Conf-920851--72

PNL-SA--20741

DE92 041338

HIGH-ENERGY CORONA FOR DESTRUCTION ON VOLATILE ORGANIC CONTAMINANTS IN PROCESS OFF-GASES

J. W. Virden
W. O. Heath
S. C. Goheen
M. C. Miller
G. M. Mong
R. L. Richardson

August 1992

Presented at the International Topical Meeting Spectrum '92: Nuclear and Hazardous Waste Management
August 23-27, 1992
Boise, Idaho

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington

HIGH-ENERGY CORONA FOR DESTRUCTION OF VOLATILE ORGANIC CONTAMINANTS IN PROCESS OFF-GASES

J.W. Virden, W.O. Heath, S.C. Goheen, M.C. Miller, G.M. Mong, and R.L. Richardson
Pacific Northwest Laboratory[a]
P.O. Box 999
Richland, Washington 99352

ABSTRACT

A small (2 scfm) High-Energy Corona (HEC) reactor was developed to produce a non-equilibrium plasma in a concentric-cylinder geometry. A volume-filling plasma was produced in a packed bed, and initial tests have demonstrated the ability to destroy up to 1500 ppm trichloroethylene at a flow rate of 1.4 scfm, with greater than 99% destruction observed. Destruction efficiency is examined as a function of inlet TCE concentration, bed height (residence time) and applied voltage. Hydrochloric acid appears to be the primary chlorinated byproduct, and can be removed by conventional wet or dry scrubbing.

INTRODUCTION

Recently, the destruction of volatile organic contaminants using a variety of plasma-generating devices (microwave, silent discharge, and corona reactors) has received considerable attention.[1, 2, 3, 4, 5] This technique is promising in terms of decontamination capabilities because treatment occurs near ambient temperature and pressure, requiring significantly lower energy and capital equipment costs than traditional thermal treatment. Also, traditional catalysts or other additives are not required. A nonequilibrium or low-temperature plasma can be produced in an air stream by passing the air through a high-voltage electrical field. Under certain circumstances, electrical discharges will occur in the gas stream that form an extremely oxidative environment capable of destroying toxic organic compounds. The successful destruction of vapor phase contaminants using plasma generating devices has been reported with the following chemicals: aliphatic hydrocarbons,[5] benzene,[2] toluene,[2, 3, 6] methylene chloride,[2, 3] trichlorotrifluoroethane,[2, 3, 5] dimethyl methyl phosphonate,[4, 7] n-heptane,[6] diisopropyl methylphosphonate,[7] 1-heptene,[6] 1-propanol,[6] aetonitrile,[8] cyanogen chloride[1] and phosgene.[1] The majority of this work has been performed on small (< 0.1 scfm) plasma reactors using a variety of reactor geometries that typically operate at power requirements as low as a few hundred watts. While small-scale application of plasma devices for the destruction of volatile organic contaminants appears promising, much work is needed towards the development of larger scale plasma reactors.

The objective of this work is to develop and conduct field tests on a prototype HEC off-gas treatment unit capable of destroying trichloroethylene and perchloroethylene at concentrations of up to 100 ppm and at flow rates of 30 scfm. Towards this end, laboratory experiments using a packed-bed corona reactor have been performed. Destruction efficiency as a function of applied voltage, bed height and inlet TCE concentration are reported. The successful completion of laboratory experiments will lead to the design of a full-scale off-gas treatment system. The project will culminate in a planned field demonstration of the HEC off-gas treatment unit for treating soil off-gases at a site in Savannah River, S.C., in 1993.

EXPERIMENTAL METHODS

A schematic of the experimental system is shown in Figure 1. The system is run under a slight vacuum with the reactor inlet at ambient pressure. Flow rates are controlled with a flow meter downstream of the reactor. At the reactor inlet, ambient air is first pulled through a water bubbler and then mixed with a controlled amount of TCE. The volumetric flow passing through the water bubbler was typically 500 times greater than that passing through the TCE bubbler.

The TCE concentration at the reactor inlet and outlet was measured using a HP Model 5840 Gas Chromatograph (GC). The GC measurements alternated between the reactor outlet and inlet every 3.5 minutes. The amount of TCE-contaminated air continuously passing through the HP-GC represented less than 0.1% of the volumetric flow through the reactor. After passing through the reactor, the gas stream passed through three caustic bubblers, a dry ice trap and a flow meter before being exhausted to the house vacuum. Samples from both the dry ice trap and the three caustic (sodium carbonate pH=9-10) bubblers were periodically analyzed for TCE and reaction byproducts.

The reactor consists of a stainless steel inner electrode (0.125 in.) centered within a borosilicate tube (diameter of 2.25 in.). A stainless steel grounding screen is attached to the outside of the borosilicate cylinder. The active part (plasma producing region) of the reactor is

[a]Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. Work supported by the U.S. Department of Energy's Office of Technology Developments VOC Non-Arid Integrated Demonstration Program.

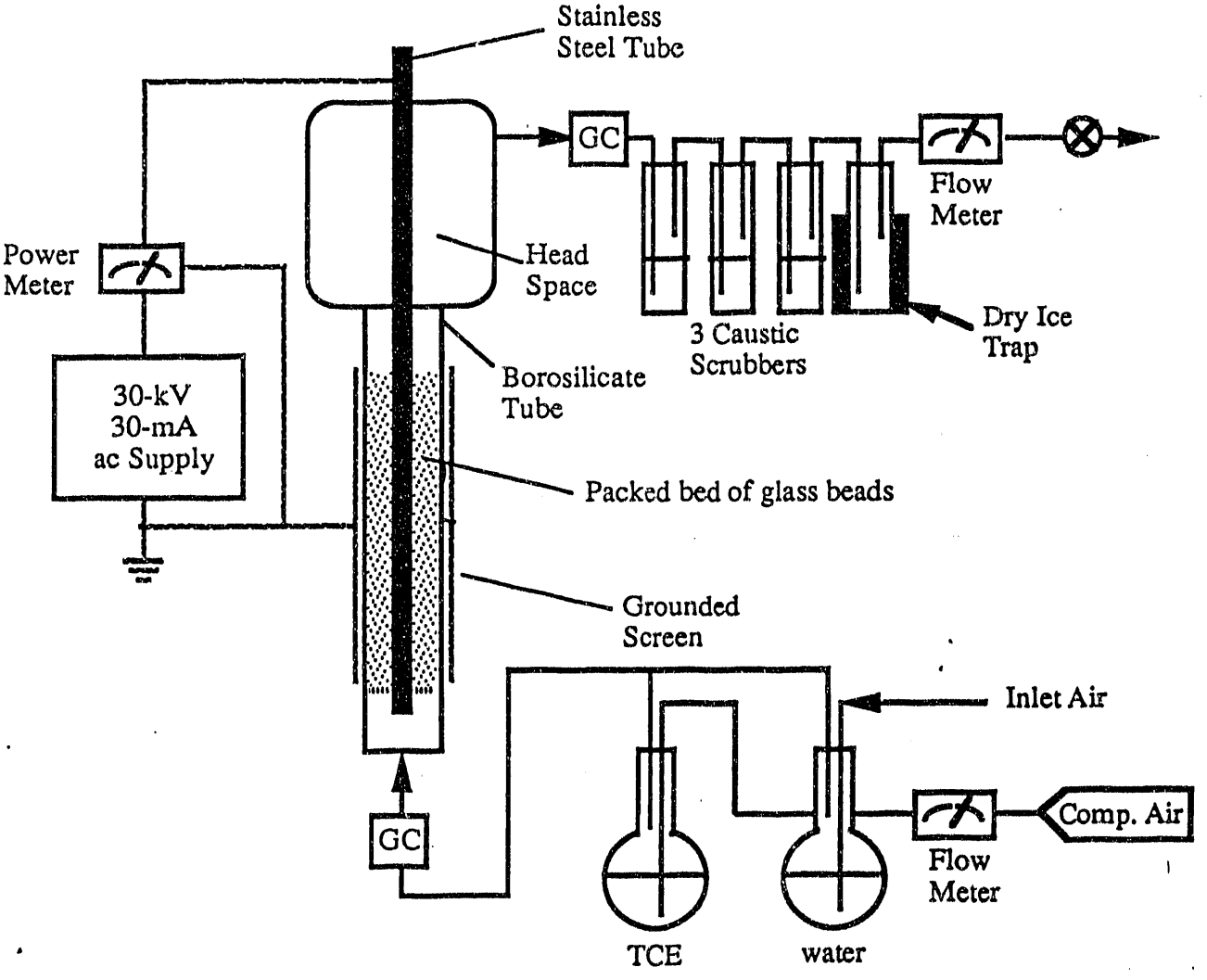

Figure 1. Bench-scale Packed Bed Corona Reactor

limited to that volume between the inner electrode and outer grounding screen. Glass beads (borosilicate or soda lime) with a diameter of 0.6 cm were used as packing between the inner electrode and the outer cylinder. The addition of the beads greatly enhanced corona activity within the cylinder volume and lowered the voltage required to initiate corona. With no beads present there was no noticeable destruction of TCE.

At the flow rates investigated, the pressure drop across the reactor was typically less than 0.5 psi. An oxidative plasma is initiated by applying an ac voltage (American HV Test Systems, Inc., Model 930-1, 30 kV maximum) to the inner electrode.[9] Typically, up to 30 kV (60 Hz) are applied to the inner electrode, resulting in currents between 3-15 mA. Experiments were typically run under ambient conditions at volumetric flow rates between 1-2 scfm. Power requirements were typically 100 watts.

RESULTS AND DISCUSSION

There are many variables that will affect destruction efficiency and thus scale-up. These variables include bed height, residence time, applied voltage, inlet TCE concentration, flow rate, bead size and dielectric constant, column diameter, electrode diameter, reactor temperature, pressure, type of contaminant, and humidity, to name a few. The effect of bed height, applied voltage, and TCE inlet concentration on the destruction of TCE are shown in Figures 2, 3, and 4.

The effect of bed height on the destruction efficiency of TCE in the corona reactor is shown in Figure 2. Bed height and thus reactor volume were adjusted by adding glass beads and grounding screen to the reactor. As beads were added to the reactor, visible discharge was observed throughout the entire reactor volume containing glass beads. At a constant overall flow rate, bed height corresponds directly to residence time within the active region of the reactor. The three reactor

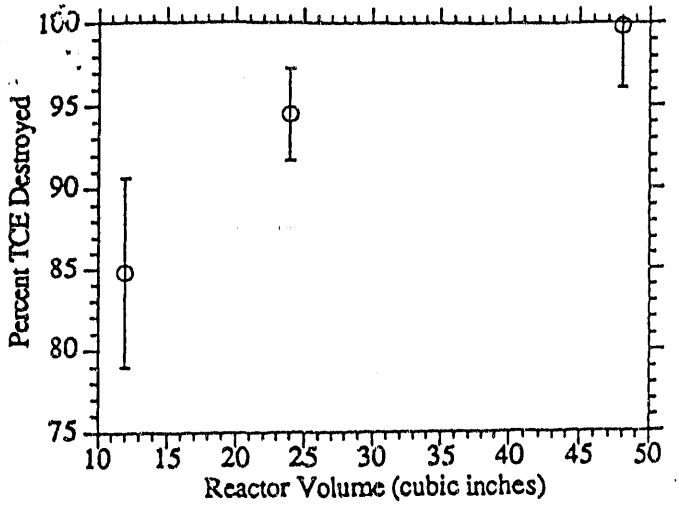

Figure 2. Percent of TCE destroyed as a function of reactor volume. Operating conditions: 1.4 scfm, 30 kV applied voltage. The inlet concentration of TCE for the reactor volumes of 12 and 24 cubic inches were approximately 230 ± 10 ppm. The inlet concentration of the 48 cubic inch reactor was 1590 ± 42 ppm.

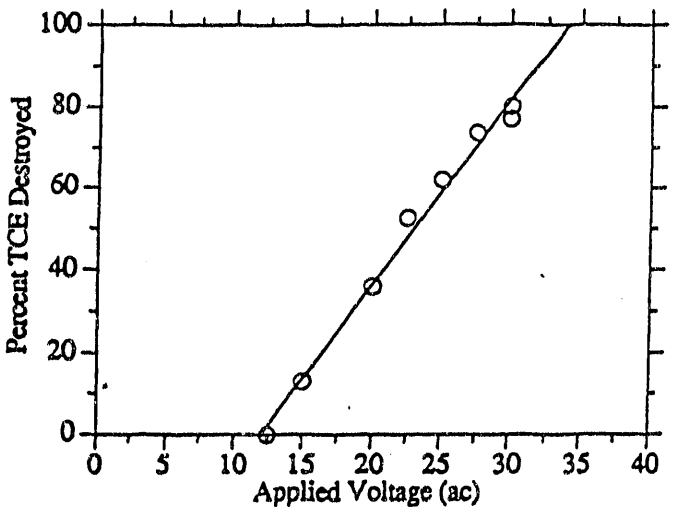

Figure 3. TCE destruction efficiency as a function of a pplied voltage. Flow rate = 1.8 scfm, TCE inlet concentration approximately 350 ppm.

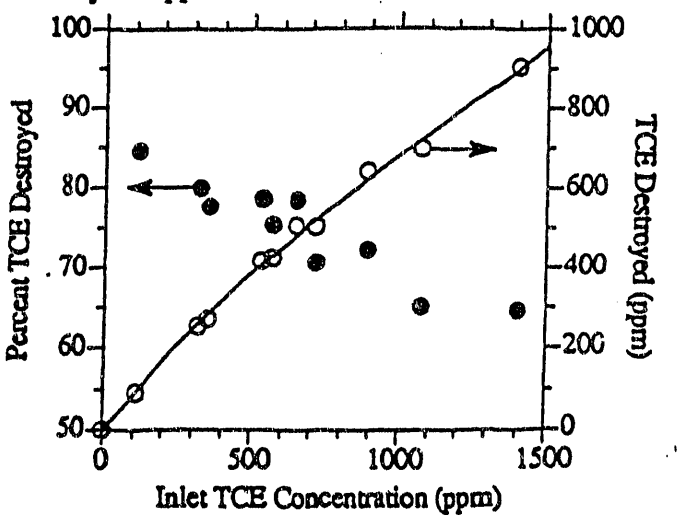

Figure 4. TCE destroyed and TCE destruction efficiency as a function of the inlet TCE concentration. Flow rate = 1.8 scfm, reactor volume = 24 cubic inches, 30 kV applied voltage.

volumes shown in Figure 2 (12, 24 and 48 cubic inches) correspond to residence times of 0.3, 0.6 and 1.2 seconds, respectively. This calculation is based on a void volume of 0.4 within the reactor column.

Greater than 99% destruction of TCE is achieved for inlet TCE concentrations of up to 1500 ppm at a reactor volume of 48 cubic inches and a flow rate of 1.4 scfm. Figure 2 suggests that destruction efficiency is strongly dependent on residence time in the reactor. As the flow rate through the reactor is increased both the residence time and destruction efficiency will decrease. A desired level of destruction efficiency may be maintained at higher flow rates by increasing the length of the packed bed reactor (as long as the pressure drop across the reactor remains reasonable).

Figure 3 reveals the effect of voltage on the destruction efficiency of TCE at a flow rate of 1.8 scfm in a reactor volume of 24 cubic inches. Destruction efficiency appears to be linear up to 30 kV. A 100 kV power supply has been obtained and will be used in future experiments to investigate the destruction efficiencies at applied voltages greater than 30 kV. There was no observable destruction at an applied voltage less than 12.5 kV. Figure 3 indicates that for a given reactor geometry (bed height, inner electrode diameter and column diameter) destruction efficiency is directly related to the applied voltage (at least up to an 80% destruction efficiency). Figure 3 suggests that the most efficient operation of a corona reactor may require a control scheme that will adjust the applied voltage depending on flow rate and inlet TCE concentration (i.e., if 25 kV will destroy a contaminant to the desired level then the voltage should be adjusted down from 30 kV).

The destruction efficiency and amount of TCE (ppm) destroyed as a function of the TCE inlet concentration is shown in Figure 4. Although the amount of TCE destroyed increases with increasing TCE inlet concentration, the destruction efficiency decreases. If the flow rate and bed height remain constant (and thus residence time remains constant), the applied voltage must be increased with increasing TCE inlet concentration to achieve a similar level of destruction efficiency.

The design of larger HEC reactors based on laboratory experiments demands that the relationship between destruction efficiency and the above-mentioned parameters be determined. Experiments to determine the relevant design parameters are ongoing.

The successful application of a corona reactor depends on the ability of the plasma to oxidize the desired contaminant while not producing any hazardous reaction byproducts. Expected reaction products for a plasma in humid air include NO_x and O_3 (ozone).[9] Oxidation products of TCE in air may include hydrogen chloride, chlorine, phosgene and dichloro acetyl chloride. Chlorine reacts rapidly with water, forming hydrogen chloride and hypochlorite ion while phosgene reacts to form hydrogen chloride (9). Dichloro acetyl chloride reacts to form dichloro acetic acid.

Gas samples obtained at both the reactor outlet and downstream of the dry ice trap at high TCE destruction efficiencies (>99% destruction) contained no detectable chlorinated organic byproducts by GC-FID and GC/Mass Spectroscopy (MS) assay. GC/MS sensitivity was approximately 10 ppm. Samples collected from the caustic bubblers and dry ice trap and analyzed using ion chromatography (IC) indicated a large increase in chloride (HCl and HClO) concentration as expected. The efficiency of the bubblers and dry ice trap appears to be fairly good, with 85% of the chloride being collected in the first trap. In other experiments, both a large increase in chloride concentration (HCl) and a reduction of pH to 1-2 has been measured using a chloride specific electrode and a pH meter in water bubblers.

Also measured in the caustic bubblers is an increase in nitrite and nitrate concentrations resulting from the NO_x produced within the reactor. The majority of the nitrite and nitrate (73%) is trapped in the first trap. Based on the total time the reactor was running and the volumetric flow rate through the reactor, the total nitrite and nitrate concentration in the bubblers and dry ice trap corresponds to an approximate gas phase NO_x concentration of 1.8 ppm. An estimate of the NO_x concentration in the head space of the corona reactor was obtained using a Dräger tube specific for nitrous fumes (NO_x, NO and NO_2). The measured NO_x concentration was 1 ppm, which compares well to the estimated concentration based on total nitrite and nitrate.

There were no detectable levels of ozone (<0.05 ppm), chlorine (<0.2 ppm) and phosgene (<0.02 ppm) in the reactor head space as measured with the appropriate Dräger tubes. Under conditions were the corona reactor is operating at a destruction efficiency of approximately 89%, using ambient air at the inlet, both phosgene and dichloro acetyl chloride were present at a concentration below 15 ppm. Absolute values of the phosgene concentration are difficult to obtain without calibration of the GC/MS with a phosgene standard. Humidifying the inlet air stream should drastically reduce phosgene[5] and will be examined in future experiments. After passing through the bubblers and dry ice traps there was no detectable phosgene and dichloro acetyl chloride.

Although levels of undesirable reaction byproducts such as NO_x and phosgene appear to be small when the reactor is operating at greater than a 99% destruction efficiency, further work is needed to quantify NO_x and phosgene concentrations. Future work will investigate the concentrations of reaction byproducts as a function of TCE destruction efficiency and experimental operating conditions (relative humidity in the inlet air).

CONCLUSIONS

Greater than 99% destruction of TCE has been observed using a HEC reactor. This has been achieved at flow rates up to 1.4 scfm and at inlet TCE concentrations approaching 1500 ppm. Power requirments are on the order of 100 watts. The destruction efficiency of TCE was found to increase with increasing bed height (residence time) and applied voltage. Although the amount of TCE destroyed increases as the inlet TCE concentration increases, the destruction efficiency decreases. When the reactor is operated such that the TCE destruction efficiency is greater than 99%, the primary reaction byproducts trapped in caustic scrubbers appear to be hydrogen chloride and hypochlorite (bleach). Phosgene is not detected under optimal operating conditions. The amount of NO_x produced in the plasma is approximately 1 ppm. Further experiments are needed to accurately characterize other TCE byproducts (i.e., phosgene and NO_x) under different experimental operating conditions.

REFERENCES

1. Birmingham,. J.G., and Moore, R.R., United States Patent #4,954,320, Sept. 4, 1990.

2. Ramsey, G.H., Plaks, N., Vogel, C.A., Ponder, W.H., and Hamel, L.E., Proceedings: Eight Particulate Control Symposium, Volume 1: Electrostatic Precipitators, November 1990.

3. Yamamoto, T., Lawless, P.A., Ramanathan, Ensor, D.S., Ramsey, G.H., and Plaks, N.,, Proceedings: Eight Particulate Control Symposium, Volume 1: Electrostatic Precipitators, November 1990.

4. Yamamoto, T., Lawless, P.A., and Sparks, L.E., IEEE Transactions on Industry Applications 25(4), 743 (1989).

5. McCulla, W.H., Rosocha, L.A., Neely, W.C., Clothiaux, E.J., Kushner, M.J., and Rood, M.J., Proceedings of INEL Plasma Application to Waste Treatment Workshop, Idaho Falls, Idaho, January 1991.

6. Kipp, E.B., Shelstad, K.A., and Castle, G.S.P., The Canadian Journal of Chemical Engineering, 51, 494 (1975).

7. Bailin, L.J., Sibert, M.E., Jonas, L.A., and Bell, A.T., Environmental Science & Technology 9(3), 254 (1975).

8. Gilman, J.P., Birmingham, J., and Moore, R., Proceedings of the 1985 Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, Maryland, November 1985.

9. McTaggart, F.K., Plasma Chemistry in Electrical Discharges, Elsevier Publishing Company, Amsterdam, 1967.

END

DATE
FILMED
11/16/92