1-29-2008

# Evaluation of Cs/Sr Waste Form for Long Term Storage and Disposal

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**Project Title: Evaluation of Cs/Sr Waste Form for Long Term Storage and Disposal**

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**AFCI/GNEP Research Area**: Separations (Waste Forms)

**Abstract:**

The goal of this project is to examine the potential long term performance of the proposed aluminosilicate waste/storage form for the isolation and eventual direct disposal of the cesium and strontium separated from recycled nuclear fuel. In the first phase of this work, researchers will investigate the sintering procedure to prepare the drum-like aluminosilicate waste/storage form from the as-received aluminosilicate powder, and then examine the basic physical properties, phase structure and microstructure of the sintered aluminosilicate with /without mixing solution with several ppm Cs/Sr. In the second phase, researchers will evaluate the interaction of the proposed waste form with structural materials proposed for the storage and disposal containers to determine if the materials are compatible with the loaded aluminosilicate waste form. In the third phase of the work, researchers will examine the leach resistance of the aluminosilicate material, with particular attention to the leachability of barium from the synthesized waste form. As a part of this work, researchers will work with researchers at Argonne National Laboratory to compare the performance of synthesized "cold" materials with archived samples of aluminosilicate minerals containing radiocesium ($^{137}$Cs, approximately 40 years old) to examine the impact of transmutation on the ability of the proposed waste form to isolate barium (the decay product of $^{137}$Cs).

**Work Proposed, Goals, and Expected Results:**

The research effort at UNLV will be divided into three subtasks: waste form preparation, materials compatibility and waste form performance. The waste form preparation will study the sintering procedure to obtain the drum-like clay. The microstructures and physical properties of the sintered material as function of sintering temperature and

cooling rate will be examined. The materials compatibility subtask will examine the potential for chemical interactions between the waste form material and proposed structural materials for the disposal container (carbon steel, stainless steel, etc.). The waste form performance task will examine the leach resistance of the waste form, with particular attention to barium retention. The performance subtask will also work with the ANL team to develop the cold analog samples for comparison with the aged $^{137}$Cs-bearing aluminosilicate.

Expected Technical Results:

- Procedure to sinter the drum-like waste form from the as-received powder.
- Evaluation of potential for waste form – container material chemical interactions
- Examination of waste form performance: alteration, leaching/dissolution
- Evaluation of waste form classification: leachability of barium
- Fabrication and characterization of cold analog samples for ANL analysis of archived $^{137}$Cs sample

**Funding Profile:**

| **Fiscal Year (DOE):** | **FY07** | **FY08** | **Total** |
|---|---|---|---|
| Total (K$) | $26 | $98.4 | $90.4 |

**Background and Rationale:**

The current GNEP waste stream management strategy calls for the separation of cesium and strontium from used nuclear fuel in order to minimize the short-term heat loading in the repository facility. It is proposed that the resulting waste stream be converted to an aluminosilicate waste form, stored for decay (approximately 300 years), then disposed as low-level radioactive waste. The goal of the proposed work is to examine two potential concerns regarding the long-term performance of this proposed cesium/strontium waste form.

The first aspect of the project will investigate the procedure to sinter the drum-like aluminosilicate waste form from as-received commercial aluminosilicate powder. The effects of sintering temperature and cooling rate on the structure and physical properties of waste form will be examined.

The second aspect of the project will explore the potential interaction of the aluminosilicate waste form with the storage canister materials to determine if there is any corrosion or chemical interaction concerns for the storage of the materials.

The third aspect of the project will examine how barium is retained by the aluminosilicate waste form. Barium is a RCRA constituent (Resource Conservation and Recovery Act [40CFR 239 – 299]), which could require that the resulting waste stream be classified as a chemically hazardous waste form, resulting in a mixed waste stream. Barium will be present in the waste form from two distinctly different sources: the initial waste stream (nascent) and the decay of cesium (transmutation). Barium present in the initial waste stream is expected to be incorporated into the aluminosilicate waste form in the same chemical environment as the strontium. Cesium, however, is monovalent and will not occupy the same chemical position within the waste as the strontium. As the cesium decays to barium, it is uncertain what chemical environment that barium will occupy, which brings into question the ability of the waste form to isolate the barium produced by the radioactive decay of the cesium. If the resulting barium is not sufficiently isolated within the resulting waste form, it will become necessary to reprocess the waste form prior to disposal.

**Research Objectives:**

- To investigate the sintering procedure of aluminosilicate waste form
- To evaluate the potential for waste form – container material interactions
- To evaluate the pre- and post-decay performance of the waste form
    - Barium leachability
    - Effect of transmutation on long-term performance

**Technical Impact:**

The proposed work will identify the sintering procedure of the drum-like aluminosilicate waste form. Also the proposed work will complete the waste form – container material compatibility studies for the proposed aluminosilicate waste form. The work will also examine the performance of the pre-decay or 'as-fabricated' material for the retention of the radionuclides and barium. Researchers will also prepare the cold samples for comparison with the $^{137}Cs$-loaded hot sample from Argonne National Laboratory, and will participate in the experiment design and analysis of the hot sample at ANL. The results of the project will provide the national project with the information necessary to evaluate the efficacy of the proposed waste form for the storage, decay, and disposal of the cesium/strontium waste stream from the recycling of nuclear fuel.

**Research Approach:**

The research effort at UNLV will be divided into three subtasks: waste form preparation, materials compatibility and waste form performance. The waste form preparation will study the sintering procedure to obtain the drum-like clay. The microstructures and physical properties of the sintered material as function of sintering temperature and cooling rate will be examined. The materials compatibility subtask will examine the potential for chemical interactions between the waste form material and proposed structural materials for the disposal container (carbon steel, stainless steel, etc.). The waste form performance task will examine the leach resistance of the waste form,

with particular attention to barium retention. The performance subtask will also work with the ANL team to develop the cold analog samples for comparison with the aged $^{137}$Cs-bearing aluminosilicate.

To study the effects of sintering temperature and cooling procedure on the microstructure and physical properties of drum-like aluminosilicate waste form, different sintering temperatures and cooling rates will be employed to fabricate the aluminosilicate clay mixed with Cs/Sr. The phase structure and location of Cs/Sr will be examined using microscopy and spectroscopy methods. Morphology of the sintered clay, phase constitute, and element distribution will be examined.

To examine the potential for waste form-storage materials interactions, coupons of container materials will be contacted with the Cs/Sr-loaded aluminosilicate waste form material. These coupons will be exposed at fixed temperatures (currently planned at 25 °C, 90 °C, and 200 °C) for up to 6 months. The samples will be analyzed for weight loss as well as structural changes to determine if any material-material interactions would be expected for this waste form.

The performance of the waste form will be evaluated using the Toxic Constituent Leaching Protocol (TCLP), established by the EPA as a standard analysis to determine if a material requires disposal as a hazardous waste. The resistance of the waste form to leaching will be examined following the TCLP, with a particular focus on barium retention. Standard dissolution/leaching tests (e.g. MCC-1) will also be performed for comparison. To evaluate the impact of radiologically produced barium in the waste form, an archived sample of $^{137}$Cs-bearing aluminosilicate material from ANL will be used to examine the chemical environment of the barium (pending funding for the ANL team, as well as access to the beam line at the Advanced Photon Source – expected FY08). Analog cold samples will be prepared at UNLV for comparison and baseline measurements, and experimental protocols will be evaluated with the cold samples to evaluate the feasibility of performing leach testing on the hot, archived sample.

**Expected Technical Results:**

- Procedure to prepare the drum-like aluminosilicate waste form with/without Cs/Sr-loaded
- Evaluation of potential for waste form – container material chemical interactions
- Examination of waste form performance: alteration, leaching/dissolution
- Evaluation of waste form classification: leachability of barium
- Fabrication and characterization of cold analog samples for ANL analysis of archived $^{137}$Cs sample

**Capabilities at the University and Argonne National Laboratory:**

The University has the laboratory space, furnaces, ovens, and analytical equipment necessary to support the experimental work proposed in this project, including the scanning electron microscopy and microprobe system required for the evaluation of the material-waste form interactions. The University also has a transmission electron microscopy capability which may prove vital to understanding the effect of transmutation due to decay on the incorporation of barium into the aluminosilicate matrix. The work with the 137Cs-bearing sample will be performed in the facilities at Argonne National Laboratory, as well as the XAFS spectroscopy work (pending support from the national program for the ANL budget).

**Project Timeline:**

Timeline Narrative

The proposed research is planned to cover 18 months, starting Spring 2008 with a project kick-off meeting at UNLV. Firstly, the procedure to sinter the target waste package materials will be identified. The microstructure and phase constitute of sintered aluminosilicate with addition of Cs/Sr will be examined and evaluated. In 2007, the tested coupons of $\alpha$-steel and stainless steels have been prepared. These coupons will then be used to start the long-term waste form – container material interaction studies, with the longest duration experiments following the identification of the sintering procedure. Following these exposures, samples will be prepared for weight loss and microscopic analysis to determine what, if any, interactions have occurred. The leaching and waste form performance testing will be performed in parallel. In collaboration with the Argonne Team, researchers will design the experiment plan for the analysis of the 137Cs-bearing aluminosilicate archive sample. The UNLV team will

then prepare the cold analogs and baseline samples for these experiments, as well as test any protocols necessary for the hot sample experiments (which will be performed at Argonne in their hot cells).

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)
M.S. in Nuclear Engineering, June 1996.

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

**PROFESSIONAL EXPERIENCE**

**University of Nevada, Las Vegas** (Las Vegas, NV) **Jan. 2000 – Current**
Assistant Research Professor, Harry Reid Center for Environmental Studies (1/00 – Current)
Deputy Director, UNLV Transmutation Research Program (3/01 – Current)

**Northeast Utilities** (Groton, CT) **May 1996 – Aug. 1996**
Engineering Intern, Safety Analysis Group

**Massachusetts Institute of Technology** (Cambridge, MA) **Jan. 1995 – Dec. 1999**
Post-Doctoral Research Assistant (9/99 – 12/99)
Research Assistant, Nuclear Engineering (1/95 – 8/99)
Teaching Assistant, Nuclear Engineering (8/93 – 12/94)

**AREAS OF INTERESTS**

Radioactive Waste Management (HLW, LLW): Technology, Science, and related Policy Issues
Nuclear Fuel Cycle: Fuel processing, actinide recycle, transmutation strategies and technology
Waste Form Engineering
Radioactive Contaminant Behavior and Transport in the Environment
Actinide and Radionuclide Chemistry: Kinetics, Thermodynamics, Engineering Applications
Interaction of Technology and Policy/Regulation in the Nuclear Fuel Cycle

**CURRENT RESEARCH ACTIVITIES**

Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process. This project examines the determination of actinide element concentrations under process conditions using optical spectroscopy techniques (UV-Visible Spectroscopy, Time Resolved Laser Fluorescence Spectroscopy) to evaluate the potential of deploying these techniques for on-line materials accountability applications.

Synthesis of Actinide Nitride Fuels via Ammonia Reduction Process. This project is developing and examining a novel process for the synthesis of nitride fuels for fast reactor applications.

Emanation of Radon from Thorium-Bearing Waste Forms. This project examines the release of radon from thorium waste forms planned for disposal at the Nevada Test Site. Work will also investigate select Uranium-bearing waste forms and diffusion of radon through soil.

Incorporation of Actinide and Fission Product Elements in Vitrified Waste Forms. This project examines a number of vitrified waste forms of interest for DOE-EM activities, including the simulation of melt glass for the underground test area at the Nevada Test Site. Work will also examine the release of these elements from the host matrix.

**PROFESSIONAL AFFILIATIONS**

American Nuclear Society
Materials Research Society

**ADDITIONAL ACTIVITIES/AWARDS/HONORS**

Affiliated Faculty Status, UNLV: Radiochemistry, Chemistry, Water Resource Management
Reviewer, DOE – NEER: 2005, 2006
Reviewer, ANS Nuclear Technology: 2004
Reviewer, Department of State ISTC Proposals: 2002, 2003
Reviewer, HPS Health Physics Journal: 2001, 2002
Honorable mention, U.S. D.O.E OCRWM Fellowship Program., Sept. 1997
Alpha Nu Sigma, Member
Sherman Knapp Fellowship Recipient, Spring 1996
INPO National Academy for Nuclear Training Fellowship, 1993-1994
Illinois Department of Nuclear Safety Fellowship, 1989-1993

**PATENTS**

Low Temperature Route to Uranium Nitride. Burrell, A.K., Sattelberger, A.P., Yeamans, C., Cerefice, G.S., Czerwinski, K.R., Hartmann, T. Patent Pending.

**PUBLICATIONS**

Smith, N.A., Cerefice, G.S., and K.R. Czerwinski. "Application of Optical Techniques for On-Line Materials Accountability in the UREX Solvent Extraction Process". *Proceedings from the 47th Annual Institute For Nuclear Materials Management Annual Meeting*. July 16 – 20th, 2006.

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. November, 2004. OECD-NEA.

Hechanova, A.E., and G.S. Cerefice. Establishment of an Advanced Accelerator Applications University Participation Program at the University of Nevada, Las Vegas. *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. Environmental Behavior of Hafnium: the Impact on the Disposition of Weapons-Grade Plutonium. 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, "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/CONFERENCES**

Smith, N.A., Cerefice, G.S., and K.R. Czerwinski. "Application of Optical Techniques for On-Line Materials Accountability in the UREX Solvent Extraction Process". 47th Annual Institute For Nuclear Materials Management Annual Meeting. Nashville, TN. July 20th, 2006.

Yeamans, C., Cerefice, G. S, Czerwinski, K. R., Sattelberger, A. "Carbon-Free, Low Temperature Synthesis of Uranium Nitride". European Materials Research Society Spring Meeting, Nice, France. June 2, 2006.

Smith, N. A., Cerefice, G. S., Czerwinski, K. R. "Optical techniques for improved materials accountability in the UREX+ process." American Chemical Society National Meeting, Atlanta, Georgia, March 30, 2006.

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.