

Solution-Based Synthesis of Nitride Fuels

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1. Project Summary

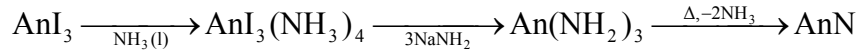
A wide variety of fuel concepts are considered for advanced reactor technology including metals, metal oxides or metal nitrides as solid solutions or composite materials. Nitride fuels have appropriate properties for advanced fuels including high thermal conductivity, thermal stability, solid-state solubility of actinides, fissile metal density, and suitable neutronic properties. A drawback of nitride fuels involves their synthesis. A key parameter for preparing oxide fuels is the precipitation step in the sol-gel process. For nitride fuels, the current synthetic route is carbothermic reduction from the oxide to the nitride. This process step is based on solid phase reactions and for nitride fuel involves a stepwise process from the metal oxide, to the carbide, and finally the nitride. This high temperature, solid-phase approach is plagued by impurities in the final nitride product and difficulties in the synthesis and fabrication steps. If the nitride could be synthesized directly by a solution route then the impurities and other synthetic problems could be eliminated or at least minimized. The proposed solution route to nitride would also have the added benefit of providing several adjustable parameters that would allow control of the properties of the final solid product (fuel).

The objective of the proposed project is to develop solution phase synthetic routes for actinide nitrides for use in nuclear fuels. In the 1970s, a proposed synthesis for actinide nitrides was proposed based on the reaction of plutonium triiodide (PuI_3) and uranium

tetraiodide (U₄I₄) with sodium metal in liquid ammonia giving PuN and UN, respectively, as the reaction products. More recent work by the LANL collaborators investigated amido reactions in non-aqueous solvents where the reaction is:



From this result, a plausible route for the synthesis of nitride fuels is:



where An is uranium, neptunium, plutonium or americium.

To achieve the solution synthesis of actinide nitrides the fundamental chemical coordination and speciation involved in the above reaction will be examined. The reaction will be performed with all the actinides listed. The non-aqueous synthetic route based on amido chemistry potentially provides property control over the nitride product similar to the sol-gel methods for actinide oxides. The resulting nitride product should be free of the impurities inherent in the carbothermic reduction technique. The experiments will be performed by a joint research team from UNLV and LANL, with actinide experiments performed at both laboratories and special emphasis on student participation in the project research. This collaboration will be strongly facilitated by the presence of LANL team member Al Sattelberger at UNLV as a visiting professor. The UNLV participants are already involved in actinide chemistry studies including the synthesis and characterization actinide-containing fuels. The LANL participants are experts in synthetic actinide chemistry including non-aqueous chemistry and materials science. The team members will collaborate in the education of graduate students and post-doctoral researchers. In addition to developing novel routes for the direct synthesis of nitride fuels, the project will also help train the next generation of radiochemists and actinide scientists with expertise in research areas crucial to the DOE and the country.

2. Project Narrative

2.1. Project Objectives

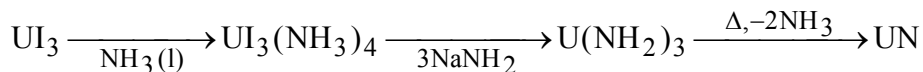
Nitride fuels are the proposed fuel matrix for a number of advanced reactor designs and are an attractive option for the transmutation of Pu and other minor actinides in advanced reactors. The current synthesis route for actinide nitrides involves the conversion of actinide oxides to carbides and finally nitrides. Unfortunately, the synthesis can carry significant levels of impurities into the final products as shown in the reaction below:



The presence of these impurities limits the utility of nitride fuels in advanced fuel cycles. The presence of oxygen and other impurities in nitride fuels can lead to the formation of phases with different properties from the bulk material including the formation of

secondary phases [1]. Oxygen present in the nitride can form oxides with fission products, altering the expected behavior of the fission products. This limits the ability to fully develop nitride fuels for advanced reactors. Even small amount of oxygen in the nitride fuel can reduce thermal conductivity by 10 % [2]. To avoid the entrainment of carbides and oxides in the final actinide nitride product a non-aqueous solution phase route is proposed.

The objective of the project is to investigate and develop a solution based synthetic route for actinide nitrides. A non-aqueous solution route for the synthesis of plutonium nitride (PuN) has been described that involves the reaction of plutonium triiodide (PuI₃) with sodium metal in liquid ammonia [3, 4, 5]. More recent efforts by proposal team members at LANL have investigated amido reactions with actinides to produce An(NR₂)₃ complexes [6,7,8], where An = U, Np, Pu. These results suggest that the amido complexes could provide a non-aqueous solution method for the synthesis of nitrides. As an example, UN can be synthesized based on the following reaction scheme:



This scheme should also be applicable for the preparation of nitrides of Np, Pu and Am. In addition to the formation of pure UN, the solution synthesis should provide control of particle size and other physical properties similar to those observed in actinide oxides when using sol-gel methods.

The objectives will be realized through a collaborative experimental project between UNLV and LANL with actinide experiments performed at both laboratories. The emphasis at UNLV will be scoping experiments with uranium. The LANL effort will focus on the later actinides starting with neptunium. However, experiments with Np will also be performed at UNLV. The PI has previously performed synthesis involving milligram quantities of Np in a university setting. The fundamental coordination chemistry and speciation in the amido synthesis will be evaluated using different spectroscopic methods. Nitride formation from the amido species will be systematically examined to determine key parameters for the product synthesis. The final product will be investigated with microscopic and X-ray methods already employed by the UNLV partner in the evaluation of fuels, including nitrides. The project results can be compared with existing methods of nitride fuel synthesis that are performed at Los Alamos for the AFCI program.

In addition to the research within the project, the team members will collaborate in educational efforts. Members of the LANL team will participate as mentors and instructors for undergraduate and graduate students, and post-doctoral researchers from UNLV. Furthermore, the young researchers from UNLV will have opportunities to perform research at LANL, helping train the next generation of radiochemists and actinide scientists with experience in DOE laboratories and an understanding of DOE and national needs.

2.2. Background

2.2.1. Nitride Fuels

At present, a wide variety of fuel concepts are under consideration for the advanced fuel cycle. The fundamental compositions include metals, oxides and nitrides. These can be in form of solid solutions or composition material. The compositions comprise CERCER (ceramic-ceramic), CERMET (ceramic-metal) or METMET (metal-metal). Nitrides are considered as potential fuels since they have high solid phase solubilities for the early actinides and excellent thermal characteristics. A comparison of properties for the oxide, carbide, and nitride of a mixed uranium and plutonium composition are provided below [9]. Of the ceramic fuel matrices, the nitride fuels have the highest theoretical density, metal density, and melting point. The metal fraction of the nitride is only slightly lower than the carbide. The thermal conductivity is slightly lower than the carbide but significantly higher than the oxide. These data indicate the suitability of nitrides as fuels.

Table 1. Comparison on actinide oxide, carbide, and nitride properties

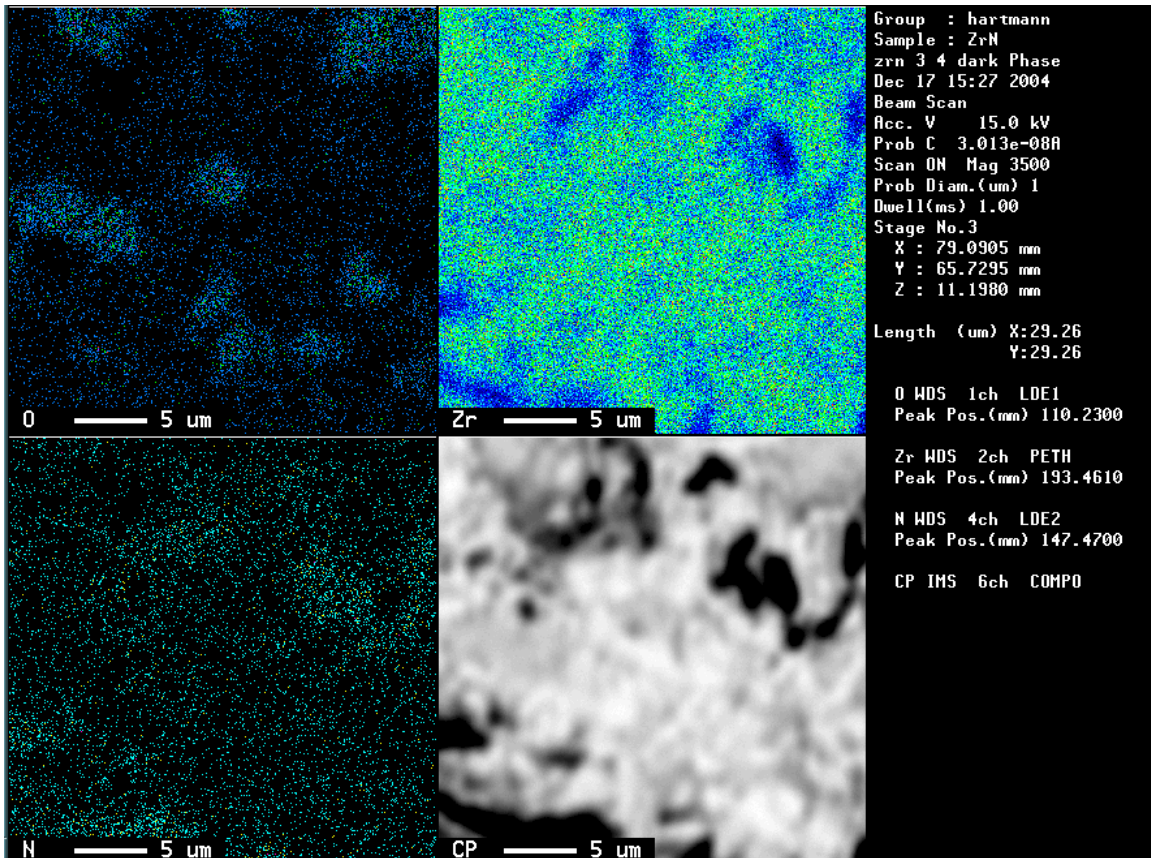
| Property | $(U_{0.8}Pu_{0.2})O_{1.98}$ | $(U_{0.8}Pu_{0.2})C$ | $(U_{0.8}Pu_{0.2})N$ |
|---|-----------------------------|----------------------|----------------------|
| Theoretical density (g/cm ³) | 11.06 | 13.62 | 14.30 |
| Metal density (g/cm ³) | 9.8 | 12.96 | 13.50 |
| Metal fraction (%) | 88.10 | 95.20 | 94.45 |
| Melting point (°C) | 2700 | 2475 | 2800 |
| Thermal conductivity (W/cm. °C) | | | |
| 700°C | 0.035 | 0.188 | 0.158 |
| 1200°C | 0.027 | 0.206 | 0.180 |
| 1700°C | 0.019 | 0.212 | 0.201 |

Uranium oxides are generally the starting point for UN as well as UC synthesis. Oxides are fabricated using a precipitation method. An example of a precipitation process consists of dissolving and mixing the chloride or nitrate salts in purified water and then creating a precipitate with NH₄OH or oxalic acid. The precipitate is washed with acetone and purified water, milled, and dried at 90 °C. The dried precipitate is milled again and redried at 150 °C for 2-3 hours. It is milled again and then calcined at 750 °C for 1 hour. The calcined powder is milled and then cold pressed into 13 or 7 mm diameter pellets for 2 minutes before being sintered under a mixture of argon and 4% hydrogen for four hours

at 1500 °C. Nitride ceramics are produced using the carbothermic reduction process [10]. In this process carbon is added in excess to actinide oxides. Heating under an inert gas such as Ar will form carbides. If the carbon/ AnO₂ mixtures are heated in the range of 1500 °C under a stream of N₂ gas, N₂-H₂ or NH₃-Ar then carbon dioxide is liberated and the intermediate actinide carbide is converted to the nitride. The carbon dioxide concentration in the outgas is used to monitor the extent of the reaction.

The UNLV team is already evaluating nitrides with researchers from the Nuclear Materials Technology (NMT) division at LANL. In studies performed by UNLV, evaluation of ZrN and CeN ceramics synthesized by a carbothermic reduction method at LANL shows the presence of oxides in the nitrides (Figure 1). In this figure the oxygen content is shown in the top left panel as the bright areas. As evident from this figure, the levels of oxygen are low but present in the evaluated ZrN. Compared to Zr (top right panel) and N (bottom left panel) the distribution of oxygen is localized in the nitride. This oxide formation is also evident with UN fuels, where surface coating by UO₂ occurs. The proposed solution phase synthesis along with removal of oxides in the furnace material should eliminate the impurities in the nitride product.

Figure 1. Microprobe analysis of ZrN showing the presence of oxides

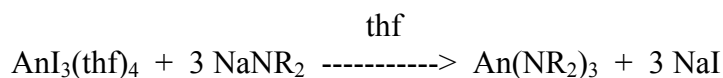


2.2.2. Actinide Amido Syntheses

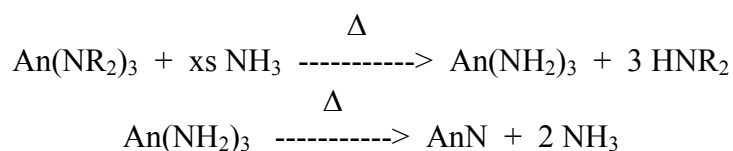
The synthetic chemistry of trivalent actinide complexes was advanced greatly with the discovery of efficient routes to soluble iodide starting materials of the type AnI_3L_4 , where $An = U, Np, Pu$, and $L =$ tetrahydrofuran (thf), pyridine, dimethylsulfoxide, etc. at Los Alamos [6-8]. We have not synthesized UI_3 or the other actinide iodides in liquid ammonia but note that PuI_3 is soluble in ammonia, presumably as its ammonia adduct $PuI_3(NH_3)_4$ [3].



These molecular species, generated from actinide metals and molecular iodine in coordinating solvents, are readily soluble in other organic solvents, and serve as convenient precursors to a variety of other trivalent actinide species including homoleptic tris amido complexes as shown below [11,12,13].



The parent amides, $An(NH_2)_3$, have not been described in the literature and it is likely that these will be polymeric materials insoluble in liquid ammonia [14]. However, sodium iodide is readily soluble in liquid ammonia and can easily be separated from the insoluble actinide product. Alternatively, we can envision reacting the pure $An(NR_2)_3$ compounds with NH_3 at elevated temperatures to yield the secondary amine HNR_2 and either $An(NH_2)_3$ or AnN .



The ammonolysis route is attractive for efficient labeling of the final nitride with nitrogen-15. For nitride fuels, enrichment is an option to prevent the formation of ^{14}C from the $^{14}N(n,p)$ reaction. The recovery of enriched nitrogen from UN has been investigated elsewhere [15]. In this work the dissolution of spent nitride fuel with an oxidizing agent in molten salt was examined. Most of nitrogen is recovered as N_2 gas resulting from the reaction of uranium nitrides above 550 °C. The recovered N_2 gas, enriched in ^{15}N , can be converted to ammonia and recycled into the above reaction.

2.3. Tasks

To achieve the project objectives research will be performed on the non-aqueous synthesis of trivalent amido complexes, decomposition of the amido complexes to the

corresponding nitrides, characterization of the nitride products, and sintering of the nitrides into fuel pellets. The description of each task is below.

2.3.1. Task 1: Non-aqueous coordination experiments

Initial efforts on this task will begin with uranium experiments at UNLV. The experiments will evaluate the optimal conditions (concentrations of reagents, time, temperature, etc.) for the formation of the uranium(III) amide, $U(NH_2)_3$, from UI_3 and $NaNH_2$ in liquid ammonia. These experiments will initially be conducted at ca. $-34^\circ C$ under nitrogen in ordinary glassware to observe color changes and the solubility characteristics of $UI_3(NH_3)_4$ and $U(NH_2)_3$. The reactions can easily be done at room temperature or above using stainless steel Parr pressure vessels. In parallel, we will examine the gas-solid reactions of ammonia and isolated uranium(III) amide complexes under flow conditions to establish the temperature at which $U(NR_2)_3$ is converted to $U(NH_2)_3$ and ultimately to UN. Once the uranium experimental conditions are identified and optimized, experiments will proceed on neptunium and the heavier actinides at LANL. The facilities at LANL will be exploited to examine and evaluate amido complexes of the transuranic elements.

2.3.2. Task 2: Formation and characterization of nitrides

In this task the formation of the nitride species and subsequent characterization of the resulting species will be performed for all the actinide nitrides examined. Based on the proposed synthetic route, the nitride will be formed from the amido actinide species under heat with the liberation of ammonia. The parameters to be examined in this task include heating temperature, time, and atmosphere. The kinetic variation in the nitrate formation as a function of the differing parameters will be evaluated. The nitride species will be evaluated by microscopic, XRD, thermal methods, and spectroscopic methods. The UNLV team is already employing microscopic and XRD methods for evaluation nitride species. Information on elemental composition and phases are expected with these methods. The spectroscopy method will be mainly XAFS, consisting of EXAFS and XANES. These methods provide information on bond distances, coordination, and oxidation state. The UNLV team is currently performing XAFS experiments with collaborators from SRNL. These efforts may be supplemented by the XAFS capabilities of the LANL team. The thermal methods will be TGA and DSC. These methods will provide information on the properties of the resulting nitrides for comparison with nitrides formed from other synthetic routes. The methods described above are available at both UNLV and LANL.

2.3.3. Task 3: Development of methods for the synthesis of nitrides

The results from Task 1 and 2 will be used to develop the optimal conditions for the synthesis of actinide nitrides. While it is expected the methods will be similar, some difference between the different actinide elements may be observed. For the formation of mixed actinide nitride solid-solutions, different routes may be needed that incorporate suitable elements of the composite actinide elements. If required, studies on the formation of mixed actinide nitride solid-solutions will be performed in this task using the methods from Task 2. The necessity of performing these studies will be evident from

results in Task 1 that identify differences in the formation of amido species for the evaluated actinide elements.

2.4. Experimental methods

The experimental methods for the synthesis of the amido actinide species relies upon the use of inert atmosphere and elevated pressure. These conditions can be reached with the use of Schlenk lines, pressure vessels, or glove boxes. A combination of these techniques will be utilized in the project. Characterization of the resulting amido species will primarily utilize X-ray diffraction employing methods and equipment already developed by the LANL partner.

For the solid phase characterization the methods will be the same as those already employed by UNLV for nitride materials. X-ray powder diffraction (XRD) in combination with Rietveld structure refinement to refine or to determine actinide occupancies within the crystal lattices of the fuels will be used. Additionally high resolution electron microscopy (transmission electron microscopy) in combination with, nano probe X-ray spectrometry (EDS), parallel energy loss spectroscopy (PEELS), energy-filter electron microscopy, electron beam microprobe analysis (EMPA) and scanning transmission electron microscopy will also be used to evaluate the actinide nitrides. The state-of-the-art analytical instrumentation on X-ray diffraction is a PANalytical X-Pert Pro with X'Celator solid state detector and Bruker AXS Topas2 Rietveld structure refinement software. The high resolution electron microscopy used a Tecnai F 30 STEM with a FEG field emission gun, scanning option, PEELS, EDS, Energy-Filter, 300 kV acceleration, and a point resolution of 2.2 Å. This project can utilize two fully equipped sample preparation laboratories, one specifically for the preparation of radioactive specimens. X-ray absorption fine structure spectroscopy (XAFS) will also be used in analysis. XAFS includes EXAFS (extended x-ray absorption fine structure spectroscopy) and XANES (x-ray absorption near edge spectroscopy). EXAFS is an atom-specific local structure probe used to determine the molecular structure of a species. Data can yield information including average interatomic distances and the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species. XANES data contains information on bound state electronic transitions and is used to determine the oxidation state of the species. The XAFS experiments can be performed at ANL with SRNL collaborators from other projects or in conjunction with LANL. Thermal analysis (DTA-DSC) can also be performed at UNLV.

2.5. Merit Review Criterion Discussion

2.5.1. Technical approach of proposed research

This project will address the current deficiencies in the synthesis of nitride fuels by developing a solution based synthesis. This project will bring experts and expertise in non-aqueous actinide chemistry to the field of nuclear fuel synthesis. This field places emphasis on coordination chemistry and reaction routes in the formation of novel and unique complexes. The addition of the knowledge and methodologies that are the basis of non-aqueous coordination chemistry will generate an improved understanding of the fundamental chemical pathways for the direct formation of nitride species. The synthesis will be combined with state-of-the-art x-ray and microscopic analysis for the

characterization of the final nitride product. These methods will identify phase, species, and coordination environments of the nitride products.

The technical approach will also include the formation of transuranic actinide species. This effort will be based on initial studies with uranium. The uranium amido synthesis will be examined by two main routes, one involving sodium metal and the other developed by LANL team members to produce $An(NR_2)_3$ complexes. The conditions for these synthesis will be systematically evaluated to determine the best methods for producing uranium amide species then subsequently the nitride species. Once these conditions are determined for uranium they can be applied to neptunium, plutonium, and americium. This methodology will also be applied to the synthesis of mixed actinide solid-solutions. The X-ray and microscopy characterization techniques will provide information on the phases in the solid-solutions.

2.5.2. Significance and Impact

A major difficulty in the potential utilization of nitride fuels in advanced fuel cycles is production of the materials. The physical properties of nitride fuels have advantages in advanced reactors and therefore an improvement in the material synthesis can enhance future options. The proposed non-aqueous solution synthetic route for actinide nitrides is based on existing amido coordination chemistry results. The control on product physical properties inherent in solution phase synthesis as observed in the sol-gel method for oxides can be applied to actinide nitrides. The successful completion of this project will provide a method of the elimination of impurities inherent in the carbothermic reduction method currently employed for nitride fuel synthesis. This will result in methods for reliable material synthesis. Furthermore, if enriched nitrogen is used, recycling can be incorporated into the synthetic route. The recovery of enriched nitrogen from UN has been investigated [15] and the method incorporated into the synthesis of actinide nitrides. In this work the dissolution of spent nitride fuel with an oxidizing agent in molten salt was examined. The benefits can be realized if the fundamental chemistry germane to the non-aqueous amido chemistry and formation of the nitride actinides is understood.

2.5.3. Principal Investigator

The PI, Professor Ken Czerwinski, is the director of the Radiochemistry Ph.D. program at UNLV, a member of the chemistry department faculty, and a researcher in the Harry Reid Center. His educational efforts are centered on providing world-class radiochemistry experience to undergraduate and graduate students. These efforts include laboratory experience as well as classroom instruction. Research is centered on determining the chemical kinetics and thermodynamics of radionuclides with an emphasis on actinide elements. Data obtained in the laboratory are incorporated into models to evaluate systems containing actinides. The results are compared to actual systems to assess the validity of the data and models. Within this broad area research is performed on the speciation of actinides in the environment, actinide separations in the nuclear fuel cycle, and actinide chemical forms in solids. The group has experience with DOE programs in EMSP, NERI, and the Advanced Fuel Cycle Initiative. The programs

include nuclear fuel development, chemical and physical separations of actinides and fission products, and environmental behavior of actinides.

At UNLV the team has access to transuranic chemistry laboratories for performing experiments with gram quantity of radionuclides and actinides. The laboratories contain hood space and glove boxes for performing these experiments. Common experimental methods performed in these laboratories include spectroscopy and separation/detection. Separation/Detection experiments divide species based on size, charge, or a combination of the two. The amount of each species is quantified by radiation detection or analytical techniques. A separate counting laboratory is maintained by the group in conjunction with the UNLV Health Physics Department. The counting laboratory provides gamma counters, alpha counters, gas proportional counters, and scintillation counters. Spectroscopic methods include IR, UV-Visible, NMR, and laser spectroscopy.

Specific methods already used by the UNLV team of importance to the project include XRD, X-ray spectroscopy, and microscopy. In XRD, X-rays are used to probe crystalline structure and to determine far ordered structure units with highest precision possible. X-ray diffraction is used in two ways: determination of the crystalline phase constitution using the PDF data base for powder diffraction, and the refinement of the individual crystal structures by Rietveld structure refinement using the ICSD data base for inorganic single crystal data. Since XRD is basically a structure sensitive technique, the XRD pattern is characterized by the structure-type of the crystalline solids present. Beside the structure-type sensitive characteristic X-ray powder pattern ("fingerprint") the UNLV team is using least square lattice parameter refinement and Rietveld structure refinement to clearly identify each individual crystalline phase. Rietveld refinement will confirm and modify the crystal structure of each phase present based on published X-ray single crystal data (ICSD). The crystal structure information provides data on interatomic distances and the coordination polyhedron of the actinide cations within the far-ordered structure to high special resolution.

Other x-ray synchrotron methods are XAFS, including EXAFS (extended x-ray absorption fine structure spectroscopy) and XANES (x-ray absorption near edge spectroscopy). EXAFS is an atom-specific local structure probe used to determine the molecular structure of a species. Data can yield information including average interatomic distances and the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species [16]. These experiments have been performed by the UNLV team members on nuclear fuel [17], environmental samples [18], and recently on separation systems.

At UNLV high resolution electron microscopy (transmission electron microscopy) in combination with nano probe X-ray spectrometry (EDS) and parallel electron energy loss spectroscopy (PEELS), energy-filter electron microscopy, and scanning transmission electron microscopy can be performed with radionuclide containing samples. UNLV's instrumentation, a Tecnai F 30 STEM, is clearly a state-of-the-art tool for high resolution electron microscopy. The Tecnai F 30 provides highest possible resolution at 300 kV by operation with a FEG field emission gun. It can be operated under scanning and energy-filtered mode and provides PEELS and EDS spectroscopy with sub-micron spatial resolution (nano-probe). The point resolution is 0.2 nm. Two fully equipped sample preparation laboratories, one for the preparation of surrogate sample, one for the preparation of radioactive containing specimens can be used. The analytical work scope

as proposed will promote the Harry Reid Center for Environmental Studies of UNLV as the top academic institution in the U.S. for analyzing radioactive samples to highest spatial resolution.

The Los Alamos partners are recognized world leaders in actinide science. One team member, Dr. Al Sattelberger, will be a visiting professor in the chemistry department at UNLV beginning fall 2005. His efforts will include development of the educational and research components of the Radiochemistry Ph.D. program, including incorporating LANL researchers into the UNLV education and research program. The extensive facilities and instrumentation for characterization of actinide compounds and materials within the NMT and C Divisions at Los Alamos will be available for use on the project. In addition, LANL participants have particular expertise and facilities for the non-aqueous synthesis and characterization of transuranic nitrides using a wide variety of physical techniques, including XAFS at SSRL.

2.6. Project Timetable

The project is divided into 3 tasks (see section 2.3). The timetable for the tasks is provided below.

Task 1: Non-aqueous coordination chemistry

- Development of amido coordination with uranium (Months 0-12)
- Development of amido coordination with neptunium (Months 10-22)
- Development of amido coordination with transneptunium actinides (Months 20-32)

Task 2: Nitride formation and characterization

- Formation and characterization of uranium nitride from amido species (Months 8-14)
- Formation and characterization of neptunium nitride from amido species (Months 15-27)
- Formation and characterization of transneptunium nitrides from amido species (Months 25-34)

Task 3: Development of methods for the synthesis of actinide nitrides

- Identification of crucial parameter of the solution based synthesis of uranium nitride (Months 12-15)
- Identification of crucial parameter of the solution based synthesis of neptunium nitride (Months 12-15)
- Comparison of solution synthesis for uranium and neptunium nitride and initial identification of required methods for solid-solution synthesis (Months 15-17)
- Experiments on the synthesis of uranium-neptunium solid solutions if large variations are identified (Months 20-30)
- Identification of crucial parameter of the solution based synthesis of transneptunium nitride (Months 28-33)
- Comparison of solution synthesis for actinide nitride and identification of required methods for solid-solution synthesis with different actinides (Months 30-36)

2.7. Evaluation Phase

The success of the project is predicated on the actinide amido non-aqueous synthesis, conversion of the amido species to the nitride, and development of methods for using the project resulting in the synthesis of nitride fuels. The plan and metrics for evaluating the project follow these areas. The follow metrics will be evaluated to ascertain the direction of the project

- Progress on uranium amido species synthesis (Month 7)
- Synthesis of uranium amido species (Month 13)
- Synthesis of uranium nitride from the amido species (Month 15)
- Progress on neptunium amido species (Month 22)
- Progress on identification of conditions for mixed actinide solid solution synthesis (Month 26)
- Synthesis of neptunium amido species (Month 28)
- Synthesis of neptunium nitride from the amido species (Month 31)
- Conditions for mixed actinide solid solution synthesis (Month 32)
- Synthesis of transneptunium nitrides (Month 36)

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