INTEGRATED RAMAN pOH SENSOR FOR IN-TANK CORROSION MONITORING

TECHNOLOGY NEED

The DOE has 332 underground tanks used to process and store over 100 million gallons of radioactive and mixed chemical waste. Some of the tanks have up to 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 a wall be compromised due to corrosion or other processes. Corrosion is of particular concern because many of the tanks contain high concentrations of nitrate, which attacks steel. To minimize the effects of nitrate, the tank contents are maintained at an elevated pH 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 monitor periodically the concentrations of NO_3^-, NO_2^-, and OH^-. If significant changes in the concentrations are observed, then appropriate measures can be exercised to restore optimum, anti-corrosive conditions. Current analytical protocols for 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 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 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 reliable analytical data at relevant concentrations under harsh conditions ranging up to 1000 rad/hr, 90 °C, and 10 M (molar) OH^-. Furthermore, the measurements of the specified analytes must be performed in turbid solutions without interference from other sample components.

TECHNOLOGY DESCRIPTION

The proposed technology will utilize a portable fiber optic Raman spectrometer with a fiber optic pOH sensor to produce an instrument that can detect all three species *in situ* over the full range of concentrations of significance to DOE. The integrated instrument will be operated remotely with only a small, lightweight probe and fiber optic cable deployed robotically in the waste tank. The instrument will be highly specific and quantitative for the anions of interest and will be able to differentiate easily between dissolved and solid materials. The Raman technique has several advantages that make it nearly the ideal choice for in-tank monitoring of 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. Raman 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 Raman is ease of sampling. Raman requires no sample preparation, so samples can be easily analyzed *in situ* if a fiber optic probe is used to deliver laser light and collect the Raman scattered light from the sample

BENEFITS

Implementing the proposed *in situ* Raman-pOH technology will significantly reduce analysis time (including sample holding time, which can be weeks or more), cost (by eliminating all the steps prior to analysis as well as the need for specialized facilities and equipment for the analysis), and risk to site workers and analysts (“hot” samples do not have to be handled or transported). We estimate conservatively that the cost per sample will be reduced to about 10% of current levels based on the procedures and equipment/facilities that are eliminated from the standard protocols. The faster, less expensive *in situ* approach will allow more samples to be analyzed in each tank, providing more reliable characterization of the contents.

CAPABILITIES/LIMITATIONS

The Raman-pOH system will provide an *in situ* real-time sensing of NO_3^-, NO_2^-, and OH^- in underground storage tanks. The Raman sensor can monitor other ions (e.g., ferrocyanide/ferricynide) 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. Operation of the Raman-pOH system will require a skilled technician.

COLLABORATION/TECHNOLOGY TRANSFER

EIC has developed both “end-viewing” and “side-viewing” type Raman probes. The former has been awarded a U.S. Patent (No. 5,112,127). Under DOE programs sponsored by Argonne National Laboratory and the Federal Energy Technology Center, EIC has also developed a portable Raman instrument that can be used in a wide variety of sensing applications, including in-tank monitoring. The deployment of the Raman system into tanks will be a joint venture between EIC and Savannah River Site personnel. EIC is committed to the commercialization of products developed from this project and making them available for use in government, industrial, academic, and medical communities.

ACCOMPLISHMENTS

The feasibility of fiber optic Raman probe measurements of nitrates, nitrites, hydroxide, and other anions of interest has been demonstrated. Limits of detection (LOD) for nitrate and nitrite over a 100 feet of fiber optic cable were determined to be 0.005 M and 0.02 M, respectively. These LODs were below the range found in tanks. Strong Raman signals were observed at concentrations that are typical of tanks in which corrosion control is being conducted. The minimum detectable concentration of 0.05 M determined for hydroxide was slightly above that found in the lowest of the SRS tanks (0.03M), but still well below the levels used to inhibit corrosion (typically over 1 M). The Raman response of individual anions was shown to be linear with concentration, and the measurement reproducibility was within 1%.

TECHNICAL TASK PLAN (TTP) INFORMATION

TTP No./Title: NV06C231 - Integrated Raman pOH Sensor for In-Tank Monitoring

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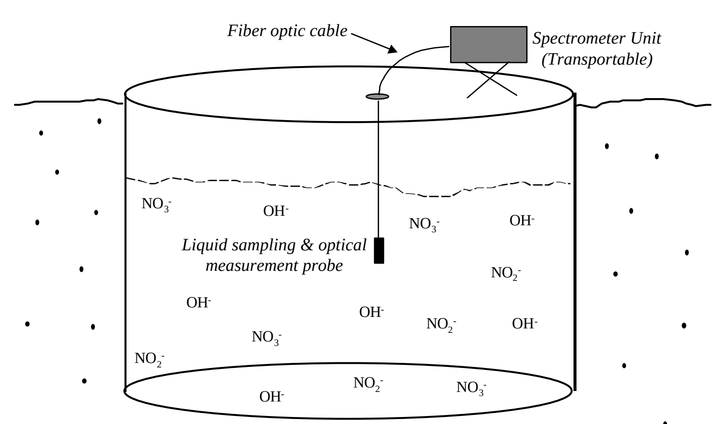
Integrated Raman-pOH Sensor for In-Tank Corrosion Monitoring



Spectral Analysis of Molecular Vibrational Information Provides Data on Chemical Species in Waste Tanks