**Nuclear Fuels Technologies
Fiscal Year 1997 Research and Development Test Plan**

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1.0 Introduction

This document details the research and development (R&D) activities that will be conducted in fiscal year 1997 (FY97) by the Nuclear Fuels Technologies project team for the Department of Energy Office of Fissile Materials Disposition. This work is a continuation and extension of experimental activities that have been conducted in support of the disposition program with regard to using weapons-plutonium in the fabrication of mixed-oxide (MOX) nuclear fuel for reactor-based disposition. The purpose of this work is to identify and if possible, resolve, technical issues associated with applying the large experience base (existing mainly in Europe) of making MOX fuel with recycled reactor-grade plutonium to the fabrication of MOX using weapons-grade plutonium. Therefore, the projects are designed to fill one or more of three needs: 1) To provide potential fabricators a technical basis upon which to evaluate the uncertainties and technical risks associated with MOX fabrication using weapons-plutonium; 2) To provide the fabricator ultimately selected for the disposition mission with a technical basis upon which to build, thereby reducing the amount of development and time required for implementation of the MOX disposition option; and 3) To identify to DOE technical issues that it is unlikely the fabricator will address (e.g., gallium removal), and to resolve these issues or provide a clear path forward for doing so. Because of the volatile nature of the disposition program as it transitions into the implementation phase, all work described within this plan is intended to be completed this fiscal year with its culmination being one of two goals: 1) a summary of the technical results sufficient to hand over to commercial MOX fabricators for their use in planning activities; or 2) an estimate with regard to cost and schedule for follow-on activities to completely resolve the issue as well as sufficient technical supporting information in order for DOE to make well-informed decisions in this regard.

Although fabrication of MOX fuel using reactor-grade plutonium is a well-developed, industrialized process, several differences exist between the reactor-grade and weapons-grade plutonium which generate technical issues that must be resolved. These differences include: variation in powder characteristics because the weapons material is to be converted using a dry pyrochemical process as opposed to a chemical dissolution and precipitation process as used in spent-fuel reprocessing facilities; the presence of gallium in the weapons material; and the variation in plutonium isotopics between the reactor-grade and weapons-grade material. All of the experiments outlined in this report address one or more of these issues. A description of how each project specifically addresses these issues is included in the narrative for each individual experiment. However, Table 1.0-1 summarizes which issues each project deals with.

The projects are divided into two categories: feed qualification, which deals with issues involving obtaining and characterizing appropriate PuO_2 sources and developing a process to remove the gallium from the PuO_2 feed; and fuel fabrication development, which includes experimental fabrication activities to evaluate the effects of various parameters on the fabrication process and fuel quality, and development of additional analytical techniques required because of the nature of the material or necessity of upgrading existing laboratory infrastructure. An overall schedule of activities is given after the description of the individual projects.

It should be noted that while this document details the experimental variables and measurements that are currently planned, the dynamic nature associated with basic research and development will likely cause variations in the characteristics of the experiments actually performed.

Table 1.0-1 Relationship Between Proposed Projects and High-Level Technical Issues

Applicable Section	Project	Difference in PuO ₂ Characteristics	Presence of Gallium	Isotopic Differences
2.1.1	PuO ₂ Production - HYDOX-derived PuO ₂	X	X	X
2.1.2	PuO ₂ Production - Aqueous-Derived PuO ₂	X		
2.2.1	Gallium Removal - Phase Diagram Assessment		X	
2.2.2	Gallium Removal - Surrogate Studies		X	
2.2.3	Gallium Removal - PuO ₂ Studies		X	
2.2.4	Gallium Removal - Industrialization		X	
3.1.1	Fabrication Studies - PuO ₂ Variability	X		
3.1.2	Fabrication Studies - UO ₂ Variability	X		
3.1.3	Fabrication Studies - Sintering Study	X	X	
3.2.1	Analytical Development - Homogeneity by Autoradiograph			X
3.2.1	Analytical Development - Homogeneity by X-Ray Microfluorescence		X	X
3.2.2	Analytical Development - Upgrade TA-55 Analytical Capability	X	X	
3.2.3	Analytical Development - Trace Analysis Validation		X	

2.0 Feed Qualification

The current disposition plan calls for the conversion of pit material (plutonium in weapons) using the Advanced Recovery and Integrated Extraction System (ARIES). This process, under development at Los Alamos and Lawrence Livermore National Laboratories, involves production of PuO_2 via hydride-oxidation, or hydride-nitride-oxidation, of plutonium metal (both of these processes are generically referred to as HYDOX). Characterization of PuO_2 produced by hydride-oxidation has shown that the particle morphology is quite different than the particles produced by conventional aqueous conversion processes. In addition, the gallium that is contained in the plutonium metal is also converted to oxide (Ga_2O_3) during this process and thus remains an impurity in the PuO_2 feed. Experimentation is required to demonstrate that the variation in morphology is acceptable for producing quality fuel, and that the gallium may be reduced to acceptable quantities (and what quantities are acceptable) in the PuO_2 .

2.1 PuO_2 Production

While previous experimentation suggests that it is possible to produce pellets of acceptable quality using PuO_2 produced via hydride-oxidation, the conversion parameters for PuO_2 production (and process, in the event that hydride-nitride-oxidation is ultimately used) were not necessarily prototypic of what will ultimately be used for the disposition mission. Therefore, in FY97, efforts will be made to obtain PuO_2 through a process that is more prototypic of what is expected for the final disposition mission, and to compare the fabrication behavior of the resulting material to the PuO_2 used in previous fabrication experiments. In addition, an attempt will be made to obtain some PuO_2 that was produced through an aqueous purification method, so that a direct comparison can be made between the fabrication behavior of aqueous PuO_2 (which is representative of what is used in commercial MOX fuel fabrication) and the HYDOX PuO_2 .

2.1.1 HYDOX-derived PuO_2

The goal of this activity is to obtain PuO_2 feed material produced in the ARIES project to be used in fuel fabrication studies.

In FY97, the amount of PuO_2 feed material required for the fuel fabrication activities will be defined, as well as schedule requirements for receipt of material. In addition, desired properties such as the Ga content and preferred particle characteristics will be communicated to ARIES project personnel in the event that options in the HYDOX process parameters will allow the production of more optimal material for MOX fabrication. Using this information, PuO_2 feed powder will then be produced in the ARIES project, using both the hydride-oxidation (2-step) and hydride-nitride-oxidation (3-step) method at LLNL. Also, PuO_2 that was produced via hydride-oxidation (2-step) at LANL in FY96 and used in previous fuels experimental activities will be obtained in sufficient quantities for use in the fabrication experiments. Once obtained, samples of each powder will be analyzed to determine the characteristics of the feed material. These characteristics are identified in Table 2.1.1-1. Use of this material in fabrication experiments is covered under section 3.1.

Milestones:

- Define Required HYDOX-Derived PuO_2 Amounts and Desired Characteristics (1 December 1996)
- Obtain HYDOX-Derived Feed Materials (1 March 1997)
- Complete Characterization of HYDOX-Derived Feed Material (1 May 1997)

Table 2.1.1-1. Summary of Experimental Variables and Measurements for PuO₂ Variability Study

Variables	Range
Plutonium Feed	LLNL 2-Step, LLNL 3-Step, LANL 2-Step
Measurements	Measurement Technique
<i>PuO₂ Powder</i>	
Ga Content	XRF, ICP, DCP
Particle Size Distribution	Sieve Analysis
Mean Particle Size	Laser Light Scattering
Mean Surface Area	BET(Braunauer-Emmett-Teller) Method
Particle Morphology	Scanning Electron Microscopy

2.1.2 Aqueous-Derived PuO₂

The goal of this activity is to obtain PuO₂ feed material produced by an aqueous process to be used in fuel fabrication studies.

In FY97, requirements will be defined in order to obtain suitable aqueous-derived PuO₂ feed material for the fuel fabrication activities. These requirements include the amount of PuO₂, process history, and schedule requirements. Using these requirements, PuO₂ powder inventories in the LANL TA-55 vault assessed for their applicability for use in these activities. Once obtained, samples of the powder will be analyzed to determine the characteristics of the feed material.

Table 2.1.2-1. Summary of Experimental Variables and Measurements for Aqueous-Derived PuO₂ Study

Variables	Range
Plutonium Feed	Aqueous-derived
Measurements	Measurement Technique
<i>PuO₂ Powder</i>	
Particle Size Distribution	Sieve Analysis
Mean Particle Size	Laser Light Scattering
Mean Surface Area	BET(Braunauer-Emmett-Teller) Method
Particle Morphology	Scanning Electron Microscopy

Milestones:

- Define Required Aqueous-Derived PuO₂ Amounts and Desired Characteristics (14 February 1997)
- Obtain Aqueous-Derived Feed Materials (1 March 1997)
- Complete Characterization of Aqueous-Derived Feed Material (1 May 1997)

2.2 Ga Removal

The presence of Ga in weapons material is a key difference between weapons-grade and reactor-grade plutonium. Experiments have shown that gallium oxide volatilizes under MOX fuel sintering conditions. This can cause problems with regard to the effect that this material has on the sintering furnace because it is corrosive and will deposit on the furnace surfaces. In addition, gallium affects the sintering behavior of the MOX ceramic. This could cause operational difficulties if frequent adjustment to the operational parameters (i.e., time and temperature) is required, or if this characteristic causes large pellet reject rates following sintering. Because of these reasons, the current approach for fabricating MOX fuel for the disposition program using weapons-grade plutonium is to remove most

of the Ga prior to fabrication. Studies were initiated last fiscal year (FY) to learn more about the behavior of Ga in general, and how the volatilization of its suboxide state can be used to provide a simple gallium removal mechanism by using a thermal treatment of the PuO_2 powder. This process, referred to as the Thermally-Induced Gallium Removal (TIGR) process, was able to reduce the residual gallium concentrations to less than 200 ppm in the PuO_2 feed. This results in a less than 10 ppm concentration of gallium in the final MOX fuel. This FY, experiments will continue to further examine its behavior, particularly with regard to the evolution of Ga under a variety of process parameters. Work will continue on the assessment of Ga phase diagrams, building on last year's efforts and incorporating the data obtained from this year's experiments. Studies will be performed using surrogate materials to examine the effect varying the process parameters has on the Ga evolution from the material. Similar experiments will be performed using PuO_2 powders, although they will be significantly more limited in scope, focusing on those differences particular to plutonium and verification of the surrogate results. An initial examination will be made as to the possible industrialization of the Ga removal, including both the thermal treatment process and an alternative aqueous process.

2.2.1 Phase Diagram Assessment

This study will attempt to optimize the Ga_2O_3 - PuO_2 , PuO_2 - UO_2 , and Ga_2O_3 - PuO_2 - UO_2 phase diagrams using available thermodynamic data.

A key to minimizing the experimental work required for the optimization of the TIGR process as well as for establishing the proper fabrication parameters for making MOX fuel is a good understanding of the underlying thermodynamic properties of the systems of interest. While the PuO_2 - UO_2 and Ga-Pu systems are well characterized, the PuO_2 - UO_2 - Ga_2O_3 and Ga_2O_3 - PuO_2 systems are less well known. The purpose of this research will be to evaluate the phase relations in the complex oxides that are being considered in the disposition effort. In particular, the systems Ga_2O_3 - PuO_2 , PuO_2 - UO_2 , and UO_2 - PuO_2 - Ga_2O_3 . These phase diagrams will be assessed by collecting and critically evaluating all available thermodynamic data. This involves conducting a thorough literature survey and critically evaluating the experimental methods used in the experiments, and statistically evaluating the various forms of data. The thermodynamic data will then be used to optimize each phase diagram using principles of thermodynamics and, where possible, aided by computer codes such as MTDATA as well as other rigorous thermodynamic models. The resulting information will then be used to assist in the development and optimization of the TIGR process as well as provided to the fuel fabricators to assist them in determining the impact of the gallium on the process parameters for the fabrication of MOX fuel.

Milestones:

- Complete Critical Assessment of Ga_2O_3 - PuO_2 Thermodynamic Data (1 March 1997)
- Optimize Ga_2O_3 - PuO_2 Phase Diagram (30 September 1997)
- Complete Critical Assessment of PuO_2 - UO_2 Thermodynamic Data (1 August 1997)
- Optimize PuO_2 - UO_2 Phase Diagram (30 September 1997)
- Complete Critical Assessment of Ga_2O_3 - PuO_2 - UO_2 Thermodynamic Data (25 August 1997)
- Optimize Ga_2O_3 - PuO_2 - UO_2 Phase Diagram (30 September 1997)

2.2.2 Surrogate Studies

This study will attempt to characterize the evolution of Ga from surrogate powder feedstock using a range of thermal treatment processes.

These experiments will utilize CeO_2 and Ga_2O_3 mixtures as a surrogate to represent the PuO_2 feed material. The use of the CeO_2 surrogate will allow covering a much wider range of processing variables than if only PuO_2 was used due to the additional complications of working with plutonium; thus, it is hoped that the performance of the surrogate studies will allow a determination by the end of this FY of a single process design to pursue in further development activities. It is recognized that important differences exist between the chemical behavior of PuO_2 and CeO_2 ; thus a critical aspect of verifying the validity of these studies is the performance of verification experiments using actual PuO_2 (covered in Section 2.2.3). It should also be noted that what is expected from the surrogate experiments is not necessarily absolute values of gallium reduction in the PuO_2 powder, but rather indications with regard to how the processing parameters can be optimized to provide for the desired gallium reduction in the PuO_2 feed (i.e., what is being sought is applicable trends that can be applied to the PuO_2 feed). The surrogate mixtures will be prepared by comilling CeO_2 and Ga_2O_3 powders (2 wt% Ga_2O_3 will be used to make the concentration analyses easier following the treatments; while this is greater than the 0.5-1% gallium concentrations expected in the PuO_2 , it still should be possible to cross-correlate the results from the PuO_2 studies to verify that the trends identified by the surrogates are representative), pressing these into pellets, and sintering in air (which will prevent any gallium loss because in an oxidizing environment the Ga_2O_3 will not be converted to the volatile Ga_2O state) to try and form a solid solution. The sintered pellets are then crushed to produce the surrogate powder for experimental use. While this process is not representative of the production of the actual PuO_2 feed material (i.e., HYDOX), it is felt that this process will result in a fairly representative distribution of the Ga_2O_3 within the CeO_2 powder. Table 2.2.2-1 summarizes the experimental variables (temperature, time, sample size, atmosphere, and particle size) to be used in FY97 to determine their effect on Ga evolution and the measurements that will be taken. Studies will be performed to analyze the effect of varying gas flow rates, sample geometries/flow geometries, and gas flow/agitation configurations. The initial composition of the mixtures will be known and chemical analysis will be performed on all samples following the experiments to determine gallium content and the gallium-to-cerium ratio in the final product. The data obtained from the experiments will be used in an attempt to model and analyze the kinetics.

Table 2.2.2-1 Summary of Experimental Variables and Measurements for Surrogate Ga Evolution Studies

Variables	Range
Temperature	600,700,800,900,1000,1100,1200 C
Time	0-8 h
Sample Size	0.3, 0.9, 2.0, 5.0 g
Atmosphere	Ar, Ar-6% H_2
Particle Size	Three size distributions (i.e., powder will be created by granulation of pellets using three different sieve sizes)
Gas Flow Rates	To be determined
Gas Flow Geometries	Flow over powder, Flow through powder
Agitation	Stirring, tumbling (i.e., in a rotating furnace)
Measurements	Measurement Technique
<i>Powder Following Thermal Treatment</i>	
Ga Content, Ga-Ce Ratio	Chemical Analyses

Milestones:

- Complete time, temperature, and sample size studies on surrogates (1 July 1997)
- Complete surrogate gallium removal studies (30 September 1997)

2.2.3 PuO₂ Studies

This study will attempt to characterize the evolution of Ga from available pit conversion PuO₂ feed material (the feed material used (LLNL 2-step, LLNL 3-step, or LANL 2-step) will be that selected as a result of the fabrication studies described in Section 3.1.1) using a range of thermal treatment processes.

The purpose of the PuO₂ studies is twofold: 1) to verify the accuracy of the surrogate studies in predicting gallium evolution trends from PuO₂ powder, and 2) to determine the effects of the processing parameters on the PuO₂ powder characteristics (which can not be determined using the CeO₂ surrogate). Table 2.2.3 summarizes the experimental variables (temperature, time, and atmosphere) to be used in FY97 to determine their effect on Ga evolution and the measurements that will be taken. A full matrix of the times and temperatures shown in Table 2.2.3-1 will be performed. However, only a single experiment will be performed in a pure argon atmosphere (1000 C for 2 h). All these experiments will use a single sample size (16 g). A larger sample size (160 g) will then be treated at 1000 C for 2 h in Ar-6% H₂ to determine the effect sample size has on the final surface area. Chemical analysis of all samples will be performed to determine Ga content. The powder properties, including particle size distribution, mean particle size, mean surface area, and particle morphology will also be measured.

Table 2.2.3-1 Summary of Experimental Variables and Measurements for PuO₂ Ga Evolution Studies

Variables	Range
Temperature	600,800,1000,1200 C
Time	15 min., 30 min., 2h, 6h
Atmosphere	Ar, Ar-6% H ₂
Measurements	Measurement Technique
<i>Powder Following Thermal Treatment</i>	
Ga Content	XRF, ICP, DCP
Particle Size Distribution	Sieve Analysis
Mean Particle Size	Laser Light Scattering
Mean Surface Area	BET(Braunauer-Emmett-Teller) Method
Particle Morphology	Scanning Electron Microscopy

Milestones:

- Complete PuO₂ gallium removal studies (30 September 1997)

2.2.4 Industrialization

The goal of this activity is to make an initial examination of how the Ga removal process could be used on the industrial scale required for the disposition program.

In FY97, a study will be initiated to examine the baseline thermal treatment process for Ga removal and its potential for industrialization. This includes defining the throughput requirements of the full scale process, identifying how the surplus material inventory characteristics affect the removal process, and using the experimental results to define what type and size of equipment is required. If possible, initial cost estimates for construction of such a system will also be generated.

Also in FY97, an aqueous Ga removal process will be examined for its potential for industrialization. This technology will serve as a backup in the event that the thermal gallium removal process is found to be inadequate for some unforeseen reason. A study will be performed using a minimum cost design objective based on existing data and a process involving off-the-shelf equipment. The study will include a theoretical design (i.e., basic process and equipment definition) of the process, equipment sizing estimates and an associated cost estimation.

Milestones:

- Generate Throughput Requirements and Surplus Inventory Effects (28 February 1997)
- Identify Thermal Treatment Equipment and Sizing (31 July 1997)
- Complete Thermal Treatment Cost Estimates (31 August 1997)
- Complete Thermal Treatment Industrialization Study Report (30 September 1997)
- Create Block Diagram of Aqueous Removal Concept (31 December 1996)
- Develop Aqueous Removal Process Specifics (31 December 1996)
- Determine Materials Balances for Aqueous Removal (31 March 1997)
- Estimate Aqueous Removal Equipment Sizing (30 June 1997)
- Perform Aqueous Removal Cost Estimation (30 June 1997)
- Complete Aqueous Removal Report (30 September 1997)

3.0 Fuel Fabrication Development

The current disposition plan calls for fabrication of MOX fuel using weapons-grade plutonium oxide and depleted uranium oxide. Any variation in the fabrication process, including the feed materials, will lead to variations in the final fuel product, and it is important to quantify the effect each variation will have on the quality of the MOX fuel. Experimentation is required to determine the range of acceptable fabrication parameters which will lead to an acceptable fuel product. Further development is also needed in the laboratory to enhance the current techniques available for measurement of certain fuel characteristics.

3.1 Fabrication Studies

Previous studies have shown that PuO_2 powder produced through the ARIES process will differ significantly, in terms of morphology, to that produced by the conventional aqueous process. Variations within the ARIES process will also produce differing powder morphologies. In addition, the sources for the depleted UO_2 powder differ widely. Experimentation is needed to determine how each of the different PuO_2 and UO_2 powders will affect the quality of the final fuel pellet quality. Therefore, in this fiscal year, pellets will be fabricated using varying PuO_2 and UO_2 feed materials and analyzed to characterize the differences in terms of density, homogeneity, oxygen-to-metal ratio (O/M) and microstructure.

3.1.1 PuO_2 Variability

This study will fabricate pellets using a single UO_2 source (Cameco ADU) and the varying PuO_2 feed materials obtained from the HYDOX (i.e., LLNL 2-step, LLNL 3-step, and LANL 2-stop) and aqueous processes. Pellets will then be characterized with regard to density, homogeneity, O/M, and microstructure.

In FY97, two PuO_2 powder samples will be obtained from the ARIES project, as well as PuO_2 produced by an aqueous process. The ARIES samples will differ in terms of their production processes (hydride-oxidation (LLNL 2-step) vs. hydride-nitride-oxidation (LLNL 3-step)). The powders will also be put through a thermal gallium removal process consisting of heating the material at 1100 C for 2 h (but with no subsequent heat treatment at 800 C for 2 hours in air, or the vibratory milling step that was used in the treatment of PuO_2 in FY96 because these steps are now thought to be unnecessary based on subsequent experimental results). Ten pellets will be made using each of these PuO_2 powders. Twenty pellets will also be produced using the PuO_2 converted at LANL in FY96 via hydride-oxidation (LANL 2-step) to provide a link to previous experimental efforts, with half of these put through the same thermal treatment as the HYDOX powders (1100 C for 2 h) and half treated identically to the way that the PuO_2 was treated in the FY96 efforts (1100 C for 2 h in Ar-6% H_2 , followed by 800 C for 2 h in air, followed by 3 passes through the vibratory mill). All pellets will have a standard 5% Pu loading. A single UO_2 source will also be used for all of these pellets to try and eliminate any variability due to the uranium. The Cameco ADU UO_2 will be used because this was the material that was used in the majority of the previous fabrication experiments at LANL, and thus has the largest experience base for experiments involving MOX fuel fabrication using weapons-plutonium. Pellets from each batch will then be sampled and characterized. The measurements that will be taken are summarized in Table 3.1.1-1.

Table 3.1.1-1 Summary of Experimental Variables and Measurements for PuO₂ Variability Study

Variables	Range
Plutonium Feed	PuO ₂ from HYDOX (LLNL 2-step, LLNL 3-step, LANL 2-step), PuO ₂ from Aqueous
Measurements	Measurement Technique
<i>Post-Sintered Pellets</i>	
Microstructure	Scanning Electron Microscopy and Optical Microscopy
Homogeneity	Scanning Electron Microscopy or autoradiograph
Oxygen to Metal Ratio	Modified Lyon's Method
Density	Geometric and Archimedes' Method
Ga Concentration (as appropriate)	XRF, ICP, DCP

Milestones:

- Fabricate Pellets with Various PuO₂ Feed (14 March 1997)
- Characterize Samples (1 May 1997)
- Complete PuO₂ Variability Study (1 May 1997)

3.1.2 UO₂ Variability

This study will fabricate pellets using one selected PuO₂ supply and varying UO₂ feed materials. Pellets will then be characterized with regard to density, homogeneity, O/M, and microstructure.

The dominant constituent in MOX fuel is UO₂. At present, there are two major production routes for UO₂ that is used in commercial nuclear fuel fabrication: ADU and direct conversion. These conversion methods yield UO₂ powders with different characteristics. While either UO₂ source should be satisfactory for use with the weapons plutonium in producing MOX fuel, the unique morphology of the HYDOX PuO₂ creates the possibility that the PuO₂ may interact differently with the different UO₂ powders. While this should not preclude the use of either UO₂, it could require additional development work or adjustment of process parameters. Therefore, a simple study will be performed to determine if any significant variations are observed when the UO₂ source is varied. In FY97, multiple UO₂ sources will be identified that have similar characteristics to the UO₂ feed currently in use by commercial MOX fabricators (i.e., ADU and direct conversion UO₂). Once identified, samples will be obtained for use in the fabrication study. Ten pellets will be fabricated using the varying UO₂ sources and a single selected PuO₂ source. A constant 5% Pu loading will be used. Pellets from each batch will then be sampled and characterized. The measurements that will be taken are summarized in Table 3.1.2-1.

Milestones:

- Obtain Various UO₂ Feed (14 March 1997)
- Fabricate Pellets with Various UO₂ Feed (14 April 1997)
- Characterize Samples (15 May 1997)
- Complete UO₂ Variability Study (15 May 1997)

Table 3.1.2-1 Summary of Experimental Variables and Measurements for UO₂ Variability Study

Variables	Range
Uranium Feed	UO ₂ from various sources (i.e., direct conversion and ADU)
Measurements	Measurement Technique
<i>Post-Sintered Pellets</i>	
Microstructure	Scanning Electron Microscopy and Optical Microscopy
Homogeneity	Scanning Electron Microscopy
Oxygen to Metal Ratio	Modified Lyon's Method
Density	Geometric and Archimedes Method

3.1.3 Sintering Study

This study will evaluate the effect that different sintering times and temperatures have on final pellet density. This study will also evaluate the effect that various H₂O partial pressures have on Ga evolution.

In FY97, UO₂-based surrogate pellets will be fabricated and sintered using various sintering profiles. Components of the sintering profile include temperature, time at temperature, and ramp times and temperatures. The parameter space to be examined is summarized in Table 3.1.3. Also using UO₂-based surrogates, the pellets will be sintered using varying H₂O partial pressures, and the resultant pellets will be analyzed with respect to amount of Ga evolution. The parameter space to be examined is summarized in Table 3.1.3-1.

Table 3.1.3-1. Summary of Experimental Variables for Sintering Study

Variables	Range
Sintering Profile Temperatures	1600-1750 C
Sintering Profile Times	4-8 h
H ₂ O Partial Pressure	To be determined
Ga Concentration	XRF, ICP, DCP

Milestones:

- Complete Temperature Effect Study Using UO₂-based Surrogates (1 July 1997)
- Complete H₂O Partial Pressure Effect Study Using UO₂-based Surrogates (30 September 1997)
- Complete Sintering Study (30 September 1997)

3.2 Analytical Development

Development of analytical techniques used in conjunction with the fabrication of MOX fuel has been identified as necessary in certain areas this fiscal year. Measurement of homogeneity for weapons-grade material could potentially be more difficult due to the lower inventories of Pu-238 and Pu-241 in the fuel matrix. Autoradiography is typically used in commercial MOX fabrication, and it will be examined to determine its applicability to this program. X-Ray Microfluorescence (XRMF) holds promise as another potentially applicable technique for measurement of homogeneity as well as spatial determination of gallium concentrations, and will be developed during this year's activities. In addition, certain existing analytical capabilities are known to be (surface finish measurement) or could potentially be (O/M measurement) inadequate for determining if the fuel pellets produced are acceptable (especially with regard for production for irradiation experiments).

The purchase of a new surface finish measurement device and the potential upgrade of the O/M measurement technique will serve to enhance the analytical capabilities within the laboratory. Finally, a validation is planned of current trace analysis methods to more accurately be able to measure Ga concentrations in the ranges applicable to this program.

3.2.1 Homogeneity

This study will develop and determine relative merits of available homogeneity measurement techniques. Autoradiograph experiments will be performed to determine the suitability of this technique for use with weapons plutonium. Experiments will also be performed with XRMF to determine the detection limit and resolution of the technique so that this method may be evaluated as a possible replacement if autoradiography is inadequate, and also as a possible technique for evaluating spatially-dependent gallium concentrations in fuel pellets and other materials (i.e., cladding).

In FY97, contracts already in place with European MOX fabricators will be used to obtain information about currently used autoradiograph techniques. Representative films and visual standards will also be obtained from each corresponding technique (the success of this depends upon vendor willingness to disclose this information for the level of funding that is available). An attempt will be made to obtain reactor-grade plutonium from the TA-55 vault, with which homogeneity standards will be fabricated, along with standards containing weapons-grade plutonium. Although the reactor-grade material will not necessarily be representative of what is currently used in commercial MOX fabrication plants (because of its age), it will have sufficient activity to produce good radiographs which can then be used as comparisons for the results obtained from the weapons material. Autoradiograph experiments will then be performed to compare the results of the reactor-grade standards to the visual standards of the European fabricators, as well as to the weapons-grade standards.

Also in FY97, experiments will be conducted to develop the XRMF technique. A comparison will be made of two focusing techniques (aperture vs. capillary), by analyzing Ga and Ce contents in a Zr matrix. One technique will then be selected and used in all further experiments. The initial capillary optic experiments will be performed at Oak Ridge National Laboratory (ORNL) because they have an existing capability. However, if the capillary optic is selected as the one for future use, a capillary optic will be procured for Los Alamos because of the necessity to analyze plutonium-bearing samples. Radioactive materials (such as U, MOX, and RG MOX) will then be introduced to determine the limit at which the radioactivity will overburden the x-ray detector. The detection limit (ppm) for Ga and Pu will then be determined through the introduction of varying amounts of each material. Finally, using a 50 μm beam, the particle size resolution of the technique will be determined for later comparison to the autoradiograph resolution. The culmination of this effort will be a report that analyzes the applicability of this technique for determination of MOX homogeneity (and comparison of it to autoradiography) as well as a cost and schedule estimate for developing the technique into a fully industrialized process. Sufficient information should be contained in this report for the applicable parties (i.e., DOE, fuel fabricators, etc.) to make a well-informed decision on whether this technique should be pursued.

Milestones:

- Identify Autoradiograph Techniques, Obtain Films and Visual Standards (1 March 1997)
- Fabricate Homogeneity Standards with Reactor-grade and Weapons-grade Pu (31 May 1997)
- Perform Autoradiograph Experiments (15 July 1997)

- Complete Autoradiograph Study (15 July 1997)
- Compare XRMF Aperture with Capillary Optics (15 November 1996)
- Determine XRMF Radioactive Burden Limit (1 March 1997)
- Determine XRMF Limits of Detection for Ga and Pu (1 June 1997)
- Determine Resolution of 50 μ m X-Ray Beam (1 September 1997)
- Complete XRMF Study (1 September 1997)

3.2.2 Upgrade TA-55 Analytical Capability

This study will serve to upgrade the analytical capabilities available in TA-55, particularly with regards to surface finish and O/M measurement.

In FY97, a new surface finish measurement device will be purchased and installed in TA-55. This is required because the existing surface finish measuring device no longer yields accurate data, and this analysis is required to verify the fuel meets the required specifications (this is particularly important for the fabrication of fuel for irradiation testing). In addition, various O/M measurement techniques will be evaluated in terms of availability and cost for eventual installation in TA-55. While the existing O/M measurement technique is sufficient for the current activities, the potential exists that future efforts will require more accurate measurements. Therefore, a small effort is planned to identify potential capabilities that could be installed if required.

Milestones:

- Obtain New Surface Finish Measurement Device (1 February 1997)
- Investigate Alternative O/M Measurement Techniques (30 September 1997)

3.2.3 Trace Analysis Validation

This study will validate the use of the inductively-coupled plasma (ICP) and direct-coupled plasma (DCP) techniques for Ga measurements in the appropriate concentration range through comparison to the x-ray fluorescence (XRF) technique.

In FY97, experiments will be performed to measure Ga concentrations using the three available techniques: XRF, ICP, DCP. The XRF technique is well calibrated for Ga concentrations within the range of 200 ppm and above. Properly calibrated, ICP and DCP techniques should yield accurate gallium concentrations down to the ppb range. However, earlier comparisons between DCP and XRF results for concentrations above 200 ppm showed variation in the results (this could be due to either the calibration being incorrect or due to mistakes in dilution of the sample which is required to get the gallium concentration within the calibrated concentration regime of the DCP). Consequently, a validation will be performed at the higher Ga concentration levels through comparison of the ICP and DCP results to those of the XRF. Adjustments will be made to the ICP and DCP calibration and sample preparation processes as required. The ICP and DCP techniques will then be used for trace analysis in the lower concentration ranges (below the limit of XRF) with higher confidence in the results.

Milestones:

- Validation of Trace Analysis (1 March 1997)

4.0 Schedule and Milestones

An overall schedule of activities for fiscal year 1997 is provided in Figure 4.0-1. A summary of the fiscal year 1997 research and development milestones for the Nuclear Fuels Technologies project are given in Tables 4.0-1, 4.0-2, and 4.0-3.

Table 4.0-1 Fiscal Year 1997 Feed Qualification Milestone Summary

Applicable Section	Milestone	Expected Completion Date
2.1.1	Define Required HYDOX-Derived PuO_2 Amounts and Desired Characteristics	1 December 1996
2.1.1	Obtain HYDOX-Derived Feed Materials	1 March 1997
2.1.1	Complete Characterization of HYDOX-Derived Feed Material	1 May 1997
2.1.2	Define Required Aqueous-Derived PuO_2 Amounts and Desired Characteristics	14 February 1997
2.1.2	Obtain Aqueous-Derived Feed Materials	1 March 1997
2.1.2	Complete Characterization of Aqueous-Derived Feed Material	1 May 1997
2.2.1	Complete Critical Assessment of Ga_2O_3 - PuO_2 Thermodynamic Data	1 March 1997
2.2.1	Optimize Ga_2O_3 - PuO_2 Phase Diagram	30 September 1997
2.2.1	Complete Critical Assessment of PuO_2 - UO_2 Thermodynamic Data	1 August 1997
2.2.1	Optimize PuO_2 - UO_2 Phase Diagram	30 September 1997
2.2.1	Complete Critical Assessment of Ga_2O_3 - PuO_2 - UO_2 Thermodynamic Data	25 August 1997
2.2.1	Optimize Ga_2O_3 - PuO_2 - UO_2 Phase Diagram	30 September 1997
2.2.2	Complete Time, Temperature, and Sample Size Studies on Surrogates	1 July 1997
2.2.2	Complete Surrogate Gallium Removal Studies	30 September 1997
2.2.3	Complete PuO_2 gallium removal studies	30 September 1997
2.2.4	Generate Throughput Requirements and Surplus Inventory Effects	28 February 1997
2.2.4	Identify Thermal Treatment Equipment and Sizing	31 July 1997
2.2.4	Complete Thermal Treatment Cost Estimates	31 August 1997
2.2.4	Complete Thermal Treatment Industrialization Study Report	30 September 1997
2.2.4	Create Block Diagram of Aqueous Removal Concept	31 December 1996
2.2.4	Develop Aqueous Removal Process Specifics	31 December 1996
2.2.4	Determine Materials Balances for Aqueous Removal	31 March 1997
2.2.4	Estimate Aqueous Removal Equipment Sizing	30 June 1997
2.2.4	Perform Aqueous Removal Cost Estimation	30 June 1997
2.2.4	Complete Aqueous Removal Report	30 September 1997

Table 4.0-2 Fiscal Year 1997 Fuel Fabrication Development Milestone Summary

Milestone	Completion Date
Fabricate Pellets with Various PuO ₂ Feed	14 March 1997
Characterize Samples	1 May 1997
Complete PuO ₂ Variability Study	1 May 1997
Obtain Various UO ₂ Feed	14 March 1997
Fabricate Pellets with Various UO ₂ Feed	14 April 1997
Characterize Samples	15 May 1997
Complete UO ₂ Variability Study	15 May 1997
Complete Temperature Effect Study Using UO ₂ -based Surrogates	1 July 1997
Complete H ₂ O Partial Pressure Effect Study Using UO ₂ -based Surrogates	30 September 1997
Complete Sintering Study	30 September 1997
Identify Autoradiograph Techniques, Obtain Films and Visual Standards	1 March 1997
Fabricate Homogeneity Standards with Reactor-grade Pu	31 May 1997
Perform Autoradiograph Experiments	15 July 1997
Complete Autoradiograph Study	15 July 1997
Compare XRMF Aperture with Capillary Optics	15 November 1996
Determine XRMF Radioactive Burden Limit	1 March 1997
Determine XRMF Limits of Detection for Ga and Pu	1 June 1997
Determine Resolution of 50 µm X-ray Beam	1 September 1997
Complete XRMF Study	1 September 1997
Obtain New Surface Finish Measurement Device	1 February 1997
Investigate Alternative O/M Measurement Techniques	30 September 1997
Validation of Trace Analysis	1 March 1997

Figure 4.0-1 Schedule of Activities

Figure 4.0-1 Schedule of Activities (Continued)