

Notes: initial TCE concentration is 100 ppm; residence time is 0.1 sec.

Table 2. CCl_4 Destruction Calculated for Different Doses and Methods of Application

Dose Method	Fractional Destruction (%)	
	50-krad	100-krad
100-ns pulse	29.3	34.1
1-kHz pulse train	77.9	91.2
10-kHz pulse train	81.2	94.1
DC	81.8	94.9

Notes: initial CCl_4 concentration is 10 ppm; residence time is 0.1 sec.

In terms of destruction effectiveness, both the 1-kHz and 10-kHz pulse trains approach the DC-case fractional removal.

Nonequilibrium Plasma Treatment of Gaseous-Based Hazardous Wastes

Background and Experimental Results

Nonthermal plasma chemical reactor work at Los Alamos has demonstrated the potential for removing hazardous organics to very low levels (approaching tens of ppb to several ppb) by free-radical "cold combustion" [7]. We employ nonthermal plasmas created by silent electrical discharges in the gas stream - arrested transient electrical discharge streamers, generated with a dielectric barrier configuration (see Fig. 4). The plasma produces energetic electrons (typical energies of 1-10 eV), which in turn generate copious quantities of highly reactive free radicals. The electrons are selectively heated, which results in an efficient transfer of electrical energy to desirable chemical reactions at near-ambient temperatures and pressures. Although the volume of the microdischarges is quite small, an extremely large number of them are statistically spread out

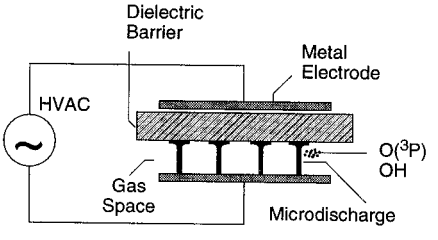

Fig. 4. Schematic drawing of representative dielectric barrier discharge configuration. Single or double barriers are typically employed in either planar (shown) or cylindrical geometry.

in space and time, resulting in a large effective processing volume. The free radicals, primarily atomic oxygen $O(^3P)$ and hydroxyl OH, oxidize organic compounds to nonhazardous, easily managed compounds such as H_2O, CO_2, and HCl. The potential of nonthermal plasma processing (dielectric barrier, corona, pulsed corona, etc.) is actively being pursued through a variety of international research efforts directed at flue gases (SO_x and NO_x) and hazardous organics (volatile organic compounds - VOCs).

We have focused on the silent discharge, which is sometimes called silent discharge plasma (SDP) because of the potential for high energy efficiency, large volume processing, scientific and technological maturity, and scalability (all typical of commercial ozone generation). Silent discharges are a natural means of creating plasmas which are potentially close to the optimal reduced electric field E/N for the production of oxidizing species. They also operate at high pressures (atmospheric and above), resulting in high rates of chemical reaction and large reactor throughput.

We have employed both single-barrier and double-barrier SDP reactors in our experiments. A typical planar cell has approximate dimensions of 71-cm length, 18-cm width, and 2.5-mm gap, giving a mean discharge area of 1238 cm^2 and an active discharge volume of 310 cm^3.

Our principal electrical power supply is a series inverter, which switches charged capacitors through a high-quality pulse transformer by means of high-power thyristors (see Fig. 5). This unit presently supplies nearly 4 kW of power at voltage pulse repetition frequencies up to 4.5 kHz. Using this power supply and the planar cell, representative operating conditions for bench-scale tests are a flow rate of 10 std lit/min and an average power of 200 W. This gives an average electrical energy density in the discharge of 1.2 J/cm^3, while the average area power density is approximately 0.16 W/cm^2.

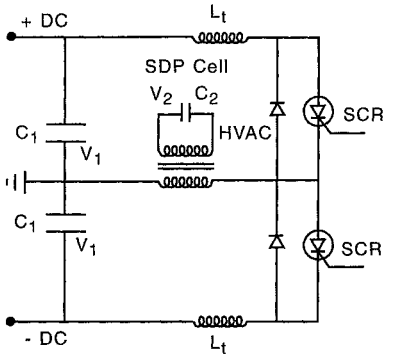

Fig. 5. Circuit schematic for the high-voltage, variable-frequency series inverter driver used in most of our experiments. Typical cell peak voltages are in the range 25 - 35 kV for 50 - 100 μs pulses. The frequency can be varied over a range of approximately 10 Hz - 3500 Hz.

We have demonstrated prototype-scale SDP destruction of aliphatic hydrocarbons, CFCs (chloro-fluorocarbons), TCE (trichloroethylene), and CCl_4. Gas flows of 10 - 20 std lit/min and TCE concentrations in the range 650 - 1,000 ppm have been typical influent parameters for our tests, although higher flow rates have now been achieved. Summary data is given in Fig. 6, which plots the destruction efficiency for TCE and CCl_4 versus energy density for both wet (~1% water vapor) and dry mixtures. At the water vapor concentrations employed in the illustrated results, the dry mixture gives greater removal for both TCE and CCl_4, which may be a consequence of Cl chain reactions in the dry case.

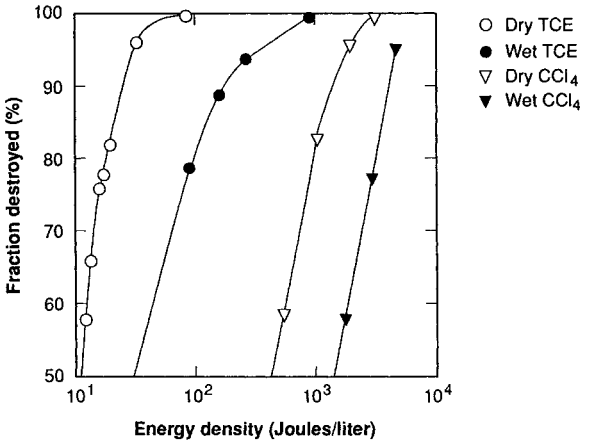

Fig. 6. Plots of TCE and CCl_4 removal versus energy density showing summary data for both wet and dry gas mixtures. The carrier gas was 80% Ar, 20% O_2, order 500 - 100 ppm chlorocarbon, and 1 - 2 % water vapor (if wet).

Silent Discharge Plasma Reactor Scaling

To scale SDP reactors, the fractional removal is related to the plasma energy density (average power <P>, divided by gas flow rate Q). For our wet experiments, doubling the reactor power or halving the flow rate will result in the same destruction. For dry mixtures, which may be dominated by chain reactions, this scaling parameter does not necessarily apply. A figure of merit for removal can be defined as the energy delivered to the plasma per hazardous molecule removed from the gas stream. A convenient unit for the figure of merit is the number of kilowatt-hours required to remove a kilogram of hazardous compound (i.e., kW-hr/kg). From the data presented previously, the removal figures of merit are determined to be approximately 12 kW-hr/kg for 90% removal of TCE, 84 kW-hr/kg for >> 99% removal of TCE (650 - 1,000 ppm to ~100 ppb) and 270 kW-hr/kg for 90% removal of CCl_4. Another way to express this is in terms of the amount of energy required to destroy the contaminant level by a factor of 10. We have named this factor the 9-factor, since if three 9's destruction (i.e., 0.999 or 99.9% destroyed) is required, three times the 9-factor must be applied to the waste stream. This factor has the units of J/lit (or J/cm^3). Preliminary values of the 9-factor for TCE are: 25.3 J/lit dry, and 75 J/lit wet. One advantage of this parameter, unlike kW-hr/kg, is that it is valid regardless of the initial concentration of waste.

Using the 9-factor, scaling calculations are simplified. For example, the removal of TCE under wet conditions can be scaled as shown in Fig. 7, a plot of degree of destruction versus gas flow rate for one, two, and four cells.

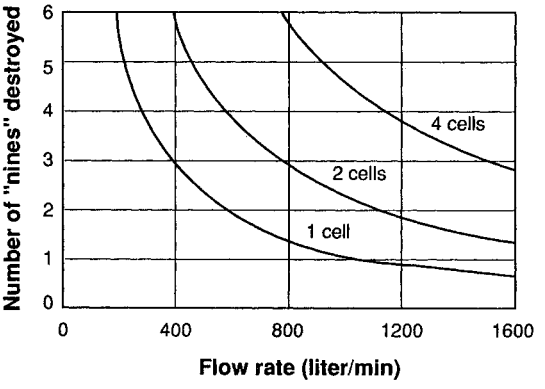

Fig. 7. Scaling plot for the destruction of TCE under humid conditions. The number of nines destroyed is plotted versus the flow rate for one, two and four plasma cells.

The scalability of SDP reactors and associated power supplies is influenced by the desired gas flow rate and the concentration of hazardous compounds to be treated. Consideration of mechanical constraints, single-point failures, and successful architectures used in the commercial ozone generation industry has led us to choose modularization as a preferred approach. Currently, we are considering scalable modules consisting of combinations of several smaller modules (see Fig. 8). This design will quickly enable a scale up of gas flow rates by factors of 10 to 100. For more corrosive compounds double barriers can be used so that there is no contact between the corrosive gas mixture and any metal surface.

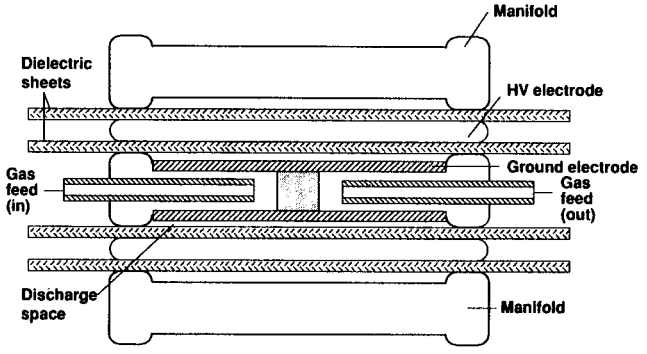

Fig. 8. Schematic diagram of stacked module containing four planar SDP cells, operated in parallel.

Future Directions

Additional factors can influence the production of free radicals in nonequilibrium plasmas. Investigations worldwide are in progress on the effects of electrical driver pulse width and rise time, electrical drive circuit coupling to plasma cells, and the role of UV light in the plasma chemistry and discharge processes. We speculate that, if free radical utilization is dominated by radical-radical recombination (which may happen in microdischarges), a fast rise time, homogeneous discharge may be more efficient in destroying contaminants. This is yet to be demonstrated, but we plan to study this effect for SDP processing.

Summary and Conclusions

We have calculated free radical production in aqueous solutions irradiated with electron beams by varying dose rate, pulse duration, and pulse repetition rate. When radical-radical recombination dominates, low dose rates are more advantageous than high dose rates. However, a suitable application of repetitive short-duration pulses (e.g., 100 ns) gives radical concentrations and fractional removals similar to a DC applied dose. New high-average-power pulsed linear induction accelerators are judged to be advantageous to conventional electrostatic accelerators for waste treatment because of relaxed requirements on high voltage isolation, ease of scaling to high power, modularity, smaller physical size, and broad range of power control.

Nonthermal discharge plasmas also show promise for the removal of VOCs and other air toxics such as SO_x and NO_x in flue gas. Removal figures of merit have been established and reactors have been scaled to energy density levels that will permit industrial service. Basic understanding of the plasma chemistry has evolved to the point where trends and equipment scaling can be predicted with reasonable confidence [8]. Because the process can simultaneously remove different types of pollutants, it is particularly attractive for future environmental applications.

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