Plasma remediation of perchloroethylene in humid gas streams

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Perchloroethylene (PCE) is one of a class of industrial solvents for which alternate disposal strategies are being investigated. Among these strategies is plasma remediation. In this paper we report on a computational study of the plasma remediation of PCE using repetitively pulsed dielectric barrier discharges. We discuss the dominant reaction pathways in the remediation of PCE and show that remediation is significantly improved in humid gas mixtures. Although plasma remediation does not totally oxidize PCE to the desired end-products (CO_2 and HCl), the dominant end-products are more easily treated than PCE and can be disposed of using conventional methods. © *1995 American Institute of Physics.*

I. INTRODUCTION

Tetrachloroethylene, C_2Cl_4, more commonly known as perchloroethylene (PCE), is extensively used as a dry cleaning and an industrial degreasing agent, and is toxic in large doses.[1] It is difficult to dispose of since it is nearly insoluble in water, nonflammable, and miscible in alcohol, ether, and other organic solvents. Due to this difficulty, alternate disposal techniques are being investigated which are both environmentally acceptable and economically viable. Plasma remediation is one such technique. In this process, the liquid is volatilized into a gas a stream to levels of 100s of parts per million (ppm) to a few percent. Electron impact dissociation of the carrier gas produces radicals which either oxidize the toxin to products which can be exhausted to the atmosphere, or converts the toxic to a form which is more readily disposed of. Plasma remediation has been demonstrated as an efficient means of disposing of a large number of volatile organic compounds.[2] For example, Rosocha *et al.* have used dielectric barrier discharges (DBDs) as a plasma source to remediate carbon-tetrachloride (CCl_4), trichloroethylene (C_2HCl_3 or TCE) and PCE.[3–5] They found that remediation of TCE is optimized in dry gas streams, whereas the remediation of PCE is optimized in humid gas streams.

We have developed a computer model for DBD processing of toxic gases to investigate and optimize the reaction pathways. In previous work, we discussed the reaction mechanisms for remediation of TCE.[5] In this paper, we extend that work to DBD processing of PCE. We show that DBD processing largely converts the chlorine in PCE into $COCl_2$ and Cl_2 which, in spite of still being toxic, can be more readily disposed of using conventional techniques. The model is described in Sec. II. We present results from the model for major reaction mechanisms and end-products during remediation and post-remediation of PCE in Sec. III. Concluding remarks are contained in Sec. IV.

II. DESCRIPTION OF THE MODEL

The model we have developed for DBD processing of toxic substances in atmospheric pressure gas streams has been described in Refs. 5 and 6 and so will only be briefly discussed here. The simulation consists of a circuit model, a solution of Boltzmann's equation for the electron energy distribution, and a plasma chemistry model. The circuit model computes E/N in the plasma. This value is then used to solve Boltzmann's equation for the electron energy distribution, using a two term spherical harmonic expansion, from which the electron impact rate coefficients are calculated. The plasma chemistry model uses the rate coefficients from the solution of Boltzmann's equation and the temperature-dependent heavy particle reaction rate coefficients to produce species densities as a function of time. The plasma chemistry model also calculates the conductivity of the plasma for use in the circuit model.

The plasma chemistry model contains 99 species and 444 reactions. The electron impact processes included in the model for Ar/O_2H_2O mixtures are discussed in Refs. 5 and 6. The heavy particle reactions and rate coefficients we used for the chlorocarbon chemistry are primarily those described in Refs. 7 and 8. The exception is the rate coefficients for the back reaction of C_2Cl_5, discussed below, which were obtained from Ref. 9. A complete list of reactions and rate coefficients used in the model can be obtained upon request from the authors.

III. REACTION MECHANISMS IN THE REMEDIATION OF PCE

Using the model described in Sec. II, we investigated processes during plasma remediation of PCE in humid gas streams. For purposes of discussion we define two timescales in the processing of PCE: remediation and post-remediation. Remediation refers to times during which plasma initiated chemical reactions with PCE reduce its density from its initial value to <1 ppm (part per million). Post-remediation refers to times after the initial concentration of PCE has been reduced to <1 ppm. Chemical reactions during this time further process the products from PCE remediation. We have assumed that the processing device is closed cycle, and so have used a gas mixture of $Ar/O_2/H_2O=80\text{-}x/20/x$ ($x=0-1$) at 300 K and 1 atm as in Ref. 5. The initial PCE concentration is 500 ppm. (For these conditions 1 ppm is equivalent to 2.5×10^{13} cm^{-3}.) These mixtures, as opposed to an atmospheric gas stream, were chosen to produce an oxidizing environment in order to avoid producing noxious products such

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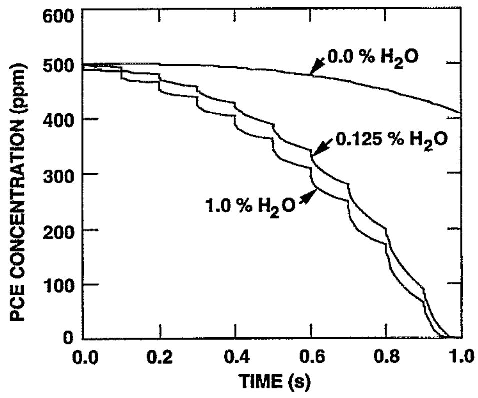

FIG. 1. The density of PCE during plasma remediation in a dielectric barrier discharge operating at 10 Hz. Results are shown for gas mixtures of $Ar/O_2/H_2O=80-x/20/x$ (1 atm, 300 K) having 0%, 0.125%, and 1% water. The initial amount of PCE is 500 ppm. Remediation is slow in the absence of H_2O. Small amounts of H_2O initiates chain chemistry involving Cl and ClO which results in rapid remediation of the PCE.

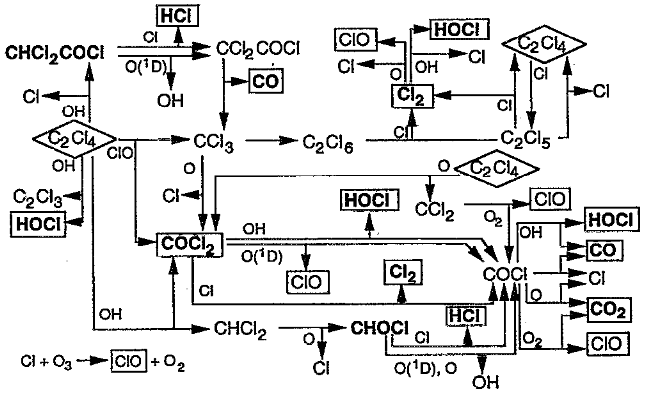

FIG. 3. Dominant reaction pathways for the plasma remediation of PCE. The initial toxin, PCE, is shown by a diamond. The dominant products of remediation are shown in bold and the dominant products of post-remediation are boxed. The dominant products of both periods are both in bold and boxed.

nitrogen oxides. The DBD was pulsed at a repetition rate of 10 Hz with a volume averaged energy deposition of 5 mJ/cm^3/pulse. The applied E/N had a maximum value of 260 Td.

The density of PCE during plasma remediation is shown in Fig. 1 for gas mixtures containing 0%, 0.125%, and 1% water. The maximum electron density during the current pulse is 2.5×10^{13} cm^{-3} for the 1% water case, as shown in Fig. 2. The maximum densities of O and OH following the current pulse, produced by electron impact dissociation of O_2 and H_2O, are 4.3×10^{15} and 7.5×10^{14} cm^{-3}, respectively. In mixtures containing at least a few tenths of percent of H_2O, removal of PCE to amounts less than 1 ppm was obtained with a total energy deposition of $\approx$45 mJ/cm^3, or 22.5 eV/molecule. In the dry mixture, remediation of PCE is slow in comparison. Significant removal of PCE occurs during and immediately after the short current pulse (10 ns in length and not resolved in Fig. 1). This remediation is as a result of direct reactions of PCE with the O and OH radicals produced by electron impact dissociation of O_2 and H_2O. The lifetimes of these radicals are only 10s–100s μs. Remediation continues, however, during the majority of the interpulse period (0.1 s) due to chain reaction chemistry involving ClO, as discussed below.

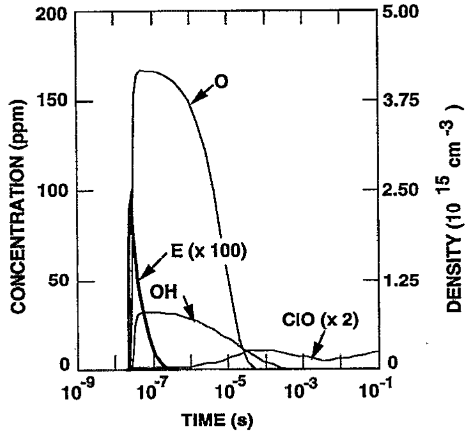

FIG. 2. The density of electrons, O, OH, and ClO for the ninth pulse of Fig. 1 using the $Ar/O_2/H_2O=79/20/1$ gas mixture. The O and OH are produced by electron impact dissociation of O_2 and H_2O during the short current pulse. ClO is produced on longer timescales, primarily by reaction of Cl atoms with O_3.

A partial reaction scheme for the remediation and post-remediation of PCE is shown in Fig. 3. Products of remediation are indicated by bold lettering and products of post-remediation are boxed. Products for both time scales are both in bold and boxed. Remediation of PCE occurs largely through a series of chain reactions with OH, O, and ClO. The chains begin by reaction of PCE with O and OH in the first 10s–100s μs after the current pulse:

$$C_2Cl_4+O\rightarrow COCl_2+CCl_2$$

$$k=1.66\times10^{-13}\exp(-2525/T)\ \text{cm}^3\,\text{s}^{-1}, \tag{1}$$

$$C_2Cl_4+OH\rightarrow CHCl_2+COCl_2$$

$$k=1.66\times10^{-11}\exp(-1010/T), \tag{2}$$

$$C_2Cl_4+OH\rightarrow HOCl+C_2Cl_3$$

$$k=1.66\times10^{-11}\exp(-6061/T), \tag{3}$$

$$C_2Cl_4+OH\rightarrow CHCl_2COCl+Cl$$

$$k=9.34\times10^{-12}\exp(-1212/T). \tag{4}$$

(In the expressions for rate coefficients, T is the gas temperature, and the activation energies are in units of degrees K.) Following these initial reactions, ClO is produced on longer timescales by reactions of the products of these initiating steps, as shown in Fig. 2. O and OH are therefore important not only in that they remediate PCE but also in that they initiate production of ClO. PCE is remediated by ClO by

$$C_2Cl_4+ClO\rightarrow CCl_3+COCl_2$$

$$k=1.66\times10^{-11}\exp(-1010/T)\ \text{cm}^3\,\text{s}^{-1}, \tag{5}$$

$$C_2Cl_4+ClO\rightarrow CCl_3COCl+Cl$$

$$k=1.66\times10^{-13}\exp(-2525/T). \qquad (6)$$

ClO is generated by a series of reactions of the remediation products. These reactions include:

$$COCl_2+O(^1D)\rightarrow ClO+COCl$$

$$k=1.0\times10^{-10}\ \mathrm{cm^3\,s^{-1}}, \qquad (7)$$

$$COCl+O_2\rightarrow ClO+CO_2$$

$$k=1.0\times10^{-13}, \qquad (8)$$

$$CCl_2+O_2\rightarrow ClO+COCl$$

$$k=1.66\times10^{-11}\exp(-505/T), \qquad (9)$$

$$Cl_2+O\rightarrow ClO+Cl$$

$$k=2.09\times10^{-11}\exp(-1414/T). \qquad (10)$$

The excited state $O(^1D)$ is produced by electron impact dissociative excitation of O_2, and so reactions with it are only important during the short current pulse. Small amounts of ClO are also likely produced by reactions of C_2Cl_3 and $CHCl_2COCl$ with $O(^1D)$.

Reactions of the initial remediation products also generate Cl:

$$CHCl_2+O\rightarrow Cl+CHOCl$$

$$k=1.66\times10^{-11}\exp(-505/T)\ \mathrm{cm^3\,s^{-1}}, \qquad (11)$$

$$COCl+O\rightarrow Cl+CO_2$$

$$k=1.66\times10^{-11}\exp(-505/T). \qquad (12)$$

These reactions are important to further remediating PCE because Cl is a precursor to formation of ClO. Ozone (O_3) accumulates in the discharge to densities $>10^{16}\ \mathrm{cm^{-3}}$ by the reaction $O+O_2+M\rightarrow O_3+M$. Reaction of Cl with O_3 is then major source of ClO:

$$Cl+O_3\rightarrow ClO+O_2$$

$$k=2.61\times10^{-11}\exp(-237/T)\ \mathrm{cm^3\,s^{-1}}. \qquad (13)$$

The production of ClO by this reaction occurs throughout the interpulse period, as shown in Fig. 2.

Although the major role of Cl in the remediation of PCE is production of ClO, Cl does directly react with PCE:

$$C_2Cl_4+Cl\rightarrow C_2Cl_5$$

$$k=4.37\times10^7T^{-7.71}\exp(-2677/T)\ \mathrm{cm^3\,s^{-1}}. \qquad (14)$$

This reaction is not a major contributor to the remediation of PCE since C_2Cl_5 quickly back reacts to regenerate PCE by

$$C_2Cl_5\rightarrow C_2Cl_4+Cl$$

$$k=91\ \mathrm{s^{-1}}(T=300\ \mathrm{K}), \qquad (15)$$

$$C_2Cl_5+Cl\rightarrow C_2Cl_4+Cl_2$$

$$k=6.61\times10^{-9}\exp(-603/T)\ \mathrm{cm^3\,s^{-1}}. \qquad (16)$$

The rates for these reactions[9] are sufficiently fast so that C_2Cl_5 does not accumulate in the discharge. However, the flux of reactants through these reactions is large enough so that significant densities of Cl_2 are produced during remediation.

The remediation of PCE by ClO [Eqs. (5) and (6)] and the generation of ClO by reaction products [Eqs. (7)–(10) and (13)] constitute a chain chemistry. The reaction of PCE with O and OH generates products which further react to generate either Cl or ClO. Cl then reacts with O_3 to produce ClO. ClO then reacts with PCE, to continue the chain. A potential chain breaking process is the reaction of ClO with OH:

$$OH+ClO\rightarrow HCl+O_2, \qquad (17)$$

which prevents ClO from further assisting in remediation. The efficiency of OH in directly remediating PCE, as well as its role in the production of ClO and Cl, outweighs any reduction in removal efficiency of PCE resulting from the loss of ClO by this reaction. As a consequence, the rate of remediation of PCE is significantly increased in humid gas mixtures, and slow by comparison in dry mixtures, as shown in Fig. 1. This result is in direct contrast to plasma remediation of TCE in which dry mixtures are more efficient than humid mixtures.[5] In that system, ClO is a major reactant with TCE. Since, however, reactions of TCE with OH are slow, removal of ClO by reactions with OH reduce the total rate of removal.

Due to the chain chemistry initiated by reactions with OH, only a small amount of OH is required to produces significant improvements in remediation compared to the dry mixtures. In fact, the chain chemistry is sufficiently efficient that above a few tenths of a percent of H_2O, additional production of OH, either by larger energy deposition or additional H_2O, does not directly impact the remediation rate. This is seen in Fig. 1 in which remediation after the later pulses occurs throughout the duration of the interpulse period.

The densities of PCE during remediation, and the resulting products during remediation and post-remediation are shown in Fig. 4. The products formed by remediation of PCE are primarily $CHCl_2COCl$, CHOCl, Cl_2, and $COCl_2$. At the end of remediation, ≈90% of the Cl atoms from PCE are in $COCl_2$ with the remainder primarily in CHOCl and Cl_2. The production of Cl_2 during remediation is due primarily to the back reaction of C_2Cl_5. With additional moderate energy deposition, CHOCl and $CHCl_2COCl$ are themselves oxidized, producing end products Cl_2, HCl, HOCl, CO, and CO_2. $CHCl_2COCl$ is remediated by reactions initiated by Cl. CHOCl is remediated by reactions with Cl and O. Note that since the reactions which consume CHOCl and $CHCl_2COCl$ are slow, these intermediate products accumulate during remediation and only decrease on the longer, post-remediative, time scale.

Although PCE can be efficiently remediated by plasma oxidation, the end-products are themselves toxic. The advantage of using a closed cycle system is that these products can be captured and disposed of using conventional and well characterized processes. For example, $COCl_2$ can be treated by water scrubbing to produce HCl, a product that can be either recovered for recycling, or by mixing further with soda ash and slaked lime.[1]

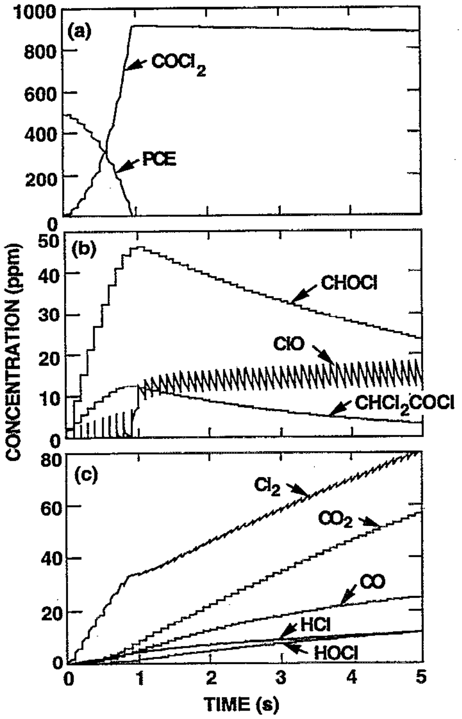

FIG. 4. Major products in the remediation and post-remediation of PCE for the $Ar/O_2/H_2O=79/20/1$ gas mixture. (a) PCE and the dominant product of remediation, $COCl_2$. (b) Products which are dominantly generated by remediation of PCE; CHOCl and $CHCl_2COCl$. ClO is also shown. (c) Products of both remediation and post-remediation (Cl_2, CO_2, CO, HCl, HOCl). After long post-remediative treatment, CHOCl and $CHCl_2COCl$ will themselves be processed.

Once PCE, which is a major reactant for Cl and ClO, is remediated, the densities of Cl_2 and ClO increase. ClO continues to be produced by the previously described processes. It is now primarily destroyed during and immediately after the current pulse by reactions with O atoms produced by electron impact dissociation of O_2 [$ClO+O \rightarrow Cl+O_2$, $k=3.0\times 10^{-11} \exp(70/T)$ cm^3 s^{-1}]. This reaction accounts for the sawtooth appearance of the density of ClO. Cl_2 is generated by reactions of the products of remediation, such as

$$COCl_2+Cl \rightarrow COCl+Cl_2$$

$$k=5.2510^{-11}\ T^{-1/2} \exp(-1010/T)\ \text{cm}^3\,\text{s}^{-1} \qquad (18)$$

and by reactions of the accumulated ClO with itself

$$ClO+ClO \rightarrow O_2+Cl_2$$

$$k=4.9\times 10^{-15}\ \text{cm}^3\,\text{s}^{-1}. \qquad (19)$$

There is little gain in the desirability of the products obtained by running the discharge after the PCE has been remediated with respect to final disposal. Large amounts of energy deposition would be required to further process the major products, at the risk of producing additional species which are difficult or more costly to remediate.

IV. CONCLUDING REMARKS

Plasma remediation in humid gas streams is an efficient technology for disposal of volatile organic compounds, and PCE in particular. In the example system, remediation of PCE by dielectric barrier discharges in Ar/O_2H_2O mixtures, PCE is converted to products that can be further treated and disposed of using conventional techniques. Conversion of PCE is primarily achieved through reactions of PCE with OH, O, and ClO. The dominant chlorine containing products after remediation are $COCl_2$, Cl_2, HCl, HOCl, CHOCl, and $CHCl_2COCl$. Further post-remediative processing can also remove CHOCl and $CHCl_2COCl$. The removal process has chain properties, as remediation reactions with O, OH, and ClO ultimately produce ClO which propagates the chain. An important intermediate in the chain is Cl. Although Cl does not directly remediate PCE, it does contribute to generation of ClO by reacting with the large amount of O_3 which is produced by electron impact dissociation of O_2. The low rate of production of ClO and Cl in the absence of the OH leads to slow remediation of PCE in dry mixtures.

ACKNOWLEDGMENTS

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[1] Details of the uses, toxicity and disposal of PCE and products of remediation can be found in L. T. Fairhall, *Industrial Toxocology* (Hafner, New York, 1969); *The Merck Index, Eleventh Edition* S. Budavari, Ed. (Merck, Rahway, New Jersey, 1989); *Toxic and Hazardous Industrial Chemicals Safety Manual For Handling and Disposal with Toxicity and Hazard Data* (The International Technical Information Institute, Japan, 1978).

[2] *Nonthermal Plasma Techniques for Pollution Control, Part B*, edited by B. M. Penetrante and S. E. Schultheis (Springer, Berlin, 1993), Sec. 2.

[3] L. A. Rosocha, G. K. Anderson, L. A. Bechtold, J. J. Coogan, H. G. Heck, M. Kang, W. H. McCulla, R. A. Tennant, and P. J. Wantuck, *Nonthermal Plasma Techniques for Pollution Control, Part B*, edited by B. M. Penetrante and S. E. Schultheis (Springer, Berlin, 1993), p. 281.

[4] L. A. Rosocha, J. J. Coogan, and M. Kang, *Proceedings of the 1994 IEEE International Conference on Plasma Science* (IEEE, New Jersey, 1994), p. 88.

[5] D. Evans, L. A. Rosocha, G. K. Anderson, J. J. Coogan, and M. J. Kushner, J. Appl. Phys. **74**, 5378 (1993).

[6] M. B. Chang, J. H. Balbach, M. J. Rood, and M. J. Kushner, J. Appl. Phys. **69**, 4409 (1991).

[7] W. D. Chang and S. M. Senkan, Environ. Sci. Technol. **23**, 442 (1989).

[8] W. D. Chang, S. B. Karra, and S. M. Senkan, Combust. Sci. Technol. **49**, 107 (1986).

[9] F. Westley, J. T. Herron, R. J. Cvetanovic, R. F. Hampson, and W. G. Mallard, NIST Chemical Kinetics Data base, NIST Standard Reference Data base 17. National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, MD 20899.