PNWD-3301
WTP-RPT-051, Rev 0

Evaluation of Corona Oxidation as Back-up Technology for Organic Destruction in the Secondary Off-Gas Treatment System

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WTP
Project
Report

Prepared for Bechtel National, Inc.
under Contract 24590-101-TSA-W000-0004

LEGAL NOTICE

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Test specification: 24590-WTP-TSP-RT-01-016, Rev 1
Test plan: TP-RPP-WTP-137, Rev 0
Test exceptions: none
R&T focus area: Vitrification
Test Scoping Statement(s): Not Applicable

Battelle - Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by 24590-WTP-TSP-RT-01-016, Rev 1 and TP-RPP-WTP-137, Rev 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager *Date*
WTP R&T Support Project

Summary

This report summarizes progress made in evaluating corona oxidation as an alternative to thermal catalytic oxidation (TCO) for organics destruction in the secondary off-gas system of the Waste Treatment Plant melters. The objective of this work was to conduct laboratory and field tests in an effort to compare the two technologies. Figures of merit included power requirements, footprint, and degree of organics destruction.

Three compounds were given as target species in the governing test specification (24590-WTP-TSP-RT-01-016, Rev 1): chlorobenzene, trichloroethylene, and naphthalene. Of these three compounds, chlorobenzene and naphthalene are the most thermally stable. Chlorobenzene was selected as a model compound for corona oxidation experiments in the laboratory. Laboratory experiments focused on determination of power requirements for oxidation using three levels of contaminant in air: 100, 500, and 1000 ppm. Results showed that degradation versus energy followed pseudo-first order kinetics and that the first order decay parameter had a value of $\beta \sim 100$ J/L. For isothermal operation, the energy requirement on a per liter basis can be determined from the necessary destruction removal efficiency (DRE) using

$$\ln\left[1-\frac{\text{DRE}}{100}\right]^{-1}=\frac{E}{\beta}, \qquad (1)$$

where E is the energy required on a standard liter basis (J/L) to obtain the DRE of interest. Once the energy requirement has been obtained on a per liter basis, power requirement scaling can be made by multiplying E by the total flow rate of the off-gas in standard liters/s. For example, using β=100 and assuming a total flow rate of 5400 SCFM for the secondary off-gas system, one can calculate that E = 921 J/L to obtain a DRE of 99.99%, which leads to a power requirement of 2.35 MW for the entire stream.

Field data were obtained at the Vitreous State Laboratory (VSL) at Catholic University, Washington, DC. A field portable corona oxidation system was shipped to VSL and DRE performance for the two technologies was compared in a pseudo-side-by-side manner using chlorobenzene and trichloroethylene as surrogates. Results showed that corona oxidation could obtain roughly the same DRE as catalytic oxidation (94% for corona vs. 96% for TCO). Here, the corona DRE was based on a comparison of WESP effluent and corona effluent, while the TCO DRE was based on a comparison of melter effluent and TCO/SCR effluent. It is expected that at least a portion of observed DRE in the case of TCO occurred in unit operations between the melter and TCO unit.

Power requirements were much greater for corona than expected from the laboratory experiments. The high power requirements limited the degree to which high DRE could be demonstrated because the portable corona oxidation unit did not have enough power capability to reach higher than 94%. The β parameter calculated from the field data was ~1000, which is 10 times the value obtained in the laboratory experiments. The requirement for high power is believed to be related to water condensation in the system resulting in power deposition into electrical conduction rather than plasma. Such conduction could result in massive losses and account for the discrepancy with lab data. Further investigation of the source of power loss was not possible with allocated funds. With 10 times the power requirements, field data indicate that 23.5 MW would be required for 99.99% DRE on the full stream. Table 1 shows a

summary of the power requirements for varying levels of DRE. Here, a power density of 15 kW per liter of reactor volume is used to estimate plasma reactor size. It should be stressed that footprint (i.e., reactor volume) could be reduced by going to higher temperature and possibly introducing a catalyst to the plasma reactor.

Table 1. Comparison of TCO to Corona for Footprint and Power Requirements[1]

	TCO (Field)	Corona (Field)	Corona (Lab)
TCE DRE (%)	96%[2,3]	94%[4]	>99.5%
Volume (95% DRE)	62.5 ft^3	17.9 ft^3	1.8 ft^3
Volume (99.99% DRE)	187.5 ft^3	55.4 ft^3	5.6 ft^3
Power (95% DRE)	1.9 MW[5]	7.6 MW	760 kW
Power (99.99% DRE)	1.9 MW[5]	23.5 MW	2.35 MW

[1] Corona and TCO Volume and Power projections are not based on official project calculations; but are calculated on a similar basis and are provided for comparison purposes only. Numerous factors such as mixed bed catalyst optimization, engineering contingency, selected components for DRE calculation will certainly make the final project projections and design different than the projections listed in this table. Basis for DREs: TCO (field) is based on Trichloroethylene results, Corona (Field) is based on Trichloroethylene and Chlorobenzene results, corona (lab) is based on chlorobenzene results.

[2] Matlack, K. S., W. Gong, T. Bardakci, N. D'Angelo, I.L. Pegg, *Final Report Integrated Off-Gas System Tests on the DM1200 Melter with RPP-WTP LAW Sub-Envelope A1 Simulant,* VSL-02R8800-2, September 03, 2002, Vitreous State Laboratory The Catholic University of America, Washington, DC.

[3] Offgas DREs for the three spiked organics were Chlorobenzene (99.6%), Trichloroethylene (95.7%), and Naphthalene (99.98%).

[4] DRE is for Trichloroethylene although results for Chlorobenzene were experimentally indistinguishable. DRE is calculated for corona is based on comparison of the WESP outlet and corona outlet, while the DRE calculated for TCO is based on comparison of the melter effluent outlet and TCO/SCR outlet.

[5] The power requirement is based on a maximum power consumption of the TCO pre-heater on the DM-1200 of 75kW. This is not a unique power cost of the TCO, since the SCR also needs pre-heated offgas. However, the power numbers are worth comparing as the Corona reactor would also benefit in DRE and overall power requirements if it were set to treat pre-heated offgas.

In addition to the laboratory and field experiments, a cost and risk-reward analysis was performed. The corona oxidation approach does have benefits such as no catalyst requirements and no evidence of partial oxidation products in the outlet. Also attractive is the aspect of a larger degree of control over the degree of oxidation through power control. However, the power requirements for the operating conditions examined thus far are too high, and the issue of water condensation should be revisited to reduce power usage. The maximum power allocated in the Bechtel National, Inc. (BNI) Waste Treatment Plant (WTP) contract is 60 MW, and the use of corona would amount to a significant portion of the allowable power draw. It may be possible to reduce power requirements by operating the corona at higher temperature and employing an oxidation catalyst in the plasma region of the device, but further work would be required to assess this strategy. It is likely that performance approaching that of the lab scale corona results can be obtained with optimum changes to the corona operating conditions

This work was performed in accordance with the Battelle - Pacific Northwest Division's (PNWD's) quality assurance project plan, River Protection Program-Waste Treatment Plant (RPP-WTP) Technical Support Quality Assurance Project Plan, RPP-WTP-QAPjP Rev. 0, as approved by the RPP-WTP QA organization. The work was performed in accordance with applicable elements of NQA-1-1989 and NQA-2a-1990, Part 2.7 as instituted through PNWD's Waster Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP).

Terms and Abbreviations

AC	alternating current
BNI	Bechtel National Inc.
CFM	cubic feet per minute
DC	direct current
DRE	destruction removal efficiency
FTIR	Fourier transform infrared
GC	gas chromatography
GC-FID	gas chromatography – flame ionization detection
ID	Internal diameter
J/L	Joules per standard liter
MW	Megawatts
MWhr	Megawatt-hour
PNWD	Battelle - Pacific Northwest Division
ppm	part per million
ppmv	part per million by volume
psia	pounds per square inch
RPP	River Protection Program
s	second
SCFM	standard cubic feet per minute
SLM	standard liter per minute
TCO	thermal catalytic oxidation
VSL	Vitreous State Laboratory
WTP	Waste Treatment Plant

Acknowledgement

We wish to thank the staff at the Vitreous State Laboratory (VSL) for their help in installing our equipment there and for taking the analytical measurements for the field test. Some of the data reported herein were taken from a their report delivered directly to Bechtel National, Inc. by the VSL (VSL-02S8800-2, Rev. 0: “Data Summary Report: Gas Phase Corona Reactor Testing During Integrated Off-Gas System Tests on the DM1200 Melter with RPP-WTP LAW Sub-Envelope A1 Simulant” prepared by K. S. Matlack, T. R. Schatz, and I. L. Pegg).

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1.0 Introduction

Oxidation technology based on non-thermal plasma has been developed by Battelle – Pacific Northwest Division (PNWD) for various U.S. government agencies and industrial clientele. Non-thermal plasma can be stably formed at atmospheric pressure by placing alternating current (AC) high voltage or pulsed-direct current (DC) high voltage across two electrodes. In the case of AC-powered devices, a dielectric barrier is placed between the electrodes to limit formation of thermal plasma. A gas can be flowed through the gap between the electrodes, resulting in chemical treatment with gas phase radicals that are formed in the plasma. When an oxygen- or water-containing gas is passed through the gap space, very aggressive species (O_3, O, OH, and $^{\bullet}O_2H$) form that can completely degrade organics present in the gas stream. This is the basis of corona oxidation. Corona alone can oxidize organics, but often the gap between the electrodes is filled with a packing material that can further catalyze oxidation.

The packed-bed corona reactor technology developed by PNWD has been used to examine degradation of many volatile organic compounds (Virden et al. 1992), some chemical and biological agent simulants (Moore and Birmingham, 1987), NOx (Rappe et al. 2001), and off-gas contaminants of interest to the semiconductor industry such as perfluorinated hydrocarbons. The technology has also been cost-compared to other technologies such as carbon adsorption, catalytic oxidation, and thermal oxidation. An independent review of destruction performance values and ownership costs, conducted by Los Alamos National Laboratory (Cummings and Booth 1996), showed corona destruction is economically favorable for large off-gas streams laden with chlorinated solvents such as trichloroethylene. Corona technology is currently being scaled up for a variety of applications including diesel engine emissions reduction and volatile organics destruction for the pulp and paper industry. Demonstrations have been conducted for slipstreams in the 10s of CFM range, and reactors have been designed to handle full-scale engine exhaust streams (>500 CFM).

1.1 Plasma-Facilitated Oxidation

Most oxidation processes in non-thermal plasmas are pseudo-first order; in other words, the rate of contaminant oxidation is proportional to the contaminant concentration:

$$-\frac{d[C]}{dt} = k_t[C] \quad \Rightarrow \quad \int_{C_0}^{C} \frac{d[C]}{[C]} = -k_t \int_0^t dt \quad \Rightarrow \quad \ln\left[\frac{C_0}{C}\right] = k_t t\,. \tag{2}$$

Here, [C] is the contaminant concentration as a function of time, t, and k_t is the pseudo-first order rate constant. Oxidation requires two reactants, the contaminant and an activated species. The activated species is typically O_3, O, OH, or $^{\bullet}O_2H$, which will be termed species X. For a given power level, the concentration of species X remains relatively constant, so its affect on the kinetics is lumped into k_t:

$$\frac{d[X]}{dt} = 0 \qquad \text{and} \qquad k_t = k_r[X]. \tag{3}$$

Here, k_r is a second order rate constant that governs the oxidation reaction. The concentration of X can be related to the power input via (Tonkyn et al. 1996):

$$\frac{d[X]}{dt} = k_p P - k_q[X] - k_r[X][C], \tag{4}$$

where P is the power deposited per liter of reactor volume, and k_p and k_q are pseudo-first order rate expressions related to production and quenching of the oxidizing species, respectively. Generally, the concentration of active species is a weak function of the contaminant concentration because most of the active species depletion is due to quenching (Tonkyn et al. 1996); therefore, d[X]/dt = 0. If that is assumed, then Equations (2) through (4) can be combined and integrated to give:

$$\ln\frac{[C]_0}{[C]} = \frac{E}{\beta} \qquad \beta = \frac{k_q}{k_p k_r} + \frac{[C]_0}{k_p} \qquad E = Pt\,. \tag{5}$$

Here, 1/β is the first order decay parameter with respect to specific energy deposition, E. Energy deposition is used to lump the effects of power and exposure time into one independent variable in this representation. Notably, β is a function of the initial concentration, which will be discussed further below. Therefore, it is expected that a contaminant will degrade in a semi-log fashion with energy deposited into the reactor provided that the reactor is kept at or near the inlet gas temperature. If sufficient power is deposited into the reactor to heat the gas substantially, β will typically drop because thermal energy input tends to offset electrical power requirements.

2.0 Experimental Methods

Testing was divided into bench scale experiments and field work. The governing test specification (24590-WTP-TSP-RT-01-016, Rev 1) indicated that chlorobenzene, trichloroethylene, and naphthalene would be used as organic surrogates for field testing. Naphthalene has the highest stability of the three compounds; however, this compound must be sampled isokinetically due to its semivolatile nature. Chlorobenzene was selected for lab studies because it is the second most stable of the three compounds in the test specification, and it could be reliably sampled for in the lab and field work.

2.1 Bench Testing

A preexisting bench scale flow system was used to carry out the laboratory experiments. All gas flows are controlled using MKS mass flow controllers (MFC - Model 1179A series controllers), and pressure is regulated using a MKS pressure controller (Model 640A 1000 Torr controller). Figure 1 shows the apparatus layout, where a bench-scale plasma reactor was used to treat streams laden with 100, 500, and 1000 ppm chlorobenzene in the 1 – 5 SLM flow range. Spikes of chlorobenzene were introduced by passing a stream of air through a bubbler of chlorobenzene liquid. This stream was merged with a higher volume air stream to obtain the low concentrations required for the tests. Analysis was performed by pulling gas chromatograph – flame ionization detection (GC-FID) samples from the inlet and outlet gas of the plasma reactor. The GC-FID system was calibrated using standards, where a known mass of chlorobenzene liquid is allowed to evaporate into a known volume of air that is enclosed in a Tedlar bag. Once the liquid evaporates, the concentration of organic is known. Several of the bag standards were used to construct a calibration curve for chlorobenzene quantification using flame ionization. The detection limit for these measurements was ~ 1 ppm chlorobenzene.

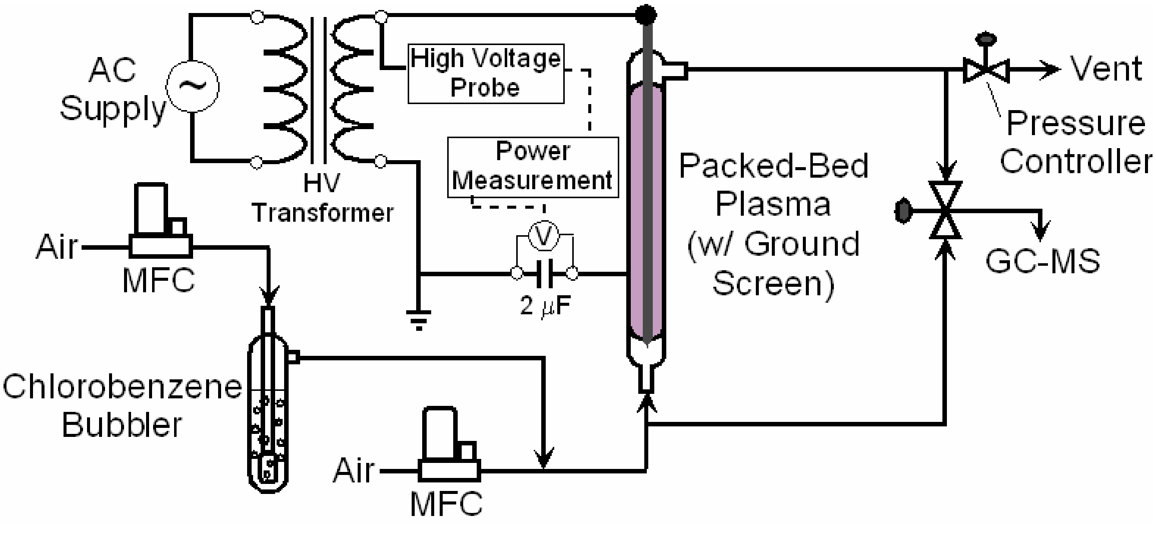

Figure 1. Layout of the Bench-scale Corona Processing System

Power is delivered to the system using a high voltage power supply. The power supply is composed of several components. A small amplitude signal (0-10V AC) is produced using a function generator (BK Precision 3011B 2 MHz function generator) and fed into an audio amplifier (QSC Audio RMX 1450). The amplified signal (~ 0-200V AC) is then fed into the primary side of a high voltage transformer

(Corona Magnetics). The secondary side of the transformer is used to drive the reactor. Power measurement is performed after the method of Rosenthal and Davis (1975). High voltage is measured using a suitable probe (Tektronix P6015A) and fed into the computer control system. Current to ground (secondary side of transformer) is passed through a 2 μF capacitor, and the voltage across the capacitor is measured continuously. The voltage across the capacitor can be used to obtain the charge on the capacitor plates as a function of time, which is proportional to the current passing through the reactor. Figure 2 shows a typical voltage and current trace as a function of time. Notice that the two waveforms are out of phase. This indicates that plasma is present. By plotting the sense capacitor voltage versus the high voltage, one can obtain the Lissajous trace shown in Figure 3. The area of the parallelogram in Figure 3 is an accurate measure of the power deposited into the plasma. Typical power conversion efficiencies for corona devices are greater than 90% when optimized. Data reported herein are taken from the secondary side of the transformer. Therefore, to assess power requirements at the wall, the transformer efficiency must be taken into account. Such efficiencies are typically greater than 90%.

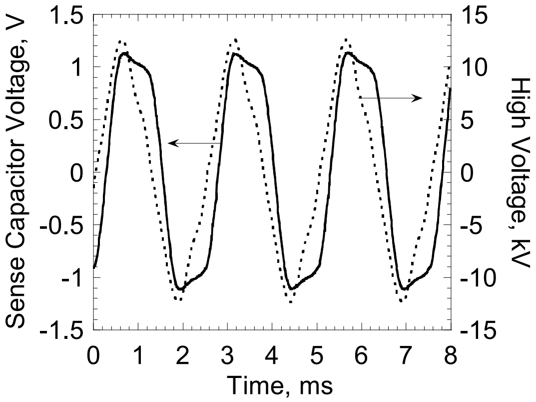

Figure 2. Typical Voltage and Sense Capacitor Traces

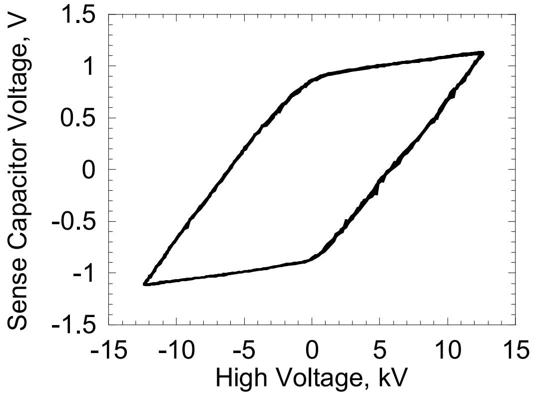

Figure 3. Typical Lissajous Trace

2.2 Corona Operation and Reactor Geometry

The reactor used for the laboratory experiments was of a cylindrical packed-bed geometry. A cross-section of the device is shown in Figure 4. A high voltage electrode is passed down the center axis of a dielectric tube, and a ground screen is placed on the outside of the dielectric tube. An inert or catalytic dielectric packing may be inserted in the gap space between the electrodes. The reactor used for this work was quartz in construction with a 1-in outer diameter and 1/8-in wall. The center electrode was 1/4-in stainless steel and the gap space was filled with quartz beads or alumina pellets.

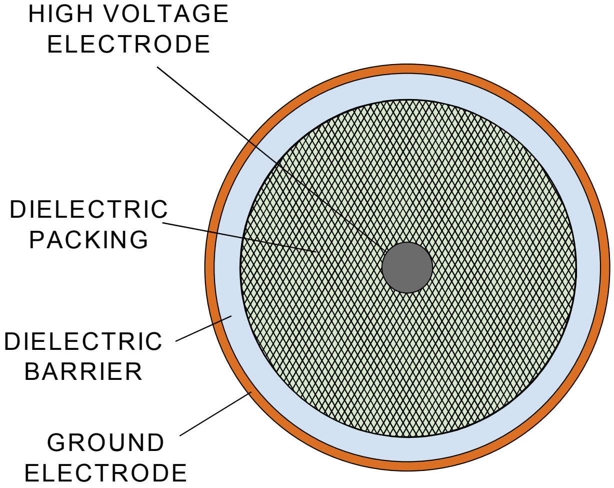

Figure 4. Cross-section of the Cylindrical Packed-bed Plasma Reactor

2.2.1 Test Matrix

A flow rate of 5 SLM was used for most of the measurements, and lower flow rates were only used to obtain very high energy density. Two configurations were investigated: 1) a discharge gap filled with quartz beads and 2) a discharge gap containing alumina pellets. The test plan originally specified an open gap be tested. An open gap reactor was not available at the time of laboratory testing, so a quartz-packed reactor was chosen. Quartz is non-catalytic and results from this reactor are expected to be equivalent to an open gap configuration. As chlorobenzene is oxidized, hydrochloric acid is produced; therefore, it is expected that the surface of the catalyst or packing material may become acidic over time. Alumina was chosen as the catalytic packing because it is active for hydrocarbon oxidation in the absence of metal dopants, and as the surface of the alumina becomes increasingly acidic, it tends to better oxidize hydrocarbon.

In general, the electrical power requirement required to obtain a specific DRE is dependent on four factors: 1) compound to be destroyed, 2) level of contaminant in the stream to be treated, 3) temperature of the stream, and 4) humidity of the stream. Because the exact levels of contaminant expected in the Vitreous State Laboratory (VSL) demonstration were not known, a range of levels was examined for chlorobenzene. Spike levels of 100 – 1000 ppm chlorobenzene in humid air were used for the bench experiments. Three temperatures (70, 100, 130^{o}C) of operation were examined in an attempt to understand how incremental heating of the off-gas will affect processing. Water vapor was added to the stream at a level of 1.5 vol% using a water bubbler. 1.5 vol% was chosen to avoid condensation at room temperature, and a system for delivery of this humidity level was already available. Particulate matter and ionic species such as sulfates and nitrates were not examined in bench testing because they should not affect performance in the field test. Based on the experimental design detailed above, a test matrix of 18 experiments was constructed and carried out. This matrix is shown in Table 2. Concentration exiting the reactor was measured as a function of power deposited into the reactor under the various conditions of interest. The data obtained were used to estimate power deposition requirements for flow rates and contaminant levels to be encountered in the fieldwork.

Table 2. Test Matrix for Chlorobenzene Oxidation

Matrix						Legend
T1, L1, A	T2, L1, A	T3, L1, A	T1, L1, Q	T2, L1, Q	T3, L1, Q	Temperature (°C) T1 = 70, T2 = 100, T3 = 130 Chlorobenzene Level (ppm) L1 = 100, L2 = 500, L3 = 1000 A = Alumina, Q = Quartz
T1, L2, A	T2, L2, A	T3, L2, A	T1, L2, Q	T2, L2, Q	T3, L2, Q	
T1, L3, A	T2, L3, A	T3, L3, A	T1, L3, Q	T2, L3, Q	T3, L3, Q	

2.3 Field Testing

A mobile plasma oxidation system was installed at the VSL for a three day test. Figure 5 shows the components that were shipped to the VSL site. The reactor used was a cylindrical packed-bed type with an alumina dielectric barrier (2-in OD & 1/8-in wall thickness). The inner electrode was 1-in stainless steel and the gap space was packed with alumina pellets. The reactor and transformer were housed in a grounded enclosure, and the control system and power supply were housed in standard racks.

Figure 5. Components for the Field Corona System. Left – Control Station and Power Supply. Right – Cylindrical Packed-Bed Corona Reactor with Inlet, Outlet, and Electrical Connections.

Figure 6 illustrates the layout of the field corona system. Installation of the unit required plumbing of a slipstream from the melter off-gas system to the unit and plumbing of an exhaust line from the unit to a suitable location downstream in the system. The slipstream was drawn from approximately a 6” water vacuum using a heated-head compressor equipped with a rotameter. A pressure sensor (MKS model 640A 1000 Torr Pressure Controller) in combination with a needle valve was placed at the exit of the corona reactor to control the pressure of the reactor at 14.7 psia. Sampling to the analytical systems was performed upstream of the reactor for inlet concentrations and just before the pressure controller for downstream concentrations. Power deposition was measured using similar circuitry as that employed in the lab testing.

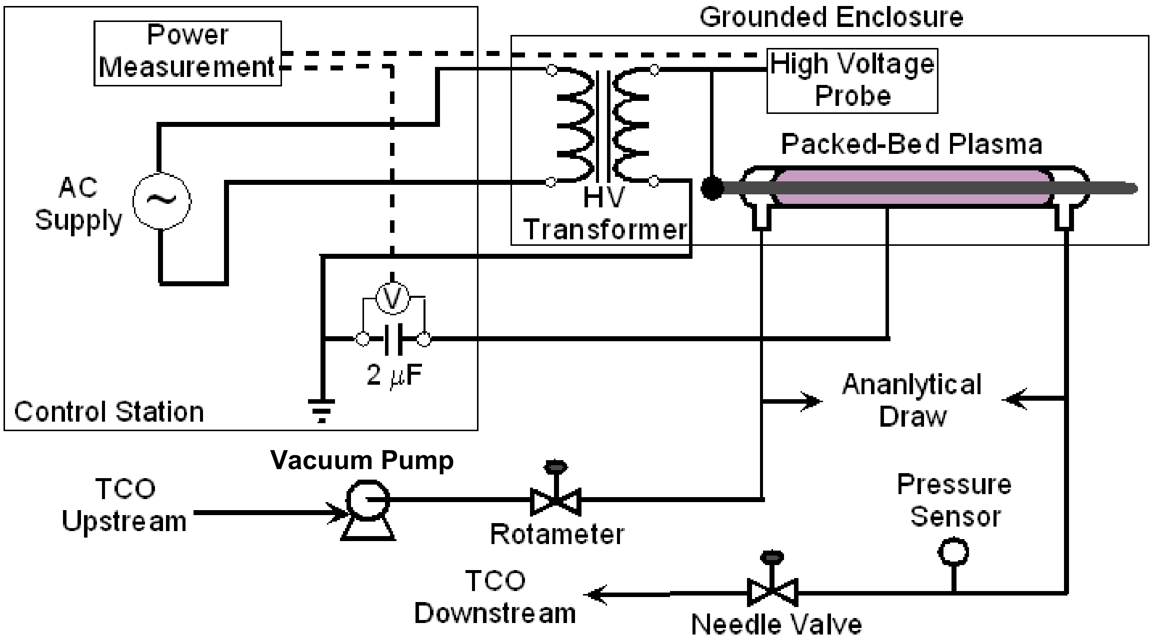

Figure 6. Layout of the Field Corona System

2.3.1 Analytical Procedures

Gas chromatographic analysis was performed using an SRI Instruments 8610C gas chromatograph equipped with a 15 m × 0.53 mm ID type MXT-1 capillary column and a photoionization detector. Fourier transform infrared (FTIR) spectroscopy was performed with an On-Line Technologies Inc. Model 2010 Multi-Gas™ Analyzer. Spectral data were recorded at 71 s intervals, corresponding to an average of 128 scans at 0.5 cm^{-1} resolution. The melter off-gas train supplied to the FTIR spectrometer and the gas chromatograph (GC - connected sequentially) was extracted using a sampling and transfer loop at a flow rate of 5 liters per minute. FTIR data were only taken for the corona system. These data were taken during the same run as the volatile organics samples described below. The sampling and transfer loop was maintained at 150 C throughout in order to prevent analyte loss due to condensation. Four major peaks were observed in the gas chromatograms of DM1200 off-gas samples. Two of these peaks were identified on the basis of their retention times as chlorobenzene and trichloroethylene. The other two peaks are as yet unidentified.

Volatile organics samples were taken using SW-846 Method 0030 and analyzed using SW-846 Method 8260. The required sampling durations were estimated from concentrations measured online by GC. Despite the use of small sampling times and flow rates, the concentrations in the absorption tubes were still sufficiently high that extraction into methanol was required.

3.0 Results and Discussion

3.1 Lab Results

All of the test results have been compiled in a form suitable for use with Equation (5). To this end, recorded data include inlet concentration, outlet concentration, flow rate, and power deposition into the reactor. Generally, data is plotted in the form of Figure 7 where laboratory results are shown for chlorobenzene oxidation at 70°C. As expected, the data are linear when plotted in this fashion. The slope of the curve has a value of β^{-1}, the pseudo-first order decay parameter for chlorobenzene. Data from an alumina-packed reactor are shown in Figure 8. Notice that initially the curves are linear, but as power deposition is increased beyond ~ 400 J/L, the curves break from the expected trend. Deviation to higher values of ln (C_0/C) indicates that oxidation takes less energy than expected from the initial linear trend. As the power is increased above a certain level, the bed is heating to the point where alumina becomes catalytically active for oxidation in the plasma environment.

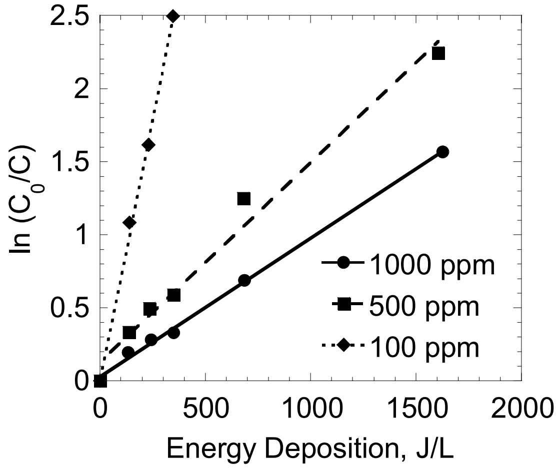

Figure 7. Data set for Chlorobenzene Oxidation in a Quartz-packed Plasma Reactor

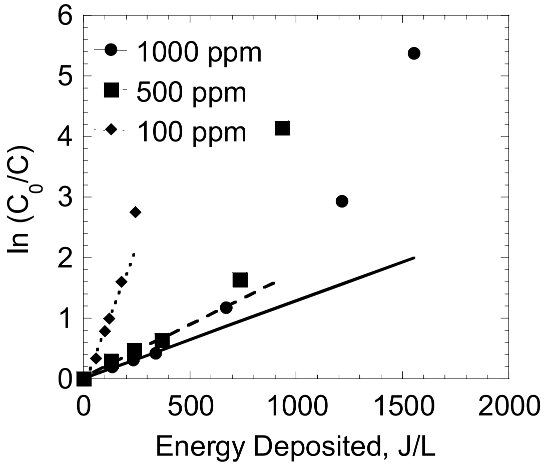

Figure 8. Data Set for Chlorobenzene Oxidation in an Alumina-packed Reactor

The β values for all of the cases tested in the experimental work are compiled into Table 3. The values for the alumina packing are taken from the linear portions of the curve at low energy density. There are several trends in the data of interest. First, β value is a strong function of inlet concentration, which is expected by Equation (5). Using extrapolation of data to total hydrocarbon levels expected in the actual off-gas train (~ 1-2 ppm), a value of β in the real application is expected to be ~ 100 if the hydrocarbons have similar stability as chlorobenzene.

Table 3. β Values for All Cases Tested in the Lab

	Quartz			Alumina		
Temp., °C	**100 ppm**	**500 ppm**	**1000 ppm**	**100 ppm**	**500 ppm**	**1000 ppm**
70	141	732	1056	109	576	781
100	203	677	1153	128	495	724
130	234	657	1055	161	543	735

In addition to the data reported in Table 3, an effort was made to assess the impact of temperature on β values for the alumina packing. The results are shown in Figure 9. Clearly, energy deposition has a large impact on β value. Using an adiabatic heat balance, the estimated temperature of the outlet was calculated using:

$$\dot{m}c_p\left(T_f - T_i\right) = EQ, \tag{6}$$

where $\dot{m}$ is the mass flow rate, Q is the volumetric flow rate at standard conditions, c_p is the heat capacity, and T_f and T_i are the exit and inlet temperatures, respectively. The product EQ is the power deposited into the reactor. Using Equation (6), a value of 180°C was calculated for 931 J/L, which corresponds to the largest energy deposition value for the 500 ppm case. A value of 290°C was calculated for 1553 J/L, which corresponds to the largest energy density for the 1000 ppm case (see Figure 8). These temperatures are likely approaching light-off conditions for catalytic oxidation on alumina. At low temperature, undoped alumina is catalytically inert for hydrocarbon oxidation.

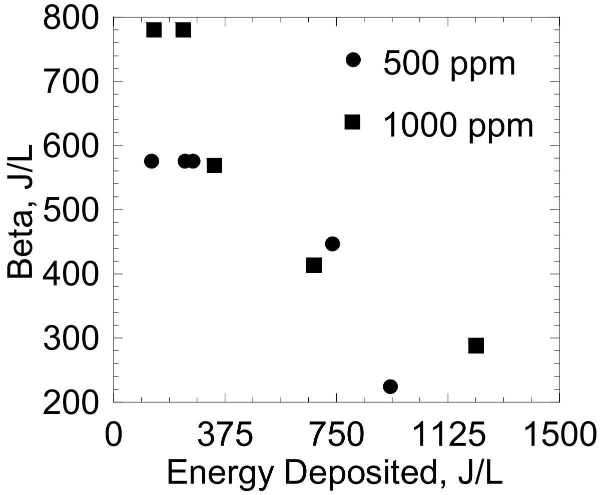

Figure 9. Beta as a Function of Energy Deposition for the Alumina-packed Reactor

3.2 Field Results

The field test took place March 1 through 4, 2002 at the VSL, Catholic University, Washington, D.C. The flow system used to perform the work is shown in Figure 6. A significantly higher power was required in the field testing than expected. Because the mobile corona system installed at VSL had limited power capability, the flow rate of the slipstream had to be minimized. The analytical systems required ~2 SLM of flow, so 2.5 SLM was used for the slipstream. This allowed power deposition to be significant enough on a per liter basis to show high conversion.

Figure 10 shows results from the field testing, where TCE and CB refer to trichloroethylene and chlorobenzene, respectively. Dotted lines represent least squares fitting of the two data sets. Two types of measurements were performed: 1) several measurements were taken using GC-photoionization (GC-PI), and 2) 1 (triplicate) measurement was taken using a certified EPA method. The EPA method data was taken to confirm that GC-PI data was giving accurate values. Generally, the data overlap quite well, so the GC-PI should be a dependable measurement of destruction levels. It should be noted that the inlet concentrations of chlorobenzene and trichloroethylene changed during testing. Trichloroethylene changed from 21 to 17 ppmv, while chlorobenzene changed from 18 to 17 ppmv. Therefore up to a 15% error in the trichloroethylene values and 3% error in the chlorobenzene values are reported in Figure 10.

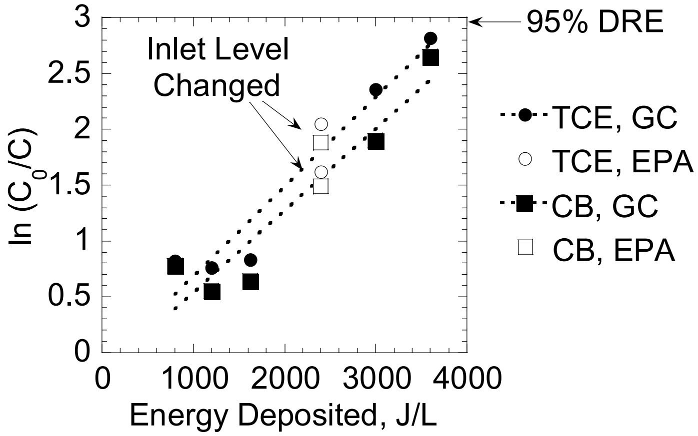

Figure 10. Field Data for TCE and CB Destruction Using Corona Oxidation

The linear fit of the trichloroethylene data lies above that for chlorobenzene, indicating that trichloroethylene is more easily oxidized than chlorobenzene. Based on the scatter in the data and the potential error in inlet levels, it should be noted that the data are statistically similar. The most important aspect to note is the larger power requirements for both compounds. Based on a linear fit of the data, β for the field test was calculated at ~1000 J/L. This represents a 10 fold increase over what was expected from the laboratory data.

Additional data were taken using FTIR, and the compiled results are shown in Table 4. There are substantial decreases in the concentrations of many of the analytes (particularly acid gases) at the corona reactor outlet, regardless of whether the power was on or off. There are several possible explanations for this including: 1) dilution due to in-leakage, 2) destruction in the corona reactor, and 3) condensation of water between the two measuring points and subsequent partitioning of analyte into aqueous phases. The similarity of the chlorobenzene and trichloroethylene values from the GC (connected in series with the

FTIR) at the reactor inlet and outlet with the power off suggests that the decrease was not due to air in-leakage dilution or destruction of the organic species. Consequently, condensation would seem to be the most likely explanation given the decrease in water, acid gases, and water soluble organics such as acetonitrile at the reactor outlet. Carbon monoxide concentrations were essentially unaffected by corona processing, as the values at the inlet and outlet indicate.

Table 4. Results from FTIR Analyses (ppm unless otherwise noted)[1]

	WESP Outlet	GPCR Outlet	GPCR Outlet, Power Off
NO	2960	1690	1010
NO_2	5070	652	1750
NH_3	<1.0	<1.0	<1.0
H_2O [%]	7.8	2.8	1.6
HNO_2	14.6	1.6	3.0
HNO_3	14.5	<1.0	<1.0
HCN	<1.0	<1.0	4.1
SO_2	2.3	<1.0	<1.0
Acetonitrile	18.6	<1.0	1.1
Acrylonitrile	<1.0	<1.0	<1.0
CO	435	409	674
HCl	48.0	<1.0	<1.0
HF	<1.0	<1.0	<1.0

[1] Taken directly from VSL – 02S8800-2, Rev. 0: "Data Summary Report: Gas Phase Corona Reactor Testing During Integrated Off-Gas System Tests on the DM1200 Melter with RPP-WTP LAW Sub-Envelope A1 Simulant" prepared by K. S. Matlack, T. R. Schatz, and I. L. Pegg.

3.3 Interpretation of Differences in Field and Lab Experiments

The large discrepancy between field and laboratory data are believed to be the result of the difference in water content between the actual and simulated off-gas. For the laboratory experiments, the water level was 1.5% while for the field tests it was 7.8%. Relative humidity can have a significant impact on the power requirements for corona oxidation. It has been previously observed that β varies in a semilog manner with relative humidity. Heath and Lessor developed an empirical expression for the dependence of β on %RH:

$$\beta(\%RH) = \beta_0 + k_{RH} \ln(\%RH), \tag{7}$$

where k_{RH} is the characteristic slope of a β vs. ln (%RH) curve, and β_0 is the value of β at 1% RH. The unpublished data resulted in fitting parameters of β_0 = 110 J/L and k_{RH} = 9.33 J/L for trichloroethylene at room temperature and 600 ppmv in air. In principle, an analogue of Equation (7) at higher temperature could be used to determine whether the higher humidity encountered in the field off-gas could result in β = 1000. An adiabatic heat balance suggests that if all power deposited into the reactor resulted in gas heating, the exhaust temperature would have been in excess of 600°C. This temperature is above the range where complete combustion of most hydrocarbons takes place over alumina. The fact that residual hydrocarbon survived the reactor indicates that the reactor temperature was less than expected. Therefore, power inefficiency must result from some other mechanism.

Another consideration is the prospect that water was condensing in the system. The FTIR data in Table 4 indicate that water condensed in the slipstream at some point. When the system was disassembled, the packing appeared to be dry, but there was a small amount of condensate between the reactor and analytical draw point. The exterior of the reactor was maintained at 100°C to prevent water condensation. In retrospect, this temperature may not have been sufficient to prevent condensation and/or adsorption on the reactor internals at the humidity and temperature levels of the field off-gas. A better design would have involved preheating the gas before corona treatment. Condensation or even adsorption could render the packing significantly more electrically conductive. The result would be significant power losses due to conduction through the bed (analogous to a short circuit) rather than conversion of electrical power to diffuse plasma discharge. It is difficult to assess the relative loss that would result within the scope of this work, but conductive losses could be quite high, accounting for the unusually high power required in the field experiment. A lower bound might be placed on the losses by examining the materials of construction of the slipstream. The tubing exiting the corona reactor was made of Teflon, yet the tubing exhibited no observable degradation. The adiabatic heat balance suggests an exit temperature of 600°C, but Teflon would have failed under these conditions. If the maximum temperature rating of Teflon (~220°C) is used to estimate conduction losses, the losses are at minimum approximately 65% and likely much greater. This would place the field test data much closer to the lab results.

The original test plan for the field work called for a second test with an unpacked reactor operating at 400°C. This test would have proved or disproved adsorbed water creating power losses due to conduction. Unfortunately, this test could not be performed due to technical problems at the VSL (forced shutdown when glycol leaked into the off-gas system).

4.0 Cost Analysis

For corona processing, the costs may be broken down into capital, installation, and operating costs. An effort was made to determine capital costs for corona systems. These costs will be dominated by the cost of the power supply. Neeltran was contacted for a power supply cost estimate. Neeltran is an original equipment manufacturer of large size 60 Hz high voltage power supplies. Power supplies of the size required are specified at 60 Hz and include a high voltage transformer. A general rule of thumb is $100K for the first 0.5MW, and cost for higher power can be obtained using Figure 11.

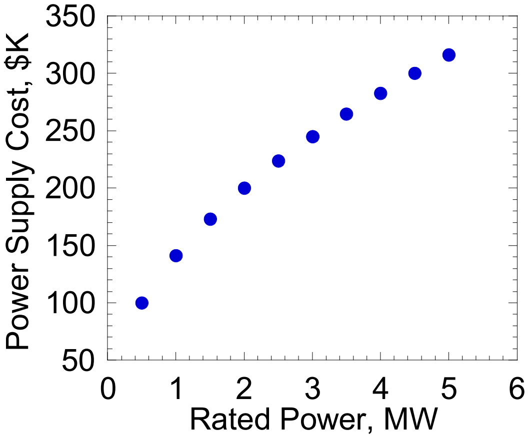

Figure 11. Power Supply Cost as a Function Of Power Rating

Other capital costs include the parts and construction of the plasma reactor. Without a specific design, costing of the plasma reactor is not possible. Costs are, however, expected to be significantly less than the power supply. Installation costs are not known for the Waste Treatment Plant (WTP). Operating costs will be dictated by power consumption. There are no consumables for this technology, unless a catalyst is used in the gap space of the plasma. Typically power costs are estimated at $30-$50/MWhr. Therefore, operating costs for the plasma unit would be on the order of $240/hr for 95% organics destruction (chlorobenzene basis) for the full stream.

5.0 Summary and Recommendations

In summary, laboratory tests and a field trial were conducted to assess the ability of corona oxidation to replace catalytic oxidation for organics destruction in melter off-gas. The projected power requirements and maturity of corona oxidation technology do not provide a sufficient basis for recommending a move away from catalytic oxidation at this time. It is expected that higher temperature operation would result in significant reduction in power, but examination of this operating regime in the laboratory was beyond the scope of this project. Corona oxidation was superior to catalytic oxidation in one aspect. Acetonitrile is produced in the melters at high levels due to the addition of sugars to achieve reducing conditions. Catalytic oxidation showed significant amounts of acetonitrile and acrylonitrile at the outlet (Matlack *et al*., 2002a), while corona oxidation showed only CO as a partial oxidation product (Matlack *et al*., 2002b). Corona appeared to handle acetonitrile quite well, while TCO appeared to have roughly 75% DRE based on melter effluent levels. In order to state with assurance that corona is superior with respect to partial oxidation product formation, additional testing examining a wider range of compounds including dioxin and furan analysis would need to be undertaken. Only the surrogates chlorobenzene and trichloroethylene along with acetonitrile and acrylonitrile were examined in this study. The potential of corona to result in fewer partial oxidation products along with the fact that corona oxidation offers greater flexibility through power control may warrant additional investigation focused on treatment of high water content streams at high temperature to reduce resistive losses. Although corona can not be recommended based on this small study, it is likely that superior performance can be obtained with optimum corona operating conditions (higher temperature). Additional work should be performed to determine if higher temperature corona oxidation can provide DRE greater than TCO.

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