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Task 29

Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process

G. Cerefice and K. Czerwinski

BACKGROUND

Increasing the proliferation resistance of the nuclear fuel cycle is one of the stated goals for the Global Nuclear Energy Partnership program. From a proliferation aspect, the greatest challenge to closing the nuclear fuel cycle is ensuring that nuclear material is not diverted during the recycling processes. As part of the safeguards-by-design concept, new separations facilities will incorporate integral systems capable of providing materials accountability for the actinide elements to minimize the potential for undetected diversion of material. The goal of this project is to evaluate technologies to meet this need. Optical spectroscopic techniques, such as Ultraviolet-Visible Spectroscopy (UV/Vis) and Laser Fluorescence Spectroscopy (LFS), are quantitative analytical techniques that have been used for measuring the concentration of the actinides under laboratory conditions.

In UV/Vis spectroscopy, the sample is illuminated by a continuous spectrum (from the UV through the Visible wavelengths). The transmitted light is measured, allowing the determination of the absorbance of the light as a function of wavelength. The wavelength of the absorbance is dependant on the electronic structure of the absorbing atom, and is proportional to the concentration of the absorbing element in the sample. For LFS, the sample is illuminated at a single wavelength, which is absorbed by the target atoms in the sample. The energy absorbed is re-emitted through fluorescence. The wavelength of the absorbance, and the fluorescence-response, is again dependant on the electronic structure of the absorbing atom, and is proportional to the concentration of the absorbing element in the sample.

Both techniques are strongly dependent on the chemical speciation of the elements to be measured, providing a tool for not only the determination of material concentrations for mass balances, but also providing inspectors and plant operators with a tool to examine the process chemistry itself. As optical techniques, both of these methods can be adapted for fiber optics, allowing the instrumentation to be



Laser induced fluorescence of a uranium sample in nitric acid

placed in shielded areas of the plant to minimize the impact of the radiation fields on the detectors and increase the accessibility of the systems for maintenance and inspection.

RESEARCH OBJECTIVES AND METHODS

The goal of this project is to evaluate the application of these analytical techniques to the on-line, real-time measurement of the actinide elements in the process streams of a solvent extraction process, with particular attention to the UREX+ and PUREX processes. Based on the experience gained through this effort, engineers will have the information necessary to decide if these technologies should be advanced to the prototype stage and tested at the pilot plant level. Through the experimental work planned as part of this effort, researchers will also develop a better understanding of the chemical interactions of the actinide elements, providing additional data for the development of first-principles based models of the solvent extraction process. The information gathered through these experiments will also add to the database on the UREX+ solvent extraction process, particularly in the off-normal operating regimes.

The research objectives are:

- To evaluate the potential for utilizing UV-Visible and laser fluorescence spectroscopy to determine actinide concentrations under process conditions, including the spectroscopic impact of acid concentration, solvent vs. aqueous product streams, ligand concentrations (TBP, AHA), and chromophoric agents (e.g. iron) from fission products or corrosion/degradation products.
- To examine what process chemistry information can be extracted from the spectroscopic signals along with the actinide metal concentrations.
- To examine the fundamental chemistry underlying the spectroscopic behavior under process conditions in support of process chemistry modeling activities.

RESEARCH ACCOMPLISHMENTS

To evaluate the potential application of optical spectroscopy techniques for the determination of uranium in the aqueous process streams of the UREX process, the impact of process chemistry on the absorbance and fluorescence behavior of the uranyl ion was examined. For the UREX flowsheet, the potential areas for deployment of these techniques was divided into four categories, based on the chemical environment, each represented by a feed or product stream: the process feed, the raffinate (actinide/fission product) stream, the technetium product stream, and the uranium product stream. These process ranges also allowed researchers to examine the potential application of these technologies to a PUREX-based flow sheet as well.

UV/Vis Spectroscopy

The UREX feed stream and uranium product will both have molar quantities of uranium present. The concentration of uranium in these streams is expected to exceed the linear range of detection for a 1 cm path length cell. To measure these high concentration streams by UV/Vis, plant designers would need to either insert a reduced path-length slip stream or add the capability for a fixed mass dilution in the slip stream. Either of these options, or more realistically the combination of the two, could reduce the absorbance in the system back to within the linear response range of the technique.

The raffinate and technetium streams are expected to have significantly lower concentrations of uranium. For the UREX process, the raffinate stream will also contain the AHA from the process. Based on the measured molar extinction coefficients for uranium under the chemical environments expected for these streams, the expected uranium concentrations will likely fall below the detection limits observed for a 1 cm optical path. While the limits of detection may be able to be extended with a longer path length, scattering and other phenomena would likely only limit this to an order of magnitude reduction in the detection limit. Even with these limitations, the technique could still be used to establish a threshold value for uranium, which may be useful in detecting changes in process chemistry. UV/Vis spectroscopy, combined with titration by a fixed mass of a caustic stream, can also be used to probe for the presence of AHA in the raffinate stream, allowing for independent confirmation that the plant is running the UREX flowsheet and has not switched to a plutonium extraction process (such as PUREX).

Laser Fluorescence Spectroscopy

The primary focus of the year two work on the project was the evaluation of Time Resolved Laser-induced Fluorescence Spectroscopy (TRLFS) techniques for the determination of uranium under process conditions. The impact of process chemistry on the observed lifetime and fluorescence yield of uranium in the aqueous process streams was investigated. TRLFS was determined to be significantly more sensitive for the detection of uranium, so much so that the signals in the feed and uranium product streams would easily saturate the detection systems. This sensitivity, however, may make the technique ideal for observing streams where the uranium concentration is expected to be very low, such as the technetium product stream and the raffinate stream. The detection limits and linear response regimes for both these process streams have been examined.

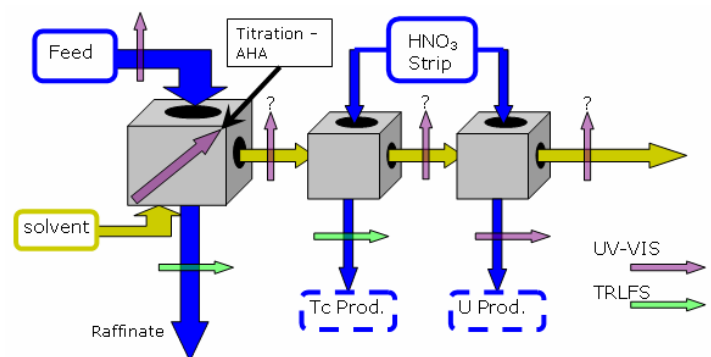
FUTURE WORK

ACADEMIC YEAR HIGHLIGHTS

- ◆ N.A. Smith, G.S. Cerefice, and K.R. Czerwinski, "Application of Optical Techniques for On-Line Materials Accountability in the UREX Solvent Extraction Process," *Proceedings, 47th Annual Institute for Nuclear Materials Management Annual Meeting*, Nashville, TN, July 16-20, 2006.
- ◆ N.A. Smith, G.S. Cerefice, and K.R. Czerwinski, "Use of UV-Vis spectroscopy and TRLFS for material accountability in solvent extraction processes," 233rd National Meeting of the American Chemical Society, Chicago, IL, March 27, 2007.

For the final project year, work will continue to apply the spectroscopy techniques to expand the fundamental understanding of the chemistry of uranium under process conditions, with the goal of providing the theoretical basis to allow a better interrogation of the observed spectra to confirm process chemistry conditions. Research will also examine the potential spectral interferences on the determination of uranium due to dissolved iron (and other corrosion products), fission products, and other actinide elements.

In parallel, the application of these techniques to the organic process streams will be examined. Initial TRLFS experiments on uranium samples extracted into the organic phase have showed no fluorescence under laser irradiation. The reason for this is being investigated, but the leading hypothesis is that the C-H oscillators of the organic matrix are acting as quenching agents in much the same way that O-H oscillators do in a water based system. As a result, it is unlikely that TRLFS will be useful for determination of uranium concentrations in the organic streams. Initial experiments suggest that UV-Visible spectroscopy, however, appears to be a viable alternative technique for these organic process streams.



Potential Application Locations for Optical Spectroscopy in the UREX Flowsheet

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