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## Short-Pulsed, Electric-Discharge Degradation of Toxic and Sludge Wastes

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### Abstract

This is the final report of a three-year, Directed Research and Development (LDRD) project funded by the Los Alamos National Laboratory (LANL). The project was a collaborative effort with the University of California at Irvine (UCI), which was the lead project performer. Short-pulse, electric-discharge streamers were used to degrade aromatic and chlorinated compounds in water aerosols. An atomizer supplies 10-50  $\mu\text{m}$  aerosol droplets to a discharge chamber containing thin wires that are driven by electric pulses of 50-90 kV amplitude, 50-150 ns pulse duration, and 100 Hz repetition rate. The combination of a high electric field, large  $\text{H}_2\text{O}$  dielectric constant and atomization provide efficient degradation of organic molecules including: paranitrophenol, di-chlorophenol and perchloroethylene. The specific energy input for degradation of a pollutant molecule depends on the particular compound, its concentration, and the operational parameters of the discharge.

### Background and Research Objectives

The pollution of air, water, and soil with halogenated chemical compounds is a continuing threat to the natural biosphere. Such compounds are characterized by extremely slow biodegradation rates and therefore remain stable and potentially toxic for a long time. Conventional methods to treat halogenated compounds—such as absorption by activated carbon, high-temperature incineration, multistage chemical processing with sodium (for PCBs), and catalytic oxidation systems (which are ineffective and costly)—have many drawbacks. For example, incineration of chlorocarbons produces more toxic compounds like dioxins and furans; and the use of metallic catalysts is uneconomical, especially for low flow rates and streams with high water content. Electric-discharge technology using energetic electrons to degrade toxic chemical wastes offers a new approach for the clean-up of refractory pollutants in aqueous- and gaseous-based media. We have employed a

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heterogeneous, highly-atomized flow of air-water droplets excited by short, high-voltage electrical pulses. This produces large densities of energetic electrons (1-100 eV) which efficiently generate reactive free radicals and uv light. At the same time increased air-liquid surface area is available for the interaction of reactive species with pollutants. Our objective is to fully degrade aqueous pollutants to the benign limit of carbon, water, and low-molecular-weight gases; or at least to the point where the products can be more easily handled by conventional techniques or biodegradation.

### **Importance to LANL's Science and Technology Base and National R&D Needs**

This project supports major Los Alamos core technical competencies and capabilities in *Earth and Environmental Systems* and *Nuclear Science, Beams, and Plasmas*. It also supports the Laboratory tactical goal of promoting great science. The Laboratory, the Department of Energy (DOE), and the Department of Defense (DoD) are concerned with effective technologies for handling the pollution of water, soil, and air with hazardous organic compounds. This project complements many ongoing national science and technical efforts on pollution abatement and environmental remediation.

### **Scientific Approach and Accomplishments**

#### **Introduction**

Our approach involves an aerosol flow of a sample compound immersed in water droplets (10-100  $\mu\text{m}$  diameter), ionized by repetitive (0.1-1 kHz), short-pulse (10-100 ns), high-voltage (50-100 kV) pulses. The high-voltage pulse duration is short to avoid spark discharge while inducing copious streamers (corona) and energetic (supra-thermal) electrons ( $T_e = 1-100 \text{ eV}$ )<sup>1</sup>. The advantages include: efficient generation of free radicals, ozone, and ultraviolet radiation, and consequently, more uniform ionization in the volume element of toxin, water, and gas; a million-fold increase in the air-liquid surface area for increased interaction with reactive components; and reduced processing cost due to the absence of bulk-discharge heating in the exposed stream-flow<sup>2</sup>. In short, the system is called a pulsed aerosol reactor. Figure 1 shows a schematic diagram of the presently-used pulsed aerosol reactor.

The reactor housing consists of a Pyrex tube (25-cm diameter, 150-cm length). The intermeshed wire electrodes are oriented vertically to increase the transparency of the system for the atomized-droplet flow. The atomizer can be located either at the top or

bottom of the reactor. In the latter case the residence time of the aerosol in the discharge was enhanced. The throughput of the system was in the range of 15-38 liter/hr.

The high-voltage pulse-modulator for the reactor consists of a dc power supply, inductive choke, hydrogen thyatron trigger generator, thyatron bias supply, pulse-forming cables (50- $\Omega$  impedance), and a step-up transformer. The high-voltage pulse generator provides pulses at a repetition frequency of 10-1,000 Hz, voltage amplitude of 60-100 kV, and 100 ns duration into the matched capacitive load of the discharge chamber.

Analysis of the initial and final concentrations of the processed compounds and the composition of byproducts was carried out using several techniques: UV spectrophotometry for chemical concentrations, pyrolytic analysis for total organic carbon (TOC) concentration, and gas chromatography with mass spectrometry (GC/MS) for chemical intermediate identification, and specific-ion-electrode argentometric methods to measure the released chloride (Cl<sup>-</sup>) concentration in halogenated organics.

## Results

During the first year of this project (FY 1995), work was focused on demonstrating the feasibility of the technique by commissioning an engineering prototype reactor, characterizing its operating parameters (voltage, current, pulse properties), and carrying out initial experiments on the degradation of a model water pollutant - the compound paranitrophenol (PNP). During the second year (FY 1996), the optimal operating parameters for voltage, pulse duration, pulse repetition frequency, flow density, and droplet dimension were established. Moreover, we expanded our studies to include chlorinated compounds and assembled a new reactor incorporating much needed design modifications in the chamber-material construction, aerosol-injection geometry, electrode geometry, and pulse-discharge circuitry. During the third and final project year (FY 1997), studies with the modified, pulsed aerosol reactor were continued in degrading aqueous solutions of contemporary interest. For the main target compounds, we selected halogenated organic compounds, e.g., various chlorinated phenols: di-chlorophenol (DCP), tri-chlorophenol (TCP), tetra-chlorophenol (TeCP), penta-chlorophenol (PCP), aromatic (PNP) and non-aromatic chlorinated organics - perchloroethylene, (PCE). The results for PNP, DCP, and PCE will be discussed here because they are representative of most of the test results.

The results of PNP scaling studies, starting with a PNP concentration of 800 ppm, a pulsed voltage of 50 kV, and a frequency of 300 Hz show that nearly 40% of PNP is degraded in 4 flow cycles through the reactor. The specific-energy cost is 40 eV/molecule

measured for the first process cycle, when the decrease in concentration per cycle is largest. Competing degradation technologies<sup>3</sup> (e.g., sonohydraulic, electrohydraulic, electron beam) report specific-energy costs of the order of several hundred, suggesting much higher energy efficiency for the present approach. The TOC concentration decreases markedly over an increasing number of processing cycles. GC/MS data suggests the formation of intermediates with higher molecular weights than that PNP (possibly due to polymerization); the exact identification of the intermediates has not been carried out.

Detailed tests with 1000 ppm of 2,4-dichlorophenol (DCP) were performed. Liberated chloride ions (in the form of HCl) dissolved in water were measured by either a selective ion probe or spectro-photometric methods. A maximum of 62% of the total possible chloride was removed after six cycles at a rate of 10% of the total possible chloride per cycle. For these conditions, the figure of merit is estimated to be 60-80 eV/molecule. Preliminary optimization experiments, in which the applied voltage amplitude and the pulse frequency were varied between 30-60 kV and 300-600 Hz respectively, keeping the same average power of the circuit, showed that operation at higher voltage provides greater released Cl<sup>-</sup> concentration. The further increase of the operational frequency up to 1,200 Hz at voltage amplitude 40 kV showed only a small change in the extent of dechlorination. This might arise from the circuit itself - with saturation of the transformer core and an resulting drop of the output voltage.

The measurement of DCP degradation was also corroborated using a gas chromatograph equipped with a flame ionization detector. Samples of treated DCP were extracted with pentane and fed to the gas chromatography system. It was found that for a 1000 ppm DCP sample in which 56% of the total possible Cl<sup>-</sup> was released, over 90% of the initial DCP was degraded. This indicates that the treatment of DCP releases on average one chloride ion per molecule of DCP rather than removing both chlorine atoms for roughly 50% of the DCP molecules.

Upon treatment of DCP, a color change was qualitatively evidenced which appeared to be related to the extent of dechlorination. After the initial, untreated, colorless DCP was processed, the sample was observed to change from a light yellowish color (10-20% dechlorination) to an aqua-green hue (50-70% dechlorination). This increase in color is probably indicative of polymerization of the oxidized, dechlorinated phenol to form quinones, as has been reported in other high-energy systems<sup>4</sup>.

Initial experiments using a 0.5 liter volume of 100 ppm perchloroethylene (PCE) solution also demonstrated efficient dechlorination, where 16-78% of the chlorine ions were removed after one to four cycles, respectively, and each cycle took 5 minutes of processing. The respective figure of merit parameter for PCE is, ~ 60 eV/molecule.

Because PCE has a high volatility, special measures were taken to keep the reactor chamber vapor tight, and treatment of the samples was done in a completely closed-loop mode - the air/droplet flow was cycled from the bottom part of the reactor to the top via atomizing nozzle using a compressor/vacuum pump. In the latter case experiments proved that atomization alone without high voltage pulse application resulted in almost total loss of the PCE from the drops to the ambient volume of the reactor chamber, so that the collected sample of initial solution of PCE did not contain more than a few percent of the its initial concentration. It means that registered progressive dechlorination of PCE molecules with the number of discharge cycles in the closed loop of the air-droplet flow (measured by the rise of the chloride ions content in the processed sample) took place mainly in the gaseous phase. Few initial tests on airborne PCE degradation (provided in the reactor via atomization of 100 ppm PCE solution) in the streamer discharge without injection of atomized water resulted in considerably lower released chlorine output, which indicates the significance of the aerosol role during the discharge.

At the present state of the reactor, as observed for both the DCP and PCE results, there were no trends toward saturation, which demonstrates the potential for multi-cycle reprocessing of halogenated organics with this technique. Table 1 below summarizes the test results for several other representative chlorinated compounds.

**Table 1.** Degree of pollutant degradation and energy-removal cost (including power supply efficiency) for representative chlorinated compounds. In the second and third columns, the first number corresponds to a liquid flow rate of 8.14 liter/hour, while the second corresponds to a flow of 18.5 liter/hour. The initial DCP concentrations were 1000 ppm, while those for the remaining compounds were in the range 100-300 ppm.

<b>Pollutant</b>	<b>Removal (%)</b>	<b>Energy cost (eV/molecule)</b>
DCP	44, 34	630, 330
2,4,5-TCP	86, 58	800, 480
2,4,6-DCP	86, 55	1300, 800
TeCP	90, 75	4400, 2100
PCP	90, 75	870, 420
PCE	94, no data	2600, no data



## Summary

We have demonstrated a means to degrade an aerosol mixture of various organic compounds (PNP, DCP, PCE) of near-term concern for environmental pollution using a medium voltage, repetitive short-pulsed discharge. The technique provides high electrical efficiency for applications involving water and airborne pollution. Future studies would be useful to identify intermediate by-products and to optimize the operating parameters that lead to a higher degree of final mineralization. UC Irvine has also started further collaborative research with the University of Notre Dame on using the pulsed aerosol reactor as an initial dechlorination stage for a bioremediation reactor<sup>5</sup>. Initial experiments with DCP have shown promising results. Future studies are expected to expand the two-stage concept to the treatment of other recalcitrant chlorinated compounds.

## Publications

1. Bystritskii, V.M., Gonzales, A., Olson, T. Puchkarev, V., Rosocha, L., Wessel, F., Yankelevich, Y., "Short-Pulsed, Electric-Discharge Degradation of Aqueous Organics," Proceedings of the International Conference on High-Power Particle Beams, BEAMS '96, Prague (July 10-14, 1996).
2. Bystritskii, V.M., Gonzales, A., Olson, T. Puchkarev, V., Wessel, F., Rosocha, L., Yankelevich, Y., "Pulsed Discharge in Aerosol for Waste Water Clean-Up," Bulletin of the American Physical Society, **41**, p. 1641 (November, 1996).
3. Bystritskii, V.M., Yankelevich, Y., Wood, T., Wessel, F., Yee, D., "Aerosol Plasma for Aqueous Waste Treatment", Abstracts of 24th IEEE International Conference on Plasma Science, San Diego, CA, p. 311 (May 19-22, 1997).
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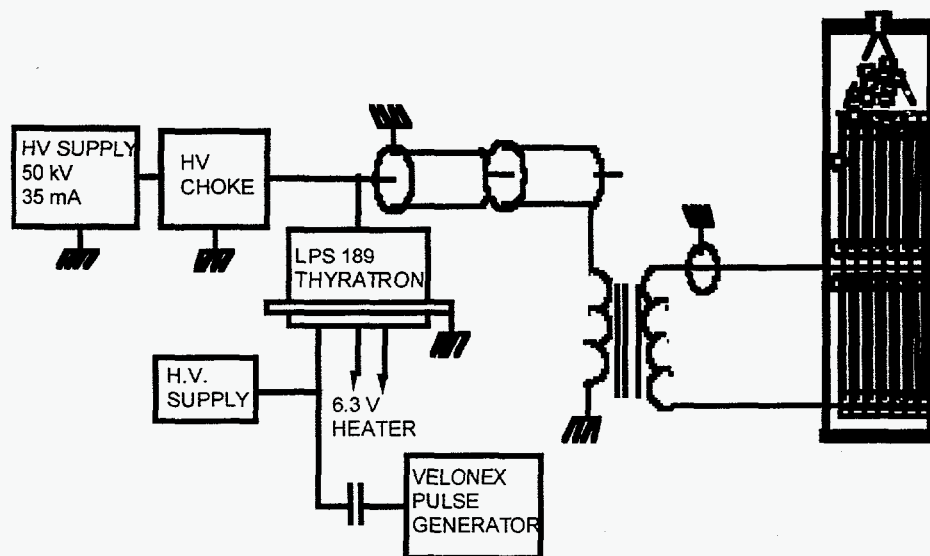


Figure 1. Schematic diagram of the pulsed, electric-discharge plasma aerosol reactor.