

EMSP Project Annual Report

Project Title: **Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces**

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Research Objective

The objective of this work is to demonstrate a practical, atmospheric pressure plasma tool for the surface decontamination of heavy metal waste. Decontamination of radioactive materials that have accumulated on the surfaces of equipment and structures is a challenging and costly undertaking for the US Department of Energy. Our technology shows great promise for mitigating the cost of this clean up effort.

Research Progress and Implications

This report summarizes the work accomplished during the second year of a three-year project. A low temperature, atmospheric pressure plasma has been developed with initial support from the Department of Energy, Environmental Management Sciences Program (see references). Now the goal is to characterize the reaction chemistry and demonstrate this technology on actual contaminated structures within the DOE complex. The group working at UCLA, headed by Dr. Hicks, is investigating the reaction chemistry in the plasma afterglow and the removal of uranium oxide from material surfaces.

A titration technique has been developed to determine the concentration of the fluorine atoms in the afterglow of CF₄-based atmospheric pressure plasmas, which are most likely the principal reactive species involved in metal etching. To our knowledge, no measurements of this type have been made on any CF₄-based atmospheric pressure plasma. This titration technique employs the rapid reaction between hydrogen molecules and fluorine atoms, $F + H_2 \rightarrow HF + H$. Infrared absorption spectroscopy was used to detect hydrogen fluoride in order to obtain the fluorine atom concentration.

The plasma source employed for this work consists of two parallel-plate electrodes made of aluminum and separated by a gap 1.6-mm across. The upper aluminum electrode is 10.2 cm wide by 2.5 cm long and is driven by RF power at 13.45

MHz, while the lower electrode is 10.2 cm wide by 20.4 long and is grounded. Just downstream of the upper electrode is a 1.0 cm x 10.2 wide ceramic plate, followed by an aluminum plate, 10.2cm x 10.2 cm. The sides of the duct parallel to the flow direction are sealed with sapphire windows so that the spectroscopic measurements of the gas can be made. For the hydrogen titration experiments, an H₂/He mixture is fed to the system through an array of 50 holes, each 0.79 mm in diameter, across the width of the lower grounded electrode. This array is located 0.3 cm downstream from the edge of the plasma discharge. The infrared light passes the gap between the two plates perpendicular to the sapphire windows at the point where the hydrogen and plasma effluent mix, and is detected with an MCT detector located at the other side.

Figure 1 shows the infrared absorption spectra of HF produced by the reaction between F and H₂. The plasma was operated at 12.8 Torr CF₄, 2.3 Torr O₂, 745 Torr He and 300 W RF power. The titration curve shown in Figure 2 has been generated by plotting the HF absorbance at 4039.7 cm⁻¹ versus different hydrogen concentrations fed in the afterglow of the CF₄/O₂/He plasma. At the titration point, the F atom concentration equals the hydrogen concentration, which is 1.6±0.1 x 10¹⁵cm⁻³. Measurement of the fluorine atom concentration is a milestone in the study of the reaction chemistry of CF₄-based atmospheric pressure plasmas. This will further benefit our efforts to develop improved designs that are more reliable and effective for TRU decontamination.

With an existing atmospheric pressure plasma source, the etching of uranium oxide samples was investigated. These samples consisted of silicon wafers coated with uranium oxide. Uranium (VI) dinitrate oxide was deposited on the silicon wafer and then converted to uranium oxide by heating to 220 °C under an O₂/He plasma for 35 min.

Figure 3 shows infrared spectra of the sample before and after treatment with the O₂/He plasma and the CF₄/O₂/He plasma for 35 min. The processing conditions during etching were 15 Torr CF₄, 4 Torr O₂, 741 Torr He, 400 W RF power, 230 °C, and 3 mm sample-to-nozzle distance. The intensities of all the peaks decreased following the O₂/He plasma treatment due to vaporization of the uranyl nitrate complex. After etching with

the fluorine plasma for 35 min, the uranium oxide was entirely removed from the silicon wafer. Figure 4 shows a close-up of the uranium oxide peaks at 949 cm^{-1} due to the UO_2^{2+} stretching mode and at 745 cm^{-1} due to the UO_3 stretching mode. No absorption is detected at these positions following the fluorine plasma etching. While these results are promising, we are nevertheless concerned that the nitrate complex is incompletely decomposed during plasma oxidation. We want to be sure the uranium is removed by chemical etching and not simply by volatilization of the uranium dinitrate oxide. Further work is underway to determine the etching rate of uranium oxide with the fluorine atom plasma.

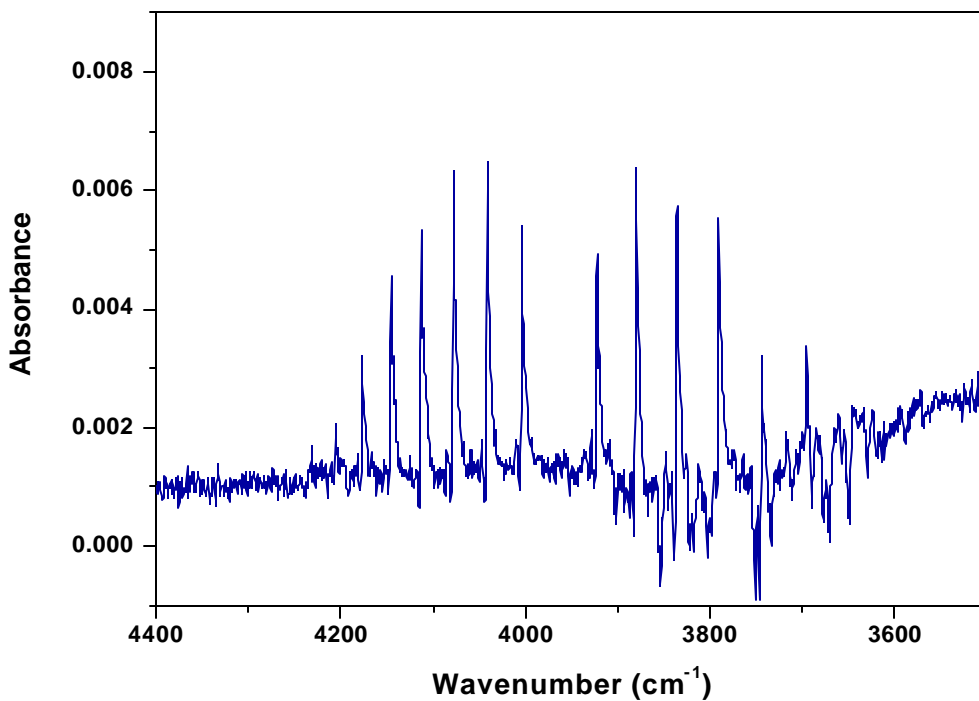


Figure 1. Infrared absorption spectra of hydrogen fluoride taken during hydrogen titration of the fluorine atoms in the $\text{CF}_4/\text{O}_2/\text{He}$ plasma afterglow.

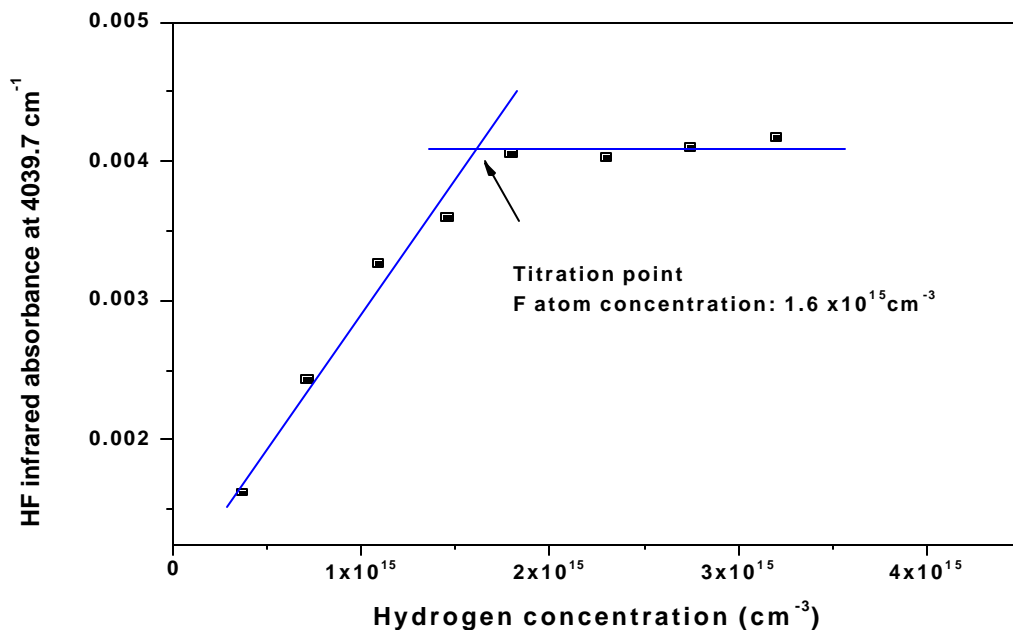


Figure 2. Titration curve for the reaction of H₂ with F atoms in the afterglow of the CF₄/O₂/He plasma. Arrow denotes the titration point.

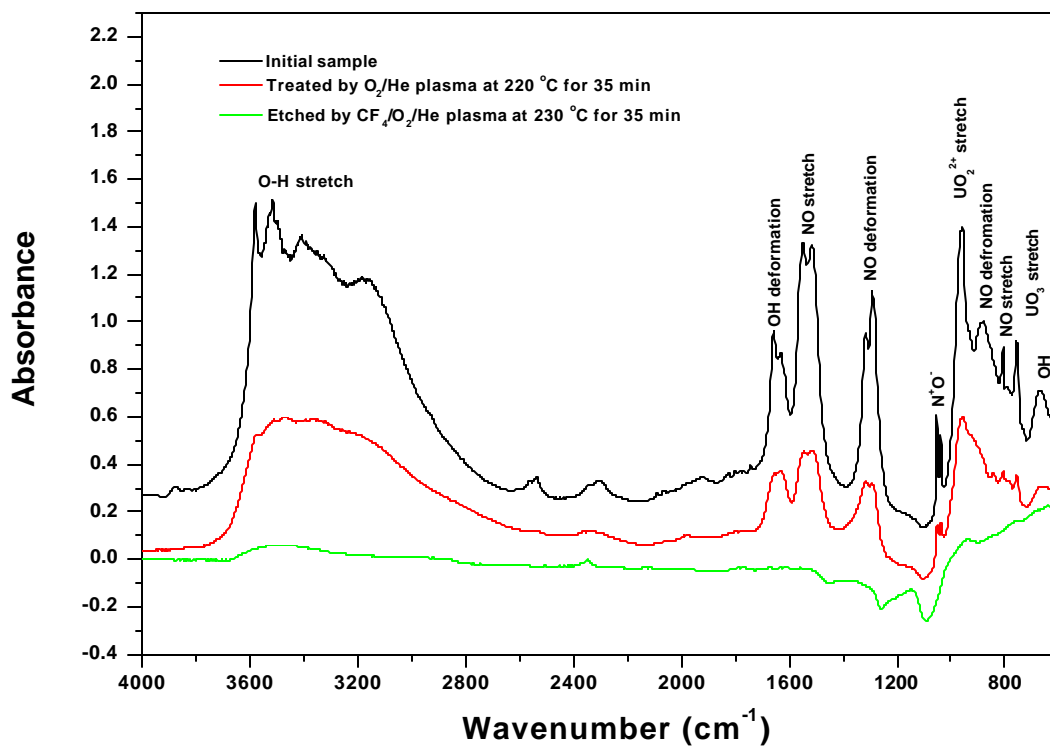


Figure 3. Infrared spectra of the uranium oxynitrate film before and after treatment with the O₂/He and CF₄/O₂/He plasmas.

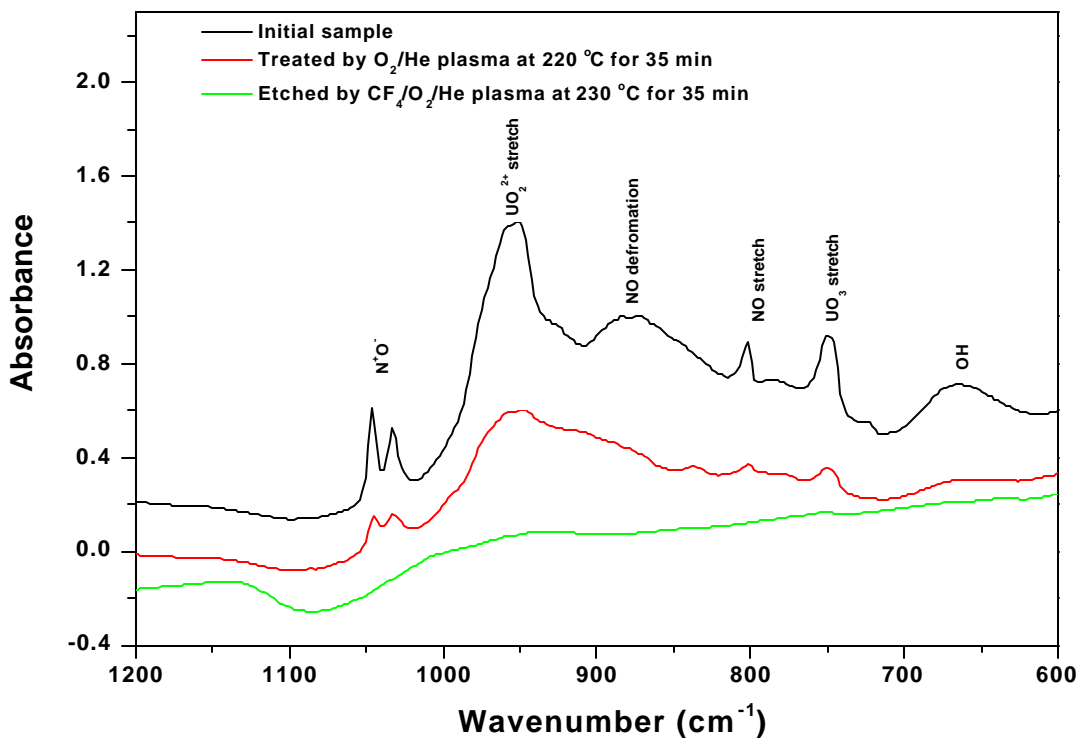


Figure 4. Close-up of the infrared spectra of the uranium oxynitrate films.

Planned Activities

We plan to publish three papers on this project by the end of this year. The first paper will focus on the determination of the fluorine atom concentration in the atmospheric pressure plasma with the hydrogen titration technique. The second paper will focus on the etching of uranium oxide with the fluorine atom plasma. The third paper will report on our study of the reaction chemistry of CF_4 -based atmospheric pressure plasmas. Below we describe the research activities that will be undertaken to accomplish these tasks.

We plan to replace the sapphire windows on the plasma source with barium fluoride windows, which are transparent to infrared light down to 900 cm^{-1} . This will enable us to study the dissociation of carbon tetrafluoride. The neutral temperature will be measured by calculating the rotational temperature from the FTIR spectra of hydrogen

fluoride or carbon tetrafluoride. These values will be compared to those obtained with an ungrounded thermocouple. The dependence of the concentration of active species, such as F atoms and CF₂ radicals, on plasma operating conditions will be determined, and compared to the rates of uranium oxide etching. Ultraviolet absorption spectroscopy will be used to study the CF₂ radicals. In the meantime, other molecules produced in the plasma, such as CO, CO₂, COF₂, and C₂F₆, also can be studied by FTIR. By comparing the experimental results with numerical models of the afterglow, we will be able to fully characterize the reaction chemistry of the CF₄-based atmospheric pressure plasma. We are also investigating the plasma etching of uranium oxide in order to verify the effectiveness of this technology for TRU decontamination. This work will identify the optimum process conditions for removing actinide films from surfaces. Once an effective decontamination procedure has been developed, we plan to demonstrate this technology at INEEL.

Information Access

1. Jeong, J. Y., Babayan, S. E., Tu, V. J., Henins, I., Velarde, J., Selwyn, G. S., and Hicks, R. F., "Etching Materials with an Atmospheric-Pressure Plasma Jet," *Plasma Sources Sci. and Tech.* **7**, (1998), 282.
2. Babayan, S. E., Jeong, J. Y., Tu, V., Selwyn, G. S., and Hicks, R. F., "Deposition of Glass Films with an Atmospheric-Pressure Plasma Jet," *Plasma Sources Sci. and Tech.* **7**, (1998), 286.
3. Schütze, A., Jeong, J. Y., Babayan, S. E., Park, J., Selwyn, G. S., and Hicks, R. F., "The Atmospheric-Pressure Plasma Jet: A Review and Comparison to other Plasma Sources," *IEEE Trans. Plasma Sci.* **26**, (1998), 1685.
4. Jeong, J. Y., Babayan, S. E., Schütze, A., Tu, V. J., Park, J. Y., Henins, I., Selwyn, G. S., and Hicks, R. F., "Etching polyimide with a non-equilibrium atmospheric-pressure plasma jet," *J. Vac. Sci. Technol. A* **17**, (1999), 2581.

5. Jeong, J. Y., Park, J. Y., Henins, I., Babayan, S. E., Tu, V. J., Selwyn, G. S., Ding, G., and Hicks, R. F., "Reaction Chemistry in the Afterglow of an Oxygen-Helium, Atmospheric-Pressure Plasma," *J. Phys. Chem.*, **104**, (2000), 8027.
6. Park, J. Y., Henins, I., Herrmann, H. W., Selwyn, G. S., Jeong, J. Y., Hicks, R. F., Shim, D., and Chang, C. S., "An Atmospheric Pressure Plasma Source," *App. Phys. Lett.*, **76**, (Jan 2000), 288.
7. Tu, V. J., Jeong, J. Y., Schütze, A., Babayan, S. E., Selwyn, G. S., Ding, G., and Hicks, R. F., "Tantalum Etching with a Non-Thermal Atmospheric-Pressure Plasma," *J. Vac. Sci. Technol. A* **18**, (2000), 2799.
8. Park, J. Y., Henins, I., Herrmann, H. W., and Selwyn, G. S., "Neutral Bremsstrahlung Measurement in an Atmospheric-Pressure Radio-Frequency (RF) Discharge," *Physics of Plasmas*, **7**, (Aug 2000), 3141.
9. Babayan, S. E., Jeong, J. Y., Schütze, A., Tu, V. J., Moravej, M., Selwyn, G. S., and Hicks, R. F., "Deposition of Silicon Dioxide Films with a Non-Equilibrium Atmospheric-Pressure Plasma Jet," *Plasma Sources. Sci. Technol.* **10**, (2001), 573.
10. Babayan, S. E., Ding, G., and Hicks, R. F., "Determination of the Nitrogen Atom Density in the Afterglow of a Nitrogen and Helium, Non-Equilibrium, Atmospheric Pressure Plasma," *Plasma Chem. Plasma Process.* **21**, (2001), 505.
11. Park, J. Y., Henins, I., Herrmann, H. W., and Selwyn, G. S., "Gas Breakdown in an Atmospheric Pressure RF Capacitive Plasma Source," *J. of App. Phys.*, **89**, (2001), 15.
12. Park, J. Y., Henins, I., Herrmann, H. W., Selwyn, G. S., and Hicks, R. F., "Discharge Phenomena of an Atmospheric Pressure Radio-Frequency Capacitive Plasma

Source,” *J. of App. Phys.*, **89**, (2001), 20.

13. Babayan, S. E., Ding, G., Nowling, G. R., Yang, X., and Hicks, R. F.,
“Characterization of the Active Species in the Afterglow of a Nitrogen and Helium
Atmospheric-Pressure Plasma,” *Plasma Chem. Plasma Process.* **22**, (2002), 255.

14. <http://prosurf.seas.ucla.edu>