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Title: **Nuclear Fuels Technologies Thermally Induced Gallium Removal System (TIGRS) Fiscal Year 1998 Research and Development Test Plan**

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Nuclear Fuels Technologies
Thermally Induced Gallium Removal System (TIGRS)
Fiscal Year 1998 Research and Development Test Plan

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1.0 SUMMARY

As TIGRS has evolved from the conceptual to application phase, the requirements have become more clearly defined, and consequently, so must the test planning. While this Test Plan is concerned with only the details of FY98, the entire test program (which is to be completed in FY99) is outlined here to aid in the understanding of the FY98 activities. It is important to note that a significant amount of TIGRS related R&D work has already occurred.

This R&D test program has been essentially divided into two major activities. These two activities form the basis of this Test Plan, and can be described as (1) process development which leads to the prototypic design, and (2) prototypic design and testing. Both of these major activities will be accomplished through testing with the use of cold surrogate (CeO_2) and hot (PuO_2) feed materials. Following feed fabrication development and validation, the surrogate feed material will be used to verify material compatibility and process material handling for the prototypic equipment. The PuO_2 feed material will be used to demonstrate adequate gallium separation and to optimize process operating conditions.

2.0 INTRODUCTION

This document details the research and development (R&D) activities that will be conducted in Fiscal Year 1998 (FY98) by the Thermally Induced Gallium Removal System (TIGRS) 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 using weapons-derived plutonium in the fabrication of mixed-oxide (MOX) nuclear fuel for reactor-based plutonium disposition. The ultimate purpose of this work is to demonstrate adequate Thermally Induced Gallium Removal with a prototypic system. This Test Plan presents more than the FY98 R&D efforts in order to frame the Task in its entirety. It is felt that to understand the motives behind each individual effort in this Test Plan, the reader must be familiar with the entire Task effort. This entire Task is essentially a two year effort culminating in the final prototypic demonstration of the TIGR process. The specifics of the FY99 effort are not discussed in this document; however, top-level objectives for both FY98 and FY99 will be explained and included in the Schedule Section.

To achieve the TIGRS Program objectives, R&D activities during the next two years will be focused on (1) process development leading to a prototypic TIGRS design, and (2) prototypic TIGRS design and testing leading to and including a prototypic demonstration of TIGRS operation. Both the process development and system testing efforts will consist of a series of surrogate-based cold tests and plutonium-based hot tests. Some of this testing has already occurred and will continue into FY99.

Surrogate-Based Cold Tests. These tests are oriented toward answering early questions regarding (1) the solid-based phase structure of gallium in PuO_2-like systems, (2) the gallium evolution mechanisms in PuO_2-like systems, and (3) the functionality and reliability of the prototype TIGRS hardware.

> Process Development. Knowledge of the solid-based phase structure can be used to infer the maximum gallium which can be separated from plutonium. This information has produced early evidence that the TIGR process has a reasonable chance of success. Additionally, it may aid in the validation of the surrogate, which will be important for cold prototypic testing. The data obtained from cold testing allows an early review of the TIGR process applicability.

Process Development. Determination of the predominant gallium separation mechanisms (i.e. diffusion within the particle, chemical kinetics, or mass transfer between the solid and gas phases) can aid in the selection of a prototypic TIGR design. For instance, early data indicate the hydrogen gas velocity and consequent mass transfer rate between the solid and gas phases may significantly affect the rate of gallium separation. From this one can infer that the TIGRS design should have the capability to adjust the gas/particle mixing. An example of how this can be achieved is an inclined-rotating versus batch-type calciner. Further testing is needed to confirm these early data. This type of data obtained from cold testing will allow an early review of potential off-the-shelf applicable TIGR processing equipment.

Prototypic Design and Testing. Use of a cold surrogate for establishing the functionality and reliability of the prototypic TIGRS is necessary for a number of reasons.

First, typical devices used for similar processing of PuO_2 such as calciners, are generally operated at temperatures significantly less than may be required for gallium separation. Consequently, while an off-the-shelf design such as that of a calciner may be selected, the materials may be different due to a higher operating temperature. The use of new materials even with an established design creates the need for some degree of mechanical and reliability testing. If hot (plutonium) feed rather than cold (surrogate) feed were used for this testing, it would be much more difficult (if even possible) to correct mechanical problems.

Second, gallium compatibility with the TIGRS materials must be established for reliability reasons. This effort will require significantly less effort and cost with a cold feed than a hot feed, with little or no compromise in the data applicability.

Third, it may be necessary to use a gallium getter, coupled with occasional bakeout of the TIGRS, to minimize degradation of system components. The efficiency of such a device can be more easily, and less expensively, demonstrated with a cold feed than with a hot feed.

And finally, the material handling itself can more easily and less expensively be demonstrated with a cold feed rather than a hot feed. In particular, should a device similar to an inclined-rotating calciner be used, the particle movement will likely need to be demonstrated due to the potentially higher operating temperature.

Plutonium-Based Hot Tests. These tests will be oriented toward (1) determining the controlling gallium evolution mechanisms in PuO_2, (2) selecting an appropriate TIGRS design for industrial application, (3) determining the optimum processing conditions, and (4) demonstrating prototypic TIGRS processing and equipment reliability.

Process Development. Determination of the controlling gallium separation mechanisms (i.e. diffusion within the particle, chemical kinetics, or mass transfer between solid and gas phases) will dictate the prototypic TIGR design. The data from hot (plutonium) testing will be used to validate the results obtained from the surrogate testing and to refine the conclusions derived from the surrogate data. For

instance, data from hot testing will be used to establish the prototypic operating temperature range which will lead to selection of materials for the prototypic design.

Prototypic Design and Testing. Preparation of the prototypic design will require evaluating the process development data to select the complete range of processing conditions, such as hydrogen gas velocity, temperature, processing time, and feed rate. Following fabrication or purchase of the prototypic processing unit, it will be necessary to evaluate its performance and reliability. While the cold testing will be used to evaluate mechanical reliability, material compatibility, and gallium getter efficiency, the prototypic hot testing will be used to demonstrate the process adequacy and to optimize the processing conditions.

3.0 PROCESS DEVELOPMENT

The Process Development task will be focused upon the following efforts to demonstrate the TIGR process adequacy and to aid in the selection of prototypic processing equipment and processing conditions.

- Producing an adequate supply of well characterized prototypic surrogate (CeO_2) and PuO_2 feed material.
- Surrogate testing to determine the phase structure of cerium-gallium oxide and the rate limiting mechanisms of gallium evolution from cerium.

  The phase structure will be determined by a variety of analytical methods including scanning electron microscope (SEM) and X-ray fluorescence (XRF) for the gallium distribution.

  The gallium evolution mechanisms to be studied are:
  (1) Diffusion within the particle (Ga_2O_3, Ga_2O, and H_2).
  (2) Chemical kinetics (Ga_2O_3 reduction to Ga_2O).
  (3) Solid/gas mass transfer (hydrogen adsorption on the particle surface and Ga_2O sublimation or vaporization from the particle surface to the gas). It is not yet known whether the Ga_2O exists as a solid or liquid on the particle surface; hence, it may sublime or vaporize.
- PuO_2 testing to validate the surrogate applicability.
- PuO_2 testing to begin the determination of prototypic processing conditions.

3.1 Feed Preparation

To conduct the process development and prototypic testing, adequate supplies of both surrogate-based and plutonium-based feed material must be fabricated. It is essential that this material, for both surrogate-based and plutonium-based feedstock, be as representative of prototypic material as possible. For this reason, multiple fabrication processes will be evaluated.

3.1.1 Surrogate (CeO_2)

The following potential methods for producing the CeO_2 will be evaluated to produce a surrogate with the proper phase structure and particle morphology.

Pressing/Sintering/Milling
: This involves pressing followed by sintering and milling of CeO_2 to achieve proper particle morphology.

Precipitation
: Dissolution in acid followed by precipitation such as the oxalate process used for plutonium. The precipitate can then be oxidized by a calcination process.

Hydride/Oxide
: This is essentially the LLNL 2-Step process developed for plutonium.

3.1.2 PuO_2

There are potentially three sources of prototypic weapons-based PuO_2 which contains gallium. This feed material in general must be characterized with regard to gallium concentration and particle morphology.

PuO_2 from the LLNL 3-Step process. As of 22 December 1997, LANL has approximately 350 g of this material remaining. All ~350 g have been characterized for gallium concentration and particle morphology (particle size and surface area).

PuO_2 from the LLNL 2-Step process. As of 22 December 1997, LANL has approximately 1500 g of this material. All ~1500 g have been characterized for gallium concentration, but the particle morphology has not been determined.

PuO_2 directly oxidized from metal ingots. Currently LANL does not have any of this material; however, production can begin in early 1998 if necessary. Characterization would be required.

3.2 Process Characterization

An important objective of the Process Development effort is the selection of prototypic processing conditions. These process conditions will dictate the type of processing equipment required and the materials.

If it is determined that the hydrogen gas velocity has a significant impact on the gallium separation rate, and that by manipulating processing temperature and processing time alone adequate gallium separation can not be achieved, a device which can significantly adjust the gas/particle interaction such as an inclined rotating kiln may be required.

If it is determined that the hydrogen gas velocity does not significantly affect the gallium separation rate, or that manipulation of processing temperature and processing time alone can achieve adequate gallium separation, then batch-type processing with a fixed bed may be satisfactory. Equipment required for batch-type fixed bed processing is of a simpler design and operation than a device like an inclined rotating kiln. For such a case, the prototypic processing unit would be less expensive to fabricate and operate.

3.2.1 Surrogate (CeO_2) Based

The plutonium-gallium oxide phase structure will dictate the maximum amount of gallium which can be separated by the TIGR process. While a single Ga_2O_3 phase should be easily reduced with hydrogen to the volatile Ga_2O species, a more complex phase with both plutonium and gallium in solution might not be amenable to Ga_2O formation. Currently, a method for characterizing the phase structure of plutonium-gallium compounds at gallium concentrations less than 10 wt% has not been found. Consequently, determining the phase structure for prototypic weapons-based material is not yet possible. However, it is possible to determine the CeO_2 surrogate phase structure with prototypic gallium concentrations of less than 1 wt%. In light of this information, surrogate phase structure studies have been initiated to ascertain the thermodynamic similarities between cerium-gallium oxide and plutonium-gallium oxide, at gallium concentrations amenable to phase structure analysis for both the surrogate and plutonium systems. Following validation of the cerium and plutonium phase structure similarities, conclusions drawn from surrogate phase structure analysis at prototypic gallium concentrations will be extrapolated to the plutonium phase structure. This may provide data regarding the theoretical maximum gallium separation from plutonium by the TIGR process.

3.2.2 PuO_2 Based

Prototypic PuO_2 will be used to establish the processing conditions which are required for the system design. The process parameters which will be studied are summarized in the following, and the detailed test matrices are shown as Tables 3.2.2-1 and 3.2.2-2.

Time

Time can affect the degree of sintering as well as the degree of gallium separation; therefore, it is desirable to maximize processing time to increase gallium separation, but to minimize process time in order to limit adverse sintering effects.

Temperature

Temperature affects the TIGR process in a fashion similar to time.

Gas velocity of the reducing agent (H_2)

The hydrogen gas velocity will alter the mass transfer coefficients for transfer of hydrogen from the gas phase to the particle, and for transfer of Ga_2O from the particle to the gas phase. Increasing gas velocity may increase the rate of gallium separation; however, increasing gas velocity can also make plutonium powder management more difficult.

Partial pressure of reducing agent (H_2)

Adjusting the partial pressure (i.e. concentration) of the reducing agent hydrogen, while maintaining the overall gas pressure and velocity constant, can provide evidence as to whether the chemical kinetics affect the gallium separation rate. However, there is little reason to use less than the maximum of 6% H_2 allowed by safety considerations. Therefore, this process parameter will probably not be evaluated.

Sample size

Sample size can affect the hydrodynamics of the gas/particle interaction. Since hydrogen must enter the particle, and Ga_2O must leave the particle, the batch size for a fixed particle bed can affect the gallium separation rate. The testing defined by Tables 3.2.2-1 and 3.2.2-2 will be conducted with a fixed particle bed.

Temperature	Gas flow Velocity 1.5 cm/s			Gas flow Velocity 3 cm/s		
	0.3 grams	0.9 grams	2.5 grams	0.3 grams	0.9 grams	2.5 grams
600°C	✓	✓	✓	✓	✓	✓
800°C	✓	✓	✓			
900°C	✓	✓	✓	✓	✓	✓
1000°C	✓	✓	✓			
1100°C	✓	✓	✓			
1200°C	✓	✓	✓	✓	✓	✓

Table 3.2.2-1. PuO_2 gallium evolution test matrix for 0.5-hr tests

Temperature	Gas flow Velocity 1.5 cm/s		
	0.3 grams	0.9 grams	2.5 grams
600°C	✓	✓	✓
900°C	✓	✓	✓
1200°C	✓	✓	✓

Table 3.2.2-2. PuO2 gallium evolution test matrix for 4-hr tests

Characterization will include gallium concentration and the particle morphology (i.e. size distribution and surface area).

3.3 Surrogate (CeO_2) Validation

The CeO_2 will be validated for acceptance as a PuO_2 surrogate by duplicating selected PuO_2 gallium evolution process optimization testing. This approach will allow leveraging of the PuO_2 process optimization data for surrogate validation. The PuO_2 process optimization test conditions are defined in Table 3.2.2-1 and Table 3.2.2-2. Not all of the conditions selected for PuO_2 process optimization testing will necessarily be duplicated for the CeO_2 validation testing. A balanced selection of the most significant test conditions will be chosen for duplication.

In the event that the surrogate can not be validated (i.e. the behavior of CeO_2 and PuO_2 do not correspond), the program will proceed with the prototypic testing, although at an increased level of risk. In particular, cold prototypic testing will be compromised

somewhat if a valid surrogate does not exist. Any required engineering changes following the initial processing checkout would be difficult incorporate on a hot (contaminated) system. It may be possible to find an alternate cold surrogate which does not duplicate plutonium-gallium evolution behavior, but duplicates PuO_2 particle dynamics.

4.0 PROTOTYPE DESIGN AND TESTING

The prototypic design effort will be focused on two primary activities. First, a system design will be selected which can provide the process conditions selected from the process development test results. As much as possible, this system design will consist of off-the-shelf equipment. Second, materials will be selected which allow operating the selected system at the design conditions. In particular, this relates to the concern over gallium reactivity with system components, and any moving parts at elevated temperatures.

The prototypic testing will consist of (1) cold checkout phase, (2) hot checkout phase, and a (3) prototypic demonstration. These tests will be conducted during FY99, and the test planning will be initiated later in FY98.

4.1 Prototype Design

As a starting point for the prototype design, consideration will be given to off-the-shelf equipment. One example of off-the-shelf equipment which is used for processing similar to that which will be needed for the TIGRS is a calciner. For instance, Los Alamos has used both fixed-bed batch-type kiln/calciners and inclined-rotary continuous-type kiln/calciners for production of PuO_2 from oxalate precipitate. While the fixed-bed can be operated at higher temperatures than the inclined-rotary, and the inclined-rotary achieves greater gas/solid mixing than the fixed-bed, it is likely that neither have been used for PuO_2 at temperatures high enough for gallium removal.

4.1.1 Mechanical

Perhaps one of the most important aspects of the mechanical design will be whether a fixed-bed batch-type processing device will suffice. If it is determined that a fixed-bed device can not provide adequate gas/particle mixing, then the design will become more complicated along the line of a inclined-rotary continuous-type device. This will add complexity to the design with regard to including more moving parts at elevated operating temperatures. While similar equipment has been used for years in the mining industry at processing temperatures far in excess of what will be required for gallium separation, the application for plutonium processing creates numerous unique challenges. For instance, locating an off-the-shelf design for TIGRS operating temperatures while matching the processing rate and satisfying the criticality requirements will probably be very difficult. For these reasons, the mechanical design effort will require a significant level of creativity if existing technology is used.

4.1.2 Materials

Two primary questions exist with regard to materials. First, what fabrication materials must be changed if the off-the-shelf equipment is operated at significantly higher than original design conditions? Second, what will be the effect of highly reactive gallium on the system materials? Should a gallium getter be included in the design, and if so what should the getter material consist of, and should it be internal or external to the processing chamber?

4.2 Prototype Testing

This is a FY99 activity.

5.0 MAJOR MILESTONES/DELIVERABLES

	Initiate	Complete
PuO_2 received for process development	ongoing	01/01/98
Systems requirement document*	ongoing	04/01/98
Hot R&D testing*	ongoing	07/01/98
Cold prototypic testing*	11/01/98	04/01/99
Hot prototypic testing*	04/01/99	05/28/99
Prototypic demonstration test*	07/01/99	09/30/99

*Report due