RAMAN AND ELECTROCHEMICAL NOISE SENSORS FOR IN-TANK CORROSION MONITORING

TECHNOLOGY DESCRIPTION

This project involves the development of a fiber-optic Raman spectroscopy sensor and deployment platform for the *in situ* analysis of chemical species in waste tanks. Specifically, the instrument can detect nitrate, nitrite, and hydroxide (NO_3^-, NO_2^-, and OH^-) over the full range of concentrations of significance for controlling corrosion in U.S. Department of Energy (DOE) high-level waste (HLW) tanks. A 670-nm diode laser is used for analyte excitation and an echelle spectrometer with a charge-coupled device (CCD) detector is used for spectral acquisition. The instrument operates remotely with only a small, lightweight probe and fiber-optic cable deployed in the tank. The miniature fiber-optic Raman sensor is housed in a miniature sampling chamber with a filtering mechanism to allow only liquid waste to enter the sampling area. A remotely operated deployment platform that interfaces with the riser opening in the waste tank will be used to deploy the Raman probe into the waste. This is done via a reel mechanism inside the platform. The deployment platform is completely sealed to protect workers from being exposed to the radiation plume emanating from the riser opening.

Using a Raman sensor for in-tank monitoring has several advantages that make it the technique of choice for monitoring anionic species such as nitrate, nitrite, and hydroxide. First, the Raman spectrum is unique for every molecule and can therefore be used as a “chemical fingerprint” to identify unknown species. The Raman technique can also differentiate between solid and dissolved species, which is important in waste tanks where the physical composition can range from liquid to sludge to hard saltcake. Another advantage of the Raman technique is ease of sampling. Furthermore, use of the Raman technique requires no sample preparation, so samples can be easily analyzed *in situ* if a fiber-optic probe is used to deliver and collect the scattered light from the sample.

Electrochemical noise (EN) sensors developed at Hanford and at the Savannah River Site (SRS) are being co-deployed with the Raman sensor. The two sensors are being integrated into a single probe head. The EN technique has the capability of monitoring both localized and general corrosion. Localized corrosion, including pitting and stress corrosion cracking, is of concern in waste tanks. EN measures the potential and current fluctuations of metal in solution. These fluctuations are perturbations resulting from the electrochemical reactions occurring at the metal surface and are low-frequency (1 Hz), small amplitude signals.

Current sampling and analysis techniques require removal of samples from tanks and subsequent laboratory analysis using ion chromatography and titration. The advantage of the Raman probe technology is that it can readily be deployed into HLW tanks and provide *in situ* analysis of ions associated with corrosion.

TECHNOLOGY NEED

This project addresses the need to monitor chemical species associated with corrosion in HLW tanks at various DOE sites. The DOE has 332 underground tanks used to process and store more than 100 million gallons of high-level, radioactive chemical waste. Some of the tanks have up to a one-million-gallon capacity, and many are of single-shell, steel construction. These tanks pose a considerable risk to the public and the environment should corrosion or other processes compromise the tank walls. Corrosion is of particular concern because many of the tanks contain high concentrations of nitrate, which attacks steel. Nitrate ion is often present in high concentrations due to the use of nitric acid in fuel nuclear weapons materials processing. To minimize the corrosive effects of nitrate, the tank contents are maintained at an elevated pH (through the addition of sodium hydroxide) and at an optimum nitrite level.

To ensure that the chemistry in a waste tank is being maintained to minimize corrosion, it is important to periodically monitor the concentrations of nitrate, nitrite, and hydroxide. If significant changes in the concentrations are observed, then appropriate measures can be exercised to restore optimum, anti-corrosive conditions. Current analytical protocols for the analysis of NO_3^-, NO_2^-, and OH^- in high-level waste tanks involve liquid sampling, preservation, transport, storage, preparation, and analysis with a pH meter and an ion chromatograph in a hot cell. These steps are slow, expensive, and present a major risk for site personnel and analysts. High costs serve to limit the number of samples collected from any one tank. There is also considerable opportunity for the sample composition to change or become contaminated from the time it is collected to when it is prepared for analysis.

An attractive alternative to existing protocols is to use one or more sensors to monitor *in situ* the three oxyanion species of interest. Small inexpensive devices that can be sacrificed, if necessary, are most appealing. Optical techniques employing fiber-optic probes are promising for this application because, unlike electrical devices, they are affected less by radiation. The important challenge for *in situ* fiber-optic sensors is for them to provide analytical data at relevant concentrations under harsh conditions such as those encountered in a waste tank. Waste tank probes will be exposed to 1,000 rad/hr, 90 ^{0}C, and 10 molar OH^-. Furthermore, the measurements of the specified analytes must be performed in turbid solutions without interference from other sample components.

The needs identified by the Site Technology Coordination Group (STCG) is as follows:

SR00-2045 - *In Situ* Waste Tank Corrosion Probe
RL-WT04 - Double-Shell Tank Corrosion Monitoring

TECHNOLOGY BENEFITS

The combined chemistry and corrosion probe will:

- Minimize or eliminate manual sampling for corrosion species.
- Minimize the quantity of inhibitors needed for corrosion control.
- Enable defining the ability of the inhibitors to mix by measuring concentration in a vertical plane.
- Implementing the combined *in situ* Raman and EN sensors will significantly reduce analysis time (including sample holding time, which normally can be weeks or more).
- Cost will be significantly reduced as well by eliminating all the steps prior to analysis as well as the need for specialized facilities and equipment for the analysis.
- Risk to site workers will be significantly reduced because “hot” samples do not have to be handled or transported.

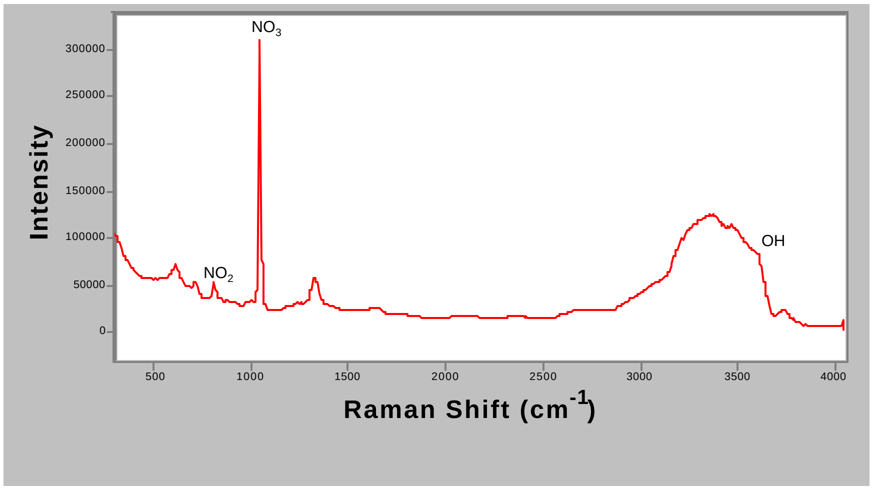
The cost per sample is conservatively estimated to be reduced to about 10 percent of current levels based on the procedures and equipment/facilities that are eliminated from the standard protocols. This faster, less expensive *in situ* approach will allow more samples to be analyzed in each tank, providing more reliable characterization of the contents.

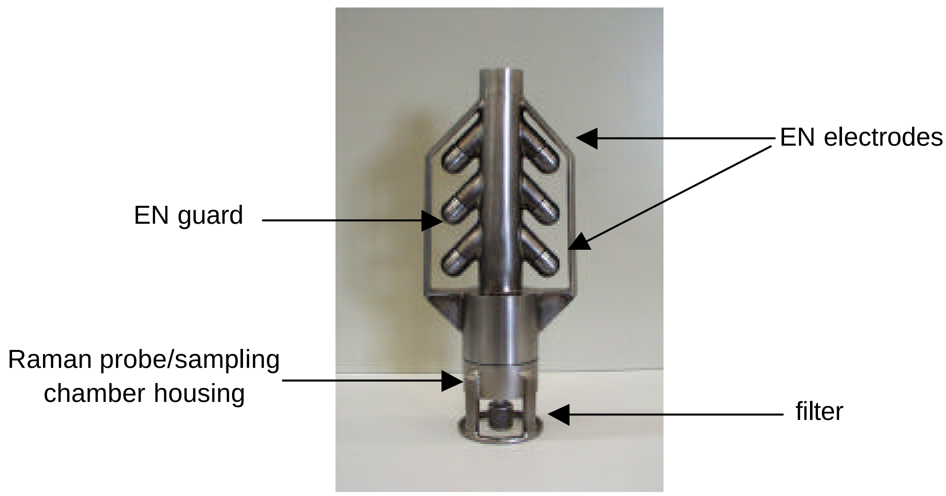
The incorporation of the electrochemical noise sensor will also provide a means to determine the type of corrosion processes occurring at the tank wall and cooling coils. Integration of the Raman and EN sensors into one probe will have the added advantage that real-time correlation between inhibitor concentrations and corrosion rates can be determined in an actual radioactive waste tank environment.

TECHNOLOGY CAPABILITIES/LIMITATIONS

Corrosion monitoring and control is the primary application. The combined Raman/EN sensors will provide an *in situ* real time quantification of NO_3^-, NO_2^-, and OH^- and a means to determine the type of corrosion processes at the tank wall and cooling coils in underground storage tanks. The Raman sensor can also monitor other oxyanions, such as ferrocyanide/ferricyanide, or organic chemicals, such as chlorinated hydrocarbon solvents, in tanks. The Raman sensor can also be used to analyze the contents of 55-gallon drums, bottles, and other waste containers slated for disposal by incineration or other means.

Safety, protocol, and mechanical issues related to operating measurement instrumentation in a radioactive environment have been the major considerations for deployment in HLW tanks. Operation of the combined Raman/EN sensor will require a skilled technician.





Raman Spectrum of Archived Waste from High-Level Waste Tank 43H (top)

Combined Raman and Electrochemical Noise (EN) Corrosion Probe (bottom)

COLLABORATION/TECHNOLOGY TRANSFER

EIC Laboratories, Inc. (EIC) has developed a small fiber-optic Raman probe under DOE programs sponsored by Argonne National Laboratory and the National Energy Technology Laboratory (NETL). The Raman probe has been awarded a U.S. Patent (No. 5112127). EIC has also developed an echelle-based Raman spectrograph under a DOE program also sponsored by NETL. This Raman spectrograph is compact and field deployable, has no moving parts, and allows the acquisition of the entire Raman spectrum ("fingerprint" to OH^- regions). These DOE-developed sensor and instruments will be used in this program. The incorporation of the electrochemical noise sensor into the Raman probe is done in collaboration with the Savannah River Technology Center. The deployment of the Raman system into waste tanks will be a joint venture between EIC and SRS personnel.

ACCOMPLISHMENTS AND ONGOING WORK

The feasibility of quantifying nitrates, nitrites, and hydroxide using the Raman technique has been demonstrated. Raman spectra of the oxyanions were also successfully obtained from various SRS archived waste samples including waste from Tank 43H where the probe will be initially deployed. All necessary steps have been taken to justify and safely deploy an *in situ* probe in HLW tanks. This technology provides costs savings and reduces employee exposure risks.

- Materials that will be used in the construction of the probe have been tested under tank conditions, such as maximum radiation exposure (1,000 rad/hr exposure for two years), high pH, and 90 ^{o}C temperature. The probe materials have been demonstrated to survive waste tank conditions.
- The fabrication of the echelle-based spectrograph that will be used with the Raman probe has been completed.
- The fabrication of the probe sampling chamber and EN housing has been completed.
- Raman analysis of archived waste samples has been completed. Raman analysis results were compared to current analytical techniques for wastes, ion chromatography (nitrate and nitrite), and titration (hydroxide). There was good agreement between the Raman results and the current analytical technique results in predicting the concentrations of nitrite, nitrate, and hydroxide in the wastes.
- Design of the deployment platform for the corrosion probe into the waste tank was completed and was submitted to SRS for review. The engineering drawings were approved by SRS with some modifications.

The remaining tasks for FY 2000 will be the fabrication of the deployment platform and cold acceptance test of the corrosion probe system.

TECHNICAL TASK PLAN/TECHNICAL MANAGEMENT SYSTEM INFORMATION

TTP No./Title: NV08C231 - Integrated Raman Probe for In-Tank Corrosion Monitoring
Tech ID/Title: 2015 - Integrated Raman Sensor for In-Tank Corrosion Chemistry Monitoring

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