Project Title: Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces
DOE-ID Grant Number: FG07-00ER45857
EMSP project number: 73835

Lead Principal Investigator:
Robert F. Hicks
Professor
UCLA Chemical Engineering
5531 Boelter Hall
Los Angeles, CA 90095-1592
(310) 206-6865
rhicks@ucla.edu

Co-Investigator:
Hans W. Herrmann
Los Alamos National Laboratory
Plasma Physics, P-24, MS E526
Los Alamos, NM 87545
(505) 665-6157
herrmann@lanl.gov

Graduate Students:
Xiawan Yang
Maryam Moravej
Gregory R. Nowling
UCLA Chemical Engineering
5531 Boelter Hall
Los Angeles, CA 90095-1592
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 CF$_4$-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 CF$_4$-based atmospheric pressure plasma. This titration technique employs the rapid reaction between hydrogen molecules and fluorine atoms, F + H$_2$ → 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 H/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 H. The plasma was operated at 12.8 Torr CF, 2.3 Torr O, 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 CF/O/He plasma. At the titration point, the F atom concentration
equals the hydrogen concentration, which is $1.6 \pm 0.1 \times 10^{15}$ cm$^{-3}$. Measurement of the
fluorine atom concentration is a milestone in the study of the reaction chemistry of CF$_4$-
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 O$_2$/He plasma for 35 min.

Figure 3 shows infrared spectra of the sample before and after treatment with the
O$_2$/He plasma and the CF$_4$/O$_2$/He plasma for 35 min. The processing conditions during
etching were 15 Torr CF$_4$, 4 Torr O$_2$, 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 O$_2$/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.

![Infrared absorption spectra](image)

Figure 1. Infrared absorption spectra of hydrogen fluoride taken during hydrogen titration of the fluorine atoms in the CF$_4$/O$_2$/He plasma afterglow.
Figure 2. Titration curve for the reaction of H\textsubscript{2} with F atoms in the afterglow of the CF\textsubscript{4}/O\textsubscript{2}/He plasma. Arrow denotes the titration point.

Figure 3. Infrared spectra of the uranium oxynitrate film before and after treatment with the O\textsubscript{2}/He and CF\textsubscript{4}/O\textsubscript{2}/He plasmas.
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.

Figure 4. Close-up of the infrared spectra of the uranium oxynitrate films.
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 CF$_2$ 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 CF$_2$ radicals. In the meantime, other molecules produced in the plasma, such as CO, CO$_2$, COF$_2$, and C$_2$F$_6$, 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 CF$_4$-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**


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