APPENDIX K
UNDER IMPLEMENTING ARRANGEMENT #1
OF THE
MEMORANDUM OF UNDERSTANDING BETWEEN
THE U.S. DEPARTMENT OF ENERGY AND RUSSIAN ACADEMY OF SCIENCES ON COOPERATION
IN SCIENCE AND TECHNOLOGY

ACTINIDE SCIENCE RELEVANT TO THE ENVIRONMENT, RADIOACTIVE WASTE MANAGEMENT, AND MIGRATION BEHAVIOR OF ACTINIDES AND FISSION PRODUCTS IN THE GEOSPHERE

This Appendix has as its aim the practical implementation of Implementing Arrangement #1 of the Memorandum of Understanding Between the U.S. Department of Energy and Russian Academy of Sciences on Cooperation in Science and Technology. It is the purpose of this Appendix to provide funding for each of the six research proposals attached as Annexes to this Appendix.

The Parties shall ensure adequate and effective protection of intellectual property created or furnished under this Appendix in accordance with Annex II of the Science and Technology Agreement signed on December 16, 1993. The Parties agree to notify one another in a timely fashion of all intellectual property created and the results of scientific and technical work obtained under this Agreement and to seek protection for such intellectual property in a timely fashion.

Background:
An Actinide Workshop entitled "Actinide Science Relevant to the Environment, Radioactive Waste Management, and Migration Behavior of Actinides and Fission Products in the Geosphere," was held on May 15-16, 2000 at the Russian Academy of Sciences in Moscow. This workshop was set up at the behest of the Joint Coordinating Committee on Science and Technology Cooperation (JCC) of the DOE/RAS MOU. As a result of that meeting, six proposals were received by the Department of Energy in response to the announcement that funding was available for collaborative basic research programs between scientists at one or more Russian Academy of Sciences (RAS) Institutions and American investigators at Universities or national laboratories in the area of actinide and fission product chemistry.

The attached Annexes describe research plans designed to provide a better understanding of; 1) the chemistry of plutonium at the mineral/water interface; 2) the development and characterization of waste forms for the immobilization of fission products & actinides; 3) the study of plutonium, neptunium and technetium behavior in the presence of silicates; 4) investigation of non-equilibrium oscillatory metal extraction methods; 5) equilibrium and kinetic studies of heterogeneous reactions of actinides hydroxide compounds in alkaline media; and 6) utilization of room temperature ionic liquids and low temperature molten salts to elucidate gallium oxychloride equilibrium in high temperature chloride melts.

Objectives:

Objective #1: Develop a fundamental understanding of the chemistry that controls plutonium (Pu) sorption or partitioning at the mineral/water interface.

To develop a fundamental understanding of the chemistry that controls plutonium (Pu) sorption or partitioning at the mineral/water interface by exploring the chemical mechanism(s) of Pu sorption to various oxide surfaces. The intention is to provide a molecular level description of the sorption process(es), along with thermodynamic data that will enable predictive modeling of Pu speciation and partitioning in an environmental system. Additionally, the research will also explore kinetic limitations for the data and systems under study.

The objectives of this Proposal are:

1. Provide fundamental information on the important chemical processes (both thermodynamic and kinetic) involved in the sorption of Pu to various environmental phases. This information is necessary to develop an understanding of the chemistry of Pu at the mineral/water interface.

2. Provide fundamental data on relevant equilibria (reactions and accompanying equilibrium constants) that describe the chemistry of plutonium partitioning at the mineral/water interface for important environmental substrates. This information is essential for improvements to modeling applications designed to predict plutonium fate and transport.

3. Apply the information obtained from Objectives 1 and 2 to actual contaminated soils and sediments from Russia and US Department of Energy (DOE) sites to predict the mechanism(s) of Pu partitioning in actual systems. Determine the mechanism(s) of sorption in contaminated soils/sediments from Russia and the US using various analytical approaches to validate the conceptual models developed from Objectives 1-3.

The information generated as a result of the proposed work will provide a foundation for describing Pu sorption or partitioning to important environmental substrates. This knowledge is necessary to understand and predict the chemistry of Pu sorption to colloidal material, and the chemistry of Pu partitioning to the geochemical phases found in soils and sediments. Consequently, with the foundation created in this research effort, both US and Russian environmental scientists who must prioritize clean-up efforts for radioactively contaminated sites will be able to rely on characterization tools such as chemical sequential extractions and reactive transport modeling to predict risks imposed by Pu environmental contamination. Such a foundation is also necessary for developing safe, cost-effective, and reliable remediation strategies for plutonium contaminated sites.

Objective #2: Development and Characterization of Waste Forms for the Immobilization of Fission Products and Actinides

Understand in detail the structure of phases potentially suitable for actinide and fission product immobilization, waste element speciation in these phases, and crystal chemical constraints for waste element incorporation into the structure of these phases and the radiation stability of candidate waste form phases.

Objective #3: Study of Plutonium, Neptunium and Technetium Behavior in the Presence of Silicates and Aluminosilicates in Aqueous Media.

The systematic study of; complexation of plutonium, neptunium, and technetium in different valent forms with the silicate ion in aqueous solutions; and preparation and investigation of plutonium, neptunium, and technetium solid silicate and aluminosilicate compounds. Based on this research, conditions necessary for the existence of particular solid phases, and the stability in solution of Pu (IV,V, VI), Np (V,VI), and Tc (IV, VII) silicate complexes, over a wide pH interval will be determined. The preparation and investigation of solid silicate and aluminosilicate compounds of Pu, Np, and Tc to be performed can then be used to constitute the basis for predicting the radioelement behavior in silicate structural materials, silicate-based waste forms, and natural minerals as encountered in D&D, waste disposal, and waste site remediation operations in the defense related nuclear processing and disposal sites both in the US and in Russia.

Objective #4: Investigation of non-equilibrium oscillatory metal extraction methods – new processes for the isotopic separation of metal ions, driven by oscillating electro-chemical reactions

To determine the kinetic extraction mechanism for the cerium catalyst of the B-Z oscillatory extraction system and to find optimal conditions for the separation of praseodymium and neodymium and isotopes of neodymium. This will involve determining their kinetic and extraction constants, elucidating how kinetic differences between the elements or isotopes affect the separation, and making adequate mathematical models of the oscillatory extraction systems. The information gained by these studies will be used for the development of improved separation technologies and a better understanding of complicated chemical heterogeneous systems. If so, the technique could extended to other elements of commercial interest.

Objective #5: Equilibrium and Kinetic Studies of Heterogeneous Reactions of Actinides Hydroxide Compounds In Alkaline Media.

- Study the composition and properties of Am (III-VI) and Pu (V-VII) solutions and compounds formed in alkaline media using structure-specific probes successfully employed for TRU speciation in alkaline media, including Raman, multinuclear magnetic resonance (NMR), X-ray absorption fine structure (XAFS), luminescence, optical absorption (UV-Vis-conventional and Photoacoustic) spectroscopes. The exact species of americium in basic solution in the solid state have not been identified.

- Investigation of the heterogeneous interaction of dissolved AM(V), (VI) and Am(III), (IV) precipitates in alkaline solutions and in solid phases, and calculation of Am(III)/Am(IV) and Am(IV)/Am(V) redox couples in the range of 0.1-10 M NaOH. Studies will include thermodynamic, kinetics, spectroscopy and electrochemistry.

- Investigation of the disproportionate reactions of Pu(VI), and redox reactions of Pu(VII) in concentrated alkaline solution.

Objective #6: Utilization of Room Temperature Ionic Liquids and Low Temperature Molten Salts to Elucidate Gallium Oxy-Chloride Equilibrium in High Temperature Chloride Melts.

Characterization of gallium oxy-chloride equilibria in high temperature molten salt systems is critical to optimizing the efficiency of the process for conversion of weapons grade plutonium to MOX fuel. Due to inherent difficulties associated with studying chemical reactions at high temperatures, >760C, the proposal is to study this complex system at ambient temperature using newly developed room temperature ionic liquids and at intermediate temperatures using low melting aluminum chloride based melts. Standard spectroscopic, dynamic electrochemical and potentiometric methods of analysis as well as mass spectrometry will be used to characterize the equilibria. Information gathered at lower temperatures can be extrapolated to higher temperatures and will be verified by potentiometric measurements carried out under typical process conditions.

Benefit to DOE:
These are important research topics to DOE that will enable us to have a better understanding of the nature and behavior of fission products and actinides. This understanding will be very important for our domestic programs regarding geologic repository science and environmental restoration and waste management technologies.

Workscope:
The attached Annexes outline workscopes for each individual research proposal.

Duration:
3 years.

Expected Results:
The attached Annexes outline the expected results for each individual research proposal.

Laboratory Tasks:
The attached Annexes outline Laboratory tasks for each individual research proposal.

Effort and Schedule:
The attached Annexes and later documents outline the effort and schedule for each individual research proposal.

Project Funding:
The budget outlined in each Annex is subject to change, but will not exceed $80,000 per annum. It is the intention of the Department of Energy to maintain the $80,000 funding level for each Annex in the second and third years provided that such funds are available and progress has been satisfactory.

Personnel:
Personnel from the Institutes of the Russian Academy of Sciences and other scientific institutions, as determined to be appropriate by consultation between the Parties, will be identified during the detailed planning process.

Proposed Period of Performance and Payment Schedule:
Refer to the attached research proposals and subsequent documentation for the proposed period of performance and payment schedule.

James F. Decker 4/26/01
James F. Decker Date
Acting Director, Office of Science
US Department of Energy

Лаверов 26/04/01
Academician Laverov Date
Vice President
Russian Academy of Sciences