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

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

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AFCI Research Area: Separations/Aqueous Processes (Proliferation Resistance)

Abstract:

The goal of this project is to examine the potential for using optical spectroscopy techniques, such as UV-Visible Spectroscopy and Laser Fluorescence Spectroscopy, for special nuclear materials accountability applications for the UREX+ and other solvent extraction processes. To increase the inherent proliferation resistance of the solvent extraction process, it is necessary to develop on-line techniques to directly measure the concentrations of special nuclear materials in-process. By providing on-line materials accountability for the processes, the potential for covert diversion of the materials streams becomes much more difficult to implement. On-line monitoring of material streams will also allow for improved plant operation, as well as serving as an additional safety measure for plant operations. Laser fluorescence and UV-Visible spectroscopy have been demonstrated for use in determining the concentration of the actinides at the laboratory scale. These processes are adaptable to flow-thru applications, and should be highly radiation-tolerant, which suggests that they should be applicable to the spent fuel treatment environment.

Work Proposed for Academic Year 2005-2006, Goals, and Expected Results:

Year 1: Impact of process parameters
Year 2: Adaptation to flowing systems
Year 3: Impact of radiation on detection systems and optics

Funding Profile:

Academic Year:	**2005-2006**	**2006-2007**	**2007-2008**
Total (K$)	$147.5	$157.7	$163.4

Background and Rationale:

One of the primary challenges facing any advanced fuel cycle is the proliferation resistance of that fuel cycle, especially the potential for illicitly diverting nuclear material from the fuel cycle for other purposes. The key step in almost all of the fuel cycles currently under evaluation in the Advanced Fuel Cycle Initiative is the chemical separation and partitioning of used nuclear fuel, either as the starting point for treating existing used fuel, or as a key step in the recycling and destruction of the higher actinides. Any partitioning of the actinides has the potential for increasing the proliferability of the fuel cycle unless the process or plant can be designed to prevent, or at least detect, the diversion of nuclear material from the process. To address this concern, the AFCI has proposed that any new separations plant include in its design an integral system capable of providing materials accountability for the actinide elements with less than 0.1% uncertainty.

It is proposed that optical spectroscopic techniques, such as Ultraviolet-Visible Spectroscopy (UV-Vis) and Laser Fluorescence Spectroscopy (LFS), would allow for the on-line, real-time analysis of the actinide elements for a solvent extraction process. UV-Vis and LFS are quantitative analytical techniques that have been used for measuring the concentration of the actinides under laboratory conditions, and are easily adaptable to multiple sampling geometries, such as dip probes, fiber-optic sample cells, and flow-through cell geometries. This research project will 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. Researchers will evaluate the impact of process conditions on the sensitivity of these techniques, providing plant engineers with the information they will be able to use to evaluate these techniques for inclusion as part of the materials accountability system for future plant designs.

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 LSF, 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. In addition to the potential materials accountability applications, UV-Vis Spectroscopy and LFS can provide information regarding the speciation of the actinides in the process stream (oxidation state, complex formation, etc.). This information will help elucidate the behavior of the actinides under process conditions, improving our understanding of the chemical interactions underlying these separations processes.

Research Objectives and Goals:

The research objectives are:

- To evaluate the potential for utilizing UV-Visible and laser fluorescence spectroscopy to determine actinide concentrations under process conditions
- To examine the impact of process environment on the sensitivity of UV-Visible and laser fluorescence spectroscopy to the actinides, including the impact of
    - Acid concentration
    - Solvent concentration
    - Ligand concentration (TBP, AHA)
    - Iron
    - Fission Products
    - Competing Actinide elements
- To examine the impact of process conditions on the sensitivity of UV-Visible and laser fluorescence spectroscopy for the determination of actinide elements, including
    - Flow rate
    - Process temperature
    - Plant Geometry (pipe diameter, shape, etc.)
- To examine the potential impact of radiation fields on the spectroscopy systems

The goals are:

- To evaluate the potential for deploying UV-Visible and Laser Fluorescence spectroscopy systems as part of an on-line materials accountability or proliferation detection system for a solvent extraction fuel processing plant.
- To assist the designers of the next-generation fuel processing facilities with the deployment of on-line materials accountability systems

Technical Impact:

The proposed work will complete the conceptual analysis and pre-prototype testing of these optical spectroscopy techniques for on-line materials accountability applications in a solvent extraction plant. 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.

Research Approach:

Detection limits for UV-Vis and LFS will be measured for the actinide elements in a dilute acid system to establish the baseline performance of the systems. The system will then be systematically explored to examine the impact of: acid concentration, nitrate concentration, redox potential, diluent concentration, ligand concentration, and contaminant/fission product concentration on the sensitivity of these techniques. The potential for interferences will also be examined. This work will be performed in a standard optical spectroscopy geometry using aliquots of know solution concentrations.

Following the examination of the chemical parameters on the sensitivity of these spectroscopic techniques, the impact of the process parameters will be examined. In the second year of the project, a flow-through cell system (flow-through optics cell, pump, etc.) will be used to examine the impact of flow velocity and process temperature on system sensitivity. Researchers will also design a modified flow-through system to examine the impacts of pipe diameter on the spectroscopic techniques, and will examine the sensititvity impacts of using dip probes, reflectance probes, and other fiber optic sampling options on the determination of the actinide elements in the solvent extraction process.

Finally, researchers will examine the potential impacts of the radiation field on the sensitivity of these spectroscopic techniques. To deploy these systems in a processing plant, it will be necessary to use fiber optics or light pipes in order to deploy the spectrometers in a shielded environment (to allow for easy maintenance and to protect the electronics). To evaluate the impact of radiation-induced degredation of the fiber optic and light pipe materials on the sensitivity of UV-Vis and LFS, sections of fiber optic will be irradiated. The irradiated fibers will be then be used to determine the impact of dose on the sensitivity of the spectroscopic techniques for the actinide elements. Additionally, the impact of fiber/light pipe length on the detection limits (due to light loss, etc.) will be examined.

Expected Technical Results:

- Sensitivity (detection limits) for the actinide elements under process conditions for UV-Visible Spectroscopy.
- Sensitivity (detection limits) for the actinide elements under process conditions for Laser Fluorescence Spectroscopy.
- Elucidation of actinide speciation under normal and off-normal process conditions for the PUREX and UREX+ solvent extraction processes.

Capabilities at the University and Argonne National Laboratory:

The University has the laboratory space dedicated to actinide and radiochemistry necessary to support the experimental work proposed in this project. The research group also has the UV-Visible spectrometer and is in the process of acquiring the laser spectroscopy system required to perform the proposed research. The laser system has been funded under another project, and is currently in the purchasing process. The research group also has access to the necessary analytical equipment, including ICP-AES, ICP-MS, alpha spectroscopy, gamma spectroscopy, and liquid scintillation to support the research, as needed. The funding for the optics tables is included in the year 1 budget of this project. To accommodate the process parameter research proposed in year 2 of the project, it will be necessary to purchase the flow-through cell and pump (included in the budget forecast).

The irradiation capability, required for the proposed year 3 work, will be obtained either through the collaboration with Argonne National Laboratory, through another national laboratory partner, or through collaboration with FZK-Karlsruhe. Travel funding to support deploying the researchers and the experiment at the appropriate site is included in year three to support this effort.

Project Timeline:

Timeline Narrative

The proposed research is planned to cover three years, starting in Summer 2005. The UV-Visible spectrometer is expected to be installed an operational at the start of the project, and initial experiments will be performed on the UV-Vis system. The laser system is expected to be installed and operational by mid-summer, and will be added to the experimental matrix. The first year of the project is expected to be focused on evaluating the impact of the chemical environment on the sensitivity of the UV-Vis and LFS techniques. Toward the end of the first year, the design of the flow-through system will be finalized to support the proposed year two work. In the second year of the project, the impact of the process parameters on the system will be evaluated, starting with the effect of process temperature (to allow for any delays in acquiring the flow-through system). The final year of the project will focus on the potential impacts of the radiation environment on the sensititivyt of optical spectroscopic techniques, and will include at least one irradiation campaign.

Expected Technical Results:
- Sensitivity (detection limits) for the actinide elements under process conditions for UV-Visible Spectroscopy.
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Milestones
- Evaluation of chemical environment impacts on UV-Visible spectroscopy sensitivity: Aug. 2006
- Evaluation of chemical environment impacts on Laser Fluorescence spectroscopy sensitivity: Nov. 2006
- Evaluation of process parameter impact on optical spectroscopy sensitivity: Aug. 2007
- Evaluation of potential radiation field impacts on optical spectroscopy sensitivity: March 2008

Deliverables
- **Monthly Updates:** Monthly updates on project progress, including the identification of recent highlights and potential upcoming problems/issues will be submitted monthly to the UNLV TRP program administration.
- **Quarterly Reports:** Brief reports indicating progress will be provided every quarter to the UNLV TRP program administration for submission to the national AFCI program.
- **Annual Reports:** Written reports detailing experiments performed, data collected and results to date.
- **Final Report:** Written report detailing experiments performed, data collected, results, and conclusions to be submitted at the end of the project.

Biographical Information:

Curriculum Vitae for Dr. Cerefice is included below, along with the statements of current and pending support.

GARY STEVEN CEREFICE

EDUCATION:

Massachusetts Institute of Technology
Ph.D. in Nuclear Engineering, August 1999. (Minor in Environmental Engineering)

Massachusetts Institute of Technology
M.S. in Nuclear Engineering, June 1996.

University of Illinois at Urbana-Champaign
B.S. in Nuclear Engineering, May 1993.

PROFESSIONAL EXPERIENCE:

Deputy Director, Transmutation Research Program
University of Nevada – Las Vegas (Las Vegas, NV) — March 2001 – Current

Associate Research Professor, Harry Reid Center for Environmental Studies
University of Nevada – Las Vegas (Las Vegas,NV) — Jan. 2000 – Current

Research Assistant, Department of Nuclear Engineering
Massachusetts Institute of Technology (Cambridge, MA) — Aug. 1993 – Dec. 1999

Engineer, Safety Analysis Group
Northeast Utilities (Groton, CT) — May 1990 – Aug. 1996

PROFESSIONAL AFFILIATIONS:

American Nuclear Society
Materials Research Society

AWARDS/HONORS:

Honorable mention, U.S. D.O.E OCRWM Fellowship Program., Sept. 1997
Sherman Knapp Fellowship Recipient, Spring 1996
INPO National Academy for Nuclear Training Fellowship, 1993-1994
Illinois Department of Nuclear Safety Fellowship, 1989-1993

PUBLICATIONS

Schmett, G.T., Kimble, G., Steinberg, S.M., Emerson, D.W., and G.S. Cerefice. "Immobilization of Fission Iodine by Reaction with Insoluble Natural Organic Matter". Proceedings from the Eighth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, November 9 – 11, 2004. OECD-NEA.

Hechanova, A.E., and G.S. Cerefice. <u>Establishment of an Advanced Accelerator Applications University Participation Program at the University of Nevada, Las Vegas</u>. Nuclear Applications in the New Millennium, Proceedings from the ANS Winter Meeting, November, 2001.

K.R. Czerwinski, G.S. Cerefice, G. Buckau, J.I. Kim, M-C. Milcent, C. Barbot, and J. Pieri. "Interaction of Europium with Humic Acid Covalently Bound to Silica Beads". Radiochimica Acta 88, 417. 2000.

Cerefice, G.S. <u>Environmental Behavior of Hafnium: the Impact on the Disposition of Weapons-Grade Plutonium</u>. Ph.D. Thesis. Massachusetts Institute of Technology. Cambridge, MA. September, 1999.

Cerefice, G.S, M. Draye, K.L. Noyes, and K. Czerwinski, "Hafnium Hydroxide and Carbonate Complexation: The Impact of Environmental Complexes on the Disposition of Weapons-Grade Plutonium," Scientific Basis for Nuclear Waste Management XX, Proceedings from the MRS Fall Meeting, Dec. 1998.

Cerefice, G.S, K.W. Wenzel, K.W.B. Sylvester, and S. Simonson, "Proliferation Resistance of Borosilicate Glass as a Host Form for Weapons-Grade Plutonium," Scientific Basis for Nuclear Waste Management XX, Proceedings from the MRS Fall Meeting, Dec. 1996.

Cerefice, G.S. Proliferation Resistance of Borosilicate Glass as a Host Form for Weapons-Grade Plutonium. S.M. Thesis. Massachusetts Institute of Technology, Cambridge, MA. June, 1996.

PRESENTATIONS

Cerefice, G.S. "Nevada, Nuclear Waste, and Transmutation." Invited Seminar. Massachusetts Institute of Technology, Department of Nuclear Engineering Seminar Series. Cambridge, MA. 5/13/2002.

Cerefice, G.S. "Nuclear Waste Management Strategies". UNLV Yucca Mountain Education Program Town Hall Meeting Series. Las Vegas, NV. 2/23/2001.

Cerefice, G.S. "Plutonium Oxide Stability: A Response to Recent Media Attention". UNLV Health Physics Society Seminar Series. Las Vegas, NV. 2000.

Cerefice, G.S., M. Draye, K. Noyes, and K. Czerwinski, "Hafnium Hydroxide Complexation and Solubility: The Impact of Hydrolysis Reactions on The Disposition of Weapons-Grade Plutonium," Material Research Society Fall Meeting, Boston, MA, 1998.

Cerefice, G.S., M. Draye, K.L. Noyes, and K. Czerwinksi, "Environmental Behavior of Hafnium for the Disposal of Weapons-Grade Plutonium," Waste Management '98 Symposium, Tucson, AZ, Proceedings, Mar. 1-4, 1998.

Czerwinski, K.R., G.S. Cerefice, G. Buckau, J.I. Kim, M-C. Milcent, C. Fleury and J. Pieri, "Sorption of Europium to Humic Acid Based Resins: The Role of Humic Coating in Sorption," 6th International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Sendia, Japan, Oct. 1997.

Czerwinski, K.R., G.S. Cerefice, M. Draye, and K.L. Noyes, "Determining Complexation Parameters for Hafnium, Lanthanides, and Plutonium for Use in Assessing Plutonium Disposition Options," First Report, Disposition of Weapons Grade Plutonium, Argonne National Laboratory, Oct. 1997.

Cerefice, G.S., K.W. Wenzel, K.W.B. Sylvester, and S. Simonson, "Proliferation Resistance of Borosilicate Glass as a Host Form for Weapons-Grade Plutonium," Material Research Society Fall Meeting, Boston, Dec. 1996.