APPENDIX L
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 (MoU) between the U.S. Department of Energy and Russian Academy of Sciences on Cooperation in Science and Technology, as renewed on December 2, 2003. It is the purpose of this Appendix to provide funding for each of the seven research proposals that are described in this Appendix. All projects undertaken as part of this Appendix shall be done in accordance with the Intellectual Property provision outlined in Article V of the MoU. Total funding for the seven proposals will be $480,000 per year for three years subject to the availability of appropriated funds.

Background:
An Actinide Workshop entitled "Actinide Chemistry and Related Topics" was held on September 11-12, 2003 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, eleven proposals were received by the Department of Energy in response to the announcement that funding was available for renewed or new 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 eleven proposals were reviewed in accordance with the policies of the DOE Office of Science. Seven of the eleven proposals were approved because they describe work of high scientific interest that is relevant to applied actinide chemistry problems of both the United States and the Russian Federation. The seven selected proposals are outlined below.

Awards:

Proposal #1: *The Chemistry of Plutonium at the Mineral:Water Interface: Role of Organic Substances to Plutonium Sorption to Model Oxides and Contaminated Soils and Sediments (renewal of 2001-2004 project)*
Principal Investigators: Dr. Stepan N. Kalmykov, Radiochemistry Division, Chemistry Department, Lomonosov Moscow State University, Moscow, Russia; Dr. Alexandre Novikov, Senior Researcher, Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia.
US Collaborator: Prof. Sue B. Clark, Chemistry Department, Washington State University, Pullman, WA.

This proposal will continue 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 environmental systems. Additionally, the research will explore kinetic limitations for the data and systems under study. This information is necessary to develop an understanding of the chemistry of Pu at the mineral/water interface and to model the transport of plutonium. The project will apply the information to actual contaminated soils and sediments from Russian and US DOE sites to predict the mechanisms of Pu partitioning in actual systems. Such a foundation is also necessary for developing safe, cost-effective, and reliable remediation strategies for plutonium contaminated sites.

Proposal #2: *Experimental Studies and Theoretical Modeling of Actinides and REEs Speciation in Solid Phases: Application for Actinide Waste Forms and U-free, Non-Fertile Fuel Development (renewal of 2001-2004 project)*
Principal Investigators: S. Yudintsev (IGEM, RAS), S. Stefanovsky (Scientific and Industrial Association "Radon") Yu. Kulyako (Vernadsky Institute, RAS). US collaborators: Rodney Ewing (University of Michigan); Richard G. Haire (ORNL).

Development of techniques and approaches for the safe management of weapon- and reactor related radioactive wastes requires an understanding of actinide chemistry and radiation damage in the solid state. The first goal of this research program will be to continue the selection, synthesis, and characterization of solid phases suitable for the safe long-term storage of transuranic actinides (neptunium, plutonium, americium, curium). The behavior of these actinides will be examined together with fission products. The second goal of this proposal is to investigate materials that may be used as matrices for uranium-free nuclear fuels, which will allow the "burning" of actinides and reduce the radiotoxicity of these radionuclides. This work will also support the development of new processing required in advanced fuel cycles. Experiments will be performed to produce materials doped with actinide and light rare earth elements, which will be followed by characterization using modern spectroscopic methods to determine:

- Content and homogeneity of distribution of the elements within the solid phases;
- Actinide solubility limits in the crystalline lattices of the host phases;
- Structural features of the phases doped with actinides and the relationships between crystal structure and composition;
- Radiation damage of the solid phase under irradiation by accelerated heavy ions and by α-decay from incorporated short-lived actinides;
- Corrosion of the actinide-REE host phases under hydrothermal conditions and after interaction with hot aqueous solutions;
- Optimal routes for industrial fabrication of the actinide-loaded phases.

Theoretical modeling of metal speciation in the solid phases will be pursued in order to predict the stability of the crystalline lattices with different types of atomic substitutions.

Proposal #3: *Fundamental Investigation of Oscillatory Metal Extraction Driven by External Periodical Disturbance to Separate Similar Elements or Isotopes (renewal of 2001-2004 project)*
Principal Investigators: Mikhal A. Afonin and Alexei A. Kopyrin, St. Petersburg State Institute of Technology. US Collaborator: Kenton Moody, LLNL.

This proposal will 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 chemically similar lanthanides and actinides and certain isotopes of these elements. The project will determine kinetic and extraction constants, elucidating how kinetic differences between the elements or isotopes affect the separation, and will make 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 be extended to other elements of commercial interest.

Proposal #4: *The Study of Chemical Behavior of Actinides in Heterogeneous Alkaline Media Containing Rare-earth and Transition Elements for Isolation and Separation of U, Np, Pu, and Am from High Level Waste (renewal of 2001-2004 project)*
Principal Investigators: B. Myasoedov, Dr. I. Tananaev (Vernadsky Institute, RAS). US collaborator: David L. Clark (LANL).

Waste tanks contains a wide variety of oxidizing agents of oxidizing actinide elements to these higher oxidation states under alkaline conditions. Chemical properties of americium and plutonium compounds and their behavior in alkaline media were studied during the first three years of this project. It was shown that the actinides in higher oxidation states (V, VI, and even VII) that are highly soluble in alkaline solutions (especially in the presence of complexing agents) may have enhanced stability under highly alkaline conditions. New separation methods of minor actinides and transition/rear-earth elements were developed, based on stabilization of actinides at high oxidation states. On the other hand, appropriate conditions were found in which Pu and Am can stabilize in a relatively insoluble form for their precipitation.

The project will continue the study of the composition and properties of americium and plutonium solutions and compounds formed in alkaline media using structure-specific probes successfully employed for transuranim element speciation in alkaline media.. The exact species of americium in basic solution in the solid state will be identified. Studies will include thermodynamic, kinetics, spectroscopy and electrochemistry. The project will investigate the oxidation-reduction reactions of plutonium in concentrated alkaline solution.

Proposal #5: *: Investigation and Modeling of the Fundamental Interactions of Actinides with Customized Humic Substances at both the Molecular and Colloidal Levels (new project)*
Principal Investigator: Irina V. Perminova, Department of Chemistry, Lomonosov Moscow State University. US collaborator: Richard G. Haire (ORNL).

This proposal addresses the fundamental interactions between actinides and humic substances. Humic substances are decomposition products of living organisms and may be encountered naturally as solids, soluble or colloidal forms. They play critical roles in the migration of actinides in various environmental conditions. The investigators will design and prepare special humic substances that will afford important controls not possible with the widely varying properties of their naturally occurring counterparts. They will model the chemical reactions between actinides and humics. The major objective will be to establish relationships between specific molecular features of humic substances and their reactions with of actinides of interest in several oxidation states (i.e., U through Am, with special focus on Np and Pu).

The research will probe the interactions between these actinides and a comprehensive group of well-characterized "designer" humic substances. Extensive modifications will be used to produce these customized materials. Innovative treatments will be performed to specifically modify the humic substances to address remediation needs. Attaching these modified humic substances to non-mobile substrates (i.e., clays, sand) can also provide "adhesive" sites for non-reversible immobilization of the actinides. The humic colloids produced will be used to probe for interfacial reactions between the sites and actinides.

This proposed quantitative structure-property approach should establish key aspects of structure and property relationships of interactions of humic substances with actinides, as well as a mechanistic understanding of the molecular reactions governing the parameters of the interactions. These approaches will advance both the basic understanding of the complex chemistries and the insights for modeling and simulating the geochemical systems in which actinides migrate in humic-rich environments. While the proposed work is focused on fundamental science of these systems, the information generated will promote the advancement of technological applications of humic materials and will suggest efficient approaches for controlling and understanding actinide migration in the environment.

Proposal #6: *Corrosion of Irradiated Uranium Alloy Fuels in Water (new project)*
Principal Investigators: V. Peretrukhine, A. Maslennikov, K. Guerman (Institute of Physical Chemistry, RAS). US collaborator: Calvin Delegard (PNNL).

Metallic uranium and alloys of uranium have been used as nuclear fuel and are stored in many places as spent nuclear fuel. The objectives are to determine the mechanisms of the corrosion of uranium metal and its fuel alloys in water and aqueous solutions. Alloys of uranium with aluminum, zirconium, molybdenum, and niobium will be chosen for the study as models of metallic fuels employed in different types of nuclear reactors. Special attention will be paid to the corrosion behavior of uranium alloys prepared to simulate irradiated uranium alloy fuel by containing fission product elements (e.g., technetium and ruthenium).

The corrosion mechanism and kinetics of uranium alloys simulating irradiated uranium metal fuel will be studied by electrochemical and hydrothermal methods. The results of the study will provide information on the corrosion rates and uranium mineral-forming reactions occurring in long-term underwater storage of uranium alloy fuel such as sludge at the Hanford Site, in spent fuel pools, and in geologic repositories.

Proposal #7: *Development of New Methods of Recognition and Separation of Actinide and Lanthanide Elements using Novel Macrocycle Ligands and Extraction Techniques (new project)*
Principal Investigators: I. Antipin, A. Konovalov (Arbuzov Institute of Organic and Physical Chemistry, Kazan State University, Kazan, RAS); B. Myasoedov, A. Tsivadse (Institute of Physical Chemistry, Moscow, RAS). US collaborator: Kenneth L. Nash (Washington State University).

Radionuclide recognition is an important research topic from environmental, analytical and industrial points of view. The research features host-guest chemistry with construction of high selective receptors for different metal ions: the "host" is a large molecule that complexes a metallic "guest." Large basket-shaped complexant molecules called calixarenes occupy an important position in host-guest chemistry due to their ability to act as selective complexing agents, carriers, catalysts and potential biomimics. The selectivity of calixarenes is provided by the cooperative multi-component binding of metal ions via pre-organized electron donor groups on the rim of the basket cavity.

The characteristic advantages of the calixarenes are low cost; accessibility of the parent molecules in a one-pot synthesis; easy functionalization by replacement of one atom with another; the existence of a variety of conformations that are rather rigid and are able to offer the required spatial orientation of the preorganized binding sites; incorporation of small water-bonding organic molecules into their molecular cavities forming stable host-guest complexes; and nontoxicity.

The goal of the project is to enhance lanthanide/actinide selectivity of extraction and recognition by formation of metal complexes with two different calixarenes. Calixarene derivatives are planned to selectively bind metal ions via inner-sphere and outer-sphere coordination, thus enhancing the extractability of the latter.

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. They will create new tools for safe disposal of nuclear waste and for controlling the migration of radioisotopes in the environment. This understanding and these tools will be very important for our domestic programs regarding geologic repository science and environmental restoration and waste management technologies.

Duration:
3 years.

Expected Results:
The above proposal descriptions outline the expected results for each individual research proposal

Laboratory Tasks:
The above proposal descriptions outline Laboratory tasks for each individual research proposal

Effort and Schedule:
The proposal descriptions and the full proposals outline the effort and schedule for each individual research proposal

Project Funding:
The budget outlined for each project is subject to change, but will not exceed $80,000 per annum, including administrative fees. It is the intention of the Department of Energy to maintain the same 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. Each project will have one or more US technical contact who

is an experienced actinide scientist from a university or national laboratory, and who will interact with the RAS project leaders by reviewing planned research and research reports.

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

Renewal and Amendment:
This Appendix can be renewed or amended to include additional proposals by written agreement of the parties.

Raymond L. Orbach 3/17/04
For the US Department of Energy Date

03/17/04
For the Russian Academy of Sciences Date