WSRC-TR-97-00345 (U)

ALTERNATIVE ALUMINUM SPENT NUCLEAR FUEL TREATMENT

TECHNOLOGY DEVELOPMENT STATUS REPORT (U)

Savannah River Technology Center Strategic Materials Technology Department Materials Technology Section

Publication Date: October 1997

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This document was prepared in connection with work done under Contract No. DE-AC09with the U. S. Department of Energy

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DOCUMENT: WSRC-TR-97-00345

TITLE:ALTERNATIVE ALUMINUM SPENT NUCLEAR FUELTREATMENT TECHNOLOGY DEVELOPMENTSTATUS REPORT (U)

 TASKS:
 SRT-MTS-96-2047, Rev. 1; SRT-MTS-97-2030, Rev. 0

 SRT-MTS-96-2063, Rev. 1
 SRT-MTS-96-2064, Rev. 0

 SRT-MTS-97-2004, Rev. 0
 SRT-MTS-97-2004, Rev. 0

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LIST OF ACRONYMS

Acronym

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Definition

AEA	Atomic Energy Act	
Al-SNF	IF Aluminum-clad, Aluminum-based Spent Nuclear Fuel	
ANL	Argonne National Laboratory	
ANSI/ANS	American National Standards Institute/American Nuclear Society	
ASME	American Society of Mechanical Engineers	
ASTM	American Society for Testing and Materials	
ATR	Advanced Test Reactor	
ATP	Alternative Al SNF Treatment Technology Program	
BOL	Beginning of Life	
CAA	Clean Air Act	
CDA	Controlled Design Assumptions Document	
CERCI A	Comprehensive Environmental Response Compensation and Liability Act	
CFR	Code of Federal Regulations	
CDD	Chemical Processing Plant (INEL)	
CDD	Cyclic Potentiodynamic Polorization	
CP	Corresion Pate	
CRWAIS	Contoston Raic	
	Defense High Level Weste	
DALW	Le Desetternet of France	
DOE EN	U.S. Department of Energy	
DOE-EM	U.S. Department of Energy Office of Environmental Management	
DOE-RW	U.S. Department of Energy Office of Civilian Radioactive Waste	
	Management (also OCRWM)	
DRR	Domestic Research Reactor	
DWPF	Defense Waste Processing Facility	
EBDRD	Engineered Barrier Design Requirements Document	
EBS	Engineered Barrier System	
EDM	Electro-Discharge Machine	
EDS	Energy Dispersive Spectrometry	
EIS	Environmental Impact Statement	
EOL	End of Life	
EPA	Environmental Protection Agency	
F&OR	Functional & Operating Requirements	
FFCA	Federal Facilities Compliance Act	
FRR	Foreign Research Reactor	
FWPCA	Federal Water Pollution Control Act	
GC	Gas Chromatograph	
HEDL	Hanford Engineering Development Laboratory	
HEPA	High-Efficiency Particulate Air	
HEU	Highly-Enriched Uranium (> 20% U ²³⁵ in U)	
HFBR	High-Flux Beam Reactor	
HFIR	High Flux Isotope Reactor	
HLW	High Level Waste	
HLWG	High-Level Waste Glass	
HVAC	Heating, Ventilation, & Air Conditioning	
IAEA	International Atomic Energy Agency	
ICPES	Inductive Coupled Plasma Emission Spectroscopy	
ID	Inner Diameter	
IMNM	Interim Management of Nuclear Materials	
INEL	Idaho National Engineering Laboratory	
IR	Infrared	
LANL	Los Alamos National Laboratory	
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ICII	Low Enriched Uranium (2 to 20% U ²³⁵ in U)
	Laurence Livermore National Laboratory
LLINL	Linear Detentiodynamic Dolorization
	Multi Canister Overbacks
MD	Malt Dilute
MCDS	Mined Geologia Dispecel System
MGDS	Mined Geologic Disposal System
	Multi Dumose Conjetes
MPC	Multi-Purpose Canister
MRS	Monitored Reinevable Storage
MTHM	Metric Tons Heavy Metal
MIR	Materials Test Reactor
MTRE	Materials Test Reactor Equivalent
MWd	Megawatt days
NDE	Non-Destructive Examination
NEPA	National Environmental Policy Act
NRC	U.S. Nuclear Regulatory Commission
NWPA	Nuclear Waste Policy Act
OCRWM	The Office of Civilian Radioactive Waste Management
OD	Outer Diameter
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Research Reactor
PCT	Product Consistency Tests
PEIS	Programmatic Environmental Impact Statement
PIN	Refers to the SNF with a pin geometry
PNNL	Pacific Northwest National Laboratory
OA	Quality Assurance
RBOF	Receiving Basin for Offsite Fuel
RCRA	Resource Conservation and Recovery Act
RH	Relative Humidity (vapor pressure of H ₂ O/saturation pressure of H ₂ O)
RHF	Réacteur à Haut Flux
RT	Room Temperature
RW	Office of Civilian Radioactive Waste Management
SARA	Superfund Amendments and Reauthorization Act
SCC	Stress Corrosion Cracking
SEM	Scanning Electron Microscone
SESD	Spent Fuel Storage Division
SI	Structural Integrity
SI	Snent Nuclear Fuel
SNI	Savannah Diver Site
SAS	Savamai Niver She Savannah Diver Technology Center
	To Be Determined
	To Be Determined
	To be venneu
	Three Mile Island
IKU	Transuranic elements
199	I ransier, storage & Snipment
VLEU	very-Low-Enriched Uranium (< 2% U ²²⁵ in U)
WAC	waste Acceptance Unterna
WP	Waste Package
XRD	X-Ray Diffraction

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PREFACE

An Alternative Aluminum Spent Nuclear Fuel Treatment Technology Program (ATP) was initiated at the Savannah River Site (SRS). The technology needed for interim storage and ultimate disposition of aluminum-based research reactor spent nuclear fuel (Al-SNF) under the jurisdiction of the U.S. Department of Energy (DOE) will be developed under this program. This report provides the status of the technology development activities for the period ending October 1, 1997.

Aluminum SNF is being consolidated at SRS in Aiken, South Carolina for treatment, packaging, interim storage, and preparation for ultimate disposal in a geologic repository in the United States. Sources of Al-SNF are domestic research reactors (DRR), foreign research reactors (FRR), and SRS production reactors. A significant portion of the Al-SNF to be consolidated at SRS will contain highly enriched uranium. Hence, although small in quantity compared to the inventory of commercial spent fuel and the high level waste (HLW) to be stored in the repository, the disposal technologies must consider and mitigate the occurrence of a criticality event in the repository. An FY97 program was initiated to evaluate technology alternatives to processing for the disposal of research reactor Al-SNF in a geologic repository. This program is referred to as the Alternative Aluminum Spent Nuclear Fuel Treatment Technology Program.

These actions followed the DOE Record of Decisions from the Programmatic Spent Nuclear Fuel Environmental Impact Statement (SNF-EIS) (Reference P.1), the Interim Management of Nuclear Materials Environmental Impact Statement (IMNM-EIS) (Reference P.2), and the Foreign Research Reactor Environmental Impact Statement (FRR-EIS) (Reference P.3). Interim management and preparation for final disposition of DOE-owned Al-SNF is programmatically managed by the Office of Environmental Management (EM) of DOE.

The Spent Fuel Storage Division (SFSD) at SRS is responsible for receipt, treatment, packaging, interim storage, and preparation for ultimate disposal of Al-SNF in a geologic repository. The SFSD is responsible for executing ATP. In addition, SFSD is also expected to initiate and implement a Request for Proposal (RFP) for a Transfer and Storage Services facility (TSS) contract. This facility will provide services to place Al-SNF in interim dry storage in a road-ready condition, awaiting shipment to the repository.

The storage and disposal of Al-SNF are subject to requirements that provide for safety and acceptable radionuclide release. Criteria for acceptance of the condition of Al-SNF for direct basin storage developed previously (Reference P.4) are presently being revised; fuels with minor cladding penetrations should be acceptable for temporary direct basin storage since there is no significant release of radioactivity impacting safety (Reference P.5). Requirements for future drying and interim dry storage of Al-SNF for up to 50 years developed previously (Reference P.6) have been updated in this status report. Requirements for repository disposal of Al-SNF have been listed in this status report. The Page xii of xiv

technical bases to demonstrate these requirements are met for Al-SNF forms are being performed under technical programs under the ATP.

Technical programs under the ATP are being led by the Savannah River Technology Center (SRTC), coordinating the efforts of a team of scientists and engineers from SRTC, SFSD, and the Projects Engineering and Construction Division (PECD). The team also includes of Argonne National Laboratory (ANL), Pacific Northwest National Laboratory (PNNL), and the DOE-RW Management and Operating (M&O) contractor. This program addresses all aspects of storage and disposal of the Al-SNF. It incorporates the recommendations of the Research Reactor Spent Nuclear Fuel Task Team appointed by the Office of Spent Fuel Management of DOE EM-67 (Reference P.7). The four main technical program elements of the ATP are:

- Development of Technologies for Direct/Codisposal of Aluminum Spent Nuclear Fuel - In Direct/Codisposal, the SNF would be placed into small waste packages, with or without high level waste glass logs, ready for disposal in a repository. The SNF quantities in a package will be limited to satisfy repository criticality requirements. This program element consists of tasks necessary to qualify the Direct/Codisposal of Al-SNF in a road ready package for the repository.
- Development of Dilution Technologies for Aluminum Spent Nuclear Fuel The Melt-Dilute option for treatment of Al-SNF consists of melting and diluting the Al-SNF with depleted uranium. This program element consists of tasks necessary to develop and qualify the Melt-Dilute process and the diluted Al-SNF form.
- Characterization of DOE Aluminum Spent Nuclear Fuel This program element consists of identifying the characterization requirements, developing and building the characterization information and the associated characterization technologies needed for both Direct/Codisposal and Melt-Dilute Al-SNF forms.
- Development of Test Protocol for Metallic Aluminum Spent Nuclear Fuel Forms - This program will develop standardized test methods for the evaluation of performance of an Al-SNF form in a repository. It is expected to serve as the test method used to qualify Al-SNF forms for repository disposal.

The data and analyses which result from the ATP will provide the technical bases for qualification of the Al-SNF for disposal in the geologic repository. This program will be integrated with the Office of Civilian Radioactive Waste Management (OCRWM) of DOE. OCRWM is ultimately responsible for the development of the license application for the geologic repository and subsequent submittal to the Nuclear Regulatory Commission (NRC).

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1.0 SUMMARY

The Aluminum Spent Nuclear Fuel Alternate Treatment Technology Program (SNF-ATP) was initiated at SRS during FY97. The purpose of this program was to develop the technologies for the disposition of a direct and a melt-dilute aluminum SNF form in a geologic repository. The SRS SNF-ATP program presently consists of the following four tasks:

- 1. Direct/Codisposal Aluminum SNF Form Development
- 2. Melt-Dilute Aluminum SNF Form Development
- 3. Development of Aluminum SNF Form Test Protocols
- 4. Development of Characterization Requirements

A brief overview and the status of each of these tasks is provided in this section.

1.1 DIRECT/CODISPOSAL TECHNOLOGY DEVELOPMENT STATUS

The overall objective of the direct/codisposal technology development program is to provide technical methodologies and analyses to support qualification of DOE-owned aluminum-based spent nuclear fuel assemblies for interim dry storage and ultimate repository disposal. The present areas of activity in the direct/codisposal technology program for Al-SNF are:

- development of storage criteria for a road ready package;
- the development of an instrumented, shielded test canister system for validation of drying and storage criteria for interim dry storage systems;
- thermal analysis of storage and disposal configurations;
- analyses of degradation and radionuclide release rates of Al-SNF in storage environments and application to repository performance assessment;
- criticality analyses of materials configurations;
- materials input for a total system performance assessment; and
- preparation of technical information base to meet regulations and requirements for repository disposal.

The path envisioned for ultimate disposition of the aluminum-based spent nuclear fuel assemblies involves transfer and processing of wet-stored assemblies into an Al-SNF form (direct or melt-diluted) in a sealed canister. The canisters would be in interim dry storage for up to 40+ years, awaiting repository disposal. The canisters would be transported to the repository and placed into waste packages for ultimate disposition. To proceed on this path, the Al-SNF form must meet requirements for both the interim dry storage system and the Mined Geologic Disposal System.

The storage criteria for aluminum SNF in a road ready package were previously developed. The storage criteria supports the basis for the interim storage and the

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repository storage requirements detailed in Section 3. An instrumented canister was designed and fabricated to validate the drying and storage criteria for road-ready storage, to validate corrosion and gaseous release models, to validate heat transfer analysis methodology, and to provide lead-assembly-surveillance for a dry storage system. The canister will house a MTR assembly in a sealed dry storage configuration and is instrumented to measure and record the temperatures of the fuel cladding and air, the gas species present, pressure, relative humidity, and the visual condition of the fuel material. The SNF and canister can be dried to any predetermined level.

Thermal modeling and analysis methodologies have been established for interim dry storage conditions. A three-dimensional CFD model has been developed using the CFX code to demonstrate that fuel temperature distributions and buoyancy-induced cooling within an enclosed spent nuclear fuel canister can be predicted and simulated with reasonable accuracy under various expected interim storage configurations and ambient boundary conditions. In addition, the conjugate thermal model has been benchmarked against the SRS full-scale experimental test data under various environmental conditions.

The engineering viability of storing aluminum-clad flat-plate spent nuclear fuel in a geological repository is also being conducted to provide an assessment of thermal performance to establish a waste package degradation model. The thermal analysis requires the decay heat load and thermal history of the proposed repository to study design options for a codisposal waste package canister. A parametric analysis approach was taken as a first phase of thermal analysis to evaluate the thermal performance for each design option of the codisposal package over the range of possible heat loads and boundary conditions. For a specified design heat load, a best estimate model will be developed later using well-defined design information.

Exposure of Al-SNF forms to environments will cause changes in the forms from their initial condition. Al-SNF degradation may result in release of radionuclides from the spent fuel matrix and reconfiguration of fissile species within the engineered barrier system (EBS). This may directly effect the performance of the proposed repository. Analytical and experimental activities are being conducted to characterize the response of the Al-SNF materials to the repository environment. Characterization of the response of these materials to the interim storage environment has been completed, except for validation testing.

One mode of degradation of the Al-SNF, while the EBS is intact, is creep due to the repository thermal environment. This creep could lead to severe slumping and cladding ruptures. Upon breach of the engineered barrier system and the DOE SNF canister, water vapor and water exposure will lead to corrosion degradation as the primary mode of attack. These modes of degradation are also being characterized.

Degradation of the Al-SNF and reconfiguration of fissile materials will be controlled by the thermochemical stability and solubility of many possible uranium compounds and rates of the many competing reactions. Based on the natural occurrence of uranium bearing minerals within ore deposits in the western United States, thermochemical data, and the

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products formed during laboratory corrosion experiments, the hydrated oxides and silicates of uranium and hydrated aluminum oxides or alumino-silicates are the most likely final degradation products. The reconfiguration and redistribution of materials within the waste package are being analyzed to support the criticality analysis.

Criticality control in waste packages for disposal at Yucca Mountain is governed by 10 CFR 60. Currently, the criticality analysis must show no possibility (probability < 10^{-6}) of criticality for 10,000 years following disposal. Therefore, both intact and degraded states of the waste package must be evaluated. Criticality within an intact DOE SNF codisposal canister was evaluated, using the MCNP4A computer code, by the Civilian Radioactive Waste Management System. Preliminary results for a degraded state of an Al-SNF canister, where the contents of the canister were homogenized with water that had flooded the free space in the canister, indicate that reactivity would be excessive, and that neutron absorber materials would need to be included in the canister to meet criticality requirements.

Neutron poison materials for loading in Al-SNF canisters have been assessed as a method for avoiding criticality with HEU SNF. Candidate materials include borated stainless steel, dispersions of europium oxide, gadolinium oxide, or samarium oxide in stainless steel, and cadmium. Mechanical properties, corrosion resistance, neutron absorption properties, cost and availability are the major factors evaluated for selection of a poison material.

The analysis of the potential long-term dose to humans from future repository release is called a performance assessment. The proposed repository for disposal of HLW, including commercial SNF, DHLW, and DOE SNF at Yucca Mountain, about 90 miles northwest of Las Vegas, Nevada, would be located in the unsaturated zone, about 200 meters above the water table. This repository is projected to be the burial site for more than 70,000 MTHM. Of this 70,000 MTHM of high-level waste, less than five percent is DOE SNF, with the bulk (63,000 MTHM) of the HLW originating from the generation of power at commercial nuclear reactors. The remainder of the waste is in the form of glass logs from DHLW and DOE SNF. The National Spent Fuel Program has categorized the DOE SNF into 15 categories for performance assessment. SRS SNF comprised three of these categories (Categories 5, 6, & 7). Results of a recent performance assessment prepared by RW for DOE indicate that the Al-SNF forms in Category 6 are one of two categories of DOE SNF that may provide a significant contribution to the dose at the accessible environment.

In order to get a reasonable estimate of the potential long-term dose to humans from future repository release, the rate of radionuclide release to the groundwater must be quantified. The release rate of radionuclides into the groundwater is primarily dependent upon the dissolution rate of the waste form and upon radionuclide solubility. These parameters are strongly dependent upon the near field environment (temperature, pH, carbonate concentration, and chloride concentration) and, in the case of the waste form dissolution rate, the physical condition of the system. Many of the parameters important to radionuclide release from the proposed repository will be generated elsewhere in the DOE complex; however, part of the SRS program is to provide input concerning the Page 1.4 of 1.8

dissolution of the DOE SNF at SRS. Preliminary investigation indicates that the dissolution rate of the aluminum-base DOE SNF at SRS (i.e., Categories 5, 6, & 7) is about one tenth the dissolution rate of uranium metal. Other important input to the performance assessment of the proposed repository may include the results of the thermal and criticality analyses of the codisposal canister and waste package.

Finally, much of the engineering analyses and the technical package development currently focused on direct and/or codisposal is directly adaptable to the analyses of a melt-dilute aluminum SNF form. Future work will include the analyses on the melt-dilute SNF form necessary to support the technical data package to meet repository requirements.

1.2 MELT DILUTE TECHNOLOGY DEVELOPMENT STATUS

The dilution of the U²³⁵ in the high enriched research reactor Al-SNF is being evaluated as the back-up option to direct/codisposal disposal of Al-SNF. The primary means of achieving the dilution is by the addition of depleted uranium or uranium oxide during a melting process. This approach is termed the Melt-Dilution technique. Benefits accrued from the melt-dilute process include the potential for significant volume reduction; reduced criticality potential, and potential for enhanced SNF form characteristics. The focus of the technology development is to evaluate the technical feasibility of a diluted aluminum SNF form through process development studies and develop the technical specifications for a melt-dilute process. The engineering and scientific data necessary to support the development of the technical data package for the disposition of a diluted aluminum SNF form in the repository will however be undertaken through the "test protocol" and "direct disposal" tasks.

The process definition and basis for a melt-dilute aluminum SNF form was established. Dilution through addition of depleted uranium is being evaluated. The SNF form compositions for three different dilution levels namely 20%, 5% and 2% were established. Alloy compositions evaluated include the eutectic (13 wt % U), an intermediate alloy (30 wt % U) and the intermetallic composition UAl₄ (67 wt % U). Of these compositions, the eutectic offers the lowest liquidus temperature for the uranium-aluminum system yielding a process with lower operating temperature and minimal release of off-gas species during melting. Analyses of the number of canisters required for the dispoal of the aluminum FRR and DRR SNF show that the number of canisters range from < 400 to > 1200 depending on the alloy composition and dilution level. The analyses demonstrated that for a typical eutectic composition (Al-13% U), only ~400 canisters will be required for the entire range of dilution levels being investigated. This compares to ~1400 canisters for the direct disposal option.

The process cycle options, namely time and temperature, for these combinations were also defined. Three different casting techniques, namely in-crucible solidification, tilt and pour and bottom pour are being evaluated. The effect of process conditions on the SNF form microstructure and characteristics for these casting approaches is also being assessed. The effect of process conditions on both graphite and carbon steel crucibles was also

evaluated. Both these crucible materials are adequate for a process at temperatures lower than 1000 °C, but graphite is preferable at higher temperatures.

The versatility and applicability of the melt-dilute process to all aluminum SNF of the melt-dilute process are also being evaluated. The aluminum FRR and DRR inventory consists of three fuel forms namely the aluminides, uranium oxides, and uranium silicides. Initial evaluation indicates that the irradiated fuel assemblies should all alloy readily with aluminum at temperatures below about 850 °C. However, uranium oxide is more stable than aluminum oxide, so if limited reaction of the oxide particles and the aluminum matrix occurs in the fuel core or meat, then some oxide could be present in the aluminum SNF form. Studies are continuing on the dissolution characteristics of oxide fuels.

Bench scale process development has focused on the casting of alloys for the range of compositions represented in the binary U-Al phase diagram. Both sub liquidus casting and above-liquidus casting processes are being evaluated. A wide range of alloys, representative of those expected in the aluminum SNF form, have been fabricated. Their product characteristics, namely microstructure, homogeneity, phase compositions etc. have been analyzed. Further, the role of ternary elements in the SNF form is also being studied. Preliminary studies show that the ternary elements from impurities or fission products will not cause any significant changes in the process cycle. Strategies for inprocess control and sampling during the melt-dilute process were also investigated. Density measurement was found to be a relatively simple test for determination of uranium content of the melt. The method may be applicable provided casting porosity is removed from the sample and at least three-place accuracy weight measurements are made. Nevertheless, this method does not seem reliable for the determination of enrichment unless highly reliable weights, both dry and water immersed, can be determined. Other characterization techniques (e.g., high-resolution inductively coupled plasma atomic emission spectroscopy) are fast for both total uranium and U^{235} analyses and are being considered for the process.

A comprehensive analysis of the radionuclides released from the melt below 1000 °C was conducted. The radionuclides include tritium, krypton, xenon iodine, cesium, rubidium, strontium, tellurium, and technetium. Calculation of the concentration of these elements in the diluted alloy indicates the content of Cs and Sr is about 0.01 wt % while the others are much less than 0.001 wt % at discharge. Data from these analyses were used to guide the definition of the off-gas systems requirements. The proposed concept for the off-gas system is condensation of the particulate, primarily cesium, on a cold surface while venting the remaining off-gas through various filters. Other methods are being evaluated. The off-gas requirements and design concepts will be evaluated through additional bench scale experiments during FY98.

A small scale resistance-heated furnace was developed for the demonstration of the meltdilute process for a full scale MTR element. Full scale MTR elements were melted to predetermined compositions based on defined dilution levels. The aluminum form was solidified in carbon steel crucibles and characterized. This demonstration will guide the integrated process demonstration (with the off-gas system) of the melt-dilute process during FY98. Page 1.6 of 1.8

1.3 DEVELOPMENT OF TEST PROTOCOLS FOR ALUMINUM SNF FORMS

The objective of the test protocol development task is to develop, validate and implement the test methodologies and associated technologies necessary to assess the suitability of aluminum SNF forms for repository disposal. Specifically, the tests will provide techniques to establish the release rate of radionuclides from the Al-SNF form and the effect of environmental variables and degradation on the release rate. The differing mechanisms for the retention of fission products in an aluminum SNF form vís-a-vís HLW or commercial SNF form require a thorough understanding and evaluation of the test methods used to develop release rate data. These are being developed in three steps, namely: 1) review and analysis of established and emerging test methods that assess commercial nuclear fuels and high level waste glasses; 2) identification of the technology needs that may be specific to the Al-SNF forms; and 3) modification and/or expansion of the established methods to provide a test protocol that will assess the relative quality of the Al-SNF forms.

Data gathered from these tests will provide input to the repository performance assessment and assist in the selection of the preferred treatment option. A draft test protocol was written to establish requirements for the data that must be gathered from a test. This draft is in the process of being submitted to ASTM for consideration as standard guide. It is anticipated that the test protocols developed will be incorporated into an ASTM Standard Guide.

Based on a literature review, three test techniques were selected as potential test methods for assessment of aluminum SNF form degradation and release characteristics. The three test methods are static immersion, low flow, and electrochemical tests respectively. These tests are being evaluated for their capability to measure the following properties/behavior as a function of environmental variables: release rate of radionuclides, forward dissolution rates of the microstructural constituents, effects of galvanic coupling on corrosion behavior, and effects of the Al-SNF form condition (i.e., microstructure, surface films, deposits, etc.).

Preliminary scoping analyses for both the static immersion and the electrochemical tests were performed. The test environments were J-13 or modified J-13 well water at 90 °C. The effects of these variables on the degradation of the aluminum matrix and the aluminide particles were evaluated. Galvanic and crevice corrosion effects were also investigated with the static tests. The results of the static tests show that the aluminum-rich phases are anodic to the aluminide particles and hence corrode preferentially. The release rate of the radionuclides is not directly related to the corrosion rate if the U-Al matrix especially if the radionuclides are retained by the aluminide particles. As a result of the corrosion process, localized particles of UAl₃ cracked or spalled from the surface. The degradation of the microstructures was independent of the solution chemistry or the galvanic couple. However, the oxide film formed on the surface of test coupons varied with test solution and couple.

The flow test was initially developed by PNNL for evaluating environmental effects on commercial SNF. PNNL has transferred this technology to SRS, and SRS has made modifications to the apparatus to accommodate Al-SNF test samples. In addition, PNNL is performing flow tests on irradiated and non-irradiated Al-SNF forms. Four types of irradiated fuel and a non-irradiated 19 wt % U-Al alloy are being tested in three simulated repository environments. SRS will conduct confirmatory tests in the SRS apparatus on the non-irradiated alloy to establish reproducibility. An extended matrix of testing has been planned to evaluate the techniques. Testing will be conducted in four different test solutions at two test temperatures on four compositions of U-Al alloy. The effects of casting and cold-working the alloy, as well as galvanic coupling of the sample, on degradation will also be assessed. The results of these tests will be the focus of a preliminary dissolution report due in August, 1998.

1.4 ALUMINUM SNF CHARACTERIZATION PROGRAM STATUS

The primary focus of the SNF characterization program has been to identify the applicable criteria and regulations which will most heavily impact pretreatment characterization of aluminum SNF, and to establish pretreatment characterization requirements for each of the two primary disposal options, Direct-Disposal and Melt-Dilution. The preliminary characterization requirements for the direct and/or codisposal and melt-dilute process have been established. A SNF characterization data manual is also being assimilated and will be issued during FY98.

From the existing regulations, acceptance criteria, and repository guidelines, pretreatment characterization requirements for the fuels to be received and processed at SRS within the Transfer & Storage Services facility were developed. The two primary disposal options were evaluated to determine process-specific characterization needs and requirements. Such requirements are expected to be used as input for the selection of a preferred alternative technology for the disposition of Al-SNF.

Although each of the two options offers individual attributes and advantages, the scope and degree of pretreatment characterization requirements for each disposal option may be a significant factor in the down-selection process. Pretreatment characterization requirements, however, are based on repository acceptance criteria which are currently under development and subject to change. In addition, the nature and scope of pretreatment characterization requirements for each disposition option is highly dependent upon the validity and acceptability of existing fuel data and operating history (Appendix A-type), with the Direct Disposal option currently deemed the more dependent method. Post-treatment characterization of Al-SNF forms produced under each disposal option is considered to be similar to meet repository requirements. However the scope for the Melt-Dilution option should be lower due to the homogeneity of the waste form produced and the reduction in number of canisters required. Page 1.8 of 1.8

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2.0 INTRODUCTION

The DOE is currently evaluating non-processing technology options for the disposal of research reactor aluminum-SNF in a geologic repository. This report provides the status of the alternative technology development program activities which are being performed under several tasks at the Savannah River Technology Center.

2.1 ALUMINUM-BASED SPENT NUCLEAR FUEL

Aluminum-based spent nuclear fuel from research reactors will account for less than 1% of the total volume of SNF and high level waste that will require disposal in a geologic repository. However, much of the Al-SNF contains HEU with up to 93% enrichment. The Materials Test Reactor design assembly which is comprised of fuel elements or plates of aluminum-clad, aluminum-uranium alloy fuel is the dominant design (approximately 80% of total) and fuel material for research reactors. In addition, some reactor fuel assemblies were fabricated from aluminum-uranium silicide alloys or aluminum-uranium oxides. The fuel elements are clad with one of the aluminum alloys 1100, 5052, or 6061 or their foreign equivalents.

Currently this SNF is typically stored under water where corrosion may be severe unless strict control of the water purity is maintained (Reference 2.1). Prolonged underwater storage is not desirable because of the high cost of operating and maintaining a properly controlled water system and the limited space and handling capabilities available at most reactor facilities. Consequently, a strategy involving interim storage followed by ultimate disposition is being pursued.

2.2 PROGRAM EVOLUTION AND TECHNICAL STRATEGY

The United States Department of Energy has selected the Savannah River Site (SRS) as the location to consolidate and store aluminum-based spent nuclear fuel (Al-SNF), originating in the United States, from foreign and domestic research reactors (FRR and DRR, respectively) (References 2.2-2.4) through the Environmental Impact Statement (EIS) process. These SNF are currently being irradiated in the research reactors, are being stored in water basins or dry storage at their sites, or have been transferred to SRS and stored in water basins (Reference 2.5). A portion of this inventory contains HEU. Since the fuel receipts would continue for several decades beyond projected SRS canyon operations, it is anticipated that it will be necessary to develop disposal technologies that do not rely on reprocessing.

The Research Reactor Spent Nuclear Fuel Task Team was appointed by the Office of Spent Fuel Management of DOE to evaluate the effectiveness, relative merits, costs, and difficulties in implementation of alternative technologies and waste forms for the treatment, packaging, and disposal of aluminum-based SNF (Reference 2.6). The base

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case for comparison of the several technologies was chemical reprocessing followed by incorporation into borosilicate glass. The principal recommendations of the Task Team were:

- parallel development of direct disposal and dilution technology options including codisposal with HLW borosilicate glass logs. Codisposal appears possible in both cases;
- utilization of the SRS canyons for chemical reprocessing of SRS fuel, failed or sectioned fuel, and other selected fuel;
- electrometallurgical treatment as an advanced technology backup to direct and dilution technologies.
- DOE-NRC agreement on requirements for SNF disposal and waste form for HEU; and
- plan, fund, and design a dry storage facility at SRS.

None of the alternative waste forms other than borosilicate glass resulting from processing is qualified for disposal in the federal repository in Yucca Mountain.

Development and licensing of the facilities of a Mined Geologic Disposal System or the repository for ultimate disposal of SNF and high level waste (HLW) is the responsibility of the Office of Civilian Radioactive Waste Management of DOE. At present, a licensing application for the disposition of SNF and high level waste glass in the proposed repository at Yucca Mountain is expected to be completed by 2002. The licensing application drives the schedule for the repository Performance Assessment and the Viability Assessment to be completed during the 1998 - 2002 period. In order to ensure that Al-SNF disposition is part of the DOE-RW licensing application, a technology development program aimed at evaluating non-processing alternatives was initiated in FY97. The purpose of this program is to complete the engineering analyses and develop the scientific bases necessary to ensure qualification of an appropriate Al-SNF form for the repository. The two candidate forms are the direct form (Al-SNF assemblies) and the melt-dilute form. The subsequent sections of this report discuss the status of the activities to enable these forms to be acceptable for repository disposal.

2.3 REFERENCES

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- 2.2 Final Environmental Impact Statement, Interim Management of Nuclear Materials. DOE (U.S. Department of Energy), DOE-EIS-0220, Savannah River Operations Office, Aiken, South Carolina (1995).
- 2.3 Final Environmental Impact Statement, Proposed Nuclear Weapons Non-Proliferation Policy Concerning Foreign Research Reactor Spent Nuclear Fuel.

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- 2.4 DOE-Owned Spent Nuclear Fuel Technology Integration Plan. DOE/SNF/PP-002, Rev. 1, Idaho National Engineering Laboratory (May 1996).
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3.0 ASSESSMENT OF ACCEPTABILITY OF DOE AL-SNF FORMS FOR INTERIM DRY STORAGE AND REPOSITORY DISPOSAL

The envisioned path for ultimate disposition of the aluminum-based spent nuclear fuel assemblies involves transfer and treatment of wet-stored assemblies into an Al-SNF form (direct or melt-diluted) in a sealed canister. The canisters would be in interim dry storage for up to 50 years, awaiting repository disposal. The canisters would be transported to the repository and placed into waste packages for ultimate disposal. To proceed on this path, the Al-SNF form must meet requirements for both the interim dry storage system and the Mined Geologic Disposal System.

Section 3.1 provides an overview of the proposed process for treatment of the Al-SNF assemblies and storing Al-SNF forms at SRS. Section 3.2 provides the requirements for interim dry storage of Al-SNF forms. Section 3.3 provides requirements for disposal of the Al-SNF forms in the MGDS or proposed repository at Yucca Mountain as currently understood. Included are the sources from which these requirements are derived and the technical bases. The Al-SNF forms can meet the requirements in Section 3.2. A technical package of information is being assembled to demonstrate that the Al-SNF forms meet the repository requirements in Section 3.3.

3.1 STORAGE OF DOE ALUMINUM-SNF FORMS

A Transfer, Storage, and Shipment facility, currently in the pre-conceptual design phase, at SRS (Reference 3.1) will provide for treatment of as-received Al-SNF assemblies, e.g., wet-stored fuel. This facility will produce an Al-SNF form that is qualifiable for geologic repository storage. Interim dry storage will be provided at the TSS facility until the canisters are transferred to the geologic repository. The storage in this configuration is termed "road-ready." The intended design life for systems to store the road-ready Al-SNF forms is 40 years (Reference 3.1).

The Al-SNF assemblies to be treated by this facility include both foreign and domestic research reactor fuel assemblies under the jurisdiction of the United States DOE. The total number of fuel assemblies in inventory at SRS and expected to be received is shown in Table 3.1. The enriched uranium contents and the burnup achieved by these fuels cover wide ranges (see Attachment 8.1 in Reference 3.1). The expected average receipt rate of these assemblies, 394 MTR Equivalent assemblies and 4 HFIR/RHF assemblies per month (Reference 3.2), has been incorporated into the pre-conceptual design requirements of the TSS (Reference 3.1).

The design and construction of the TSS shall meet the established requirements necessary for licensing by NRC as an interim dry storage facility (References 3.4- 3.5). Provisions in the Standard Guide for extended service of interim dry storage facilities (Reference 3.6) will also be considered in the design for a 40+ year life. The Al-SNF forms in their

canisters shall also meet requirements for the MGDS so that the DOE can obtain a license from the NRC for the geologic repository which includes these forms.

	Mass (MTHM)	Volume (m ³)	MTRE (Note 1)
Inventory (end 1995)	0.44	8.2	1230
Domestic Research Reactors	7.5	128	9194
Foreign Research Reactors	13.4	94	15000
Transfer from INEEL	2.5	36.2	6986
TOTAL (Note 2)	23.84	266.4	32410

Table 3.1. Estimate of the Inventory and Expected Receipts of Al
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Note 1.Materials Test Reactor Equivalent (MTRE) fuel assembliesNote 2.Compiled from Reference 3.3.

Definitions important to the intended receiving, handling, treatment, storage, and disposal of spent nuclear fuel are contained in Section 2.1.2 of Reference 3.1. The following definitions are added for clarification:

<u>DOE Aluminum-based Spent Nuclear Fuel (Al-SNF)</u> - Nuclear fuels under the jurisdiction of the U. S. Department of Energy that have been exposed in a nuclear reactor whose fuel material is characterized as uranium compounds in an aluminum matrix and whose cladding is an aluminum alloy.

<u>Treatment</u> - Any conditioning or treatment to which the fuel is subjected in preparing it for dry storage (e.g., drying, melt-diluting, etc.), ready for repository disposal.

<u>Road-Ready</u> - The term used to indicate that the Al-SNF form in a canister is ready for direct transfer to and placement in the geologic repository. The term "disposable canister" is also used in the DOE-RW WAC (Reference 3.7).

<u>DOE Al-SNF form</u> - The material from the Al-SNF assemblies to be disposed of in the repository. Two candidate forms are the direct fuel assembly form and a treated (e.g. melt-diluted) form.

The TSS facility will treat the Al-SNF form to create a "road-ready" package and will provide for storage. That is, the SNF will be canistered and interim dry-stored at the TSS facility without the need for further treatment until transfer of the SNF canisters to the federal repository is authorized. Only statistical sampling of the canisters to ensure canister integrity and verify compliance with storage criteria is envisioned to be performed prior to transportation to the geologic repository.

3.2 REQUIREMENTS FOR THE AI-SNF FORM FOR ROAD-READY, INTERIM DRY STORAGE

The TSS facility at SRS will be designed and operated in compliance with a NRC license. The Al-SNF form and the interim dry storage system shall be in compliance with the requirements of this section. These requirements are derived from 10 CFR 72, applicable standards, and site-specific criteria and other requirements (References 3.1; 3.4-3.6; 3.8-3.10). These requirements are based on the fundamental requirement that the Al-SNF form (e.g. direct Al-SNF or melt-dilute SNF) be maintained in a condition that enables full, safe retrievability from time of receipt throughout treatment and storage. That is, the limits to the treatment and storage conditions provide for preventing excessive fuel degradation and unsafe conditions throughout the interim dry storage period. Testing is being performed to validate the technical bases for the requirements (see section 4.1) and therefore the requirements may be revised in the future. These requirements are being codified to be included as an appendix to the ASTM standard guide for extended, interim dry storage (Reference 3.6) and thereby receive national consensus.

Up to approximately 10% of the Al-SNF assemblies have corrosion or mechanical damage that has resulted in minor penetrations (breaches) of the aluminum cladding and exposure of the fuel core to the ambient environment. Although the cladding integrity is compromised, these assemblies still retain a fully handleable geometry. In addition, since the fuel is metallurgically-bonded to its cladding, a minor penetration of the cladding only allows a minor area of fuel exposure to the environment, thus maintaining general confinement under dry storage conditions. Therefore, these assemblies do not require special, additional canning before placement within the canister to meet the interim dry storage requirements and the repository requirements.

The following requirements for the Al-SNF form in its canister for road-ready, interim dry storage, originally reported in Reference 3.8, have been revised for purposes of clarity in this report. A discussion of the requirements is provided in italics. The canister used for the storage at SRS would be the DOE SNF canister to be placed within the waste package in the repository. An interim dry storage system for both the direct Al-SNF form and the melt-diluted Al-SNF form should be able to meet these requirements.

1. Free water remaining within the sealed storage canister after drying is limited to maintain the hydrogen content less than 4 vol %.

The typical transfer of the Al-SNF assemblies from basin storage to dry storage will involve drying the fuel. The fuel may be dried separately, or it may be loaded underwater into a canister followed by drying the fuel/canister system before backfilling with helium (see item 5 below) and sealing for the direct-stored Al-SNF form. With time, the residual free water within the sealed canister will be consumed through corrosion and hydrogen gas would be evolved. The limit of 4 vol % for hydrogen buildup is based on the generally recognized range of flammability of hydrogen in air as being from 4 vol % to 75 vol % with anything less than 4 vol % being considered as nonflammable (Reference 3.11). Hydrogen generation can be predicted from the following (References 3.8-3.10):

$$\frac{\text{Free Water (g)}}{\text{Canister Volume (m^3)}} = 292,505 \left[\frac{\text{P}_{\text{H}_2} \text{ (atm)}}{(273.15 + \text{T (°C)})} \right]$$

The requirement for a helium back-fill (see item 5 below) provides additional assurance that a flammable mixture will not be generated (4% hydrogen in helium is a non-flammable mixture). Drying of the melt-dilute Al-SNF form would occur as an initial step in the melt process.

2. The lag storage, treatment, and canister storage environments shall limit general corrosion or pitting corrosion to less than 0.0076 cm (0.003 in.) in depth in SNF cladding or in exposed fuel material.

This requirement is related to retrievability as it defines the acceptable degradation or change in condition of the direct-stored Al-SNF form that is allowable throughout the transfer, treatment, and dry storage steps. The requirement is based on engineering judgment to provide for full handleability of the fuel if retrieval is necessary.

3. The canister storage environment shall preclude the plastic deformation of SNF elements to less than 2.54 cm (1.0 in.) over a fuel assembly length of 91.44 cm (3.0 ft) and deformation not to exceed 75% of the clearance space between the fuel assembly and storage grid throughout the period of storage.

This requirement is related to retrievability as it defines the acceptable degradation or change in condition of the direct-stored Al-SNF form that is allowable during the interim dry storage period. The requirement is based on engineering judgment to provide for ready removal of the fuel from a canister and handleability of the fuel.

4. The interim storage environments shall prevent rupture of the SNF cladding due to creep or due to severe embrittlement.

This requirement is related to retrievability as it defines the acceptable degradation or change in condition of the direct-stored Al-SNF form that is allowable during the transfer, preparation, and dry storage steps. The requirement derives from 10 CFR 72 (Reference 3.4) which precludes a gross cladding rupture during the storage and handling of spent fuel.

5. Canisters shall be backfilled with helium to 1.5 times atmospheric pressure at room temperature.
This requirement is based on the desire for compatibility of gases used within the canisters and the waste package itself as recommended by the DOE SNF Canister Task Group (Reference 3.12). The heat transfer properties of helium would result in lower fuel temperatures (note that there is a temperature limit of 200 °C for interim dry storage) and reduced degradation rates over that of other cover gases.

6. The storage facility shall be capable of handling canisters from 10 to 15 feet in length.

This requirement is primarily based on the present uncertainty associated with standard canister design development. Current approved designs include a 10 foot long canister for West Valley and DWPF and a recently approved 15 foot long canister for Hanford HLW (Reference 3.12). Final determination of the preferred waste form for DOE SNF to be treated at SRS may result in a canister length other than 10 or 15 feet based on space utilization and criticality requirements, but the length finally selected is anticipated to be bounded by these two values.

7. The interim storage environment shall prevent the SNF cladding temperature from exceeding 200 °C.

A fuel temperature limit of 200 °C was identified to avoid excess creep and the potential for hydrogen blistering of the aluminum fuel and cladding materials during drying and storage (Reference 3.9).

3.3 REQUIREMENTS FOR REPOSITORY DISPOSAL OF THE AI-SNF FORM

The Al-SNF in its codisposal canister shall be in compliance with the applicable waste acceptance criteria specified for disposal within the Mined Geologic Disposal System (Reference 3.7). These requirements, drawn from several sources including References 3.13-3.16, were recently issued and are based on repository designs and concepts of operation as of September 1997; they are likely to evolve further before the repository becomes operational. Several of the acceptance criteria and most of the required documentation are yet to be determined.

The body of requirements in Reference 3.7 supersedes the initial list of requirements provided in Reference 3.8. The documentation demonstrating that the two Al-SNF forms, namely the direct disposal SNF form and the melt-dilute form, meet these requirements needs to be prepared. Several of these requirements may be met through testing, analysis, and characterization as described in Sections 4-7 of this report.

The following is a listing of the requirements from Reference 3.7 that would be applicable to the intact and non-intact Al-SNF forms in disposable (road-ready) canisters. A brief

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discussion/description is provided in italics. Placement of the Al-SNF forms in road-ready canisters is a current requirement (Criterion 2.1.4) of Reference 3.7.

Reference 3.7 contains the complete specification of each requirement (criterion) including a description of the criterion, acceptance criteria, source of criteria, and documentation required. Note that the term "SNF" used throughout Reference 3.7 refers to commercial spent nuclear fuel and that the term "DOE SNF" applies to the Al-SNF forms. With the exception of Criterion 2.1.4, the requirements for SNF are adopted for the Al-SNF form.

1. Compliance with Nuclear Waste Policy Act Definition of Spent Nuclear Fuel (Criterion 2.1.1 of Reference 3.7)

This requirement includes the definition of SNF as "fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing." The DOE AI-SNF forms should readily meet this requirement.

Minimum Cooling Time Since Reactor Discharge (Criterion 2.1.2 of Reference 3.7)

This requires SNF to be cooled for a minimum of five years following reactor operation for repository acceptance. The DOE Al-SNF should readily meet this requirement.

3. Provision that SNF be a Solid (Criterion 2.1.3 of Reference 3.7)

The SNF must be a solid at the range 25 to 400 °C and a pressure of 1 to 5 atmospheres. The DOE Al-SNF should readily meet this requirement.

4. Provision that Wastes Other than Intact SNF be Canistered. (Criterion 2.1.4 of Reference 3.7)

This criterion includes wording that limits the DOE Al-SNF forms to be canistered for acceptance in the repository.

5. Provisions for Disposable Canister Materials (Criterion 2.1.20 of Reference 3.7)

This criterion assures that the canister materials will be compatible with the waste package.

6. Requirement that Canisters be Sealed (Criterion 2.1.21 of Reference 3.7)

The canisters must be sealed for repository emplacement.

7. Limits on Free Liquids in Canistered SNF (Criterion 2.1.22 of Reference 3.7)

Free liquids are not acceptable because they provide a mechanism for radionuclide transport.

8. Maximum Allowable Quantity of Particulates (Criterion 2.1.23 of Reference 3.7)

This criterion limits the acceptable level of particulates.

9. Limits on Pyrophoric Materials (Criterion 2.1.24 of Reference 3.7)

The SNF must not be contain pyrophoric materials in amounts that could compromise surface-facility or repository preclosure safety or long-term performance. The DOE Al-SNF forms should meet this requirement.

 Limits on Combustible, Explosive, or Chemically Reactive Waste Forms (Criterion 2.1.25 of Reference 3.7)

This criterion assures that the waste form will not be reactive under repository conditions of 25 to 400 °C, 1 to 5 atmospheres.

Provisions for Unique, Permanent Canister Labeling (Criterion 2.1.26 of Reference 3.7)

The DOE Al-SNF forms should readily meet this requirement.

12. Provisions for Tamper Indicating Devices on Canisters not Seal-Welded (Criterion 2.1.27 of Reference 3.7)

The DOE Al-SNF forms should readily meet this requirement..

- Physical Condition of Disposable Canisters (Criterion 2.1.28 of Reference 3.7)
 The DOE SNF canister must meet minimum structural capacity requirements.
- 14. Limits on Radionuclide Inventories in Canistered SNF (Criterion 2.3.20 of Reference 3.7)

The performance requirements limit the content to a upper bound on selected radionuclides.

Limits on Disposable Canister Criticality Potential (Criterion 2.3.22 of Reference 3.7)

The canistered Al-SNF shall be shown to have a calculated k_{eff} of 0.95 or less.

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16. Limits on Organic Materials in Canistered SNF (Criterion 2.3.23 of Reference 3.7)

The DOE Al-SNF forms should readily meet this requirement..

17. Limits on Total Thermal Output for Disposable Canisters (Criterion 2.4.20 of Reference 3.7)

This requirement specifies that no single-element [assembly] SNF canister shall have a thermal output in excess of 1500 watts at time of shipment to the MGDS. The DOE Al-SNF forms should meet this requirement.

 Limits on Disposable Multi-Element Canister Thermal Design (Criterion 2.4.21 of Reference 3.7)

This requirement specifies that the temperature of the SNF cladding shall not exceed 350 °C and shall be demonstrated to be achievable over 1000 years. The assumed canister surface temperature is 200 °C after 50 years in the repository.

The DOE Al-SNF forms should meet this requirement; however if the cladding temperature of the Al-SNF direct-disposed form is 350 °C, retrievability of the individual assemblies may not be readily achievable due to creep-induced deformation.

19. Limits on Disposable Canister Surface Contamination (Criterion 2.4.22 of Reference 3.7)

The DOE Al-SNF forms should meet this requirement..

20. Provisions for Canister Internal Pressure (Criterion 2.4.23 of Reference 3.7)

The DOE Al-SNF canister is limited to 50 psig (TBV).

21. Limits on Disposable Canister Leak Rates (Criterion 2.4.24 of Reference 3.7)

The DOE Al-SNF canister shall have no detectable leak rate at time of receipt at the MGDS.

3.4 REFERENCES

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- 3.5 "American National Standard Design Criteria for an Independent Spent Fuel Storage Installation (Dry Type)", *ANSI/ANS-57.9*.
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4.0 DIRECT/CODISPOSAL TECHNOLOGY DEVELOPMENT PROGRAM

The overall objective of the direct/codisposal technology development program is to provide technical methodologies and analyses to allow qualification of DOE-owned aluminum-based spent nuclear fuel assemblies for interim dry storage and repository disposal. The present areas of activity in the direct/codisposal technology program are:

- the development of requirements for aluminum-based spent nuclear fuel forms for the road-ready package;
- the development of an instrumented, shielded test canister system for validation of drying and storage criteria for interim dry storage systems;
- thermal analysis of storage and disposal configurations;
- analyses of degradation and radionuclide release rates of Al-SNF in storage environments and application to repository performance assessment;
- criticality analyses of materials configurations; and
- materials input for a total system performance assessment.

The status of these activities is provided in the following subsections.

4.1 DEVELOPMENT OF REQUIREMENTS FOR ROAD-READY STORAGE OF ALUMINUM-BASED SPENT NUCLEAR FUEL

Requirements for interim dry storage of Al-SNF forms are listed in Section 3.2 of this report. These requirements were, in large part, derived from acceptance criteria for drying and storing Al-SNF assemblies (direct forms) which were developed at SRS (Reference 4.1). The criteria were based on degradation testing and analyses of the aluminum cladding and fuel materials under dry storage environments. Degradation testing and analysis of the Al-SNF melt-dilute form will also be performed to verify that the criteria developed for the Al-SNF direct form are directly applicable to the Al-SNF melt-dilute form.

Similar testing and analyses are being performed for repository disposal environments as described in Sections 4.3 and 4.4 below to develop the technical bases for meeting repository disposal requirements.

4.2 VALIDATION OF THE ROAD-READY DRYING & STORAGE CRITERIA-INSTRUMENTED, SHIELDED TEST CANISTER SYSTEM

The validation of the drying and storage criteria for road-ready storage will be performed through tests in which a spent nuclear assembly is housed in a special instrumented canister to monitor both the environment of storage and the fuel behavior. This section describes the development of an instrumented, shielded test canister system to store and Page 4.2 of 4.78

monitor an Al-SNF assembly under dry storage conditions. Additional information may be obtained from Reference 4.2.

The primary test objectives using the instrumented canisters are to:

- validate drying and storage criteria for road-ready storage;
- validate corrosion models;
- validate gas release models;
- validate heat transfer analysis methodology; and
- provide lead-assembly-surveillance for a dry storage system.

These objectives will be achieved following the loading of MTR fuel assembly into the canister and the analysis of data collected under the test environmental conditions of storage.

An instrumented, shielded test canister system has been designed and fabricated (see Figure 4.1). The canister can house an MTR assembly in a sealed dry storage configuration and is instrumented to measure and record the following parameters, during storage to characterize the environment internal to the canister and the fuel material's response:

- fuel clad and air space temperatures
- gas species (corrosion reaction products released from fuel)
- pressure
- relative humidity
- visual condition of fuel material

The canister is capable of being dried to any desired level. Tests to demonstrate unheated vacuum drying of the test canister containing a mock Materials Test Reactor fuel assembly and water have been performed. The results show that free water can be removed to a minimal vapor. A vacuum of less than five torr at room temperature is readily achievable, meeting the site-established criteria for road-ready storage. Drying of a representative FRR/DRR MTR assembly using the unheated vacuum drying technique will be performed as part of the validation testing.

The unique instrumented test canister system design monitors the storage environmental conditions and the response of nuclear fuel in a dry storage system. In calendar year 1998, two canisters will be loaded with FRR MTR assemblies; dried using unheated vacuum drying; backfilled with air and a finite level of water corresponding to the environmental limit prescribed for dry storage; sealed; and staged in the SRS L-Area disassembly dry cave. These actions will be performed following preparation of the area and documentation of safety reviews. Data will be accessible at the staged location, and also remotely via computer network. The response of the SNF to varying environmental conditions will be monitored to validate the storage criteria.



Figure 4.1. Instrumented, Shielded Test Canister System for Dry Storage of Al-SNF. The Test System includes the Fuel/Canister Monitoring System, the Data Acquisition System, and the Canister with Shielding.

4.2.1 Design Objectives for Tests Using the Instrumented, Shielded Test Canister System

The test canister system is designed to be an apparatus for tests of MTR fuel assemblies in dry storage although other fuel, fuel segments, and waste forms could be accommodated. The storage environments can be set by water injection and gas back fill. Self-heating of the waste form is the heat source in the canister.

The drying and storage criteria governing the handling, processing, and interim dry storage of Al-SNF, originally developed and reported in Reference 4.2, have been adopted as technical functional performance requirements for a road-ready dry storage system in Reference 4.3. These were further clarified in Section 3.1 of this report. A summary of these requirements are as follows.

Fuel Temperature Limit:	200 °C
Canister Storage System:	Sealed
Free Water Limit in Canister:	Limit H ₂ Build-up to 4%
Fuel/Clad Consumption Limit:	0.003"
Canister Cover Gas:	Helium

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An estimate of 10% of the fuel assemblies have corrosion or mechanical damage that has resulted in minor penetrations (breaches) of the aluminum cladding and exposure of the fuel core to the ambient environment. Fuels with minor breaches are acceptable for direct placement in the dry storage canisters (References 4.2-4.3). The basis for this acceptance is that the materials and structure of the Al-SNF provide a measure of confinement of the radionuclides. The corrosion of any exposed fuel material is expected to be on the same order as the cladding (Reference 4.4). In addition, significant diffusion and release of species through the fuel matrix and cladding is not expected during low-temperature (<< 200 °C), short term (less than 50 years) storage (Reference 4.5). The canister test will verify that the release of volatile products from exposed fuel is low.

The MTR assembly placed in the canisters during the tests will be based on availability, existing degraded condition, and fission product inventory which affects heat generation and radiation field. Two fuels have been tentatively selected, fuel with exposed meat from the SAPHIR and fuel with exposed meat from the R2 reactor. Figure 4.2 shows fuel plate 243 from the SAPHIR assembly SES02 with an apparent exposure of fuel meat.



Figure 4.2. Fuel Plate #243 with Cladding Breach from SAPHIR Assembly SES02

In fiscal year 1998, the L-dry cave will be prepared to stage the canister system (Reference 4.6). Safety documentation and a fuel/canister handling procedure will be issued. The fuels will then be transferred from RBOF to L-disassembly basin. The fuels will be loaded underwater into the shielded canisters. The canister will be vacuum dried, then vented to air and injected with a controlled amount of water. The system will be sealed and staged in the L-area dry caves and the collection of data will begin.

4.2.2 Design and Fabrication of the Instrumented, Shielded Test Canister System

Vacuum drying at slightly elevated temperatures (~120 °F) appears to be an acceptable method of preparing aluminum SNF for extended dry storage. Achieving a vacuum below the triple point of water (~4.5 torr) within a heated canister will vaporize all free liquid water. High temperature drying to remove water of hydration from the aluminum oxide on the SNF cladding is not practical, as the temperature required to dehydrate the oxide is high (greater than 300 °C). There is no requirement nor technical need to remove this hydrated water.

Two complete independent systems to store and monitor two Al-SNF assemblies under test conditions were designed and fabricated. These include two canisters, two shields, two camera brackets, two air monitoring loops with instrumentation, and one data acquisition system with uninterrupted power supply to manage and record data on environmental conditions inside the two test canisters.

Instrumented Canister

The instrumented canister (Figure 4.3) provides sealed containment for a MTR fuel assembly, which is approximately three inches square and just over two feet long. The fuel assembly is supported by an aluminum sensor rack to center it and to allow positioning of thermocouple tips on the fuel surface. The canister body is made from a section of 6" outside diameter Type 304 stainless steel tubing with a wall thickness of 1/8". The top of the body is welded to a commercial 8" vacuum flange. A blank flange, which is welded to the shield lid, bolts to twenty threaded holes in the flange of the canister and gives the vacuum tight enclosure. The bottom of the canister tube is seal welded to a flat 1/8-inch thick 304 stainless steel plate.

Three stainless steel tubes, ½ inch OD. with .050" wall thickness, are welded to the canister. One lower tube and one upper tube serve as air inlet and outlet ports, respectively, to mate with the air circulation loop for air sampling. For air sampling during the test, air enters the canister through the bottom tube, passes the fuel assembly and exits one of the top tubes. All thermocouple wires exit through the third port which serves as a conduit. The canister is housed within a lead shield (see Figures 4.4, 4.5, and 4.6) to reduce the radiation exposure and to allow limited access to the L-area dry cave where the canister will be staged. It also has a four-inch-diameter sealed quartz viewing window to allow direct visual inspection of the fuel surface approximately eight inches from the bottom. This observation will be done with the aid of a video camera that can be seen in the cross section plan view, in Figure 4.5. The camera is mounted around a 90° corner



Figure 4.3. Photograph of Test Canister for Housing an MTR Fuel Assembly. The visible features are the quartz viewing window, the thermocouple feed-through line, and the circulation inlet and outlet lines.



Figure 4.4. Schematic of Side View 1 of Test Canister within Lead Shield for Containing an MTR Fuel Assembly



Figure 4.5. Schematic of Side View 2 of Test Canister within Lead Shield for Containing an MTR Fuel Assembly. Note the lifting bails for the shield/canister assembly.



Figure 4.6. Schematic of Top View of Test Canister within Lead Shield for Containing an MTR Fuel Assembly. Note the camera mounted around a 90° corner to view the assembly through a front surface mirror (item 17) mounted in the viewing tunnel to avoid the high direct radiation field directly in front of the assembly.

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and views the assembly through a front surface mirror mounted in the viewing tunnel to avoid the high direct radiation field directly in front of the assembly.

<u>Shield</u>

Shielding (Figure 4.7) is needed due to the high radiation field expected from a spent fuel assembly. A shielding analysis was performed to determine shielding requirements. The shield consists of a 1/8 inch-thick stainless steel shell construction filled with molten lead. Based on the analysis, the shield has 4.25" of lead shielding to keep the dose rate below 100 mR/hr on the shield surface for one High Flux Beam Reactor assembly. The approximate weight of the shield with the canister is 6,640 pounds.



Figure 4.7. Photograph of Shield for Test Canister. Note the lifting bails and skid mounting of the shield.

Fuel Monitoring System

The fuel monitoring system consists of a cabinet containing one complete instrumentation loop for each canister (Figure 4.8). Each loop has two primary components; a GC and an instrument manifold. The gas chromatograph takes a one microliter sample of air from the canister once per day. This sample is combined with a carrier gas in the instrument and is analyzed for hydrogen, nitrous oxides, and oxygen content. The carrier gas is ultra high purity argon which is contained in a cylinder just outside the cabinet. A calibration gas system is programmed to periodically confirm the GC output and automatically purges itself to prevent dilution of subsequent samples. Calibration gas bottles containing a mixture of hydrogen, nitrogen, and oxygen are located in the bottom of the cabinet.



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The instrument manifold houses a temperature/relative humidity sensor and a pressure transducer. A radiation detector is included between the instrumentation manifolds which monitors the loops of both canisters simultaneously. The radiation detector senses the presence of gamma radiation which indicates that radioactive material has been released from the fuel element and is circulating within one or both instrument loops. This material is retained by the system such that no radioactive particles are released to the atmosphere. Each loop is also equipped with a circulating pump, a flow meter, and line for introducing outside air in the event that pressure decreases with time. Solenoid valves are controlled by the data acquisition computer. These valves are used to direct air flow to the gas chromatograph during sampling and calibration procedures. Signals to and from all instrumentation are linked to the data acquisition system in an adjacent cabinet.

Data Acquisition System

A computer-based data acquisition system has been developed to monitor environmental parameters associated with two identical shielded test canisters. The system consists of a central computer cabinet, instrumented process cabinet and two instrumented canisters (Figure 4.9). The computer provides real-time display of data, data storage, and remote data access via network/internet connection. Sensors in the process cabinet allow monitoring of air temperature, air flow, canister gas composition, pressure, relative humidity, and radiation. Sensors in the canister measure surface temperatures of the fuel and canister wall and temperatures of inlet and outlet air. Circulating pumps located in the instrument cabinet (Figure 4.8) ensure continuous circulation of system air past all sensors. The visual appearance of stored fuel is monitored by a video camera mounted on each canister.

Data acquisition, storage and display are accomplished in four basic levels: sensor output, signal conditioning, communication and computer translation. All process sensors, except gas composition, video, and radiation, provide voltage or current level analog outputs proportional to the measured parameter. Each analog signal is converted to digital form by a dedicated signal conditioning module located in close proximity to the sensor. The signal conditioning modules reside in backplanes which convert the digital information to a robust serial format which ultimately enters the computer through a standard serial (RS232) communication port. Gas composition information is conditioned and transmitted directly from one of two gas chromatographs to a dedicated serial port on the computer. Video information is provided by one camera mounted on each of the canisters. Standard video signals are transmitted directly to the computer and received through one of two ports on a video capture board. Radiation detection is accomplished with a single dedicated sensor and meter. At a predetermined level the meter generates a contact closure. The contact closure is detected by a signal conditioning module where it is transmitted along with other signal data. The computer translates all received signals to tabular and/or graphical form for storage and display. Video from observation cameras can be displayed exclusively or concurrent with parameter information on the computer display.





Vacuum Drying Test Program

A vacuum drying test program at SRS began in August 1997 to demonstrate the feasibility of drying mock MTR SNF assemblies to below 5 torr. The tests quantified vacuum drying times versus initial water volume, and provided operating experience with the drying apparatus and instrumentation. All drying tests were conducted within the Building 105-L assembly area. The primary objectives in the drying tests are as follows:

- Demonstrate feasibility of drying to below 5 torr in an unheated canister system; and
- Provide check-out of drying apparatus in preparation for underwater loading followed by drying of the MTR SNF in the instrumented canister.

A test canister, similar in design to the instrumented canisters, and a mock MTR fuel assembly were designed for these tests. The canister, constructed of Type 304 stainless steel, is 6 inches in diameter, 35.4 inches high, with a volume of ~934 cubic inches. The removable lid is sealed with a standard copper vacuum gasket. The mock assembly contains 18 aluminum plates and variable wattage heaters on the outer two plates. A photograph of the canister and mock-up in L assembly is in Figure 4.10. A photograph of the vacuum canister stand and scale is in Figure 4.11. A photograph of the assembled canister in a test is in Figure 4.12. A photograph of the assembly in the canister is in Figure 4.13. A photograph showing the dry can post-test is in Figure 4.14.

Vacuum Equipment

Drying tests utilized a 480 VAC skid-mounted Kinney KLRC 300KFA liquid ring rotary vacuum pump in series with a KMBD 1604 blower and an air ejector, as shown in Figure 3.15. The oil-free liquid ring pump utilizes water as the vacuum chamber sealant and coolant. Nominal pump capacity is 300 cfm at 100 torr, and the pump and blower combination can achieve a maximum vacuum of ~0.5 torr. The pump was connected to the canister via 50 feet of 1-1/2 inch diameter flexible stainless steel hose. The 1/2-inch diameter port on the test canister was connected to the stainless steel hose via ~6 inches of 3/8-inch ID Tygon tubing.

Water mass changes within the canister during tests was measured with new Mettler Toledo precision bench scales. The scales have a readability of 0.0002 pounds with a maximum capacity of 70 pounds. The canister and assembly weighed ~47 pounds and remained on the scales during drying.

Instrumentation and Data Acquisition

Two calibrated vacuum gauges monitored the approach to dryness during tests. A Varian model WV110-2 digital vacuum gauge with a range of 0.001 to 1500 torr was installed in the canister lid to monitor pressure. A Varian model 801 thermocouple vacuum gauge with a range of 0 to 2 torr was installed at the 1-1/2 inch hose inlet. SRTC equipped the canister with two thermocouples and a humidity sensor to monitor interior conditions. The thermocouples measured side plate temperatures at the top of the assembly. A thermocouple was also taped to the canister exterior below the initial water level for selected tests.



Figure 4.10. Vacuum canister and electrically-heated fuel mock-up



Figure 4.11. Stand to hold vacuum canister. Note the scale on which the canister rests.



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Figure 4.12. Assembled Canister in a Test



Figure 4.13. Assembly inside the Canister



Figure 4.14. Post Test Canister Interior



Figure 4.15. Vacuum Pump

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The digital scales, humidity sensor, interior thermocouples, and vacuum gauge were connected to a computerized data acquisition system that displayed and stored readings every five seconds during tests. Readings were also recorded manually at ~10 minute intervals during tests.

The empty canister and mock SNF were weighed prior to the start of each test to establish baseline weights. A measured quantity of water was then added directly to the canister or poured over the assembly, and the lid was sealed. The sealed canister was weighed at least five times to establish the gross weight of the canister, mock SNF, and water. The weight/volume of water added was determined by the weight difference. The vacuum hose and instrumentation cables were connected to the canister after weighing, and data acquisition was initiated upon startup of the vacuum pump. Vacuum immediately stabilized at 25-30 torr as water inside the canister began to boil.

Strip heaters on the mock SNF were operated at 5 or 14 watts during selected tests to simulate heat generating SNF. Heat generation was controlled by regulating the voltage and current on an adjustable power supply.

Temperatures, vacuum, and humidity readings were recorded throughout each test. Drying continued until a vacuum of one torr or better was achieved inside the canister indicating all water had been removed. Typical final vacuum was 0.4 to 0.7 torr. The canister was backfilled with room air to atmospheric pressure after completing drying. Hoses and cables were disconnected prior to obtaining a final gross weight.

Condensate on the exterior of the canister and scale platform during nonheated drying tests skewed weights. The scale platform and canister were hand-dried to remove all condensate prior to final weighing for these tests. The canister was opened after drying was completed, the mock SNF was removed, and the canister and assembly were visually inspected to ensure no moisture remained.

A series of drying tests was conducted over a two week period with varying initial quantities of water and heat inputs to obtain baseline drying performance data. The water content inside the test canister varied from 15 to 689 ml. The 300 milliliter tests equate to \sim 1 inch of standing water (0.6 pint) inside the canister, and the 450 milliliter tests equate to \sim 1-1/2 inches of standing water (1.5 pints) inside the canister. The actual instrumented test canisters are expected to retain 1/2 to 1 inch of water after the SNF is loaded and the bulk water is pumped out. The power input to the test varied from 0.0 to 14 watts, compared to an estimated decay heat from a spent MTR fuel assembly of one watt. The results from the high power input conditions provide information to improve the drying time when the vacuum dry system is used to dry the MTR fuel assemblies. Short duration drying tests with a dry assembly, damp assembly, and dripping assembly were also conducted to provide reference data. Table 4.1 lists the major test matrix.

Water Volume in Canister (ml)	Heat Input (Watts)	Drying Duration (Minutes)
14.3	14.0	6
15.5	0.0	27
300	14.0	230
448	14.0	378
297	4.8	290
297	0.0	348
461	0.0	518
689	0.0	779

Table 4.1. Test Matrix and Measured Drying Time

Drying tests with the mock MTR assembly demonstrated that vacuum drying is feasible for the two shielded, instrumented canisters after loading SNF. The general configuration of the vacuum pump, hose, and instrumentation was satisfactory.

Any of the measurements (pressure, relative humidity and temperature) could be used as an indication of dryness during the vacuum dry process. To minimize personnel radiation exposure and design complications, the pressure measurement on the vacuum hose is recommended to monitor dryness for vacuum drying of irradiated SNF.

Drying tests using the shielded SNF canisters and the mock MTR assembly are planned prior to loading irradiated SNF. The SAPHIR SES02 assembly proposed for loading into one of the canisters has a very low heat output (~1 watt), which suggests that drying of this assembly could be expedited by external heating. Simple concepts such as a warm air purge also will be evaluated.

Thermocouples within the instrumented canisters are intended for long-term monitoring after drying is completed. Consideration will be given to using thermocouple data to confirm dryness.

4.3 ROAD-READY PACKAGE THERMAL ANALYSIS

The temperature of the fuel in interim storage and disposal environments is the most important parameter in predicting the degradation processes and rates. Sections 4.3.1 and 4.3.2 provide the status of the development of thermal modeling methodologies and the results of analyses for interim and repository configurations, respectively.

4.3.1 Interim Dry Storage Environment

Thermal modeling and analysis methodology have been established for the interim dry storage conditions prior to a geological repository. To demonstrate that fuel temperature distributions and buoyancy-induced cooling within an enclosed spent nuclear fuel canister can be predicted and simulated with reasonable accuracy under various expected interim storage configurations and ambient boundary conditions, a three-dimensional CFD model has been developed using the CFX code. In addition, the conjugate thermal model has been benchmarked against the SRS full-scale experimental test data under various boundary conditions. An overview of this analysis and principal results and conclusions are described in References 4.7-4.8.

4.3.2 Repository Disposal Environment

4.3.2.1 Thermal Analysis for Codisposal Waste Package Canister

The prediction of the behavior of Al-SNF in a geological repository requires an accurate assessment of the thermal conditions to establish the degradation rates of the Al-SNF. The temperature of the Al-SNF forms is highly dependent on the canister and waste package structures and on the heat sources within the canister and waste packages. Well-defined heat source terms for the Al-SNF direct and melt-dilute forms are being developed along with the term for the HLW glass canisters. Concurrently, a best estimate thermal analysis was performed using a detailed thermal model that considered convective heat transfer in addition to conductive and radiative transfer in a detailed structural model of the waste package internals. The well-defined heat source term information is not available at this time. Therefore, a parametric analysis approach was taken as a first phase of thermal analysis to evaluate the thermal performance for each design option of the codisposal package over a range of possible heat loads and boundary conditions. When these heat source terms are developed, the best estimate analysis will be performed.

4.3.2.2 Analysis Approach for Codisposal Waste Canister

A codisposal canister contains HLWG and a SNF canister. The codisposal canister is horizontally laid down at the center of a geological drift tunnel as schematically shown in Figure 4.16. In this case, HLWG and SNF regions have different decay heat sources, and the SNF canister is surrounded by five HLWG canisters inside the codisposal waste package. The package canister will be filled with air, helium, or other filler material such as a neutron absorber depending on the design.

A general energy balance equation on a control volume of the waste package is given in a vector form as follows:

$$\rho C_{p} \frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T = \beta T \frac{DP}{Dt} + \nabla \cdot (k \nabla T - q_{r}) + q^{\prime \prime \prime}$$
(1)



Figure 4.16. Horizontal Emplacement of Codisposal Waste Package in the Center of an Emplacement Drift

Energy terms within a control volume of the package includes convection $(\vec{v} \cdot \nabla T)$, conduction ($k \nabla T$), radiation heat transfer (q_r), internal heat sources (q'''), compression work of back-filled gas ($\beta T DP/Dt$), and energy storage due to transients ($\rho C_p \partial T/\partial t$). For steady state with no heat source in a transparent gas medium, Equation (1) becomes

(Heat Convected into Surface I, $q_{conv,I}$) + (Heat Conducted into Surface I, $q_{cond,I}$) = (Radiant Heat lost from Surface I, $q_{rad,I}$) (2)

If convective heat transfer is neglected, the heat conducted into a wall surface is balanced by the radiant heat lost from the wall surface. For the present parametric analysis, a twodimensional, steady state, conduction-radiation model was developed using uniformly distributed heat generation sources within HLWG and SNF canisters to predict the package thermal performance within a geological repository. The buoyancy-induced natural convection term will be considered later for the best estimate model to simulate thermal performance of the waste package and to quantify the conservatism of the conduction-radiation model. A 1/5 sector model of the codisposal waste package was used for a better computational efficiency by imposing symmetrical boundary conditions Page 4.20 of 4.78

on both sides of the model. Figure 4.17 presents the present 1/5 sector model. CFX code has been used as a tool to model and simulate the thermal performance for the codisposal waste canister in a geological repository, since it had been previously used to simulate and benchmark the test data for the interim spent nuclear fuel dry storage canister with reasonable accuracy (Reference 4.7). The CFX modeling results were also compared with those of FIDAP code. The schematic diagram for the thermal analysis methodology is shown by Figure 4.18. Finally, the thermal analysis results will be used in the development of the waste package degradation model.







Figure 4.18. Simplified Diagram for Thermal Analysis Approach Methodology of Codisposal Waste Package

4.3.2.3 Modeling Assumptions and Design Parameters

The computational modeling domain is shown in Figure 4.17. A quasi-steady state temperature distribution was assumed for a selected time since the waste package transient temperatures will reach equilibrium in a few days. The package was assumed to be laid down horizontally in the repository drift tunnel. It was also assumed to have no solid conduction paths among the SNF and HLWG canisters such that HLWG canisters, SNF

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canister, and codisposal canister inner wall do not touch each other. The temperature around the package wall circumference was assumed to be uniform. A typical natural convective heat transfer coefficient of 1.5 W/m².°C (Reference 4.7) was used as an external wall boundary condition for the present parametric analysis. Natural convection due to internal gas movement inside the waste package is neglected in the present model, but it will be considered later for the best estimate model. An effective thermal conductivity for the SNF canister and its contents was generated as a volume-weighted average thermal conductivity of the constituents in the SNF canister. Heat loads, as volumetric source densities, for the SNF and the HLWG regions were provided to the model (see Equation (1)) by assuming that heat generation for each region is uniformly distributed.

The main design parameters involved in the thermal performance of the waste package are:

- Different combinations of back-filled gases or porous filler materials in the SNF canister and the waste package container (e.g., air-air, helium-helium, or iron oxide)
- Various sets of combinations of two heat sources (SNF and HLWG decay heat sources)
- Internal structural materials of the codisposal canister
- Repository temperature history since emplacement of waste package
- Waste package placement within a drift (center or off-center of a drift): The present analysis assumes that the waste package is located at the center of a drift.

4.3.2.4 Results and Discussions

Based on the approach methodology and the assumptions, a two-dimensional conductionradiation coupled model was developed to investigate key parameters and to find sensitivities to the changes of the design parameters involved in the thermal performance of an intact codisposal waste package. CFD codes such as CFX and FIDAP were used as a tool to create a geometry file under a non-orthogonal mesh environment and a bodyfitted coordinate system and to solve the non-linear equations by using a discrete radiation transport technique.

The package consists of typical aluminum-clad flat-plate fuel, such as MIT-type fuel, and five HLWG canisters. Table 4.2 shows the thermal properties of the codisposal package components used for the present analysis.

The following key parameters were mainly considered in performing a parametric thermal analysis for the codisposal waste package design:

• Gas Back-fill: Air or helium is used as the back-fill gas for the SNF canister and for the entire codisposal canister. The maximum temperature for air-filled waste package is about 5 °C higher than that of helium-filled package for given heat load and natural

Regions in Figure 4.17	Materia	als	Thermal Conductivity	Emissivity
\square	Spent Nuclear Fuel		38.13 W/m·K	0.60
	(SNF) Canister	er He-filled	38.21 W/m·K	0.60
2	High-level Waste Glass Log (HLWG)		1.046 W/m·K	0.60
3	Back-filled A Gas H	Air	0.031 W/m·K	—
		Helium	0.173 W/m·K	—
4	Co-Disposal Canister Inner Wall		11.104 W/m-K	0.80
3	Co-Disposal Canister Outer Wall		36.322 W/m·K	_

Table 4.2. Thermal/Radiation Properties of the Codisposal Canister Components used for the Present Analysis

convective boundary conditions. Figure 4.19 shows the radial temperature distributions for air-cooled and helium-cooled designs as a function of decay heat load.

- Iron Oxide Back-fill Material: When iron oxide is used as a neutron-poison material, • the effective thermal conductivity of back-fill region inside the waste package increases about four times compared to that of the helium back-fill design. Decay Heat Loads: Transient decay heat sources for typical MIT-/ORR-type SNF fuel and HLWG canisters are being estimated by using a Monte Carlo code, SCALE 4.3 - ORIGEN-S. In the meantime, a range of decay heat loads for the SNF canister was used for the present parametric analysis (10 W to 1000 W). Figure 4.19 presents the temperature distributions from the center of the codisposal canister to the canister wall. The distribution was calculated along the centers of the two canisters (SNF and HLWG) for the heat loads between 10 W and 640 W in SNF region and 460 W in each HLWG canister. In addition, the present CFX model calculates a maximum temperature of 267 °C for a 1000 W heat load in SNF and 460 W for each HLWG canister within a nitrogen-cooled waste package. This result agrees with the FIDAP finite element model. In the FIDAP model, the external wall heat transfer coefficient of 5.68 W/m². C was used, but this value is higher than a typical literature value (about 1.5 W/m².°C) for a horizontal natural convective wall surface.
- Internal Conduction Path Between SNF and HLWG Canisters: The FIDAP conduction model examined the effect of internal structure between the canisters on the peak temperature of the waste package. The conduction model results showed that the maximum temperature is reduced by about 13 °C through the use of internal structure. It should be noted that this model considers conduction only.

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Figure 4.19. Temperature Distribution along the Radial A-B Line for Various Decay Heat Loads and Different Back-Filled Gas (air or helium)

• Repository Temperature History: The temperature history of a repository is closely related to the heat loads of the waste package and the surrounding geological conditions. A reasonably accurate model is not available now. Consequently, the present parametric studies were performed over a range of possible repository temperature conditions (27 to 100 °C). Figure 4.20 shows peak temperatures with respect to repository temperatures for two different decay heat conditions, corresponding to 10 W and 640 W heat loads in SNF canister. The results of the conduction-radiation model indicated that the predicted peak temperature of the waste package increases linearly with repository temperature as shown in Figure 4.20.



Figure 4.20. Maximum temperature of helium-cooled codisposal canister as a function of repository temperature for two sets of internal decay heat sources (heat transfer coefficient at canister wall = 1.5 W/m².°C)

It is noted that the peak temperature location of the waste package is moved from the central edge of the HLWG region to the SNF region as decay heat load for the central SNF canister increases for a given heat load in HLWG (460 W per canister). The graphical results for the radial temperature distributions within the package are shown in Figure 4.19. Figure 4.21 shows the computational results for 640 W in SNF and 460 W per HLWG canister in helium-cooled waste package.

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Figure 4.21. Temperature contour plot for the helium-cooled waste package with internal heat sources of 640 W in SNF canister and 460 W per HLWG canister

4.4 DEGRADATION OF ALUMINUM-BASED SPENT NUCLEAR FUEL IN DISPOSAL ENVIRONMENTS

Exposure of Al-SNF forms to environments will cause time-dependent changes in the forms from their initial condition resulting in reconfiguration in physical and chemical conditions. These changes include release of radionuclides and reconfiguration of fissile species that directly effect the performance assessment and criticality analysis of the repository. Analytical and experimental activities are ongoing to characterize the behavior of the materials of the Al-SNF forms in repository environments. Characterization of the response of the materials of the Al-SNF direct form to interim storage environments has been completed except for validation testing.

The primary mode of degradation while the Al-SNF is isolated from the repository environment is creep. Creep could lead to severe slump and cladding ruptures. With a breach of the engineered barrier system and the DOE SNF canister (i.e., postcontainment), the Al-SNF forms would be exposed to water and water vapor in air conditions which would result in thinning and pitting of the Al-SNF forms due to corrosion. The principal mechanism for radioactivity release from the Al-SNF form, a metallic form, would most likely be corrosion-based. The status of activities to provide the characterization of materials' behavior of Al-SNF forms in repository environments is discussed in the following sections. Consideration of the final chemical and physical states of the materials in the repository disposal systems is discussed in Section 4.5.3

4.4.1 Creep Analysis

Previous work for time/temperature conditions applicable to interim dry storage has shown that plates on the MTR design assemblies can slump 0.1 inches in 50 years at 200 °C (Reference 4.9). The prediction of slumped configurations is desired for temperatures up to 350 °C and times up to 10,000 years to assess behavior under repository disposal conditions. Beyond this time the Al-SNF materials will likely have been exposed to the repository environment and corrosion attack.

A model of a complete MTR assembly will be constructed for finite element analysis to evaluate the impact of time/temperature on the deformation for various:

- i) creep models;
- ii) fuel orientations; and
- iii) fuel material conditions.

The results of this analysis will become part of the technical bases package to obtain NRC licensing for the repository storage of these fuels.

4.4.1.1 Theoretical Background

It is observed that high temperature creep of polycrystalline engineering alloys most frequently terminates in intergranular creep fracture associated with very small strains. It is well recognized that intergranular creep damage starts to accumulate at the very beginning of creep and generally involves grain boundary sliding, grain boundary diffusion, surface diffusion and matrix creep flow.

The deformation response of a structural element to applied loading is a function of the structural configuration, kinematic boundary conditions, thermal boundary conditions, material properties, and the loading rate. The stress-strain state in the specific structural element may consist of elastic, inelastic (e.g., viscoelastic, viscoplastic, etc.), and plastic components. The time dependent component of plastic deformation is designated as creep.

An alternative definition of creep states that creep is the plastic deformation proceeding at constant stress or at constant load and constant temperature in time. The graphical representation of the time dependence of strain is known as the creep curve (Figure 4.22). The curve is an implicit function of temperature and stress. In the first stage, the homologous temperature is low. The initial strain rate is high which includes instantaneous elastic strain and viscoelastic as well as plastic strains. The strain rate decreases with time in this primary or transient creep stage. In the second stage, the creep rate remains constant with respect to time. This creep rate is designated as steady-state or secondary creep rate. The steady-state creep takes place only at relatively high homologous temperatures, at which the recovery rate is sufficiently high to compensate the effects of deformation strengthening at any instant of time. In the third stage of creep, the creep rate increases with time. This time increase of creep rate can follow either from increasing (true) stress or from metallurgical changes in structure taking place during creep. The tertiary creep stage terminates in fracture.

The time dependence of creep strain has been investigated by many researchers (References 4.10-4.12). In general there are three major approaches in formulating the creep curves.

Empirical Description

The dependence of creep rate on time can be described by a power series:

$$\dot{\varepsilon} = \sum_{i} a_{i} t_{i}^{-n_{i}}$$

where a_i and n_i are functions of both temperature and stress. In most cases, $0 \le n_i \le 1$ and n generally decreases with increasing temperature. At low homologous temperatures, at which the rate of recovery is negligible, a logarithmic dependence of strain on time - the logarithmic time law - is frequently observed. The "logarithmic creep" rate can be



Figure 4.22. Schematic Representation of a Creep Curve

described using a single term in the above equation with n = 1. Integration of this equation then leads to the time relation, which can be expressed in the form

$$\varepsilon = \alpha \cdot \ln(\gamma t + 1) + \varepsilon_0$$

where α and γ are constants and ε_0 is an instantaneous strain, i.e., the strain corresponding to t = 0.

For steady state creep, n = 0 in the strain rate equation. The creep can be put in the form:

$$\varepsilon = \dot{\varepsilon}_s t + \varepsilon_0$$

where $\dot{\varepsilon}_s$ is the steady-state creep (strain) rate. The steady-state strain rate as described by this equation can be interpreted as resulting from dynamic equilibrium of the processes of deformation strengthening and recovery. The law expressed by this equation, with $\varepsilon_0 =$ 0, can, under certain conditions also describe the diffusional Nabarro-Herring and Coble creep. Page 4.30 of 4.78

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An exponential time law was proposed as:

$$\varepsilon = \varepsilon_o + \varepsilon_1 \left[1 - \exp\left(-\frac{t}{\tau_1}\right) \right] + \dot{\varepsilon}_s t + \varepsilon_3 \exp\left[\frac{t - t_f}{\tau_3}\right]$$

where ε_1 is the strain in the primary stage, t_f is time to fracture ε_3 the strain in the tertiary stage and τ_1 , τ_3 are constants.

In the literature, numerous attempts to analyze time laws of creep with the aim of generating ideas about the operating creep mechanism encounter serious difficulties. One is the fact that the parameters in equations describing these time laws depend on the previous deformation history and structure.

Phenomenological Description

Phenomenological models of creep based on ideas of accumulation of damage during creep also lead to the time laws of creep. Among various models published, a model started from Lepin's phenomenological theory of creep can be written as:

$$\varepsilon = m\varepsilon \exp[\alpha\sigma (1-k\varepsilon + K)]$$

In this equation $K = k_2\varepsilon + k_3\sigma t$ is the damage factor, which consists of the deformation component, the term $k_2\varepsilon$; and the stress-time component, the term $k_3\sigma t$; m, n, α and k_1 , k_2 and k_3 are constants.

Physical Description

Based upon the concepts of average behavior of a large number of dislocations and ideas of dislocation dynamics, a number of physical models have been developed in the past. The equation developed by Webster can be put in the form:

$$\varepsilon = a_1 t + a_2 \cdot \ln\{1 + a_3[1 - \exp(\alpha t)]\} + R[\exp(-\alpha t)]$$

where a_1 , a_2 , a_3 and α are constants and R is a fractional rational function of exp(- α t). The constants a_1 , a_2 , a_3 and α relate to the dislocation structure characteristics and can be determined by measurements of these characteristics and interpreted by the dynamic behavior of dislocations.

From the point of view of the needs of engineering practice, the phenomenological description is more appropriate, while the physical description may contribute to an understanding of participating dislocation processes such as dislocation generation, dislocation motion and annihilation and immobilization, respectively.

A characteristic behavior of diffusional Coble creep is that the creep rate is a linear function of stress. The dislocation creep rate is practically independent of grain size, while
the diffusional creep rate is inversely proportional to the second power of mean grain diameter when the diffusion mass transport occurs via the lattice, and to the third power of mean grain diameter when it occurs through grain boundaries. Theoretically, diffusional Nabarro-Herring and Coble creep is well elaborated, and agreement of theory with extensive experimental data for pure metals is remarkable.

The creep rate of Coble creep (low stress and low homologous temperature) with diffusion can be written as

$$\dot{\varepsilon} = 44 \frac{\sigma \Omega D_{\rm B} \delta_{\rm B}}{{\rm d}^3 {\rm kT}}$$

The rate of diffusional creep of a metal or a solid solution containing finely dispersed particles of a second phase can be expressed as

$$\dot{\epsilon} = 44 \frac{D_{B} \delta_{B} \Omega}{d^{3} kT} (\sigma - \sigma_{0})$$

The threshold stress σ_0 can be expressed by the relation

$$\sigma_0 = \frac{2\Gamma_B}{b_R l}$$

where b_B is the Burgers vector length and Γ_B is the line energy of a grain boundary dislocation and l is the interparticle spacing.

By putting $\Omega = 0.7 b_B^3$ and assuming $\delta_B \approx 0.2 b_B$, the strain rate equation for the Coble creep can be written as

$$\dot{\varepsilon} = A_{co} D_{o(gb)} \frac{G b_B}{kT} \left(\frac{b_B}{d}\right)^3 \left(\frac{\sigma}{G}\right) \exp\left(-\frac{Q_{gb}}{RT}\right)$$

for pure aluminum, where

 A_{co} =dimensionless Coble creep constant = 66.8, $D_{o(gb)}$ = grain boundary frequency factor = 1.86 cm² sec⁻¹ = 1.86E-04 m²·sec⁻¹, R = gas constant = 8.31441 J·mol⁻¹·K⁻¹, k = Boltzmann's constant = 1.38E-23 J·K⁻¹, Q_{gb} = grain boundary diffusion activation energy = 86.04 kJ·mol⁻¹, G = shear modulus at temperature $T = G_o - \Delta GT = 3.022E+04$ MPa - (16.0 MPa K⁻¹)T, b_B = Burgers vector = 2.86E-08 cm =2.86E-10 m. d = average grain size (cm) σ = von Mises equivalence stress (MPa or psi) T = absolute temperature (K)

4.4.1.2 Mathematical Modeling and Numerical Calculation of the Fuel Element

The fuel assemblies in dry storage are under the influence of temperature changes, the gravitational load and the grain size of the fuel elements. Since the mass density of the aluminum is comparatively low, the stress generated by gravity is insignificant. The thermal expansion effect is confinement dependent. For an unconfined element, the thermal expansion in the element has little or no stress variation. Therefore, this type of fuel assembly will deform with the Coble creep strain rate. In the Coble creep strain rate formula, the effect of the grain size is cubic in power. The variation of grain size in the fuel element will tremendously influence the rate of long term deformation of the fuel assemblies.

In order to predict the long term creep deformation of the fuel assemblies, a detailed finite element analysis model was constructed. The general purpose nonlinear mechanics code, ABAQUS (Reference 4.13), was used for this calculation. The rate dependent plasticity (creep) models provided in ABAQUS was used to model inelastic straining of materials which are rate sensitive. High temperature creep in structures are one important class of examples of the application of such a material model. Because such problems generally involve relatively small amounts of inelastic straining, the explicit, forward Euler method (References 4.14-4.15) is often satisfactory as an integrator for the flow rule. This method is only conditionally stable, but the stability limit is usually sufficiently large compared to the time history of interest in such cases that the explicit method is very economic. Cormeau (Reference 4.16) has developed formulae for the stability limit for most common cases of stress-induced creep, and these results are used to monitor stability.

There also exist many problems involving rate dependent plastic response in which the characteristic relaxation times for the material under the stress states to which it is subjected are very short compared to the time period of interest in the analysis, so that the conditional stability of the explicit operator will only allow very short time increments. For such cases (actually the fuel assemblies creep analysis falls within these cases), it can be more economical to use the backward Euler method because of its unconditional stability. ABAQUS always uses the implicit method for high strain rate applications to avoid time increment restrictions being introduced by considerations of stability in the integration of the constitutive model.

Based upon mathematical derivations, in the finite element analysis, the fully integrated solid continuum element provides reliable solutions for most complicated problems. Nevertheless, for certain specific problems, shell elements and elements with reduced integration are much more economical (for fewer elements and shorter computation time). Since for the creep analysis of the fuel assemblies, a great deal of cases will be analyzed, all the favorable elements for this analysis should be considered.

The solid continuum element model, consists of 81,400 eight-node brick elements with 10,353 nodal points. Taking advantage of the double symmetry of the fuel assemblies, a single fuel plate is modeled only within the planes of symmetry. The finite element model represents a quarter of the real fuel plate. Since the creep of the fuel assemblies is a long term process, any slight variation in the fuel plate will eventually be magnified in a long term deformation. Therefore, the geometry and the boundary confinements are meticulously modeled.

4.4.1.3 Preliminary Results

For the low stress and moderately high temperatures, the creep strain rate is governed by the Coble creep law in which the material grain size is the most influential factor. A parametric study has been performed for two grain sizes (10 and 50 μ m) at two different temperatures (200 and 350 °C). The fuel plate is subject to its own weight (gravity) and each plate end is free to slide in a frictionless but fixed supporting slot. The temperature is assumed to remain unchanged throughout the entire duration of creep. Thermal stresses are neglected since thermal equilibrium is assumed. The times for the center of the curved plate to reach 0.1-inch slump and the times for the fuel plate to slide out of the slot are listed respectively in Tables 4.3 and 4.4:

Table 4.3. Time for a Fuel Plate to Slump 0.1 inches

	Grain Size	Grain Size
	10 µm	50 µm
200 °C	11 years	> 1000 years
350 °C	13 days	4 years

|--|

	Grain Size 10 µm	Grain Size 50 µm
200 °C	41 years	> 1000 years
350 °C	49 days	16 years

Creep deformation of the fuel plate is shown in Figure 4.23. The originally arched fuel plate is deformed with two curvatures - one in the center of the plate and the other near the end of supporting slots. Figure 4.23 is at a time/temperature condition when the fuel plate is about to slide out of its supports.



Figure 4.23. The Slumping of a Fuel Plate Sliding out of the Slot

4.4.2 Vapor Corrosion of the Materials of Aluminum-based Spent Nuclear Fuel-Repository Environments

Previous vapor corrosion tests of the materials of the Al-SNF direct form were performed using atmospheric condensate as the water source. The previous results, reported in Reference 4.4, are summarized in Section 4.4.2.1. In that work, corrosion equations in the form of a power law with an Arrhenius relation were developed for aluminum cladding alloys 1100, 5052, and 6061to allow prediction of their corrosion behavior at vapor environments from approximately 100 °C to 200 °C and 0 to 100% relative humidity. Results from initial corrosion tests of fuel materials and from gamma radiation and air/water vapor tests at 78 °C and 200 °C on the cladding alloys were also reported.

The planned tests for aluminum cladding alloys (including the on-going tests) and for the proposed aluminum-19 wt % uranium are listed in Section 4.4.2.2. Section 4.4.2.3 contains the recent results of aluminum cladding alloys in 200 °C and 250 °C vapors. Diluted nitric acid water vapor and repository well (J-13) were used in some cases. The radiation tests were carried out in the SRTC gamma cell ambient temperature (about 78 °C). A strong dependency on water chemistry was observed. In high temperature tests (250 °C), severe hydrogen blistering occurred in the specimen exposed to condensate water vapor even without radiation effect. The degradation mode has been shifted from the uniform surface oxidation with layers of oxides (amorphous aluminum oxide, bayerite or gibbsite, and boehmite) to non-uniform attack, both externally and internally. Oxide spalling from the specimens occurred in the high temperature tests, even at a low (50%) relative humidity.

4.4.2.1 Vapor Corrosion with Condensate Water-Summary of Previous Work (from Reference 4.4.)

Behavior Under Unlimited Corrodant Species

An autoclave facility was used to investigate the corrosion behavior of the aluminum cladding alloys (Al 1100, 5052, and 6061) in saturated vapor (constant 100% relative humidity) at 150 °C (for up to about 1400 hours) and at 200 °C (for up to about 5100 hours). The corrosion of alloys 1100 and 6061 can be described by a general power law with Arrhenius relation:

• Alloy 1100: Wt. Gain (in μ g/dm²) = 2.19x10⁸ • exp[-9.82(kcal/mole)/RT(K)] • (Hours)^{0.40}

• Alloy 6061: Wt. Gain (in $\mu g/dm^2$) = 3.30x10⁶ • exp[-6.82(kcal/mole) / RT(K)] • (Hours)^{0.47}

where R is the universal gas constant (R=8.31434 J/g·mole·K or 1.98717 cal/mole) and T is the absolute temperature in Kelvin.

It was discovered that the alloy 5052 exhibits normal parabolic corrosion behavior initially (<1400 hours at 200 °C). However, break-away corrosion occurred at a weight gain of about 100,000 μ g/dm². The post-break-away behavior is a linear relationship between the weight gain and the time of exposure. Therefore, the corrosion of alloy 5052 is described by

Alloy 5052:
Before break-away corrosion
Wt. Gain (in μg/dm²) = 2.81x10⁸ • exp[-11.13(kcal/mole)/ RT(K)] • (Hours)^{0.55}
Post-Breakaway
Rate of Weight Gain (μg/dm² per Hour)= 1.67x10¹² • exp[-19.92(kcal/mole)/ RT(K)]

The following conversion formulae in terms of weight gain are useful. These equations are not valid if sloughing-off of corrosion product (oxide) occurs.

- Aluminum Consumed (or Metal Loss in mils) = (1.19x10⁻⁶) x Weight Gain (in μg/dm²)
 ----- Valid for both pre- and post break-away corrosion;
- Oxide Film Thickness (Boehmite Film in nm) = $(5.33 \times 10^{-2}) \times \text{Weight Gain (in } \mu\text{g/dm}^2)$ ------ Valid only prior to break-away corrosion.

In the above equations the aluminum alloy density of 2.7 g/cc and the boehmite density of 3.41 g/cc are used.

Behavior Under Limited Corrodant Species

Sealed stainless steel capsules were used to test the corrosion behavior of the cladding alloys 1100, 5052, and 6061 under fixed initial environmental conditions including the

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relative humidity and water chemistry. Tests were carried out at 150 °C for up to twelve months. Various levels of initial relative humidity up to 100% were achieved by injecting a calculated amount of solution into the capsules before sealing. The solutions include the condensate water and the diluted nitric acid simulating the radiolysis effect. The relative humidity decreases due to the consumption of water in the corrosion process. The results show that :

- (1) Vapor from the nitric acid solution, or the simulated radiolysis environment, is significantly more corrosive than water vapor.
- (2) Corrosion is more extensive in an environment with higher relative humidity.
- (3) The corrosion rate will decrease, and corrosion will eventually cease. The capsule is a completely closed system. The amount of air, water, and/or acid was fixed when the capsules were sealed; the corrodant species were depleted due to the oxidation reaction $(2Al + 4H_2O \rightarrow Al_2O_3 \cdot H_2O + 3H_2)$.
- (4) Under a water vapor environment, a critical relative humidity between 40 and 70% exists below which practically no corrosion occurs at room temperature (Reference 4.17). It appears that in the current capsule test, the critical relative humidity at 150 °C is 20% for 1100 and 6061, because no weight gain was observed after exposures up to 9000 hours below 20% relative humidity.
- (5) Based on the present data, the critical relative humidity for alloy 5052 under a water vapor environment at 150 °C is less than 20%. All three aluminum alloys (1100, 5052, 6061) exhibited weight gains in the acidic or simulated radiation environment at 20% relative humidity; therefore, a threshold water level below which corrosion does not occur was not observed.
- (6) In a closed system, the corrosion will stop when all the corrodant species (e.g., free water and oxygen) are consumed. The absence of a critical relative humidity (in a radiation field) below which no corrosion is detected does not preclude acceptable fuel storage in a completely sealed containment system. The amount of corrosion that takes place during storage can be controlled by limiting the initial amount of water present in the canister at closure.

Effects of Gamma Radiation in Air/Water Vapor Environments

Actual storage of spent nuclear fuel will be under a radiation field which depends on the package configurations and co-disposed waste forms, the type of fuel, fuel burn-up, and decay times. As has been demonstrated in nitric acid water vapor environments, the corrosion rates were significantly increased under this simulated radiation environment. To investigate corrosion behavior under an ionizing radiation field, the test capsules with initial relative humidities of 20, 50, and 100% were tested at 200 °C for 1, 4, 8, and 12 weeks in the SRTC gamma cell facility. Each capsule contains an 1100, a 5052, and a 6061 specimen. The gamma cell contains a cobalt 60 source and has a fixed dose rate of 1,810,000 R/hr (value during test). This intensity is higher than that expected during spent nuclear fuel storage in the repository.

Test results show a significant increase in the corrosion rate. In the case of 100% relative humidity with radiation in the water/air environment, a weight gain about three times as

great from that in the water/air environment without radiation was observed in the early stage of the corrosion. After a very short period of time, less than a week, most of the corrosion has occurred and either the usable water vapor corrodant has been depleted or the oxide film has reached a thickness sufficient to significantly decrease the corrosion rate. The post-exposure surface is no longer an even layer of boehmite crystals. The morphology appears to be a result of hydrogen blistering which normally occurs in the aluminum alloys when the temperature is above about 250 °C in moist air (Reference 4.5). Boehmite crystals form in irregular clusters with various sizes. The test showed that no critical value for relative humidity exists in gamma radiation field at 200 °C.

A separate test was carried out at the normal operating temperature of the gamma cellabout 78 to 80 °C. Test results confirmed that corrosion rates increase with gamma radiation.

Fuel Materials Corrosion Test

Most of the FRR/DRR fuels to be returned to SRS are UAl_x fuel. The fuel material will be subject to vapor corrosion when the aluminum cladding is penetrated or consumed.

Aluminum-10 wt % uranium alloy was tested in an autoclave at 200 °C under saturated vapor conditions. The specimens were taken out of the autoclave at selected intervals for weight gain measurement up to exposure times of 1500 to 1700 hours (about 70 days). Two types of specimens were used: rectangular coupons (hot rolled with broken fragments of UAl_x, most likely UAl₄, in the microstructure) and circular disks (extruded with large eutectic areas in the microstructure).

The results show that although the total weight gains for these two types of specimens differed, the corrosion rates (the slopes of the curves) appear to be consistent. In general, the weight gain for the UAI alloys is greater than that for aluminum 1100 under the same exposure conditions. The microstructural inhomogeneity of the alloys may contribute to the discrepancy. In fact, for a hot-rolled specimen with only four days of exposure, a blistered region had formed. In addition, a large number of uranium aluminide particles are scattered both in the metal matrix and in the oxide layer. Therefore, the corrosion resistance of the uranium aluminide will be further investigated.

Aluminum-18 wt % uranium and aluminum-33 wt % uranium are more representative of high enriched and low enriched FRR/DRR fuels than the aluminum-10 wt % uranium. Additional tests have been planned to investigate specimens equivalent to these compositions.

4.4.2.2 Conditions for Additional Tests

Additional vapor corrosion tests have been planned. The corrosion of aluminum cladding alloys and fuel materials (aluminum-uranium) in vapors will be characterized as a function of temperature, water chemistry, gamma radiation, and relative humidity. Two test

matrices are devised for the cladding alloys and for the aluminum-19 wt % uranium fuel alloy (see Tables 4.5-4.6)

Temperature	Test Duration		
(°C)	(weeks)	Radiation	Water
250	4/12/24/36/48	No	Condensate, RH ≤ 100% Initial
200	4/12/24/36/48	No	Condensate, RH ≤ 100% Initial
200	4/12/24/36/48	No	Nitric Acid, RH ≤ 100% Initial
200	1/4/12	No	J-13, RH = 100% Saturated
200'	up to 12	Gamma	Condensate, RH ≤ 100% Initial
78	1/4	Gamma	Condensate, RH = 100% Saturated
78	78 1/4 Gamma J-13, RH = 100% Saturated		
†: This test has been completed and the result is reported in Reference 4.4.			
It is included here for completeness.			

Table 4.5. Test Matrix of Aluminum Cladding Alloys (Al 1100, 5052, and 6061)

The aluminum-19 wt % uranium is chosen to represent the majority of the FRR/DRR fuel materials for the vapor corrosion test. Both high and moderate temperatures will be considered. The effects of water chemistry on corrosion with and without a radiation field will be investigated.

4.4.2.3 Recent Results

Capsule tests with aluminum cladding alloys 1100, 5052, and 6061 at high temperatures (200 and 250 $^{\circ}$ C) are in progress. These data have not been reported in Reference 4.4. The recent tests with high temperatures, J-13 water, and gamma radiation are described in Table 4.7.

Corrosion in the Absence of a Radiation Field

The weight gain data for aluminum alloys 1100, 5052, and 6061 under (initial) 100% RH in 200 °C are plotted in Figures 4.24 to 4.26, respectively. Two additional sets of test data are included in these figures for completeness: 1) 200 °C autoclave test data; and 2) 200 °C gamma cell data. It is apparent that the water chemistry has a significant impact on corrosion: the weight gain in the J-13 vapor is greater than that in the condensate water vapor environment.

In the simulated radiation condition (i.e., the water vapor contains diluted nitric acid) at 200 °C, it was found that the corrosion product has fallen off the test specimens. XRD

	Test		
Temperature	Duration		
(°C)	(weeks)	Radiation	Water
200	1/4/12	No	Condensate, RH = 100% Saturated
200	1/4/12	No	J-13, RH = 100% Saturated
200 ‡	1/4/12	Gamma	Condensate, RH = 100% Saturated
200 ‡	1/4/12	Gamma	J-13, RH = 100% Saturated
78 or Gamma Cell Ambient Temperature	1/4/12	No	Condensate, RH = 100% Saturated
78 or Gamma Cell Ambient Temperature	1/4/12	No	J-13, RH = 100% Saturated
78 or Gamma Cell Ambient Temperature	1/4/12	Gamma	Condensate, RH = 100% Saturated
78 or Gamma Cell Ambient Temperature	1/4/12	Gamma	J-13, RH = 100% Saturated
‡: The high temperature test with the SRTC gamma cell is on hold until it is reviewed/modified by the equipment vendor and the SRS safety committee.			

Table 4.6.	Test Matrix	of Aluminum-19	wt %	Uranium	Allovs
1 abic 4.0.	I COL MALLIA	vi / mummum-1/	116 70	Oramum	ппоуз

Table 4.7. Preliminary Results of Aluminum Alloy Vapor Corrosion Testing

Temperature	Test Duration		
(°C)	(weeks)	Radiation	Water
200	1/12/24	No	Condensate, Initial $RH = 10, 20, 50,$ and 100%
200	1/12/24	No	Nitric Acid, Initial $RH = 10, 20, 50,$ and 100%
250	1/12/24	No	Condensate, Initial $RH = 10, 20, 50,$ and 100%
200	1/4	No	Condensate, RH = 100% Saturated
200	1/4	No	J-13, RH = 100% Saturated
78	1/4	Gamma	Condensate, RH = 100% Saturated
78	1/4	Gamma	J-13, RH = 100% Saturated

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Figure 4.24. Corrosion of Aluminum 1100 in Various 200 °C Vapor Environments



Figure 4.25. Corrosion of Aluminum 5052 in Various 200 °C Vapor Environments



Figure 4.26. Corrosion of Aluminum 6061 in Various 200 °C Vapor Environments

analysis indicated that this substance is boehmite. Although weight gain measurement is no longer valid for the acidic vapor environment, the data points are still plotted in Figures 4.24 to 4.26 for reference purpose. Because of the sloughing-off of oxide, the "weight gain" in the nitric acid vapor is less than that in the case of water vapor.

The weight gains of the specimens in initially 100% RH condensate water vapor at 200 °C should be comparable to or less than those obtained in autoclave tests. The cause of higher weight gain obtained in equivalent capsule tests will be investigated.

The condensate water vapor test at 250 °C resulted in oxide sloughing off the specimen surfaces. No weight gain data can be reliably reported. Since internal oxidation (Reference 4.4) and hydrogen blistering (Reference 4.5) may have occurred in these specimens, there is no effective way to remove all the oxides so that metal loss can be measured.

Corrosion in Radiation Field

The gamma radiation effects on vapor corrosion at the ambient temperature (78 to 80 °C) of the SRTC gamma cell (about 1,600,000 Rad/hr when the test was being performed) has been investigated. Note that cobalt source has decayed since the last set of data was reported in Reference 4.4 at which time the dose rate was reported as 1,810,000 Rad/hr. In Figure 4.27, the weight gains of the cladding alloys in the water vapor containing the impurities found in J-13 well water are about 2 to 3 times greater than those in the condensate water vapor. The oxide forms found with XRD on the specimen surfaces are a

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combination of bayerite and boehmite due to the low ambient temperature of the test environment.



Figure 4.27. Water Chemistry Effects on Aluminum Alloy Corrosion in Gamma Radiation Field

Post-Exposure Metallography (250 °C)

It has been observed that the oxide may fall off from the specimen surface at 200 °C in the 100% relative humidity condensate vapor environment. When the vapor contains nitric acid (or NO_x gases), the sloughing-off occurs in the capsules with 50% relative humidity. At 250 °C, the oxide was observed to slough off even in 50% relative humidity condensate water vapor. At this temperature, it is well known that hydrogen blistering may occur.

Figure 4.28(a) shows the aluminum 1100 specimen after an exposure of six months in the 100% relative humidity water vapor at 250 °C. Unexplained circular spots, each with depth about 30 to 40 mils (0.8 to 1.0 mm or 24 to 32% of the test coupon thickness) appeared on both the front and back surfaces of the specimen. The XRD results indicate that the center of the spot has been oxidized (Figure 4.28(b)). Note that the oxide no longer has distinct facets even at 2000 times magnification. A section of the specimen was examined by SEM (Figure 4.28(c)). No oxide layer was detected in the dipped region. However, part of the oxide layer can be seen at the edge of the spot (upper right corner in Figure 4.28(c)). The metal matrix seems to have undergone grain boundary attack.



(c) Metallography of the Section in the Dip Area (Left side shows the bottom of dip; remaining oxide layer is visible on the right side.)

Figure 4.28. Aluminum 1100 Exposed to 250 °C Water Vapor for Six Months (Initial Relative Humidity 100%)

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No apparent peculiarities in the exposed specimen of aluminum 5052 in 250 °C vapor were observed. The surface morphology is similar to that in the gamma radiation field at 200 °C reported in Reference 4.4. As shown in Figures 4.29, the specimen surface is covered with broken blisters and oxide crystals (Figure 4.29(b)). Under the oxide layer in the cross-section of the specimen (Figure 4.29(c)), massive cavities formed in the metal matrix very similar to the internal oxidation sites found in Reference 4.4. In addition, smaller holes formed inside the oxide layer. It indicates that external and internal oxidation can occur simultaneously, leading to a very rapid degradation mode (for all three alloys).

In a 250 °C water vapor environment, local areas of the aluminum 6061 specimen surface were attacked and chipped away. Figures 4.30 show the chipped area and cross-section of the specimen. The morphology is similar to that of aluminum 1100 (Figures 4.28). Grain boundary attack occurred in the metal matrix.

High Temperature Degradation Mode

The tests of aluminum alloys in 200 °C and 250 °C vapors have been completed for four, twelve, and 24 weeks (or equivalently, one, three, and six months). This on-going test will be completed after a total exposure of 48 weeks. The XRD analysis of the oxide form on the specimen surface and the analysis of the sloughed-off substance left inside the bottom of the capsules are all boehmite in 200 °C tests and in 250 °C test up to 3 months. However, with extended exposure time in 250 °C condensate water vapor, the XRD results not only show boehmite (Al₂O₃•H₂O), but also corundum (Al₂O₃). This may suggest that dehydration would occur with high exposure temperature and long exposure time. The oxide layer would slough off as a result of hydrogen blistering with internal corrosion along the grain boundary. Because the weight gain data are no longer valid and the oxide forms are not unique and cannot be completely removed, the rate of corrosion is impossible to characterize. In such a case, the final forms of corrosion products and their stability may be more relevant to the long term repository storage environments.

Summary

The corrosion rates and products of Al SNF cladding and fuel materials exposed to repository vapor environments are presently being characterized through testing and analysis. The corrosion rate or, equivalently, the rate of conversion from a metallic form to an oxide form under vapor conditions, is highly dependent on temperature, relative humidity, water chemistry, and ionizing radiation. Models for the conversion of cladding and fuel materials under vapor conditions are being developed to facilitate prediction of the time-dependent form of materials. Dissolution of the materials and release of radionuclides would primarily occur under aqueous conditions. The release would occur from the metallic form, if unconverted, or from the oxide form, if converted.

4.4.3 Aqueous Corrosion

Characterization of the dissolution of the Al-SNF fuel materials in a metallic form in aqueous environments is being performed under the Test Protocol program (see Section 6

of this report). The preliminary assessment considers the dissolution rate to be equivalent to the corrosion rate of the fuel. A first approximation is the that rate of dissolution of Al-SNF materials (U-Al, U_3Si_2 -Al, and U_3O_8 -Al) is 0.1 times that of uranium metal.

The corrosion rate of uranium metal in aqueous systems is directly related to its rate of dissolution. A corrosion model for uranium- and uranium alloy-based spent fuel was incorporated in a performance assessment developed by SNL (Reference 4.18):

 $M = A e^{-B/T} (t_2^c - t_1^c) D E S$, where

M is the metal loss due to corrosion from time t_1 to time t_2 , A is an empirical coefficient, B is an Arrhenius activation energy term, c is a power law exponent, D is a function of saturation, E is a function of oxygen concentration, and S is the surface area of the metallic spent fuel. In the performance assessment developed by SNL (Reference 4.18), the equation was simplified to a linear relationship by assuming that c = 1 (linear in time), D = 1 (fully saturated system for conservatism), E = 0.2 (approximated by the volume concentration of oxygen in dry air. This model is inappropriate for aluminum-based metals with corrosion rates that do not vary significantly with temperature below 100 °C and which, like aluminum, exhibit passive film formation under neutral pH chemistries.

From SRTC corrosion tests in storage basin water (high purity), preliminary data using linear polarization testing showed that the consumption rate for both a cladding alloy, 8001 aluminum, and a fuel alloy, aluminum-10%uranium, is 0.2 mpy for a 600-grit fresh surface. For an 1100 aluminum specimen with a boehmite film approximately 1 μ m thick, the immersion testing indicated that the rate is 0.02 mpy. No dissolution tests has been carried out for aluminum-uranium alloys. Based on the vapor corrosion test of the extruded aluminum-10 wt % uranium disk specimens (Reference 4.4), the rate of metal consumption is in the order of 0.5 mpy. The reaction in the higher temperature vapor environment is more severe than that of the lower temperature water environment.

The results of initial testing of U-Al materials in vapor environments show that the weight gain (or, equivalently, metal consumption) rate is reduced as exposure time increases consistent with the formation of a passive film (Reference 4.4). This general behavior is similar to with that of the aluminum cladding in the same environment and to the literature data for aluminum corrosion in high purity water at temperatures less than 100 °C (Reference 4.19). The corrosion of aluminum in water proceeds in accordance with

 $W = A + B \ln(t)$

where W is the metal consumption, t the exposure time, and A, B are the empirical coefficients.

Corrosion and dissolution behavior is being investigated as discussed in Section 6 of this report.



- (c) Metallography of the Section showing Interconnected Cavities in and under the Oxide Layer.
- Figure 4.29. Aluminum 5052 Exposed to 250 °C Water Vapor for Six Months (Initial Relative Humidity 100%)

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(a) Exposed Coupon Sample

(b) Morphology of the Chipped Area on the Left Side



(c) Metallography of the Section in the Chipped Area (Remaining Oxide Layer is visible on the right side.)

Figure 4.30. Aluminum 6061 Exposed to 250 °C Water Vapor for Six Months (Initial Relative Humidity 100%)

4.4.4 Hydrogen Generation

The hydrogen generation can be estimated either by the bayerite/gibbsite reaction (predominant below about 80 $^{\circ}$ C - Reference 4.2)

$$2A1 + 6H_2O \rightarrow Al_2O_3 \cdot 3H_2O + 3H_2$$

or by the boehmite reaction (predominant above about 80 °C)

 $2Al + 4H_2O \rightarrow Al_2O_3 \cdot H_2O + 3H_2$.

In the above equations, one mole of hydrogen is generated by two moles of water when the corrosion product is bayerite or gibbsite; and is generated by 4/3 moles of water when boehmite is formed at higher temperature. For the Al-SNF in the canister storage condition, the hydrogen generation depends on the amount of moisture allowed inside the canister before it is sealed. For example, if the volume fraction of hydrogen is limited to X and the free volume of the canister is V, then the allowable water in milligrams (mg) is approximately XV, where V is in cubic centimeters (cc). In general, the explosion limit for hydrogen volume fraction is 4%. Therefore, the water in the canister should dry to less than 0.04V mg. Note that the more conservative boehmite reaction was used. However, in a breached canister where water may be unlimited, the hydrogen will continue to generate until all the aluminum alloys are consumed by corrosion process.

4.4.5 Volatile Species Release

The release of volatile radionuclides from an intact Al-SNF in a codisposal waste package would directly affect the performance assessment of the geologic repository. Argonne National Laboratory is conducting furnace tests for SRTC to evaluate fission product release from irradiated aluminum-based fuel elements. Two heating tests on segments of irradiated aluminum-based fuel have been completed. No radionuclide release was detected from segments of either U_3Si_2 -Al or UAl_x-Al during furnace tests at 275 °C for times up to four months. Further tests of the UAl_x-Al fuel at 400 to 425 °C for times up to four months are planned in an attempt to establish a temperature threshold for change in fuel behavior.

In the first test, a segment of fuel element irradiated in the Oak Ridge reactor was heated at 275 °C for 30 days. The fuel was a dispersion of U_3Si_2 (19.8% enriched) particles in an aluminum matrix clad with 6061-T6 aluminum. Average burnup was 51.4%. The area of fuel exposed to air in the test chamber was 0.6 cm². In the second test, the fuel element segment was a dispersion of UAl_x particles (19.8% enriched) in aluminum clad with 6061-T6 aluminum. The fuel element had been irradiated in the Oak Ridge reactor to an average burnup of 66.5%. The area of fuel exposed to air in the test chamber was 0.5 cm². There was no release of volatile fission products in either test nor were there any significant changes in fuel microstructure, core-clad interface, or surface oxide thickness detectable by optical microscopy.

4.4.6 Pyrophoricity

The potential pyrophoricity of aluminum plate fuels retrieved from underwater storage has been evaluated (Reference 4.20). Results of this evaluation indicate that the possibility of pyrophoricity in aluminum plate fuels should be significantly lower than for uranium metal. Several contributing factors to this conclusion are given as follows:

- The rate of UH₃ production is lower because of the greater corrosion resistance of UAl_x compared to uranium metal.
- The extent of corrosion is expected to be much lower because exposure of UAl_x occurs by localized pitting corrosion rather than cladding removal by general corrosion.
- The extent of corrosion is expected to be lower in the penetrated areas because of the microstructure of the fuel meat, where the extent of corrosion is limited by the more resistant aluminum matrix.
- The rate of aluminum corrosion (cladding thinning rate) is much lower than the rate of uranium corrosion, resulting in a lower rate of UO_2 and UH_3 formation.
- The lower rate of aluminum reaction (lower propagation rate) and the presence of hydrated alumina will favor more complete digestion of the UH₃.
- Any residual UH₃ is further diluted by the major product of the corrosion reaction, Al(OH)₃.

Additional analyses are being performed to demonstrate that the aluminum-based fuels $(UAl_x-Al, U_3Si_2-Al, and U_3O_8-Al)$ are not pyrophoric under repository conditions.

4.5 CRITICALITY ANALYSIS

Criticality control in waste packages for disposal at Yucca Mountain is governed by 10 CFR 60. Currently, the criticality analysis must show no possibility (probability $< 10^{-6}$) of criticality for 10,000 years following disposal. Therefore, both intact and degraded states of the waste package must be evaluated. Further, the Total System Performance Assessment - License Application should report the impact on total system performance in the event of a criticality incident.

The criticality analysis of Al-SNF forms is being performed in separate phases. Analysis of the Al-SNF direct form within an intact DOE SNF canister has been completed by CRWMS. Analysis of the melt-dilute form within an intact canister will be performed in FY98. Analysis of degraded configurations of the direct form within the waste package is being performed by CRWMS. Supporting investigation of materials reconfiguration and candidate neutron poison materials is in progress.

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Criticality within a DOE-SNF codisposal canister was evaluated, using the MCNP4A computer code, by CRWMS (Reference 4.21). Two DOE-SNF fuel types were analyzed: high-enrichment MIT reactor fuel; and the low-enrichment ORR fuel. Although the initial configuration of materials in each canister within the WP will meet repository criticality requirements, initial calculations for a degraded state of an Al-SNF canister, where the contents of the canister were homogenized with water that had flooded the free space in the canister, indicate that reactivity would be excessive unless neutron absorber materials are included in the canister.

Degradation of the Al-SNF and reconfiguration of fissile materials will be controlled by the thermochemical stability and solubility of many possible uranium compounds and rates of the many competing reactions. Based on the natural occurrence of uranium bearing minerals within ore deposits in the western United States, thermochemical data, and the products formed during laboratory corrosion experiments, the hydrated oxides and silicates of uranium and hydrated aluminum oxides or alumino-silicates are the most likely final degradation products.

Neutron poison materials for loading in Al-SNF canisters have been assessed as a method for avoiding criticality with HEU SNF. Candidate materials include borated stainless steel, dispersions of europium oxide, gadolinium oxide, or samarium oxide in stainless steel, and cadmium. Mechanical properties, corrosion resistance, neutron absorption properties, cost and availability are the major factors evaluated for selection of a poison material.

Section 4.5.2 discusses the criticality analysis for the Al-SNF within an intact codisposal canister. Section 4.5.3 discusses degradation and reconfiguration of the Al-SNF. Section 4.5.3 discusses neutron poison materials.

4.5.1 Background

The current rule concerning NRC's disposition on criticality control in waste packages for disposal at Yucca Mountain is given in 10 CFR 60. The rule states that a 5% shut down margin ($k_{eff} < 0.95$) must be demonstrated for all SNF for the entire compliance period. The current time period of concern is 10,000 years.

Currently, 10 CFR 60 is under revision. This revision may eliminate design criteria for the proposed repository at Yucca Mountain. In the event that the design criteria are removed from the rule, a performance criterion would be effected. This performance objective will likely be based upon dose to the general population. We would therefore be required to determine the likelihood and dose consequences of the criticality event.

Historically, however, NRC has taken the 'defense-in-depth' approach in dealing with radioactive waste. If NRC follows their 'defense-in-depth' philosophy, we will end up with a rule that would combine the two regulatory philosophies: a performance based standard that also has design criteria. In the event that the design criteria remain in the

rule, it would be necessary for our analysis to show no possibility (probability $< 10^{-6}$) of criticality for 10,000 years following disposal. In any event, the Total System Performance Assessment - License Application should report the impact on total system performance in the event of a criticality event.

Assessing the likelihood of criticality scenarios will require modeling groundwater flow, materials degradation, geochemical reactions, nuclide transport, and reprecipitation. Groundwater flow modeling should include both matrix and fracture flow and should consider chemistry and thermal effects. Materials degradation modeling must include the degradation of the waste package, the SNF and/or HLW, the absorber material, and the invert/lining/backfill materials. The degradation modeling should also include the consideration of the chemical environment (pH, oxygen partial pressure, carbonate concentration, chloride concentration), saturation, and temperature. Modeling of the geochemical reactions should include consideration of pH, temperature, saturation, and the degradation products of the waste package, SNF and/or HLW, absorber material, and the invert/lining/backfill materials. The degradation and geochemical modeling together should provide insight to nuclide dissolution, phase formation, and colloid formation. Nuclide transport modeling should consider chemistry and geology to predict retardation, dispersion, and reconcentration of dissolved solids, particulates, and colloids. The transport and geochemical modeling together should provide information on the likelihood of reprecipitation of fissile material and other degradation products. It will be necessary to complete criticality calculations to determine if the possible configurations produce a critical mass. Therefore, the modeling program suggested above should be run in parallel with criticality calculations. The results of this extensive modeling effort and the criticality calculations will be the possibility and probability of achieving a given critical configuration and the total probability of a critical event. Further, data gathered from this modeling effort can be input to a dose model to determine the consequence of a criticality event. The modeling and calculations described above constitute a simplified performance assessment. The criticality calculations are an integral part of this performance assessment. We must therefore exercise diligence in our selection of the tools and assumptions that will be used in our criticality analysis.

There are several computer codes that have been used or are being used for determining the multiplication factor, k_{eff} , of a given geometry and chemistry. Two of these codes, KENO and MCNP, have been used in previously accepted transport/storage/shipment NRC license applications. KENO-VI is an extension of the KENO Monte Carlo criticality program developed for use in the SCALE system. The primary purpose of KENO-VI is to determine k_{eff} in three-dimensional systems (Reference 4.22). Other calculated quantities include lifetime, generation time, energy-dependent leakages, energy- and region-dependent absorptions, fissions, fluxes, and fission densities. Special features of KENO-VI include simplified data input, supergrouping of energy-dependent data, the use of quadratic equations to represent geometry input, a P_n scattering treatment, extended use of differential albedo reflection, and restart capabilities. MCNP is a general-purpose, continuous-energy, generalized-geometry, time-dependent, coupled neutron/photon/ electron Monte Carlo transport code (Reference 4.23). It can be used in several transport Page 4.52 of 4.78

modes and can handle a wide range of particle energies. The capability to calculate k_{eff} eigenvalues for fissile systems is a standard feature of MCNP. The computer code that we use for criticality calculations for disposal will require benchmarking and/or validating the code.

A DOE SNF canister loaded with Al SNF will contain more fissile material than necessary to attain a critical mass in the incredible event that the fissile material selectively reconfigures into a spherical geometry. A complete criticality analysis of credible configurations of fissile material in the repository is a complex task. It requires consideration of all possible configurations for a given canister and a given waste package, but also, consideration must be given for possible configurations outside a waste package in the near-field and far-field environments as provided by other aspects of our performance assessment modeling effort. Each configuration that is shown to be possible from our performance assessment modeling effort should be evaluated for the possibility of achieving criticality.

The most likely place for achieving a critical configuration is within the DOE SNF canister itself. This is because: i) the geometry provides the lowest surface-to-volume ratio relative to the other possible configuration of fissile materials within the waste package; and ii) the full, initial inventory of fissile material is contained within the canister. The assemblies placed within a canister in the waste package are in a nearly optimal configuration for criticality (slightly under-moderated). Increasing the space between rods or plates, e.g., swelling of the assembly spacer grids or basket degradation that increases spacing, will increase the reactivity.

Outside the waste package, reliance must be placed on the performance assessment models to determine possible configurations. In a matrix flow system, the tendency would likely be towards dispersion of the radionuclides by diffusion and advection due to concentration gradients. However, if the groundwater flows through the fractures, then fissile species from several waste packages may be concentrated in the fractures, possibly creating a critical plane. It may also be postulated that fissile material will form a critical plane on the invert, within the emplacement drifts.

In the criticality analysis for direct/codisposal of aluminum-based DOE-SNF, one is concerned only with the possibility of achieving criticality internal to the disposal waste package. The possibility of achieving a criticality event external to the disposal waste package will be considered elsewhere. Limited work has been done concerning criticality in a waste package containing aluminum-base DOE-SNF. This work, described below, will provide a foundation upon which to build a model for generating a defensible approach to direct/codisposal of aluminum-based DOE-SNF.

4.5.2 HEU/LEU in Intact SNF Canister

It has been proposed that Al-SNF in a codisposal waste package with five canisters of HLW. The EBDRD contains the design criteria for engineered barrier segment design.

5

The EBDRD requirements 3.2.2.6 and 3.7.1.3.A both indicate that a WP criticality shall not be possible unless at least two unlikely, independent, and concurrent or sequential changes have occurred in the conditions essential to nuclear criticality safety. These requirements also indicate that the design must provide for criticality safety under normal and accident conditions, and that the calculated effective multiplication factor (k_{eff}) must be sufficiently below unity to show at least a five percent margin after allowance for the bias in the method in calculation. Assumption EBDRD 3.7.1.3.A of the CDA, which provides guidance for requirements listed in EBDRD that have unconfirmed or unqualified data with the requirement, clarifies that the above requirement is applicable to only the preclosure phase of the MGDS, in accordance with the current DOE position on postclosure criticality.

An evaluation was prepared to provide a preliminary assessment of the viability of disposing of the Al-SNF in accordance with the above design requirements. The disposal characteristics of the codisposal canister with regards to criticality safety, structural strength thermal limits, and effect on the waste package surface dose rates have been analyzed (Reference 4.21). Following is a summary of the criticality safety portion of this analysis.

Two Al-SNF fuel types were considered in the analysis. These two fuel types are the high-enrichment MIT reactor fuel and the medium-enrichment ORR reactor fuel. MIT and ORR fuel types were chosen to represent near-bounding conditions for the wide variations found in Al-based research reactor fuels. The MIT and ORR fuels have 93.5 wt $\% U^{235}$ and 20.56 wt $\% U^{235}$, respectively. Criticality calculations were performed for intact fuel contained within the codisposal canister for repository conditions. Also, sufficient criticality analyses were performed in order to establish the quantity of stainless steel/boron alloy needed to ensure subcriticality if the fuel degrades within an intact basket.

The MCNP4A computer code was used to calculate the nuclear reactivity of the codisposal container within a waste package. MCNP4A calculates the effective multiplication factor (k_{eff}) for a variety of geometric configurations with neutron cross sections for elements and isotopes described in ENDF-B/V.

The MIT fuel assemblies are constructed from 15 plates tilted at a sixty degree angle so that the resulting assembly has a rhomboidal cross section. The fuel plates consist of an aluminum cladding over an uranium/aluminum (U-Al_x) alloy. The maximum fuel mass for the MIT assembly is 514.25 grams of U^{235} . The aluminum present in the U-Al_x alloy is 30.5 wt %. The analysis considered the void volume that would be present if the U-Al_x alloy is distributed over the maximum dimensions. The void volume fraction in the fuel alloy was calculated to be 0.6353. For the criticality calculations, this void volume was assumed to contain water at different densities, up to unity. The result of increasing the density of water occupying the pore volumes is increased reactivity.

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The ORR fuel assemblies are constructed from 19 curved fuel plates which are held within two opposing aluminum comb plates. The fuel plates consist of an aluminum cladding over a U-Si-Al fuel material. The maximum fuel mass for the ORR assemblies 347 grams of U^{235} . The uranium present in the U-Si-Al alloy is 77.5 wt %. The void volume fraction in the fuel alloy was calculated to be 0.4064. For the criticality calculations, this void volume was assumed to contain water at different densities, up to unity. The result of increasing the density of water occupying the pore volumes is increased reactivity.

For the criticality analysis of the MIT and ORR fuel, the codisposal waste package is assumed to contain 16 MIT or 10 ORR DOE-SNF assemblies in the basket cross section, and assemblies are assumed to be stacked four high within each position in the fuel basket for a total of 64 MIT or 40 ORR assemblies. This assumption is consistent with the maximum number of assemblies of each type that can physically fit in the DOE-SNF canister. The MIT and ORR fuel is assumed fresh, and the waste package is assumed to be fully flooded with water for all criticality calculations. The fully flooded condition is the most reactive and is conservative. Boron neutron absorbers modeled in the criticality analysis are assumed to no more than 75% effective, and neutron absorbers were assumed to stay in the fuel/metal matrix when degradation occurs.

The analysis included both intact assemblies and assemblies at different stages of degradation. For the intact configurations, a fully flooded condition was analyzed for both MIT and ORR fuel in their respective baskets within the WP. For the configuration of assemblies degraded within the codisposal container, the potential progressive degradation of fuel was evaluated (MIT SNF only, to allow sizing of stainless steel/boron components). Optimum moderation was evaluated by varying the water content of the fuel alloy and the surrounding moderator volume for the degraded configurations. The progressive degradation of the fuel and codisposal basket was evaluated in stages as follows:

- 1. Homogenize fuel plates and inter-plate moderator volume
- 2. Homogenize entire assembly (fuel plates plus structural combs plus water)
- 3. Disperse homogenized material throughout basket free space

Both MIT fuel assemblies and ORR fuel assemblies were explicitly modeled in the criticality analysis, including the slightly different fuel alloy U^{235} content of the plates at either end of the nineteen plate array and the aluminum side plates of the ORR fuel assemblies. The fuel alloy and aluminum cladding were modeled as separate layers in close contact for each fuel type, and the actual design spacing of the fuel plates within the assembly was used.

The MIT SNF codisposal basket consists of a round disk with rhomboidal slots to accommodate the fuel assemblies. Each slot, which holds one, two, or four MIT SNF assemblies are lined on one side with a stainless steel/boron plate to neutronically isolate each row of fuel assemblies. Further, adjacent assemblies are separated by stainless steel/boron separator plates. The ORR SNF codisposal basket design consists of ten square tubes aligned so that straight structural load paths progress from one side of the basket to the other. Stainless steel/boron separator plates are used in both basket designs to isolate axial layers of assemblies. All stainless steel/boron separator plates used in the analyses are SS316B2A (0.6 wt % B). Considering the assumption of 75% neutron absorber effectiveness, this corresponds to using SS316B3A (0.87 wt % B).

The waste package is modeled with the codisposal canister in the center of the package with five HLW canister arrayed around the codisposal container. The codisposal canister was modeled with the minimum thickness which might be expected to allow the DOE-SNF fuel and HLW canisters to approach each other to the minimum possible separation, which yields a conservative calculation of k_{eff} . The codisposal container is sealed at the top and bottom ends, however, the steel thickness of these closures were modeled as a water reflector to add conservatism. Further, the steel wall of the HLW canisters was omitted to allow the plutonium-bearing glass to interact neutronically with the codisposal canister fuel to the maximum extent possible. The waste package structural wall was modeled in the radial direction, however, the ends of the waste package were modeled as a water reflectors to maximize the neutron return from these zones.

Results for the MIT and ORR fuels in the intact configuration with varying amounts of water moderator in the maximum potential void volume within the fuel alloy indicate that the maximum reactivity is reached when the void volume within the fuel alloy is filled with water (see Table 4.8). The reactivity maximum reactivity for the MIT and ORR fuels in the intact configuration are 0.90295 and 0.89724 (calculated k_{eff} plus two sigma plus 0.02 bias allowance), respectively. The intact configurations for both the MIT and ORR fuels therefore comply with EBDRD requirements 3.2.2.6 and 3.7.1.3.A.

Percent H ₂ O in	Estimated keff for	Estimated keff for
Fuel Matrix Voids	MIT fuel	ORR fuel
0	0.83413	0.86768
25	0.85541	0.87867
50	0.87191	0.88306
75	0.88881	0.89334
95	0.90159	0.89714
100	0.90295	0.89724

Table 4.8. Intact Codisposal Canister Criticality Calculations

For degraded state calculations, data for the MIT fuel indicate that the reactivity of the fuel is excessive if stainless steel alone is used to separate adjacent assemblies within a basket slot (see Table 4.9). Data for the ORR fuel indicate that the reactivity of the fuel is excessive if the four layers of assemblies are stacked within each basket tube directly on top of one another, without the axial stainless steel/boron separator plates (see Table

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4.10). Calculations for the MIT and ORR fuels, in degraded configurations, suggest that neutron-absorbing materials are necessary to preclude the possibility of a criticality event.

Divider Plates Between	Degraded Fuel Geometry	Estimated k _{eff}
Assemblies		
Stainless Steel	Plate Array with Comb Teeth in Assembly Envelope	0.94853
Stainless Steel	Plate Array Homogenized	0.98117
Stainless Steel	Entire Assembly (Including Side Plates)	0.98045
Stainless Steel	Entire Cell Homogenized	1.01618
Stainless Steel	High Boron in Divider Plates	0.97309
SS316B2A	Plate Array with Comb Teeth in Assembly Envelope	0.87667
SS316B2A	Plate Array Homogenized	0.91009
SS316B2A	Entire Assembly (Including Side Plates)	0.90323
SS316B2A	Entire Cell Homogenized	0.93855

 Table 4.9. Degraded MIT SNF Codisposal Canister Criticality Calculations

Table 4.10. Degraded OKK SIVE Coursposal Callister Criticality Calculation
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Model Description	Estimated keff
No Boron	
Homogenized Assembly	0.95185
Homogenized Water Gap	0.96700
Axial Boron Separator Plates	· · · · · · · · · · · · · · · · · · ·
Homogenized Assembly	0.88411
Homogenized Water Gap	0.91181

There is no mechanistic basis for the conservatism in the above approach to modeling degraded SNF. It is more likely that the assembly degradation would result in a volume reduction within the waste package as the assembly components lose integrity and allow the SNF to collapse. This volume reduction may decrease the reactivity of the system and should be considered. Further, although the borated stainless steel absorber material will likely outlive the aluminum-base SNF assemblies by a significant margin, the absorber material will eventually degrade. However, it is likely that some fraction of the boron within the stainless steel will be incorporated in the corrosion products of the stainless steel due to the very stable nature of borides of irons. Therefore, careful consideration must be given to the transport of fissile material out of the waste package, to the transport

of the boron, and to the chemical reactions that will occur as the absorber material degrades.

The steps necessary to develop a mechanistic model are to demonstrate subcriticality in a DOE-SNF codisposal canister are:

- Select a material from our list of candidate neutron absorbing materials.
- Identify degradation modes of and possible configurations for the degrading components of the SNF assemblies within the degrading codisposal canister.
- Identify the stable phases that will be generated as the materials degrade.
- Perform geochemical calculations to identify the reactions that will take place.

This will be an iterative process as the criticality analysis will provide required absorber material concentrations back to the geochemistry model for consideration. The completed process will indicate the quantity of absorber material required to preclude criticality in the codisposal canister. Further, consideration should be given to alternative loading strategies that will limit the initial mass loading of U^{235} within a single codisposal container or that will reduce the available space for moderator infiltration.

4.5.3 Material Reconfiguration Analysis

Materials reconfiguration analysis is being performed to support the criticality analysis of Al-SNF and the performance assessment of the proposed repository. This analysis focuses on the chemical compounds that the fissile species may assume during degradation of the waste package and internals, solubilities of these compounds in groundwater, and the final chemical and physical state of the fissile species.

The proposed WP for codisposal of Al-SNF would contain one canister of Type 316L stainless steel containing intact Al-SNF fuel assemblies surrounded by five canisters that contain HLW incorporated into borosilicate glass. Although the initial configuration of materials in this codisposal WP will meet repository criticality requirements, initial calculations for a degraded state of a single Al-SNF canister, where the contents of the canister were homogenized with water that occupied the free space in the canister, indicate that reactivity would be excessive unless neutron absorber materials were included in the canister (3.5.2). Degraded states for the fissile material based on thermochemical and kinetic analysis and degradation sequences that include the HLW canisters, structural, and filler materials within the WP have not been evaluated.

Modeling of the degradation of the WP and its contents is based on thermochemical and kinetic analyses that simultaneously considers all possible soluble species, chemical reactions among these species, formation of complexes, precipitation of amorphous, colloidal, or crystalline substances, changes in the water composition from contact with the WP and its contents, the influence of the radiation field, and temperature changes in the water as it moves from the repository into the WP (Reference 4.24). Processes can occur which could lead to a transitory or final state that compromises criticality:

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separation of the fissile elements from any neutron absorbers placed in the canisters; entrainment of water or other means of neutron moderation with the fissile material.

The naturally-occurring uranium bearing minerals within ore deposits in the Western United States and the products formed during laboratory corrosion experiments provide guidance as to which chemical compounds might form from reaction between ground water, Al-SNF, and other materials present within the WP. Published thermochemical data allow estimation of the relative stability and solubility for many uranium and aluminum compounds that are of interest. Unfortunately, reliable chemical thermodynamic data do not exist for all of the uranium compounds that are possible degradation products. The physical form to be expected may be judged from mineralogical information and corrosion experiments.

The most-likely products from degradation of Al-SNF would be the hydrated oxides and silicates of uranium and hydrated aluminum oxides or alumino-silicates. Amorphous, microcrystalline, and colloidal forms of these compounds are possible. These compounds would be modified by subsequent chemical reaction with fission products, HLW, borosilicate glass, the carbon and stainless steel canisters, and other barrier, support or poison materials included as part of the WP. The presence of borosilicate glass and aluminum fuel assemblies within the WP suggests that clay could form. Clay retains water and could affect criticality. The final chemical form of the degradation products would be independent of whether the WP contained intact Al-SNF assemblies or the product of a dilution process as the waste form would consist of uranium-aluminides and aluminum alloys in both cases.

The degradation products from intact fuel assemblies and from the melt-dilute process are expected to be the same, as the alloy phases are closely similar: an alloy of 1100, 5052, and 6061 aluminum; uranium aluminides - UAl₂, UAl₃, and UAl₄; canister materials - Type 304L and Type 316L stainless steels, carbon steel, and Alloy 625; and borosilicate glass containing HLW. Also, minor quantities of the uranium silicides - U₃Si₂, USi₃, and UO₂ would be present.

4.5.3.1 Potential Alteration Phases of Fuels in Repository Disposal Systems

Uranium-bearing ore bodies in the Colorado Plateau, the Wyoming basin, the Basin and Range Province, and the Texas Coastal Plain occur primarily within sandstone and were formed by weathering of granites, volcanized sediments, or arkoses (a sandstone consisting of quartz and feldspar) (References 4.25-4.28). These ores are referred to as "unoxidized" as a large fraction of the uranium is in the +4 valence state (U(IV)-uranous) rather than the +6 valence state (U(VI)-uranyl).

The most common mineral is uraninite, UO_2 (ideal formula), which has a calcium fluorite crystal structure. Uraninite occurs as crystals of various size or as aggregates of small crystals. Uraninite oxidizes readily forming mixed valence oxides such as U_3O_8 which are thermodynamically more stable than UO_2 provided that the oxygen potential is high

enough (Reference 4.26). All naturally occurring uraninite contains some U(VI), but the predominance of U(IV) indicates that the uraninite deposits formed under conditions of low oxygen potential and that subsequent weathering by oxidizing ground water led to formation of minerals where U(VI) is dominant. In uraninite, charge neutrality is maintained by interstitial oxygen O or OH which compensate for the presence of U(VI). At high oxygen potentials, all U(IV) is converted to U(VI) and the uraninite reconstitutes to form the hydrated oxide schoepite, $UO_3 \cdot 2H_2O$, which occurs in microcrystalline or tabular form.

Coffinite, a hydrated silicate of U(IV) with formula $U(SiO_4)_{1-x}(OH)_{4x}$, is the other dominant uranium bearing mineral in United States ore deposits. Coffinite occurs as small crystals (less than 5µm) in association with amorphous coffinite and uraninite. The hydroxyl group substitutes for the silicate where x~0.5. An anhydrous form of the mineral is not known (Reference 4.27).

Minerals that contain hexavalent uranium occur in association with uraninite and coffinite in US ore deposits and are often referred to as alteration products as they are believed to arise from weathering of the primary minerals. The more common minerals are:

schoepite	UO ₃ ·2H ₂ O (ideal formula);
carnotite	$K_2(UO_2)_2(VO_4) \cdot nH_2O;$
uranophane	$Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O;$
autunite	$Ca(UO_2)_2(PO_4)_2 \cdot nH_2O;$
sabugalite	HAI(UO ₂) ₄ (PO ₄) ₄ ·16H ₂ O;
vanuralite	$Al(UO_2)_2(VO_4)_2OH \cdot 11H_2O.$

Phosphates and vanadates of uranium appear to be the only naturally occurring uranium compounds that also contain aluminum which have been observed in mineral deposits (Reference 4.27). Both carnotite and uranophane are commonly found in small concentrations in ore deposits worldwide, whereas only minor amounts of schoepite, sabugalite, and autunite have been found in the sandstone deposits of the western United States. Minor concentrations of a copper variant on autunite have been found among ore deposits in the Basin and Range region (Reference 4.28). Usually all of these minerals have oxides of the alkali or alkaline earth metals, iron oxide, lead and other radioactive decay products associated with them. Mixed oxides of uranium with iron, chromium, nickel, or manganese are also known and could form following corrosion of the stainless steel canisters and their contents (Reference 4.27). Uranium also forms complexes with the inorganic ligands present in the ground water, such as fluoride, nitrate, carbonate, and sulfate. The final chemical form taken by uranium will depend on competition among all of these chemical species, the pH, the oxidizing potential of the water, temperature, and kinetic factors.

The stability of the uranium minerals offers further information relevant to possible degradation products of aluminum based fuel elements. Natural uraninite recrystallizes when heated in air changing to UO_2 , U_3O_8 , U_4O_9 or to a mixture of these oxides

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(Reference 4.27). The final product depends upon the temperature, atmosphere, and duration of heating. Given sufficient time at temperature uraninite converts to U_3O_8 when heated in oxygen at temperatures up to 185 °C. Colloidal formations of UO_2 change to U_3O_8 at room temperature when exposed to air. In the case of schoepite, water loss begins when the mineral is heated above 60 °C leading finally to anhydrous UO_3 when heated to about 300 °C (Reference 4.27).

Commercial grade aluminum ores consist of hydrated oxides mixed with iron oxides, silica, water, and occasionally clay or titania (Reference 4.29). The most common aluminum-bearing minerals in the ore bodies are:

-	$\alpha - Al_2O_3 \cdot H_2O$
-	$\beta - Al_2O_3 \cdot 3H_2O$
-	$\alpha - Al_2O_3 \cdot 3H_2O$
-	Al ₂ Si ₂ O ₅ (OH) ₄
-	Al ₂ Si ₂ O ₅
-	Al ₂ Si ₂ O ₅
-	Al ₂ Si2O ₅
	- - - -

Kaolinite and the three forms of $Al_2Si_2O_5$ are clay forming minerals. The trimorphous forms of $Al_2Si_2O_5$ are distinguished by differing crystal structures (Reference 4.30). The presence of borosilicate glass and aluminum fuel assemblies within the WP provides the necessary ingredients for clay formation during degradation of the WP.

4.5.3.2 Corrosion and Oxidation Products of Uranium-Aluminides

 U_3O_8 was the only oxide identified following oxidation of aluminum-uranium compounds in an atmosphere of purified oxygen over the temperature range 350 - 600 °C (Reference 4.31). Phases studied were UAl₂, UAl₃, specimens of the UAl₄-Al eutectic, and mixtures of 30, 65, and 90% primary UAl₄ with balance eutectic. Exposure times were short, from several minutes to 200 hours. Oxidation rate laws and activation energies are given in Table 4.11. The activation energy for UAl₄ was obtained by extrapolating activation energies for eutectic - UAl₄ mixtures containing 30, 65, and 90 % UAl₄ to pure UAl₄.

Oxidation of the UAl₄-Al eutectic followed a logarithmic rate law, but the data were too erratic to allow calculation of an activation energy. Weight gains for the specimens that contained varying amounts of massive UAl₄ (30, 65, and 90%) were measured at 500 °C. After 100 hours exposure, the weight gains were a factor of ten to one hundred greater than for a sample that was entirely eutectic, indicating a more rapid oxidation of UAl₄ than of aluminum (Reference 4.31).

Compound	Activation Energy (cal/mol)	Temperature Range (°C)
UAl ₂	22,100	250 - 350
UAl ₃	23,600	350 - 600
UAl₄	36,500	400 - 550

Table 4.11. Oxidation of Uranium - Aluminides

X-ray diffraction examination of the surfaces of oxidized compounds of UAl_2 , UAl_3 , and 90% UAl_4 indicated the presence of U_3O_8 only; however, a very thin layer of aluminum oxide at the metal-oxide interface would not have been detected. Oxidation products on the Al / UAl_4 eutectic were not determined (Reference 4.31).

UO₂ was the only identifiable reaction product from oxidation of USi₃ and U₃Si₂ (Reference 4.32). In an earlier study of the reactions of U₃Si₂, USi₃, and UAl₂ with oxygen, weight gain was measured continuously on a microbalance at temperatures of 200 to 500 °C for times up to about 2 hours. Weight gain followed the general relation, w = ktⁿ, where w is the weight gain in $\mu g/cm^2$, t is the time in seconds, and k is the rate constant. The value of n varied: n = 1 for a linear rate law, 0.5 for a parabolic rate law; and 0.33 for a cubic rate law. Specimens were made by powder metallurgy techniques. Reaction rates followed parabolic rate laws for USi₃ and U₃Si₂, whereas the rate law for the UAl₂ was cubic. Constants for the Arrhenius equations (k = s·exp(-E/RT)) for oxidation of the three compounds are given in Table 4.12. The reaction product on the UAl₂ was not identified (Reference 4.32).

		Activation Energy, E	Temperature Range
Compound	Frequency Factor, A	(cal/mol)	(°C)
USi ₃	3.00 x 10 ⁹	23,600	300 - 400
U ₃ Si ₂	3.20 x 10 ⁵	10,600	300 - 500
UAl ₂	2.70 x 10 ¹⁵	26,000	200 - 300

 Table 4.12. Reaction of Uranium Compounds with Oxygen

4.5.3.3 Evaluation of Corrosion Product Results from SRS Corrosion Studies

Boehmite, α - Al₂O₃·H₂O, and possibly U₃O₈ were detected by X-ray diffraction on specimens of Al-10%U exposed in an autoclave at 200 °C for times up to 60 days in air that was saturated with water vapor (Reference 4.4). Specimens had been cut from extruded rod or from strip that had been repeatedly heated to 500 °C and rolled. In both

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cases, the original microstructure consisted of primary aluminum and eutectic. The extruded alloy generally retained this microstructure, but the rolled strip had recrystallized to a microstructure with no evidence of primary aluminum and somewhat larger UAl₄ particles. After ten days exposure, boehmite, $\alpha - Al_2O_3 \cdot H_2O$, and possibly some U₃O₈ were detected by x-ray diffraction on specimens of rolled strip. Although boehmite was detected after 1250 hours exposure of the extruded alloy, no uranium oxides were detected even after 1500 hours exposure. Microscopic examination of the specimens indicated little if any corrosion of the UAl₄ particles, confirming the x-ray diffraction data. This behavior is in direct contrast to the elevated temperature oxidation studies of uranium-aluminum alloys where uranium oxide formed, but no aluminum oxide was detected (Reference 4.31).

Corundum, boehmite, U_8O_{19} , and U_3O_7 were the compounds formed during corrosion of UAL_x in synthetic ground water at 100 °C or water vapor at 200 °C. Specimens of an alloy of 67 wt % uranium in aluminum, consisting of particles of UAl₃ and UAl₄, were exposed to a solution with the nominal composition of J-13 ground water at 100 °C or to saturated water vapor from the same solution at 200 °C. The high temperature tests were in sealed stainless steel capsules. Corundum, the anhydrous form of Al₂O₃ was the only oxide detected after the 100 °C corrosion test. Corrosion in water vapor yielded both corundum and boehmite after one week exposure, but only boehmite after two weeks exposure. Two mixed valence uranium oxides were identified from the water vapor corrosion tests, U₈O₁₉ after one week and U₃O₇ after two weeks.

Corrosion products obtained from Mark 31A slugs that were stored in L-reactor basin have been identified as bequerelite, CaU_6O_{19} ·11H₂O, and compreigmacite, $K_2U_6O_{19}$ ·11H₂O, which is the potassium form of the bequerelite (Reference 4.33). Uranium is in the +6 valence state in these compounds indicating strong oxidizing conditions in the L-reactor basin.

Aluminum alloys corrode in ground water forming bayerite at temperatures below 80 °C or boehmite at temperatures above 80 °C (Reference 4.34). There is evidence that oxidation proceeds by formation of an amorphous hydroxide followed by its conversion to one of the oxides mentioned above. Boehmite was formed during corrosion of the aluminum cladding alloys, 1100, 5052, and 6061, in water vapor at temperatures of 80 to 200 °C (Reference 4.4). These results are applicable to the pH range of 6 to 9 that is expected during storage of a WP in a geologic repository.

Aluminum corrodes more rapidly in the presence of a radiation field than without radiation. Specimens of aluminum exposed to moist air at room temperature for 30 days corroded more rapidly when in the presence of alpha radiation from a polonium source (Reference 4.35). Corrosion rates increased both with increased relative humidity from 44 to 100% and with intensity of the alpha radiation from 0.15 to 1.5 curies. There was essentially no corrosion at zero or 9% relative humidity. The corrosion product consisted of boehmite and $Al(NO_3)_3$ ·9H₂O. Corrosion of the cladding alloys in a gamma radiation

field of 1.81×10^6 Rad/hr at 78 °C and 200 °C was more rapid than without radiation (Reference 4.4). The corrosion product was boehmite.

4.5.3.4 Chemical Thermodynamics - Uranium and Aluminum Compounds

Thermodynamic data for selected compounds are presented in Table 4.13. These data have been obtained from the *Chemical Thermodynamics of Uranium* published in 1992 (Reference 4.36), the *Handbook of Thermochemical Data for Compounds and Aqueous Species* (Reference 4.37), the IAEA publications on *The Chemical Thermodynamics of Actinide Elements and Compounds, Part 3 and Part 5* (References 4.38-4.39), and *Thermochemical Data for Reactor Materials and Fission Products* (Reference 4.40). The first publication is an exhaustive review and critical assessment of published data on uranium from the early 19th century through 1991, and the authors report experimental data that are not included in the tabulations because of uncertainties with identification of either the initial reactants or the reaction products.

The temperature dependencies of the free energy of formation of the uranium aluminides from α -uranium and solid aluminum over the temperature range 298 - 933 K are given by (Reference 4.39):

 $\begin{array}{lll} \Delta_{f}G^{\circ} (UAl_{4}) &= -133,972 - 21.42T^{*}ln(T) + 178.57T \ , \ kJ/mol \ U \\ \Delta_{f}G^{\circ} (UAl_{3}) &= -103,930 + 9.96T^{*}ln(T) - 67.11T \ , \ kJ/mol \ U \\ \Delta_{f}G^{\circ} (UAl_{2}) &= -92,174 + 6.53T \ , \ kJ/mol \ U. \end{array}$

The free energy of formation of U_3Si_2 , for temperatures between 1675 and 1840 K was derived from vapor pressure measurements (Reference 4.39).

 $\Delta_{f}G^{\circ}(U_{3}Si_{2}) = -180,121 + 4.39T$, kJ/mol U.

Reliable data for the free energy of formation of U_3Si are not available, but the enthalpy of formation has been reported as -104.2 kJ/mol U (T = 298 K). The enthalpy of formation of U_3Si_2 is reported as -169.45 kJ/mol U (T = 298 K).

Aluminum and uranium-aluminides have a natural tendency to react with water or oxygen to form the more stable oxides as shown by the negative standard free energy changes for representative reactions between aluminum or uranium-aluminide (UAl₄ (s)) and water or oxygen. The reaction products at temperatures of 75 °C and 200 °C are assumed to be $\alpha - Al_2O_3 \cdot H_2O$ (s) and U_3O_8 (s) which are the oxides observed in corrosion experiments. The standard free energy changes are based on one mole of Al or one mole of UAl₄ and assume that the reactants and products are in their standard states at unit activity. For a gas, the standard state is the pure gas at a pressure of 0.1 MPa (one atmosphere) in a state that exhibits ideal behavior and for a solid, the pure solid at one atmosphere pressure. For intermetallic compounds, such as the uranium-aluminides, the activity of the uranium or aluminum is equal to its atom fraction for ideal behavior; however, behavior is seldom Page 4.64 of 4.78

ideal and activity coefficients as small as 0.01 have been measured (Reference 4.41). Whether a reaction would take place under conditions encountered in a repository may be controlled, however, by kinetic factors or surface conditions which are not considered here.

The reaction of UAl₄ with water assumes that the product is U_3O_8 and does not consider the possible formation of intermediate species such as hydroxides, hydrated oxides of uranium, or compounds of single +4 or +6 valence state all of which are possible depending on the pH and oxidizing potential of the water. Corrosion of aluminum is assumed to produce boehmite, $\alpha - Al_2O_3 \cdot H_2O$ (s), at 75 °C.

Al (s) + $2H_2O(l) = 0.5Al_2O_3 \cdot H_2O(s) + 1.5H_2(g)$ $\Delta G^{\circ}(348 \text{ K}) = -108,100 \text{ cal/mol Al}$ UAl₄ (s) + 10.66H₂O(l) = 0.33U₃O₈ (s) + $2Al_2O_3 \cdot H_2O(s) + 8.66H_2(g)$ $\Delta G^{\circ}(348 \text{ K}) = -555,800 \text{ cal/mol UAl}_4$

 U_3O_8 (s) and corundum, Al_2O_3 (cr) are the oxidation products of uranium and aluminum at 200 °C.

Al (s) + 1.5 O_2 (g) = 0.5Al₂O₃ (s) $\Delta G^{\circ}(473 \text{ K}) = -182,500 \text{ cal/mol Al}$ UAl₄ (s) + 8.66 O_2 (g) = 0.33U₃O₈ (s) + 2Al₂O₃ (s) $\Delta G^{\circ}(473 \text{ K}) = -962,500 \text{ cal/mol UAl}_4$

Reaction of aluminum or aluminum-uranium compounds with water vapor at 200 °C is assumed to yield U_3O_8 and boehmite, $Al_2O_3 \cdot H_2O$ (s), the corrosion product that has been observed in vapor corrosion experiments at SRTC. Hydrogen is assumed to form a gas and neither diffuse into the aluminum nor form uranium hydride.

 $\begin{array}{ll} Al(s) + 2H_2O(g) &= 0.5Al_2O_3 \cdot H_2O(s) + 1.5H_2(g)\\ \Delta G^{\circ}(473 \ K) &= -102,154 \ cal \ / \ mol \ Al\\ \\ UAl_4(s) + 10.66H_2O(g) &= 0.33U_3O_8(s) + 2Al_2O_3 \cdot H_2O(s) + 8.66H_2(g)\\ \Delta G^{\circ}(473 \ K) &= -505,800 \ cal \ / \ mol \ UAl_4 \end{array}$

4.5.3.5 Solubility of Compounds

Aluminum, uranium-aluminides, uranium-silicides and the oxides of aluminum and uranium are sparingly soluble in water. The extent of solubility is controlled by temperature, pH of the water, oxidizing potential, and the chemical composition of the water. For the case of ground water in a geologic repository, the expected range of pH is between 6 and 9 without considering pH changes associated with reaction between the water and the contents of the WP (Reference 4.4). Water temperatures could reach the boiling point and canister temperatures as high as 260 °C have been calculated for some WP configurations (Figure 4.20).

Equilibrium constants for the solubilities aluminum, uranium, and their respective oxides in pure water at 25 °C in the pH range 6 to 9 may be evaluated by considering suitable reactions in conjunction with data from Tables 4.13 and 4.14. The species of interest for U(VI) are $UO_2(OH)_2$ (aq), and $UO_3 \cdot 2H_2O$ (cr) (Reference 4.36).

$$\begin{split} UO_{3} \cdot 2H_{2}O(cr) &= UO_{2}(OH)_{2} (aq) + H_{2}O(l) .\\ log_{10}K^{\circ} &= -5.52 \qquad \Delta_{r}G^{\circ} &= 31.40 \text{ kJ} \cdot \text{mol}^{-1} (298.15 \text{ K})\\ [UO_{2}(OH)_{2} (aq)] &= 10^{-5.52} \text{ M} \end{split}$$

Table 4.13. Thermochemical Parameters of Selected Aluminum and UraniumCompounds - 298.15 K

		−∆ _f G°	-∆ _f H°	S°	
Compound	Formula	(kJ/mol)	(kJ/mol)	(J/K·mol)	Ref
uraninite	UO ₂	1031.8	1085	77.03	4.36
	$U_4O_9(U_{2.25})$	1069.1	1128.0	83.53	4.36
	$\beta - U_3O_7(U_{2.33})$	1080.6	1142.0	83.51	4.36
	$U_{3}O_{8}(U_{2.66})$	1123.2	1191.6	94.18	4.36
	UO ₃	1145.7	1223.8	96.11	4.36
schoepite	UO ₃ ·2H ₂ O	1636.5	1826.1	188.54	4.36
coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$	1883.6	1991.3	118	4.36
carnotite	$K_2(UO_2)_2(VO_4) \cdot nH_2O$	*			4.36
uranophane	$Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$	*			4.36
autunite	$Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$	*			4.36
sabugalite	HAl(UO ₂) ₄ (PO ₄) ₄ ·16H ₂ O	. •			4.36
boehmite	$\alpha - Al_2O_3 \cdot H_2O$	1825.5	1974.9	97.1	4.37
bayerite	$\beta - Al_2O_3 \cdot 3H_2O$	2292.4	2567.7	140.2	4.44
gibbsite	$\alpha - Al_2O_3 \cdot 3H_2O$	2287.4	2562.7	140.2	4.37
kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	3778.2	4098.6	202.9	4.37
kyanite	Al ₂ Si ₂ O ₅	2596.2	2746.4	83.7	4.37
andalusite	Al ₂ Si ₂ O ₅	2596.6	2744.3	93.3	4.37
sillimanite	$Al_2Si_2O_5$	2625.9	2772.3	96.2	4.37
aluminide	UAl ₂	90.2	92.5		4.39
aluminide	UAl ₃	107.0	108.4	•	4.39
aluminide	UAL4	117.1	124.7		4.39
silicide	U ₃ Si ₂	178.8**	169.45		4.39
silicide	U ₃ Si	*	104.2		4.39

• •

* Reliable data are not available

** Extrapolation from data at 1675 - 1849 K

	$-\Delta_{\rm f} {\rm G}^{\circ}$	-Δ _f H°	S		
Compound	(kJ/mol)	(kJ/mol)	(J/K-mol)	Ref	
U(OH)4 (aq)	1452.5	1655.8	40.0	4.36	-
$UO_2(OH)_2$ (aq)	1368.0			4.36	
UO ₂ ⁺⁺	952.5	1019.0	-98.2	4.36	
UO_2^+	961.0	1025.1	-25	4.36	
U ⁺⁴	529.9	591.2	-416.9	4.36	
U ⁺³	476.5	489.1	-188.2	4.36	
AlO ₂ .	823.4	918.8		4.37	
Si(OH)4 (aq)	1307.7	1456.9	189.9	4.36	

The free energy change with reactants in their standard states yields an equilibrium solubility where M is molarity, mol·dm⁻³. Although experimental verification of the existence of $UO_2(OH)_2$ (aq) is lacking, thermochemical functions have been estimated based on compatibility with solubility data for $UO_3 \cdot 2H_2O$ (cr) at 25 °C (pH 6.2 - 8.2) (Reference 4.36). A measured value of $log_{10}(K) = -5.96$ was determined for schoepite, $UO_3 \cdot 2H_2O$ (cr), which yields a somewhat lower solubility than the calculated value of -5.52 (Reference 4.36). For pH values below 5.2 or above 9, additional aqueous species appear.

For U(IV), solubilities of uranium and uranium oxide may be estimated from reactions that involve the aqueous species U(OH)₄ (aq) and U⁺⁴ or UO₂ (cr) (Reference 4.36).

 $U^{+4} + 4H_2O(l) = U(OH)_4 (aq) + 4H^+$ $log_{10}K^\circ = -4.45 \qquad \Delta_r G^\circ = 25.40 \text{ kJ} \cdot \text{mol}^{-1} (298.15 \text{ K})$ $[U(OH)_4 (aq)] / [U^{+4}] = 0.145 - 4pH$ $UO_2 (cr) + 2H_2O(l) = U(OH)_4 (aq).$ $log_{10}K^\circ = -9.55 \qquad \Delta_r G^\circ = 54.50 \text{ kJ} \cdot \text{mol}^{-1} (298.15 \text{ K})$ $[U(OH)_4 (aq)] = 10^{-9.55} \text{ M}$

The solubility of UO₂ (cr) has been measured and found to be essentially independent of temperature in the range 100 to 300 °C for a pH above 4 (Reference 4.36). Both hydrous and amorphous forms of UO₂ are known. However, the degree of crystallinity, crystal size, extent of surface oxidation, and extent of hydration are not constant or not known, so that thermochemical properties and equilibrium constants can not be determined unequivocally, but must be measured for the material at hand.
The solubilities of aluminum and boehmite as treated by Pourbaix (Reference 4.43) for the pH range of 6 to 9 yield the following:

Al (s) + $2H_2O(l) = AlO_2^{-}(aq) + 4H^{+} + 3e^{-}$ log₁₀(K) = 64.01 $\Delta_r G^\circ = -87.33 \text{ kJ} \cdot \text{mol}^{-1}$ (298.15 K)

and solubility is related to the reduction potential, Eo, and pH by

$$E_0 = -1.262 - 0.0788 pH + 0.0197 \log (AlO_2)$$
.

For boehmite, the relations are:

$$Al_2O_3 + H_2O = 2AlO_2^{-1}(aq) + 2H^{+}$$

$$log_{10}K^{\circ} = 12.3 \qquad \Delta_rG^{\circ} = -33.58 \text{ kJ} \cdot \text{mol}^{-1} (298.15 \text{ K})$$

$$log (AlO_2^{-1}) = -12.32 + \text{pH}.$$

Summary

All metallic phases present in the Al SNF forms are thermochemically unstable in water. The focus of the present work has been to assess the speciation of uranium in aqueous systems. The speciation is a function of pH, oxidizing potential, and anion/cation species. Speciation is also dependent on relative rates of competing reactions.

Speciation can not be predicted unequivocally in complex systems since i) the knowledge of conditions is always incomplete; and ii) reliable thermochemical data is lacking for some compounds. The most likely compounds of uranium would be oxides or silicides if silicon from the waste glass in the co-disposal package enters the water. Carbonates, sulphates, and chlorides are also possible compounds.

All possible uranium compounds are sparingly soluble in water. Oxide solubility is highly valence dependent with valence dependent on pH and oxidizing potential of the water. Continued solution of a compound is possible if fresh water is supplied.

4.5.4 Assessment of Neutron Poisons

An assessment of neutron poison materials is being performed to support the criticality analysis and the performance assessment of the potential repository. Results of the criticality analysis described in Section 4.5.2 indicate a need for additional criticality control within the codisposal canister to preclude the possibility of achieving criticality. The addition of neutron absorbing materials in the codisposal canister is one method of criticality control. Therefore, the assessment of neutron poison material efficacy focuses on those characteristics that will impact the selection of a neutron poison.

One aspect of SNF disposal is the potential for achieving a criticality event. Many of the DOE SNF assemblies are composed of HEU, that have the greatest likelihood of achieving a critical configuration. Among the possible methods available to avoid

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criticality are the consideration of alternate loading patterns (to limit the amount of fissile material disposed of in a single waste package) and the consideration of loading neutron absorbing materials, poisons, with the HEU SNF. The following is a brief summary of the current understanding of potential poison materials as described by Anderson and Theilacker (Reference 4.45) and by McDonell and Parks (Reference 4.46). Table 4.15 lists the properties of possible poison materials, and Table 4.16 reports more detailed data on specific absorber elements and nuclides.

The most predominantly utilized poison materials are boron and borated metals. This is primarily due to the availability and excellent nuclear characteristics associated with boron. A boron-stainless steel alloy has been used for discreet burnable poison and control rod applications. A compound of boron-boron carbide (B_4C) in the bulk ceramic form has been used in control applications and as small particles in distributed burnable poison applications.

An advantage of boron as a neutron absorber is the experience gained through the use of boron in control rod and burnable poison applications. Another advantage of boron is that its reaction products, helium and lithium 7, do not become significantly radioactive. Further, the cross section of the neutron absorbing isotope of boron, ¹⁰B, is inversely proportional to the velocity of the incident radiation, which simplifies boron burnable poison physics calculations when compared with those for silver, hafnium, europium, or indium which have relatively complicated resonance absorption cross sections.

While the reaction products of boron are not radioactive, the production of helium and lithium 7 can cause metallurgical problems in a metal matrix. Boron has an atom size such that it has neither appreciable interstitial nor substitutional solid solubility in structural materials such as stainless steel or aluminum. The result of irradiation of metal-boron alloys is accelerated embrittlement of the alloys. The helium gas generated when ¹⁰B captures a neutron is extremely mobile and tends to accumulate at points of stress concentration. The lithium generated by neutron capture in ¹⁰B puts additional stress on the metal matrix.

The incorporation of up to about three or four percent boron in stainless steel by powder metallurgical processes results in a material with good mechanical and good corrosion resistance in oxidizing and saturated environments. However, sites for crack initiation result from the coarse boride particles produced by conventional methods of ingot metallurgy, when boron content is increase above about one percent boron. The addition of boron to stainless steel increases the alloy's yield stress and tensile strength, while decreasing ductility, workability, and impact strength due to the limited solubility of boron in the stainless steel that results in boron combination with iron and chromium to form a brittle, dispersed boride phase in the austenitic matrix. Increasing the boron content above three to four percent results in the rapid degradation of mechanical properties and corrosion resistance. Embrittlement has been found to occur in borated stainless steel alloys is known to cause pitting in regions adjacent to boride precipitates; as pits grow, they tend

Material	Atomic number	Atomic weight	Melting point (°C)	Density (g/cc)	Atoms per cubic centimeter (×10 ⁻²⁴)	Microscopic thermal neutron- absorption cross section (barns)	Macroscopic thermal neutron- absorption cross section (cm ⁻¹)	Approximate resonance integral	Decay half life	Approximate cost of raw material (\$/Ib)	Abundance in earth's crust (ppm)
Boron 10	5	10	2,300	2.45	0.148	3,840	568			1,500	2.8
Boron	5	10.82	2,300	2.45	0.136	755	104	280		410	14
Cadmium	48	112.41	321	8.65	0.046	2,450	118	••	43 days	1.4	0.15
Cobalt	27	58.94	1,495	8.71	0.089	37	. 3.4	48	5.3 yr	2.5	0.23
Dyprosium	66	162.51	1,400	8.56	0.032	950	35	1,000	2.3 hr	260	4.5
Erbium	68	167.27	1,550	9.10	0.033	173	5.7		7.5 hr	260	2.5
Europium	63	153.0	900	5.22	0.021	4,300	92.5	1,000	16 yr	590	1.1
Gadolinium	64	157.26	1,350	7.95	0.030	46,000	1,390	67	18 hr	75	6.4
Gold	79	197.00	1,063	19.3	0.059	99	5.8	1,530	2.7 days	420	0.005
Hafnium	72	178.50	2,222	13.1	0.044	105	4.8	1,800	46 days	65	20
Holmium	67	164.94	1,500	8.76	0.032	65	2.1		_27 hr	260	1.2
Indium	49	114.82	156	7.3	0.038	196	7.3	2,700	54 min	23	0.1
Iridium	77	192.20	2,442	22.4	0.071	440	31	2,000	19 hr	2,500	0.001
Lithium	3	6.94	186	0.53	0.046	71	3.3	28	0.8 sec	10	65
Lutetium	71	174.99	1,750	9.74	0.033	112	3.8	720	3.7 hr	2,600	0.8
Manganese	25	54.94	1,245	7.42	0.081	13	1.08	11	2.6 hr	0.3	1,000
Mercury	80	200.61	39	13.6	0.040	380	15.1	70	47 days	2.5	0.5
Osmium	76	190.2	3,000	22.5	0.071	15.3	1.1	180	32 hr	2,000	0.001
Rhenium	75	186.22	3,180	21.0	0.068	86	5.85	650	90 hr	910	0.001
Rhodium	45	102.91	1,960	12.4	0.073	156	10.8	575	44 sec	1,800	0.001
Samarium	62	150.35	1,052	7.75	0.031	5,600	166	1,800	47 hr	180	0.5
Silver	47	107.88	961	10.5	0.059	63	3.7	700	253 days	12	0.04
Tantalum	73	180.95	2,996	16.6	0.055	21	1.2	500	117 days	41	2.1
Thulium	69	168.94	1,650	9.35	0.033	127	4.2	••	129 days	2,600	0.2
Tungsten	74	183.86	3,410	19.3	0.062	19	1.2	170	24 hr	15	69
Zirconiumt	40	91.22	1,852	6.57	0.043	0.180	0.008	3.5	65 days	\$11	220
Iront	26	55.85	1,535	7.86	0.085	2.53	0.222	2.3	45 days	"0.5	50,000

 Table 4.15. Properties of Possible Poison Materials (Reference 4.45)

Raw material in the form of oxide. *

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Added for comparison with poison materials. The alloy Zircaloy-2 contains about 98% zirconium, 1.5% tin, 0.15% iron, 0.10% chromium, and 0.05% nickel. +

Price of Zircaloy-2 strip.
** Price of austenitic stainless steel strip.

[Melting	(
Element or	Abundance %	Density	Point	.	Σ
Isotope	or (half-life)	(g/cc)	(°C)	(barns/atom)	(cm^{-1})
Cadmium		8 64	321	2450	113.56
¹¹³ Cd	12.3	0.01	521	25.000	115.50
Boron	12.3	2.54	2030	755	97.23
	19.8		2050	3800	526.41
	80.2			05	520.41
Zirconium(pure)		65	1845	0.18	0.0079
(3% hafnium)	_	0.5	1045	3 32	0.15
Hafnium		13.1	2222	105	4 598
¹⁷⁴ Hf	0.18	15.1		1500	1.550
177Hf	18 38			380	
¹⁷⁸ Hf	27.08			75	
¹⁷⁹ Hf	13.77			65	
Europium		5.22	826	4600	95.17
¹⁵¹ Eu	47.8			9000	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
¹⁵² Eu	(13v)			5500	
¹⁵³ Eu	52.3			420	
¹⁵⁴ Eu	(16v)			1500	
¹⁵⁵ Eu	(1.7y)			14.000	
Gadolinium		7.94	1312	46.000	1492.0
¹⁵⁵ Gd	14.73			61.000	
¹⁵⁷ Gd	15.68			240.000	
Samarium		6.93	1072	5600	161
¹⁴⁹ Sm	13.84			41,000	
¹⁵¹ Sm	(T _{1/2} =73 yr)			10,000	

Table 4.16. Properties of Significant Absorber Elements and Nuclides (Reference 4.46)

to act as crack initiation sites and increase the alloys susceptibility to stress corrosion cracking and embrittlement. Weight gain of borated stainless steel in high temperature water is four to seven times higher than that of 304 stainless steel. General corrosion resistance of 304 stainless steel - 1.75 percent boron alloy is inferior to stainless steel in salt spray and pitting tests. A further effect of boron in stainless steel is a volume change of the material as boron is depleted. Measurement of the volume change indicates that borated stainless steel changes in volume about ten percent per depletion of one weight percent of boron 10 at temperatures below about 750 °F.

Boron may also be added to aluminum alloys. Four to five percent boron may be added to aluminum alloys without degrading strength or ductility. The resulting borated aluminum alloy has good thermal conductivity and well established mechanical properties for short exposures. Only limited data are available, however, on mechanical properties after

prolonged exposures at elevated temperatures. Also, the mechanical properties of the alloys are inferior to other poison materials. The aluminum alloys are susceptibility to pitting, blistering, and general aqueous corrosion, particularly at elevated temperatures. Also, the aluminum alloys have a lower corrosion potential than do the stainless steels. Therefore, consideration must be given to the galvanic corrosion of the aluminum alloys if there is to be contact between aluminum alloys and stainless steel. In waste packages (100 - 300 °C), surface pitting and blistering would be of primary concern. Available data suggest that pitting and crevice corrosion may be a problem with aluminum - boron alloys.

Silver-base alloys were first considered for power reactor application in 1950. Early work was based on alloys of silver containing 20 to 40 percent cadmium, which has good corrosion resistance, plus small amounts of other elements, such as copper, to add strength. These early alloys exhibited poor corrosion resistance in high temperature water and tended to lose weight during corrosion and, thus, release their high activity nuclides to the coolant. A silver-base alloy containing 15 percent indium and 5 percent cadmium was soon developed, and a nickel plated version of the alloy was used in the Yankee Atomic Power Station at Rowe, Massachusetts. The nickel plate was used to improve the corrosion resistance in the event of abnormal water chemistry. The silver-indiumcadmium materials have attractive nuclear properties. Silver and indium provide a thermal cross section similar to that of hafnium, and like hafnium, these alloys have large epithermal resonance absorption. The cadmium strengthens the neutron absorption in the thermal energy range, but due to its high thermal cross section (2,450 barns), it is rapidly depleted. Silver-base alloys are readily available and can be easily fabricated, and unlike hafnium, these alloys are not sensitive to impurities. Also, they are ductile and retain their ductility even after irradiation.

The main drawbacks of the silver-base alloys are their relatively low strength, their poor corrosion resistance in water containing even small amounts of oxygen (5 ppm), and the resultant release of high activity silver nuclides. However, the strength of the silver-indium-cadmium alloy can be improved by dispersion strengthening techniques, and the corrosion resistance can be improved by nickel plating the alloys. Also, small additions of tin have been found to improve the corrosion resistance. These nickel-plated silver-indium-cadmium alloys have evidently been used in commercial power reactors, where corrosion in high temperature (400 - 600 °F) water is of concern. In addition, a number of test and research reactors, that operate at around 100 - 200 °F, have used either cadmium or silver-cadmium alloys based primarily on their nuclear properties, without extensive consideration of strength and corrosion at higher temperatures. A final note on the use cadmium is that its vapors and salts are toxic.

Gadolinium has the highest absorption cross section of any element. However, its high absorption cross section results in a very high burnup rate. Further, gadolinium has very poor corrosion resistance. Typically, it is used as an oxide dispersion in a metal matrix; however, Gadolinia (Gd_2O_3) dispersions are limited for practical purposes to about 40 percent by volume. Gadolinia has been used in transport/shipment casks as a criticality control mechanism.

Another rare earth element, europium, has been used as a control material in power reactors. Europium has the unique quality that capture of a neutron by ¹⁵¹Eu begins a chain of four daughter isotopes that each have relatively high absorption cross sections. This quality provides for a relatively long lived absorber material. Problems with europium include cost and scarcity. Further, due to its high vapor pressure and relatively low melting point, europium is difficult to alloy with common reactor materials such as stainless steel and zirconium. Once alloyed, europium tends to impair the corrosion resistance of stainless steel and zirconium at concentrations as low as one weight percent. Europia (Eu₂O₃) has however found use as an oxide dispersion in stainless steel and zirconium. Control rods using a europia dispersion in stainless steel were used in the second core of the Army Package Power Reactor. Europia has been successfully dispersed in stainless steel and zirconium by powder metallurgy and used as burnable poisons in boiling water reactors and fast breeder reactors. A further disadvantage of using europium is that there is very little published data on mechanical properties of europium and on the corrosion resistance of europia in a metal matrix.

Zirconium alloys have found extensive use in light water reactors based entirely upon their excellent high temperature mechanical properties and their good corrosion resistance. From Tables 4.15 and 4.16, it is readily apparent that zirconium has a very small absorption cross section, and this is its major disadvantage with respect to criticality control. One further disadvantage is its affinity for impurity atoms (nitrogen and carbon) that can have a detrimental effect on the corrosion resistance of zirconium alloys. However, zirconium is abundant, relatively inexpensive, and has a low burnup rate. Therefore, zirconium is a good candidate, provided that the absorption cross section is sufficient to control criticality.

Of the materials considered for control rod applications, hafnium is the least complicated metallurgically. In its pure form, hafnium has about the strength of Zircaloy-2 and about one third its corrosion rate in 500 to 600 °F water. Hafnium, therefore, requires no cladding or protective plating for water-cooled reactor application. Hafnium was first used in the prototype reactor of the submarine Nautilus at Arco, Idaho. This reactor went into service on 31 May, 1953, and its satisfactory performance resulted in the use of that metal in a variety of water-cooled reactors. The disadvantages with the use of hafnium are primarily economic rather than difficulties with performance. The only significant source of hafnium is from zirconium ores that contain only about 2 percent hafnium by weight. However, the absorption cross section of hafnium is more than 500 times that of its sister element, zirconium.

Many of the neutron absorbing materials discussed above involve dispersions in stainless steel or some other corrosion resistant material. Several others require a cladding of stainless steel or some other noble material (e.g., nickel plating of the silver-base alloys). In any case, the resulting neutron absorbing material would be more corrosion resistant than the aluminum-base SNF meat and cladding materials. Based upon their relative positions in the galvanic series, these neutron absorbing materials would also be expected to be noble (passive) to the aluminum-base materials in the event of the development of a galvanic cell. Therefore, the neutron absorbing materials can be expected to remain intact as the aluminum-base SNF degrades and reconfigures. Table 4.17 contains mechanical and absorptive properties of several neutron absorbers for comparison.

		Thermal	Modulus of	Tensile		
Material	Σ_{a}	Conductivity	Elasticity	Strength	Yield Stress	%
Composition	(cm ⁻¹)	(W/m °K)	(×10 ⁻⁶ psi)	(psi)	(psi)	Elongation
Pure Cd	113.56	98.6	•	13,700		126
304SS - 1% ¹⁰ B	38.24	21.0	27.6	103,000	42,000	31.7
304SS - 1% nat Boron	7.79	21.0	27.6	103,000	42,000	31.7
6351-T5 Al - 1.2% ¹⁰ B (@ 300 °F)	45.83	199.2	10.2	21,3200	18,000	17.2
Unrefined Zr (3% Hf)	3.16	22	24.9	64,000	40,000	25
50% Hf - 50% Zr	52.50	22	-	60,100	35,600	35
70% 304SS - 30% Gd ₂ O ₃ - Sm ₂ O ₃	93.70	3.9	18.06	42,900	37,500	.75
70% 304SS - 30% Eu ₂ O ₃	11.85	-	4.5	-	-	-

Table 4.17.	Mechanical and Ab	sorptive Properties of
Some	Neutron Absorbers	(Reference 4.46)

4.6 REPOSITORY PERFORMANCE ASSESSMENT CONSIDERING DOE ALUMINUM-BASED SPENT NUCLEAR FUEL

The performance assessment of the proposed repository will require data for the existing physical and chemical conditions of the Al-SNF forms as well as data on the performance of the forms under repository conditions. Data from completed and future testing and analyses reported in Sections 4, 6, and 7 of this report will be incorporated into the performance assessment of the proposed repository.

A performance assessment is defined as the analysis of the potential long-term dose to humans from future repository release (Reference 4.47). The proposed repository for disposal of HLW, including commercial SNF, DHLW, and DOE SNF at Yucca Mountain, about 90 miles northwest of Las Vegas, Nevada, would be located in the unsaturated zone, about 200 meters above the water table. This repository is projected to be the burial site for more than 70,000 MTHM. Of this 70,000 MTHM of high-level waste and SNF, Page 4.74 of 4.78

less than five percent is DOE SNF, with the bulk (63,000 MTHM) of the HLW originating from the generation of power at commercial nuclear reactors. The remainder of the waste is in the form of glass logs from DHLW and DOE SNF. The National Spent Fuel Program has categorized the DOE SNF into 15 categories for performance assessment. SRS SNF comprised three of these categories (Categories 5, 6, & 7). Containment of HLW within the waste packages will be substantially complete for a period to be determined by the NRC taking into account the factors specified in 10 CFR 113(b)), provided, that such period shall be not less than 300 years nor more than 1,000 years after permanent closure of the geologic repository, as dictated by 10 CFR 60.113(a)(1)(ii)(A). Therefore, the time periods of consideration for the release of radionuclides are the containment and post-containment periods. During the postcontainment period, the waste packages can be expected to be breached at various times, due to the degradation of the waste packages. Recent estimates have indicated that waste packages, that are not defective at the time of emplacement, will begin to fail after about 2,700 to 12,000 years, depending upon the degree of galvanic protection afforded the inner barrier of the waste package by the outer barrier of the waste package. Upon breaching of the waste package, the HLW will be exposed to the environment, and waste form dissolution will ensue. Release of radionuclides from the proposed repository is expected to be transported downward through the unsaturated zone to the water table and then laterally in the saturated zone to the accessible environment.

The primary mechanism for movement of radionuclides from the repository to the accessible environment is expected to be by groundwater flow, after the waste packages have failed. Therefore, in order for the radionuclides to be released, the waste container must fail, to either allow formation of a water film from moisture in the drift on the waste form through which release can occur by diffusion or to allow advection through the failed waste package. Radionuclides leached from the wastes may travel out of the failed waste package either by diffusion or advection, migrate to the water table through the unsaturated zone, and be transported to the accessible environment in the saturated groundwater flow. The presence of radionuclides at the accessible environment may result in human exposure to ionizing radiation (i.e., a dose). It is this dose to humans that is predicted by a performance assessment.

In order to get a reasonable estimate of the potential long-term dose to humans from future repository release, the rate of radionuclide release to the groundwater must be quantified. The release rate of radionuclides into the groundwater is primarily dependent upon the dissolution rate of the waste form and upon radionuclide solubility. These parameters are strongly dependent upon the near field environment (temperature, pH, carbonate concentration, and chloride concentration) and, in the case of the waste form dissolution rate, the physical condition of the system. Many of the parameters important to radionuclide release from the proposed repository will be generated elsewhere in the DOE complex, however, part of the SRS mission is to provide input concerning the dissolution of the DOE Al-SNF. Preliminary investigation indicates that the dissolution rate of the DOE Al-SNF (i.e., Categories 5, 6, & 7) is about one tenth the dissolution rate of uranium metal. Other important input to the performance assessment of the proposed

repository may include the results of the thermal and criticality analyses of the codisposal canister and waste package. Details of these analyses were provided previously in this section.

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5.0 MELT AND DILUTE TECHNOLOGY DEVELOPMENT PROGRAM

Major challenges associated with the direct disposal of research reactor fuel in a repository include nonproliferation and criticality control, both of which may be a concern for HEU Al-SNF. Consideration must be given to the potential desirability and/or regulatory necessity of diluting the HEU SNF to below 20% enrichment. The probability for a criticality event as well as the issue of proliferation are greatly lowered by reducing the enrichment. The melt-dilute technology development program is focused on the development and implementation of a treatment technology for diluting HEU Al-SNF to LEU levels and qualifying this LEU Al-SNF form for geologic repository storage. The present areas of activity in the melt-dilute technology development program are:

- Development of process options, including candidate alloys, casting techniques, and process cycles
- Demonstration of process benefits, including volume reduction, proliferation, criticality, and process versatility
- Bench-scale process development to evaluate candidate alloys, crucible materials, microstructures, and ternary constituent effects
- Off-gas system development to analyze fission product release, system requirements and to develop a preliminary system design

The overall goal of these development activities is driven by the ability to produce an Al-SNF form that will meet repository waste acceptance criteria. The status of the these activities is provided in the following sections.

5.1 MELT-DILUTE AI-SNF FORM TECHNOLOGY DEVELOPMENT

The melt-dilute process is a method of preparing DOE spent nuclear fuel for long term storage. The process melts the fuel assemblies to reduce their volume and then adds depleted uranium to dilute the U^{235} concentration and reduce the potential for criticality and proliferation concerns. The resulting alloy is cast into a form for long term geologic repository storage. A flow diagram of the melt-dilute process is shown in Figure 5.1.

The process shown in Figure 5.1 is simple; however, there are many variations on how the process can be executed, depending on the isotopic dilution and chemical composition of the final product. The process described below provides a final product with an isotopic uranium content of $20\% U^{235}$ and a chemical composition of 13.2% uranium in aluminum. The process described below is our current best estimate of the equipment and methods required; however, there are alternative approaches that may prove suitable as the melt dilute process technology matures.

5.1.1 Preliminary Process Description

This section describes a preliminary description of the equipment and methods necessary for the melt-dilute processing of Al-SNF. The technology is under development and thus, changes in this outline are expected during the coming year. The basic steps in our best estimate of the process are shown in Figure 5.1.



Figure 5.1. Schematic Diagram of Melt-Dilute Process

The key elements of the melt-dilute process developments are as follows:

• Fuel Assembly Preparation:

MTR fuel that has been irradiated has been stored under water, and even though some of the fuels may have been out of water for some time, potentially some water could be inside of the assembly. Water is incompatible with molten metal; thus, the first step in preparation of the MTR fuel for processing is to oven dry at 110 °C for thirty minutes

• Fuel Assembly Melting:

One or more MTR assemblies will be remotely positioned with the bottom end in the furnace crucible. The assemblies are several times longer than the crucible in which they will be melted, so only the bottom end will be in the crucible. Heat from the crucible will melt the bottom end of the assembly allowing it to slump down into the molten pool of alloy. This process continues until the assembly is completely melted.

Isotopic Dilution and Chemical Composition Adjustment:

Once the assembly is melted and the uranium aluminum alloy in the crucible is at a temperature between 750 and 850 °C, isotopic dilution is accomplished by adding a measured amount of depleted uranium metal. This addition reduces the isotopic content of the uranium to $20\% U^{235}$. Aluminum metal is also added, if necessary, to adjust the chemical composition of the alloy to 13.2% uranium in aluminum. Induction stirring of the alloy is done to insure rapid and complete reaction of the uranium metal with the aluminum and complete mixing of the constituents of the alloy solution. The isotopic dilution is done to reduce the possibility of criticality, and the chemical adjustment is done to achieve an alloy with a low melting point and a homogeneous microstructure.

Alloy Sample:

A sample is withdrawn for analysis. The temperature of the alloy is above 750 °C (100 °C above liquidus temperature). An immediate measurement of the uranium composition, such as bulk density measurements, will be made to verify that the alloy can be poured. The same sample is then submitted for chemical analysis for documentation of the elemental content of the alloy. Metal remaining from the sample after analysis can be added to subsequent melts unless an archive of the sample is required. Liquid waste from the chemical analysis will be sent to the high level waste stream.

Casting of SNF Form:

As soon as the uranium content has been measured to confirm alloy composition, the alloy will be either cast into a mold or solidified in the crucible. For bottom pouring, the plug in the bottom of the crucible is lifted and the alloy flows into the storage canister, preferably stainless steel. The volume of the storage canister is much larger than the capacity of the crucible, so the melt cycle will be repeated many times before the storage canister is filled.

• Off Gas System:

The fuel assembly and furnace crucible are enclosed in a chamber that has slight negative pressure relative to atmospheric. Any gases that are released from the fuel assembly will be confined to the chamber and subsequently processed through the offgas system. The process is designed to condense cesium vapor, collect iodine, and filter particulate material from the gas prior to releasing the processed gas to the stack.

• Identification of Waste Streams:

There are two sources of solid waste generated by this process: used crucibles from the melting operation and used filters from the off gas system. The only liquid waste from the process results from chemical analysis of samples taken to measure uranium content and filter wash stream if chemical cleaning is used in the off-gas process. Gases released to the stack may contain some iodine, xenon, and krypton provided they are not absorbed on filter beds.

5.2 PROCESS DEFINITION AND BASIS

The melt-dilute technology is a relatively simple and versatile process that can alleviate . both nonproliferation and criticality concerns for the long-term storage of HEU spent nuclear fuel. This section provides general background concerning pertinent characteristics of the spent fuel inventory and the uranium-aluminum alloy system. Additionally, potential process/casting options are discussed as well as the overall benefits of this treatment technology compared to the direct/codisposal option.

5.2.1 Melt-Dilute Process Options

Many MTR and other research reactor fuel elements were originally fabricated using 93% highly enriched uranium and aluminum alloy, and they were generally clad with 6061 aluminum. These fuel assemblies have been irradiated, and some have been stored for up to 40 years in water basins after being discharged from the reactors. During irradiation, the fissile content of the fuel core is reduced about 30-60% leaving approximately 70-40% of the U^{235} remaining in the fuel assembly. To dilute the enrichment and reduce criticality and proliferation concerns for long term repository storage, the melt-dilute technology was proposed for treatment of spent nuclear fuel. When SNF assemblies are melted, the composition of the molten alloy is expected to range from 3 to 10 wt % uranium in aluminum. For dilution, depleted uranium metal is added to the melt to reduce the enrichment of the uranium to about 20% or less. Aluminum can be added to the melt, if needed, to adjust the casting composition of the alloy in the crucible to production requirements, such as the eutectic or the intermetallic composition.

When depleted uranium metal is added to dilute the fissile content to $\leq 20\%$, the phases present in the melt and in the final microstructure of the casting are affected. According to the phase diagram in Figure 5.2, phases vary from liquid to liquid plus solid as the uranium content increases at temperatures above 660 °C. Once inside a two phase region,

the solid intermetallic phases of either primary UAl₃ or UAl₄ become thermodynamically stable and begin to precipitate from the liquid solution. Because the density of the intermetallics is greater than the liquid alloy, they tend to segregate at the bottom of the crucible unless it is stirred continuously. Heating the melt above the liquidus temperature dissolves the intermetallic compounds and forms a single liquid phase. Above the liquidus temperature, there is complete isotopic homogenization or uniform dilution of the uranium fuel.

There are various uranium compositions that can be cast for the uranium-aluminum system, but for the melt-dilute process, a specific alloy content or an adjusted composition is desired for the waste form. This simplifies both the production process and waste form qualification for the geologic repository. The composition selected for the process basically depends on the isotopic dilution required for the spent nuclear fuel waste form and the waste volume criteria for repository storage. Three basic isotopic dilutions have been investigated and include 20%, 5%, and 2%. Each dilution can be achieved by either adding depleted uranium metal or by adding both depleted uranium and aluminum metal to the molten alloy. The process used for treatment affects the waste volume as indicated in Figure 5.3 where the waste volume is shown as a function of the dilution factor (%) for aluminum-base SNF. Advantages of a 20% dilution and the eutectic composition include: (1) lower process operating temperatures, (2) minimum gravity segregation in the casting, (3) lower volume of off-gas products and (4) lower associated costs. When compared to other dilution methods, the 20% dilution offers the greatest versatility because waste forms containing about 5 to 67 wt % uranium can be produced and stored in less than 400 canisters each. If the waste form is diluted to approximately 20% U²³⁵, criticality and proliferation concerns are reduced or eliminated for geologic repository storage.



Figure 5.2. Binary Phase Diagram of the Uranium-Aluminum System

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The bar graph in Figure 5.4 shows the percent SNF fuel vs. MD melt composition for fuel assemblies diluted to 20%. The data include foreign research reactor, domestic research reactors, Argonne Test Reactor, and High Flux Isotope Reactor fuel assemblies. About 96% of all fuel elements have a composition within the 0-30 wt % uranium range when diluted using depleted uranium metal only.



Figure 5.3. Total Waste Volume for FRR, DRR, HFIR, and ATR Fuel Assemblies as a Function of the Dilution Factor, Process Additions and Waste Composition (Reference 5.1).



Figure 5.4. Percent Fuel Assemblies vs Weight Percent Uranium in Aluminum for 20% Dilution of Irradiated Research Reactor Fuel Assemblies includes FRR, DRR, ATR, HFIR Fuels (Reference 5.1).

As a comparison, the waste form alloy could be diluted further by adding additional uranium to the melt in the crucible. For example, if the dilution required for the MD process was 5%, then the optimum casting composition would be 67 wt % uranium in aluminum to achieve the minimum number of canisters. The percent of fuel elements vs uranium alloy compositions for 5% dilution using depleted uranium only is shown in Figure 5.5. More than 90% of the fuel assemblies would have a uranium composition less than 67 wt % uranium. Aluminum would have to be added to the remaining assemblies to achieve the casting composition of 67 wt % and a 5% dilution of U^{235} .

It should be noted from Figure 5.2 that when the composition of the alloy exceeds 30 wt % uranium, the liquidus temperature becomes greater than 1000 °C and can reach 1500 °C for a 67 wt % alloy of the intermetallic UAl₄ composition. At these temperatures, the release of fission products from the melt increases as will be discussed in a later section. The solubility of hydrogen in the melt also increases with temperature



Figure 5.5. Percent Fuel Assemblies vs Weight Percent Uranium in Aluminum for 5% Dilution of Irradiated Research Reactor Fuel Assemblies, includes FRR, DRR, ATR, and HFIR Fuels (Reference 5.1).

which produces additional porosity in air-melt castings. Subliquidus casting is a low temperature option for higher wt % alloys, but uranium homogeneity of the melt and isotopic dilution of the primary phase may be questionable.

5.2.1.1 Candidate Uranium Alloy Compositions

There are three alloy compositions that are considered for the MD process. They are the eutectic composition, 30 wt % uranium-aluminum, and the intermetallic composition of

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UAl₄ The eutectic compositions is of particular interest because it has the lowest liquidus temperature in the U-Al alloy system. The 30 wt % uranium alloy has a liquidus temperature of less than 1000 °C, and UAl₄ has the lowest liquidus temperature of the intermetallic compounds.

The eutectic composition contains about 87 wt % aluminum and only 13 wt % uranium. Aluminum must be added to the melt for diluted alloy compositions above the eutectic. The amount of aluminum depends on dilution requirements of the process and tends to increase the waste volume. Aluminum adds about 370 cc/Kg to the waste volume, whereas uranium adds only about 50 cc/Kg. However, solidification of the eutectic composition is unique in that it occurs at a constant temperature of 646 °C. The solidification characteristic of the eutectic produces a uniform microstructure with little or no gravity segregation of the aluminide intermetallic phase. Because the composition range is narrow, the microstructure generally consists of a small amount of primary aluminum or UAl₄.

For the 30 wt % uranium composition, the liquidus temperature is about 1000 °C, and there is a 350 °C two-phase zone where separation of primary aluminides can occur during solidification. The aluminides are dense and will separate from the liquid without stirring and settle to the bottom of the casting during slow cooling. Photographs, shown in Figure 5.6, show approximately a 5% difference in the aluminide phase concentration at the bottom of a 30 wt % uranium casting. The alloy in the figure was heated above the liquidus temperature in a graphite crucible and poured into a graphite mold.

The uranium-aluminum alloy system has three different intermetallic compounds, UAl_2 , UAl_3 , and UAl_4 . The composition of UAl_4 is about 67 wt % uranium and 33 wt % aluminum. The liquidus temperature for this composition is approximately 1500 °C, and the peritectic reaction temperature is 731 °C. The low temperature of the peritectic reaction requires a relatively long diffusion time at temperature for completion. Thus, the microstructure of a slow cooled casting most often consists of a mixture of both UAl_3 and UAl_4 intermetallic compounds. These compounds generally have different physical and chemical characteristics from the alloy which could prove beneficial for corrosion resistance of the waste form.

5.2.1.2 Process Cycle Options

Two process cycles have been developed for the production of uranium-aluminum alloys with the aforementioned compositions. For the eutectic and 30 wt % uranium alloy cases a the process cycle is depicted in Figure 5.7. This process cycle involves heating the alloy to above the liquidus temperature to ensure maximum homogeneity and distribution of the elements. This processing cycle can also be adapted to the 67 wt % uranium alloy but with a liquidus temperature in excess of 1500 °C it may not be feasible on a production/ commercial scale basis. Thus, another potential processing cycle option has been outlined in Figure 5.8. This processing cycle relies on a casting technique that can be termed subliquidus or mushy zone casting. With this technique, the alloy is produced by heating the



(a) Top



(b) Middle



(c) Bottom

Figure 5.6. Photomicrographs of a 30 wt % Uranium-Aluminum Alloy showing Gravity Segregation of the Primary UAL



Figure 5.7. Process Melt Cycle for Eutectic and 30 wt % Uranium Alloys



Figure 5.8. Process Melt Cycle for Sub-Liquidus/Mushy Zone Casting

materials to a temperature below the liquidus within a two phase region where one of the two phases is a liquid. Two potential drawbacks to this casting cycle are the need for longer dissolution time and the relative inability to ensure alloy homogeneity. While this technique is possible for all three compositions it would only make sense to explore this option in cases where the liquidus temperature is unobtainable or significant negative impact on the overall process is brought about by going to the liquidus temperature.

5.2.1.3 Melt-Dilute Casting Techniques

Production of the Al-SNF form may be done by three casting methods, two of which involve a separate crucible and solidification vessel and one in which the crucible is used as the actual solidification vessel. The use of a separate crucible and casting vessel necessitates a pouring operation, which may be accomplished by top pouring or bottom pouring. Each of these techniques has distinct advantages and disadvantages.

A top pour is a physically simple operation that merely requires rotating the crucible to allow the molten metal to pour into the mold or casting vessel. There are several disadvantages to this process. Melt slag and oxides that are present on the top of the melt will be the first liquid to pour into the mold unless they are removed by skimming. Because of the radioactive nature of the product and the necessity of remote handling, this would not be a trivial operation to accomplish. Another potential issue is the disposal of solidified crucible skull.

Bottom pouring avoids all of these problems but introduces one additional difficulty. For bottom pouring, there are two means of regulating the flow. One of these is the stopper rod, a plunger which is raised or lowered from above the crucible and which opens and closes a hole in the bottom of the crucible. The stopper rod produces good regulation of pour rate and long life of the assembly. The other method is the slide gate, which is a sliding portal that either lines up with or blocks an opening in the bottom of the crucible. The slide gate offers more reliable shutoff than the stopper rod valve but may have a shorter service life. Slide gates are also more expensive and offer less control of the pour rate. In either case there is a potential problem with blockage of the flow regulation device or of the pour spout which is an integral part of the assembly and which guides the flow into the mold. Previous work with aluminum alloys, however, has shown that these alloys may be reliably processed by a bottom pour system with no clogging or flow problems.

The final method of producing a solid SNF form is solidification in crucible. This avoids all of the aforementioned problems and reduces the complexity of the off-gas system needed for capture of the volatile radioactive species that are released from the melt. Solidification in crucible provides the slowest cooling rate and simplifies the microstructure of the SNF form. It is an inherently safe process because there is no chance of spillage. The lack of melt disturbance (as would be present after pouring) reduces the potential for porosity in the casting and reduces the amount of volatile species released to the off-gas system. Solidification in crucible also allows the slag and oxides to become an integral part of the casting and eliminates the need for separate disposal.

5.2.2 Process Versatility

An attribute of the melt-dilute process is its applicability to various types of FRR and DRR SNF. The viability of the melt dilute option and its ability to treat these different fuel materials has been addressed herein.

5.2.2.1 Applicability to Different Research Reactor Fuel Types

There are three basic fuel types that have been fabricated for research and test reactors. Originally fuel was made from cast aluminum-uranium alloys; later it was made using powder metallurgy techniques. These fuels include UAl_x, U₃O₈ and U₃Si₂ powders that are mixed with aluminum powder and hot/cold rolled to produce flat plates. Fuel elements are irradiated from 30 to 60% burnup. Photomicrographs of these fuels at high burnup are shown in Figure 5.9. During irradiation, centerline temperatures up to about 200 °C can occur which enhances diffusion of uranium and aluminum in the fuel meat. These effects produce chemical reactions between various fuel particles and matrix materials. For example, in U₃O₈ fuels a UAl_x type phase is formed while in silicide fuels other aluminumsilicon phases form at the aluminum - U₃Si₂ particle interface. These phases can be seen in Figure 5.9(b) and (c) for the oxide and silicide fuels, respectively. For aluminide fuels, no reaction occurs at the particle-matrix boundary because of the thermodynamic stability of the aluminide phase present in the fuel as shown in Figure 5.9(a).

The kinetics of oxide dissolution in molten aluminum are slow because of the stability of the oxide phase, but the diffusion reactions in oxide fuels during irradiation will enhance the solubility of the fuel phase. During MD reprocessing, all fuels are expected to dissolve adequately when melted. For irradiated oxide and aluminide fuels, the melting behavior is expected to be governed by the uranium-aluminum phase diagram shown in Figure 5.2 of this report. With silicide fuels, the uranium-aluminum-silicon ternary phase diagram is necessary to predict process conditions. The ternary diagram at 950 °C was constructed from binary phase diagrams and is shown in Figure 5.10.

At 950 °C the aluminum-uranium-silicon system has a relatively large liquidus region near the aluminum-rich end of the phase diagram. Calculations, based on aluminide fuels, for the silicide loading indicate that the melt composition will be in the range of about 1 to 10 wt % uranium, 0.1-0.8 wt % silicon, and 98.9-89.2 wt % aluminum for various MTR assemblies. According to these calculations, the alloy is expected to melt between 660 and 960 °C. Melting of silicide fuels can be accomplished using the same melt-dilute process; however, dilution may not be a concern for these low enriched elements. Melting and casting would, however, consolidate the fuel and produce a waste form consistent with other fuel types.



(a) UAl_x-Al



(b) U₃O₈-Al



Figure 5.9. High Burnup Fuels Irradiated in Research and Test Reactors



950° C ISOTHERM OF THE U-AI-SI TERNARY SYSTEM

Figure 5.10. Ternary Isothermal Section from the U-Al-Si System at 950 °C

Besides the composition of the fuel meat used during the fabrication of these research and test reactor fuel assemblies differences in the compositions of the Al-cladding alloys also exists. MTR fuel assembly manufactured by the French used cladding alloys that had relatively significant amounts of magnesium, iron, and nickel. Assemblies manufactured in both the US and Germany typically used the 6061 aluminum alloy which has magnesium and silicon as its major alloying additions. Other alloying additions that occur in much smaller concentrations than either magnesium or silicon but which have the potential to impact the melt-dilute process are also being identified. For example, zinc is a common alloying additions in small concentrations for 6061 aluminum alloys. Zinc's relatively low boiling point could impact the design of the off-gas system if it is deemed necessary to collect/trap any volatilizing zinc atoms during melting. Further evaluation of the potential impact of these and other cladding alloy additions on the melt and dilute processing technology will be performed in the future.

5.2.3 Process Benefits

The advantages/benefits of the melt-dilute processing technology option as compared to the direct disposal option have been evaluated. The two greatest concerns with the direct disposal option are proliferation and criticality. With the majority of the SNF inventory to be returned possessing levels of enrichment greater than 20 % the ability of a direct disposed SNF form to demonstrate criticality stability is an uncertainity. Additionally, the inefficient packaging achieved with the direct disposal option leads to greater numbers of repository canisters and space both of which can be shown to have significant direct increases in total disposal cost. This section addresses similar factors for the melt-dilute option and demonstrates the benefits that this option has to offer over direct disposal.

5.2.3.1 Volume Reduction

In order to provide a direct comparison to the direct/codisposal technology regarding SNF form volume and packaging, canister dimensions and fuel data from Brewer's report (Reference 5.2) and Matos Database (Reference 5.3) were used. Burnup credit was taken in the following manner: for the FRR fuel, burnup information from the Matos database was used, and for DRR, ATR, PIN, and HFIR/RHF fuel types, an across the board 30% burnup was assumed in the calculations. Additionally, since the as-solidified melt will not be 100% dense it is necessary to consider an increase in volume resulting from porosity. Thus, calculated average total volumes for the castings were increased by 10% to reflect this porosity effect. In addition, since some of the repository canister volume will be wasted by the stainless steel packing container for the melts, it was necessary to reduce the repository canister volume number used in the calculations to reflect this inaccessible volume. The adjusted repository canister will be determined by reducing the previous value (368,859 cc) by 25% providing a repository canister volume of 276,644 cc.

The combined effect of accounting for porosity and some inaccessible volume results in reduction of the total canister volume by 35%.

5.2.3.1.1 Repository Canisters Necessary for SNF Disposal

Analysis of the DOE SNF inventory reveals that there are approximately 28,492 domestic and foreign fuel assemblies for disposal. These 28,492 fuel assemblies are comprised of 9,755 foreign research reactor MTR assemblies, 11,625 DRR assemblies, 4,097 ATR, 2,721 PIN, and 294 HFIR/RHF type fuel assemblies. The initial enrichment of these assembly types ranges from 20 to 93%. Volume calculations have been performed to examine the dilution of these assemblies to 2%, 5%, and 20% enrichment using the Melt-Dilute technology. A compilation of the dilution compositions for the typical DOE SNF at 20% and 5% is shown in Figures 5.4 and 5.5, respectively.

Once the amount (kg) of uranium and aluminum were known for each dilution treatment (2%,5%,20%) the following relationships-- uranium 50 cc/kg and aluminum 370 cc/kg-- were applied to calculate total waste volumes. The value of 50 cc/kg for uranium does

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not account for alloying with aluminum, and any increasing volume that would arise from alloying can be offset by the overall 35% reduction in total canister volume used in these calculations. From these total volume calculations, an average value was determined for each type of assembly which was then used to determine the number of necessary repository canisters for disposal. Table 5.1 summarizes the results of the volume calculations for the melt dilute technology for each isotopic dilution.

From these initial calculations it is quite obvious that the number of repository canister savings simply based on dilution is considerable when compared to the direct/codisposal technology. For processing the DOE SNF to 2, 5 or 20% dilution the total number of repository canisters needed is 328, 272, and 253 respectively. This is approximately only 23-30% of the number of canisters needed for direct/codisposal.

5.2.3.1.2 Determination of Casting Composition Following Dilution

As a result of the variation in the as-manufactured compositions of the fuel assemblies, the compositions of diluted uranium-aluminum alloys are quite varied. From the standpoint of commercial/production viability, it may be necessary to specify a single composition to which all of the alloy melts will be cast. This "adjusted casting composition" will most likely be different from the as-diluted composition for most of the fuel assemblies and will require either the addition of aluminum or uranium. Thus, it is necessary to examine some preliminary casting compositions and determine how the waste form volume and in turn the number of canisters are affected. Initially, three "adjusted casting compositions" have been examined. The eutectic composition (Al-13.2 wt % U) is attractive from two standpoints. First, the low liquidus temperature at this composition makes processing easier as well as allowing for less fission product release. Additionally, because of the nature of the eutectic equilibrium during solidification the problem of gravity segregation is reduced if not eliminated. A potential drawback to this composition is the two-phase lamellar microstructure which could affect the corrosion resistance from natural galvanic coupling of the different constituents. The corrosion behavior of this two-phase eutectic microstructure is being explored under a separate task of the Al-SNF Treatment Technology program and is reported in Section 6. Another casting composition under consideration is Al-30 wt % U. This casting composition is attractive because much like the eutectic composition the liquidus temperature is relatively low (<1000 °C). Furthermore, much of the early cast U-Al alloy test reactor fuel were produced at or near this composition and as a result much information concerning melting practices exist for this composition. A potential drawback is that potentially SNF form microstructure characterization could be more difficult due to the varied and complex microstructures that result on casting an alloy of this composition. The last casting composition that is being considered at this time is that of the intermetallic compound UAl₄ (Al-67 wt % U). The attractiveness of this casting composition stems from once again reducing alloy segregation by producing a single phase structure. Furthermore, it is speculated that the corrosion resistance of this compound may be better than a conventional multi-phase microstructure. This particular intermetallic compound of the U-Al system is attractive

Type of	Dilution	Avg.Total	# of
FA	%	Volume at	canisters
	U ²³⁵ /U	Dilution	at
		per FA	Dilution
Foreign			
MTR			
9,755			
	2	2139	76
	5	1901	68
	20	1793	64
Domestic			
MTR			
11,625			
	2	2677	113
	5	2281	96
	20	2142	90
ATR			
4,097			
	2	2927	44
	5	2451	37
	20	2269	34
PIN			
2,721			
	2	2680	27
	5	1016	10
	20	638	7
HFIR			
294			
	2	63378	68
	5	57355	61
	20	54343	58

Table 5.1. The Number of Repository Canisters Required for Melt-Dilute Waste Form Disposal of Isotopically Diluted DOE SNF

*note all volumes in cc

TOTALS: 2%-- 328 5%-- 272 20%-- 253 Page 5.18 of 5.82

because it is not a line compound. UAl₄ has been shown to exist over a limited compositional range (65-69 wt % U) of compositions thus, making it easier to process. With other U-Al intermetallic compounds any slight deviation from stoichiometry results in a two phase mixture instead of a single phase monolith.

For the sake of examining SNF form volumes all of these compositions have been considered and calculations performed to determine the necessary number of repository canisters if the fuel assemblies are diluted to 2%, 5%, and 20% and then cast at one of these compositions. A summary of the calculations is given for the eutectic, 30 wt % U, and for the intermetallic composition (67 wt % U) in Tables 5.2-5.4.

Examination of the total number of canisters required for disposal based on the three different casting compositions provides the following: (i) For the eutectic composition at 2, 5 and 20 % dilution--1796, 1234, and 396 repository canisters are needed respectively, (ii) For Al-30 wt % U at 2,5, and 20% dilution-- 1103, 479, and 283 canisters are needed, and (iii) For Al-67 wt % U at 2,5, and 20% dilution-- 386, 326, and 320 repository canisters are needes. From Tables 5.2-5.4 it can be shown that following dilution to 20% enrichment all of the "adjusted casting compositions" result in similar numbers of repository canisters. This makes the eutectic casting composition attractive because of the lower processing temperature associated with the eutectic invariant in this system. For the case of diluting to a 5% enrichment, only the 30 wt % U and the intermetallic (67 wt % U) compositions are attractive from a number of canisters standpoint. The eutectic casting composition at this enrichment would require more repository canisters than the direct/codisposal option. If the DOE SNF is diluted to a 2% enrichment the only casting composition that is feasible is that of the intermetallic--67 wt % U.

5.2.3.1.3 Fissile Mass Loading per Repository Canister

According to the report issued by the Research Reactor Spent Nuclear Fuel Task team in June of 1996 (Reference 5.4), the following limits have been specified for fissile mass loading of repository canisters:

- * HEU -- each package limited to 14.4 kg U²³⁵
- * LEU -- each package limited to 43 kg U²³⁵
- * VLEU -- each package limited to 200 kg U²³⁵

where HEU refers to > 20% U^{235} , LEU to 2-20% U^{235} , and VLEU to < 2% U^{235} . With these limits in mind calculations have been performed to examine the fissile mass loading per repository canister for the melt-dilute technology. For the case of direct/codisposal most of the DOE SNF will be classified as HEU and will thus be limited to 14.4 kg U^{235} per repository canister. With the melt-dilute technology all of the waste will be classified as LEU and thus will allow 43 kg of U^{235} per canister. Table 5.5 shows the resulting fissile mass loading per canister for DOE SNF processed using melt-dilute to dilutions of 2%, 5%, and 20%.

Type of FA	Dilution %	Avg. Total	# canisters
		Volume at	at Casting
		Casting	Ŭ
		per FA	
Foreign			
MTR			
9,755			
	2	16290	575
	5	7220	255
	20	2219	79
Domestic			
MTR			
11,625			
	2	9072	382
	5	9362	394
	20	3288	139
ATR			
4,097			
	2	30203	448
	5	12148	180
	20	3485	52
PIN			
2,721			
	2	17892	176
	5	19388	191
	20	6901	68
HFIR			
294			
	2	201666	215
	5	200937	214
	20	54404	58

Table 5.2. Number of Repository Canisters Needed for Disposal with anEutectic Casting Composition of Al-13.2 wt %U

TOTALS: 2%-- 1796 5%-- 1234 20%-- 396

Type of FA	Dilution %	Avg.Total Volume at Casting per FA	# canisters at Casting
Foreign MTR 9,755			
	2	6593	233
	5	2813	100
	20	1857	66
Domestic MTR 11,625			
	2	8276	348
	5	3821	161
	20	2304	97
ATR 4,097			
	2	11110	165
	5	4580	68
	20	2335	35
PIN 2,721			
	2	16318	161
	5	7132	71
	20	2539	25
HIFIR 294			
	2	183927	196
	5	73910	79
	20	56396	60

Table 5.3. Number of Repository Canisters Needed for Disposal with anAlloy Casting Composition of Al-30 wt %U

TOTALS: 2%-- 1103 5%-- 479 20%-- 283

Type of FA	Dilution %	Avg. Total Volume at Casting	# canisters for Casting
Foreign MTR 9,755			
	2	2407	85
	5	2237	79
	20	2237	79
Domestic MTR 11,625			
	2	3174	134
	5	2699	114
	20	2668	113
ATR 4,097			
	2	3548	53
	5	2812	42
	20	2812	42
PIN 2,721			
	2	4150	41
	5	1820	18
	20	1300	13
HFIR 294			
	2	67935	73
	5	67935	73
	20	67935	73

Table 5.4. Number of Repository Canisters Needed for Disposal with anIntermetallic Casting Composition of Al-67 wt %U

*note all volumes in cc

TOTALS: 2%-- 386 5%-- 326 20%-- 320

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From Table 5.5, all of the fuel assemblies in the diluted and adjusted casting composition cases meet the requirements for fissile mass loading. These values were calculated by taking the total amount of U^{235} for 28,492 fuel assemblies and dividing by the number of repository canisters necessary based on volume from Tables 5.1-5.4. The total amount of U^{235} for all of the DOE SNF is approximately 9 metric tons and the average initial fuel assemblies U^{235} loading values for the different fuel types FRR, DRR, ATR, PIN, and HFIR are 200, 229, 315, 436, and 5215 grams, respectively.

Dilution %	Kg U ²³⁵ / Canister Dilution	Kg U ²³⁵ / Canister Eutectic	Kg U ²³⁵ / Canister 30 wt % U	Kg U ²³⁵ / Canister 67 wt % U
2	27	6	8	23
5	32	7	19	27
20	35	22	31	27

Table 5.5. Determination of the Fissile Mass Loading per Repository Canister for the Melt-Dilute Technology

5.2.3.1.4 Total Loaded Mass Canister Plus Contents

An additional concern in the development of a qualifiable SNF form via the melt-dilute process is the maximum mass of the canister and contents. The mass (kg) of the repository canister based on the following assumptions--43 cm inner diameter, 47 cm outer diameter, 300 cm in length, and constructed from 316L SS with a density of approximately 8 gm/cc--is calculated to be 678 kg. The preliminary limit for canister and contents is 2270 kg as stated in EPS-26-97, Draft of Preliminary Specification for DOE Standardized Canisters (Reference 5.5). Table 5.6 shows the total loaded mass for the canister and contents summed for FRR, DRR, ATR, PIN, and HFIR fuels.

From Table 5.6, it can be seen that except for the case of the intermetallic composition (Al-67 wt % U) at 5 and 20% dilutions, the preliminary requirements for total mass of the canister and contents are met. For the cases that are not within the preliminary specified limits, the excess contents needs to be distributed over 3 and 2 extra repository canisters for the 5 and 20% dilution treatments, respectively.

5.2.3.1.5 <u>Analysis</u>

The melt-dilute technology has been shown to offer clear advantages with respect to criticality, proliferation and volume when compared to the direct/codisposal technology for geologic repository storage of aluminum based DOE SNF. With the dilution of the DOE SNF, the enrichment can be reduced to 2-20% U^{235} without any increase in the

Dilution %	Total Loaded	Total Loaded	Total Loaded	Total Loaded
	Mass per	Mass per	Mass per	Mass per
	Canister for All	Canister for All	Canister for All	Canister for All
	Fuel Types at	Fuel Types at	Fuel Types at	Fuel Types at
	Dilution (kg)	Cast (Al-13.2U)	Cast (Al-30U)	Cast (Al-67U)
		(kg)	(kg)	(kg)
2	2151	1394	1594	2202
5	1750	1412	1591	2285
20	1474	1372	1592	2283

Table 5.6. Average Total Loaded Mass Canister and Contents for Typical DOE SNF

number of repository canisters necessary for disposal and with meeting all of the repository requirements concerning fissile mass loading and total loaded mass. If one considers diluting the fuel to 20% enrichment and casting at 30 wt % U, the total number of necessary repository canisters is 283, the fissile mass loading per canister is 31 kg U^{235} , and the total loaded mass canister and contents is 1592 kg. All of these values are well within the preliminary repository specifications of 1200 canisters, 43 kg U^{235} per canister and 2270 kg for total loaded mass. Comparing the value of 283 repository canisters for disposal to the values of 1,361 of direct/codisposal shows a decrease of almost 80% or 1078 canisters. If one merely considers the canister construction cost of \$21,000 per canister as outlined in Volume 2 of the Research Reactor Spent Nuclear Fuel Task Team Report, June 1996 (Reference 5.6), this would result in a cost savings of approximately 20 million dollars.

5.2.3.2 Proliferation Resistance

One of the concerns with the disposal of HEU SNF is the potential for the proliferation of weapons feasible material The attractiveness of the melt-dilute treatment technology option with respect to proliferation is that when the SNF is diluted to LEU levels it is by definition non-proliferable.

5.2.3.3 Criticality Stability

The direct disposal of HEU Al-SNF without the addition of poisons has recently been shown to result in a k_{eff} value greater than 0.95. The addition of borated stainless steel to the canister does however, lower the k_{eff} value to below 0.95. For the melt-dilute technology option the potential for criticality is lower than direct disposal. This results from the fact that the enrichment of the SNF is reduced as the fuel is melted and depleted uranium is homogeneously incorporated into the alloy during the dilution treatment. An Page 5.24 of 5.82

additional advantage to the melt-dilute option concerning criticality is that should more detailed criticality calculations show that poison additions are necessary, these poison additions will be integral to the SNF form since they are incorporate directly into the alloy during melting where as, for the direct disposal case the poisons are only incorporated mechanically.

5.2.3.4 Characterization Requirements

Potentially the characterization needs for the direct disposal option could be extensive if characterization is required on a per fuel assembly basis. For the direct disposal option, if the Appendix A information for incoming fuel is missing or suspect it will be necessary to establish a pedigree and condition for the SNF to include information such as burnup, fissile content, and chemical constituents.

Characterization needs for the melt-dilute option will be significantly less. The extent of the required Appendix A data is reduced since the history of the SNF is erased through melt-dilute processing.

The strategy for characterization as a tool for process control is to limit in-line characterization. Currently, the only measurement being considered for in-line process control is that of uranium concentration. Quick response techniques such as density measurements or glow discharge emission spectroscopy are being considered.

5.2.3.5 Al-SNF Form Stability

Al-SNF form stability involves two aspects namely, phase stability and chemical stability. The issue of phase stability addresses the impact of SNF form microstructural features as they pertain to geologic repository storage performance. The area of chemical stability is influenced by phase stability and addresses issues such as dissolution and corrosion of the SNF form. Chemical stability will be discussed in Section 6.

5.2.3.5.1 Phase Stability

The ability to select/tailor the final Al-SNF form composition and microstructure allows for the potential to increase phase stability which in turn results in increased chemical stability. For example, the eutectic microstructure of a 13.2 wt % uranium alloy is relatively stable but with time and temperature the lamellar eutectic tends to spheroidize as the alloy system attempts to minimize surface/interfacial energy. This spheroidal structure possesses superior phase stability. Additionally, for the intermetallic composition case the production of a single phase monolith will possess superior phase stability when compared to the mixed phase microstructure inherent to the direct disposal Al-SNF form.
5.3 PROCESS DEVELOPMENT

The melt-dilute process is a simple concept. An MTR fuel element will be placed into a heated crucible. When heated, the fuel assembly will begin to melt and slump into the bottom of the crucible to form a pool of molten uranium-aluminum alloy. The average research and test reactor fuel assembly will have a uranium content of approximately 8 wt % uranium when melted. Depleted uranium will be added to the alloy to dilute the percentage of U^{235} . During melting, fission gases will be released as well as any fission products whose boiling point are below the temperature of the melt. These fission products will be collected in an off-gas system and disposed of in an appropriate manner.

Although the concept is simple, there are many technical issues, surrounding each of the processing, steps that must be resolved before the technology can be implemented. Thus, numerous tests and studies have been conducted to develop an understanding of the behavior of alloys and crucibles materials under conditions that simulate a broad range of possible melt-dilute process conditions.

5.3.1 Bench Scale Development

Bench-scale process development activities afford the researcher opportunity to explore different and varied processing conditions in a timely manner. This section provides the results from the current bench scale process development activities and includes the evaluation of cast microstructures and crucible materials, ternary constituent effects, melt stirring techniques, and in-line process control.

5.3.1.1 Evaluation of Cast Microstructures and Crucible Materials

The influence of microstructure on material properties is well documented within the realm of materials science. The distribution, size, and morphology of the individual phases within the microstructure ultimately determine extensive material behaviors such as thermal, mechanical, and corrosion stability. In reference to the processing of DOE SNF via the melt-dilute technology, the microstructure will play a significant role in determining the SNF form characteristics. Thus, it is necessary to understand the influences of various processing parameters such as temperature, composition, mold materials, and impurity/addition elements on the resulting microstructure of aluminum-based DOE SNF forms. Several significant issues requiring consideration are segregation of the primary intermetallic phase formed during cooling, the ability to tailor microstructures by controlling processing to achieve desired Al-SNF form characteristics, and the effects of impurity/addition elements on the alloy transformation behavior during heating and cooling.

Fundamental experimental investigations of the solidification microstructure resulting from different processing treatments have been carried out in order to provide information for the development of the melt and dilute processing technology for U-Al, UAl_x, U-Si, and Al-U₃O₈ research test reactor fuel assemblies. These investigations have been centered on

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uranium-aluminum alloys with compositions varying from the eutectic (13.2 wt % U) to the intermetallic UAl₄ (67 wt % U) compound. Two sets of investigations have been carried out; one involving carbon steel crucibles and one using graphite crucibles. The processing treatment for these two studies has been similar and is as follows: (i) heat an aluminum charge in the desired crucible to a temperature between 800 and 850 °C, (ii) add pre-weighed portions of depleted uranium and stir, (iii) after all uranium portions are added heat the alloy to 50 °C above the liquidus temperature, (iv) take dip samples from the liquid melt for compositional analysis, and lastly, (v) for graphite crucibles pour molten alloy into a graphite mold and allow to cool in air, and for carbon steel crucibles shut-down the furnace and allow molten alloy to furnace cool in the crucible. The microstructures of the dip samples as well as sections from the cast billets were characterized using light optical microscopy, X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy. Additionally, chemical analysis was performed to determine uranium and iron content.

5.3.1.1.1 Carbon Steel Crucible Melts

Uranium-aluminum alloy melts were prepared using carbon steel crucibles for compositions from 13.2 to 50 wt % uranium. Figure 5.11 shows typical microstructures for dip samples collected from these alloy melts. It is rather easy to distinguish between the UAl₃ and UAl₄ phases in optical metallography pictures because the UAl₃ phase is blocky whereas the UAl₄ phase is chevron shaped.



Figure 5.11. Typical Microstructures from Dip Samples collected from Uranium-Aluminum Alloy Melts with 13.2-40 wt % U in Carbon Steel Crucibles

13.2 wt % U-AL

For an alloy with 13.2 wt % U, the expected microstructure would consist of the eutectic microconstituents. However, in the microstructure of Figure 5.11(a), the matrix consists of primary Al (solid solution) phase with the interdendritic regions occupied by the eutectic. Quantitative microscopy, to determine the volume fraction of the primary phase, led to a determination of the alloy composition of approximately 10 wt % U. This would explain the discrepancy in the expected and experimental microstructures. XRD analysis found only two structurally distinct phases present in the microstructure. These were identified as the Al (solid solution) phase and the UAl₄ intermetallic compound. Compositional analysis via Inductively Coupled Plasma Emission Spectroscopy reported a uranium concentration of approximately 12 wt % and also indicated that approximately 0.5-1.0 wt % Fe was found in the melt. SEM/EDS analysis from dip samples collected during processing shows a matrix of primary aluminum dendrites surrounded by the eutectic, Figure 5.12.







Figure 5.12. SEM Images of Primary Al Dendrites and the UAl₄ Eutectic Microconstituent (a,b) and their Corresponding EDS Peaks(c,d)

<u>20 wt % U-Al</u>

For a 20 wt % uranium alloy the microstructure, according to the equilibrium phase diagram, should be comprised of a two phase mixture with approximately 13% UAL and 87% eutectic. From Figure 5.11(b), it is clear that a three phase mixture is present. XRD analysis identified three crystallographically distinct phases as UAl₃, UAl₄, and Al (solid solution). The appearance of primary aluminum dendrites within this hypereutectic microstructure is contradictory to the equilibrium phase diagram. A plausible explanation of this phenomenon has been given by Bramfitt and Leighly (Reference 5.7) and Munitz et al. (Reference 5.8), based on their previous studies of the uranium-aluminum alloy system. As the primary UAl₄ phase forms during cooling, growth is sluggish allowing for the possibility of liquid undercooling. Examination of the metastable liquidus extensions and the coupled eutectic growth region proposed by Munitz et al (Figure 5.13) shows that it is conceivable that the liquid may reach a level of undercooling such that Al nucleation is energetically favorable. With the subsequent nucleation and growth of these non-faceted Al dendrites, heat is released thereby raising the liquid temperature to a level such that formation of the eutectic results. Thus, as in Figure 5.11(b) we would expect to observe the Al dendrites adjacent to areas of eutectic. A further interesting observation is the appearance of the UAl₃ phase in this room temperature microstructure. This can be accounted for by non-equilibrium cooling conditions and the sluggish nature of the peritectic (L + UAl₃ \rightarrow UAl₄) reaction. Primary UAl₃ forms on cooling a 20 wt % uranium alloy below the liquidus temperature; further cooling to below the peritectic temperature (731 °C) will result in the formation of the UAl4 phase by the peritectic reaction L + $UA_{1} \rightarrow UA_{4}$. The manner in which this reaction takes place, as shown in Figure 5.14, results in the sluggish formation of UAL, and as the temperature continues to decrease a temperature (646 °C) is finally reached whereby any remaining liquid transforms to the eutectic via the reaction ($L \rightarrow UA_{L} + Al$). Thus, any unreacted primary UA₁ is retained in the room temperature microstructure. Compositional analysis of these samples reported an iron concentration of 0.5 wt %. This level of iron impurity can be directly traceable to the starting materials of the melt.

<u>30 wt % U-Al</u>

The 30 wt % U alloy sample (Figure 5.11(c)) shows a complex three phase microstructure. From the phase diagram, an alloy with this composition should contain approximately 32% primary UAl₄ and 68% eutectic. Once again the previously mentioned non-equilibrium cooling and sluggish nature of the peritectic reaction can account for the retained UAl₃ which results in the three phase microstructure. Additionally, evidence of Al dendrites in this hypereutectic alloy is documented. XRD analysis also detects three distinct phases with the amount of the UAl₃ phase being slightly greater than in the 20 wt % alloy. From Figure 5.11(c), it is quite interesting to notice the blocky UAl₃ phase with a distinct layer of second phase around its edges. This phenomenon is often referred to as peritectic envelopment since it results from the peritectic reaction as UAl₄ is formed at the interface between the liquid and the UAl₃ phases. Compositional analysis of this alloy melt yielded a value of approximately 1 wt % Fe. Once again the low level of iron in these samples can be traced back to the impurities within the raw materials (Al and



Figure 5.13. Metastable Liquidus Projection and Coupled Eutectic Growth Zone for Undercooled Uranium-Aluminum Alloys



Figure 5.14. Schematic Representation of the Peritectic Reaction that Occurs during the Solidification of Uranium-Aluminum Alloys (adapted from Reference 5.9)

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depleted U) and no substantial melt-crucible interactions seem to be occurring. SEM/EDS analysis of this sample shows a complex three phase microstructure consisting of UAL₃, UAl₄, and Al, Figure 5.15.



(a) 30 wt % U

Figure 5.15. SEM Micrographs showing the Complex Multi-Phase Microstructure of an Al-30 wt % U Alloy

40 wt % U-Al

Optical metallography for the 40 wt % U melt samples (Figure 5.11(d)) shows a complex three-phase microstructure. In these samples it is difficult to distinguish between the UAl₃ and UAl₄ phases. Some evidence of a secondary phase forming at the periphery of a primary phase provides some indication of peritectic envelopment and allows for the identification of the individual phases. The amount of primary intermetallic phase in these microstructures whether it is UAl₃ or UAl₄ is greater than in the lower wt % U alloys. From the equilibrium phase diagram one can predict the relative amounts of the equilibrium phases as 52% UAl₄ and 48% eutectic. XRD data confirm the occurrence of a three phase mixture with UAl₃, UAl₄, and the Al phases. For this composition, the XRD results seem to indicate a slightly larger amount of UAl₃ compared to UAl₄.

Compositional analysis reported a value of 38.5 wt % U and 4 wt % Fe for these samples. It thus appears that some additional iron above the impurity levels of the starting materials has been incorporated into the melt. The obvious source for this additional iron is through crucible wall dissolution.

50 wt % U-Al

An additional alloy melt with a composition of 50 wt % uranium was attempted and results are shown in Figure 5.16. The processing temperature of this melt was approximately 1400 °C. It is quite apparent from the condition of the crucible that significant attack of the carbon steel by the molten alloy occurred. XRD results from dip samples collected during melting identified a ternary Fe₄Al₈U compound. Compositional analysis from granular materials collected from the crucible returned values of 25 wt % Fe. Thus, it is evident that carbon steel crucibles are limited to below 1400 °C which correspondingly limits their use to alloys below 50 wt % U.



Figure 5.16. Carbon Steel Crucible from an Al-50 wt % U Melt Heated to 1400 °C

Billet Samples from Carbon Steel Melts

Additional microstructural investigations were performed on samples sectioned from the cast billets. For the melts using carbon steel crucibles, the billets were formed by allowing the molten alloy to solidify in the crucible after the induction furnace power had been turned off. This allowed for slower cooling of the melt resulting in near-equilibrium solidification conditions. It is believed that these slower cooling conditions will be more representative of the final melt and dilute process. As a result, one of the main questions to be investigated is the issue of density driven alloy segregation during cooling. The

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density of the intermetallic compounds in the uranium-aluminum system are greater than the corresponding liquid from which they form (i.e., for a 30 wt % alloy the density of liquid is 3.56 g/cc whereas the theoretical densities of UAl₄ and UAl₃ are 6.06 and 6.80 g/cc respectively). Thus, it might be expected that any intermetallic phases formed during solidification would settle to the bottom of the crucible.

Figure 5.17 shows microstructures from samples sectioned from the top, middle, and bottom of a 30 wt % uranium alloy billet. Examination of these micrographs reveals a 5% difference in the amount of primary intermetallic phase from the bottom of the billet to the top. XRD analysis determined that the only phases present were the UAl₄ intermetallic and the Al phase. This differs somewhat from the dip sample results where XRD data reported a three phase microstructure. Thus, it would appear that the slow cooling offered by allowing the melt to solidify in the crucible as the furnace cooled provided adequate time for the sluggish peritectic transformation of L+UAl₃ \rightarrow UAl₄ to go to completion. It should be noted, however, that one explanation for XRD analysis failing to find any UAl₃ phase could result from the sensitivity of the technique. XRD analysis will only detect phases that are present in approximately 5 vol % or greater. Thus, it is possible that only a small fraction of the unreacted primary UAl₃ could be present in the microstructure. As a result, detailed SEM/EDS analysis was performed to provide further insight into the details of the microstructural transformations in this alloy melt.

Figure 5.18 shows the micrographs of these samples and the corresponding EDS patterns from regions within these samples. From these SEM micrographs, the presence of three distinct phases is observed. EDS analysis confirms this with the UAl₃, UAl₄, and Al phases being documented. It is interesting to note that from the EDS patterns of the UAl₄ phase a peak is present for iron. As previously mentioned this iron can result from either impurities from the starting materials or from crucible wall dissolution. The interesting point here is that iron appears to selectively partition to the UAl₄ intermetallic phase rather than either the UAl₃ or Al phases. A search of the literature reveals that in the iron-uranium system two intermetallic compounds UFe₂ and UFe₆ have been documented (Reference 5.10). Additionally, it has been shown that in ternary U-Fe-Al alloys the compound U(Fe,Al)₂ forms as a result of the two UM₂ type phases being isomorphic. In this situation, it is possible for Fe or Al to substitute for each other and to occupy similar sites in the U(M)₂ crystal lattice.

Given these results it thus seems plausible that Fe could substitute for Al in the UAl₄ compound. A further question that arises is why does this same simple substitution phenomenon also not occur in the UAl₃ phase with Fe substituting on some of the Al sites. The reason for Fe substituting for Al in the case of UM₂ compounds is that the UAl₂ and UFe₂ compounds have the same crystal structure. If we look at the UAl₄ and UAl₃ cases there are no analogous compounds in the U-Fe binary system. However, the UFe₆ compound is closer in stoichiometry to the UAl₄ compound and the crystal structures of both are similar. Thus, it would seem that Fe should preferentially partition to this phase rather than the UAl₃ phase.



(a) 30 wt % U Top



(b) 30 wt % U Middle



(c) 30 wt % U Bottom

Figure 5.17. Typical Microstructure from the Top, Middle, and Bottom of an Al-30 wt % U Casting in a Carbon Steel Crucible



(a) SEM Image of Al-30 wt % U



(b) EDS Trace from a UAl₄ Particle

Figure 5.18. SEM Image from a Billet Sample of Al-30 wt % U and the Corresponding EDS Scan

5.3.1.1.2 Graphite Crucible Melts

Following the initial experiments involving carbon steel crucibles, it was decided to perform similar experiments using graphite crucibles which would allow for higher wt % uranium alloy melts and no chance for iron contamination via crucible dissolution.

Figure 5.19 shows typical microstructures from the dip samples collected during melting. These microstructures are similar to those previously documented from the carbon steel crucible experiments. Once again, the 13.2 wt % U melt shows evidence of primary aluminum dendrites indicating a composition slightly aluminum rich with respect to the intended eutectic composition. The 20-40 wt % uranium alloys also show evidence of complex three phase microstructures comprised of the UAl₃, UAl₄, and Al phases. XRD analysis identifies three crystallographically distinct phases with the amount of metastable UAl₃ increasing in the dip samples as overall uranium concentration increases. Evidence of the sluggish nature of the peritectic reaction resulting in envelopment of the primary phase is also observed. One distinguishing characteristic of the graphite melt dip samples is that the sizes of the intermetallic phases are larger than those seen in the carbon steel melt samples. Additionally, preliminary compositional analysis for iron levels in these samples has shown a maximum of 0.5 wt % Fe. This level of iron is attributable to the impurities in the starting materials and does not increase with the increasing processing temperatures necessary for higher wt % U alloys as in the carbon steel melts. With the use of graphite crucibles, it was possible to make melts with compositions of 50 wt % U and 67 wt % U. For the 67 wt % U melt, XRD analysis documented only two phases present in the microstructure. This two-phase mixture was comprised of the UAl4 and UAl₃ intermetallic compounds.

SEM analysis of these graphite crucible dip samples has shown similar results to the carbon steel melts. Iron has been shown once again to selectively partition to the UAl₄ phase in these samples. Additionally, however, it has also been shown that Si appears to preferentially partition to the UAl₃ phase (Figure 5.20). This can be explained by examining the phases and their respective crystal structures in both the U-Al and U-Si binary systems. Both binary system have an intermetallic phase of the form UM₃ and in both systems the crystal structure of these UM₃ type phases is the ordered Cu₃Au structure. Thus, it is quite conceivable based on crystal structure and similar atom size that impurity silicon atoms can simply substitute for Al atoms to form a U(Al,Si)₃ compound.

Billet samples for compositions from 20-40 wt % U have also been examined. Results for the 30 and 40 wt % U samples were similar to the carbon steel billet samples of the same composition. XRD data identified only two phases present (Al and UAl₄) in samples sectioned from the top, middle and bottom of the cast ingot. The amount of intermetallic phase appears to increase slightly on going from the top to the bottom of the casting owing to density driven segregation of the aluminides. Table 5.7 shows results for concentration of uranium on going from top to bottom of the cast billets as determined by quantitative metallography. For the 20 wt % U samples XRD analysis identified three phases present in the microstructure. These phases were the UAl₄, UAl₃, and Al phases. It is not completely unexpected for some metastable UAl₃ phase to be present based on the processing treatment for these samples. For the carbon steel billet samples the cast ingots were produced by simply shutting off the induction furnace power and allowing both furnace and crucible to cool simultaneously. The cooling rate for this procedure was quite slow, thus providing adequate time for the peritectic reaction to go to completion. Page 5.36 of 5.82

For the graphite melts, cast ingots were produced by pouring molten alloy into graphite molds and allowing these molds to cool in air. Due to the relatively high thermal conductivity of graphite, the cooling rate should be increased in this case. As a result, the peritectic reaction may not have sufficient time to go to completion which would in turn account for the small amount of UAl₃ documented by XRD analysis.



(c) 30 wt % U

(d) 40 wt % U





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(a) SEM Image of Al-30 wt % U



(b) EDS Trace from UAl₃ Particle

- Figure 5.20. SEM Image of a Primary UAL Phase and Its Corresponding EDS Scan for an Al-30 wt % U Dip Sample
- Table 5.7. Uranium Concentration Determined via Quantitative Metallography forthe Top, Middle, and Bottom Sections of an Al-30 wt % U Cast Ingot

Location	Concentration wt %U	% Error
TOP	30	+/- 1 wt %
MIDDLE	26.5	+/- 1.5 wt %
BOTTOM	35	+/- 1 wt %

Summary of Evaluation of Cast Microstructures and Crucible Materials

Uranium-aluminum alloy melts have been produced with compositions from 13.2 to 67 wt % U using both carbon steel and graphite crucibles. For the lower wt % U melts (< 30 wt % U) neither crucible seems to offer any advantage over the other. The liquidus temperatures for alloys of these compositions are below 1000 °C and dissolution of the carbon steel crucibles by the molten alloy is not appreciable. Impurity elements found during compositional and SEM/EDS analysis can all be attributed to the original starting materials. However, for the case of higher wt % U melts (> 40 wt % U) graphite is the crucible material of choice. The liquidus temperature for alloys of these compositions rises rapidly to a maximum of 1550 °C for the UAl₃ intermetallic compound. Significant dissolution of the carbon steel crucible at these temperatures resulted in extensive melt contamination and crucible failure. This is evident in Figure 5.21 which shows %Fe in the dip samples versus melt temperature of the carbon steel melts. Below 1000 °C, little attack (approximately 2%) is documented but above 1000 °C the amount of attack increases quickly.





Figure 5.21. Iron Content of the Carbon Steel Dip Samples versus Melt Temperature

Dip samples taken from both sets of experiments showed similar results. The relatively small volume of molten metal collected cools rapidly resulting in non-equilibrium microstructures as evident by the observation of the UAl₃ phase in room temperature microstructures. Billet samples from these experiments solidified under near-equilibrium conditions. Typically, these samples showed only a two phase mixture of the equilibrium phases as predicted by the equilibrium binary U-Al phase diagram. It is believed that these samples will be more representative of the final melt-dilute SNF form microstructures. Segregation of the aluminides initially appears to be of little concern. Relatively little difference is discernible between optical photomicrographs of the microstructures taken from the top, middle, and bottom of the cast ingots.

The documentation of the selective/preferential partitioning of impurity atoms (Fe and Si) to the intermetallic phase could prove to be invaluable. For the melting of irradiated assemblies the issue of where and how the fission products are incorporated into the melt has been raised. The results for iron and silicon may allow for the development of a prediction criterion for the incorporation of fission products into the different phases in this system which could subsequently be assessed using non-radioactive surrogates. Additionally, if it is necessary to add poisons for enhanced criticality stability, information gained from knowing how Fe and Si selectively partition may help in selecting possible poison elements, such as B or Gd, and also in predicting where they may reside in the final microstructure.

5.3.1.2 Evaluation of In-Line Process Control

Proper dilution of the DOE SNF assemblies during melt and dilute processing is required to ensure that the HEU has been properly treated. Thus, the use of density measurements as a method of determining the composition of uranium-aluminum alloys was investigated. The possible extension of this method to the determination of fissile uranium enrichment level in uranium-aluminum alloys was also evaluated.

5.3.1.2.1 Theoretical Considerations

A technique to use density (specific volume) measurements to infer uranium composition in uranium-aluminum alloys was developed by Aronin and Klein in 1954 (Reference 5.11). The reproducibility of measurements under optimum conditions for 7-21 wt % uraniumaluminum alloy was found to be ± 0.03 wt % uranium using density measurements. The technique was shown to give accurate results provided the following conditions could be met:

- 1. Compositions of the phases present must be known;
- 2. Densities of the phases present must be known;
- 3. Volume of the solid must be the same as that measured (no voids present);
- 4. Impurities or non-equilibrium phases must not interfere;

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5.3.1.2.2 Preliminary Studies

A blind application of the method was performed at SRTC. A number of grab samples were taken of an aluminum-uranium alloy; a sample of pure aluminum was also taken. The aluminum sample and fourteen alloy samples were weighed in air (dry) and then while immersed in water at a temperature of 23 °C. The results are shown in Table 5.8. The density of a sample can be determined using the dry and immersed weight measurements as follows:

$\rho = \rho_{\alpha} (\underline{Wg})$	7)
$Wg-W_{\alpha}$	

Table 5.8. U-Al Alloy Sample Weights, Dry and Wet

Dry Weight, g	Wet Weight, g
16.4	10.00
24.4	17.12
23.6	16.48
26.8	18.63
24.5	17.21
25.1	17.28
25.5	17.72
24.9	17.15
27.3	18.76
26.9	18.81
26.0	18.17
25.0	17.27
24.8	17.16
24.2	16.87
24.3	16.93
	Dry Weight, g 16.4 24.4 23.6 26.8 24.5 25.1 25.5 24.9 27.3 26.9 26.0 25.0 24.8 24.2 24.3

* aluminum-only sample

The sample densities were measured and then used to determine the uranium weight fraction in the sample, assuming depleted (0.2% enriched) uranium. The calculated density of the aluminum-only sample and the theoretical density of aluminum were used to account for porosity in the samples and an adjusted uranium composition was also calculated for each sample. The results are shown in Table 5.9. The nominal uranium composition ranged from 19% to 24%, with a mean of 22%. The adjusted composition ranged from 23% to 28%, with a mean of 26%. The actual average uranium composition of the melt from which the samples were taken was 33% by weight. Thus, the calculated compositions in Table 5.9 are too low, even when adjusted for porosity. This implies that the porosity of the alloy samples is greater than that of the pure aluminum sample.

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5.3.1.2.3 Effect of Porosity Reduction

A scoping investigation of the benefit of cold pressing the samples was conducted at SRTC. Aluminum and uranium were melted to create a molten mixture with a nominal uranium composition of 24.3% by weight. Two samples were taken from the aluminumuranium melt and, after cooling, their dry and immersed weights measured. The roughly cylindrical samples were approximately 0.5 inches in diameter and 0.75 inches long, with one nearly flat end and one hemispherical end. The two samples were then cold pressed in a 75-ton press to a thickness of less than 1/8 inch. Sample #1 was pressed axially and Sample # 2 was pressed longitudinally. While in the press, the edges of the samples were unconstrained, resulting in radial cracks around their circumference. The pressed samples were then weighed dry and immersed in water. Table 5.10 shows the results of the weighing and the calculated densities and uranium compositions by weight.

The uranium compositions in Table 5.10 were calculated using the same formula as in Table 5.9; hence, the U^{235} content of the uranium was assumed to be 0.2%. The two samples "as cast" were quite consistent in their calculated densities and uranium compositions; the average composition of 21.6% is low compared to the nominal value of 24.3%. As expected, the two samples after pressing have higher calculated densities and, hence, higher calculated uranium content. The average uranium composition of 24.6% is quite close to the nominal value. The pressed samples show more spread in the calculated densities and compositions; this may be due to measurement error or the result of the handling of the samples. Two samples do not provide enough data upon which much meaningful analysis can be done. However, the results suggest that a significant improvement in the accuracy of the density method may be realized by cold pressing the samples before weighing. More samples over a range of uranium compositions should be taken and measurements made to confirm and better quantify this benefit.

5.3.1.2.4 Determination of Uranium Enrichment

The investigations discussed to this point have dealt with a method for determining the uranium content (weight fraction) of a binary aluminum-uranium alloy. The quantity of primary interest to the melt and dilute program, however, is the uranium enrichment, i.e., the fraction of the uranium that is the fissile isotope U^{235} . It is the U^{235} that is to be diluted by adding depleted uranium (i.e., having less than 0.7% U^{235}) to yield a mixture that has a resulting enrichment below some criterion (e.g., 20%). The density method can account for the enrichment level by adjusting the average weight of the uranium as the ratio of U^{235} to U^{238} changes. These effects are small, as the difference in the weights of the two isotopes is a small fraction of their weights. This effect is "diluted" even further by the addition of the much lighter element aluminum and the mixture of isotopes that constitute fission products.

		Uranium Compos	sition (by weight)
Sample ID	Density (gm/cm ³)	nominal	adjusted
97-25-6	3.35	0.241	0.281
97-25-7	3.31	0.229	0.269
97-25-8	3.27	0.216	0.257
97-25-9	3.36	0.244	0.284
97-25-10	3.21	0.197	0.239
97-25-11	3.27	0.216	0.257
97-25-12	3.21	0.197	0.239
97-25-13	3.19	0.191	0.233
97-25-14	3.32	0.232	0.272
97-25-15	3.31	0.229	0.269
97-25-17	3.23	0.204	0.245
97-25-18	3.24	0.207	0.248
97-25-21	3.30	0.226	0.266
97-25-23	3.29	0.223	0.263
mean	3.28	0.218	0.259
st. dev.	0.22	0.017	0.016

Table 5.9. Uranium Composition Inferred from Density of U-Al Alloy

Table 5.10. Improvement in Accuracy of Density Method **Resulting from Cold Pressing of Samples**

Sample Number	1	1	2	2	
Sample Condition	As Cast	Cold Pressed, Axially	As Cast	Cold Pressed, Longitudinally	
Dry Weight, g	25.13	25.18	22.78	22.76	
Immersed Weight, g	17.44	17.58	15.82	16.13	
Calculated Density, g/cm ³	3.27	3.31	3.27	3.43	
Inferred Uranium	21.5	22.8	21.6	26.4	
Weight percent					
Actual Uranium	24.3	24.3	24.3	24.3	
Weight percent					

Average calculated uranium weight % as cast:	21.6
Average calculated uranium weight % cold pressed:	24.6

Average calculated uranium weight % cold pressed:

The method of Aronin and Klein provides a means to see the sensitivity of alloy density to uranium enrichment for a range of aluminum-uranium mixture fractions. Equation 5) can be written with the enrichment level as a variable and solved for the density in terms of the enrichment and overall uranium weight fraction. Fission products are not accounted for in this technique. Table 5.11 shows the results of calculating the variation in alloy density for uranium weight fractions ranging from 10% to 60% and enrichments ranging from 10% to 95%. The results in Table 5.11 show clearly that, for a given overall uranium weight fraction, the alloy density is insensitive to enrichment, particularly at lower uranium compositions. Thus, to determine the enrichment from an alloy density measurement, one would have to get a very accurate density measurement, and it would be necessary to obtain independently a very accurate overall uranium composition. Given this, the task of determining uranium enrichment from an alloy density measurement appears to be intractable.

The results in Table 5.11 (and those reported in Reference 5.11 and earlier in this report) show that the density method has utility as a means of calculating overall uranium composition; pressing the samples to reduce porosity improves the accuracy of the method. However, in an application where significant quantities of fission products or other impurities will be present, even that utility is unclear. It does seem clear that another technique will be required to determine the uranium enrichment level in a melt-dilute alloy sample.

	U-Al Density (gm/cm ³)								
f \ x * 0.10	0.20	0.30	0.40	0.50	0.60				
0.10 2.937	3.219	3.561	3.984	4.522	5.227				
0.20 2.94	3.22	3.56	3.98	4.52	5.23				
0.30 2.94	3.22	3.56	3.98	4.52	5.22				
0.40 2.94	3.22	3.56	3.98	4.52	5.22				
0.50 2.94	3.22	3.56	3.98	4.52	5.22				
0.60 2.94	3.22	3.56	3.98	4.52	5.22				
0.70 2.94	3.22	3.56	3.98	4.52	5.22				
1 0.80 2.94	3.22	3.56	3.98	4.52	5.22				
0.95 2.936	3.217	3.558	3.979	4.514	5.214				

Table 5.11. Effect of U²³⁵ Enrichment on Density of U-Al Alloy

* x is the alloy uranium fraction by weight and f is the U^{235} atom fraction in the uranium component (enrichment).

The results reported in Table 5.11 assume an ideal two-component alloy of aluminum and UAI₄, no porosity or impurities (e.g., fission products).

5.3.1.1 Evaluation of Melt Stirring Technique

Stirring of the molten material inside the crucible may be accomplished by either conventional mechanical stirring, which must be used if a resistance furnace is employed, or by the natural stirring action that is found in an induction furnace. There are distinct advantages in the induction melting process because of the inherent agitation of the melt that accompanies the action of an induction coil.

5.3.1.3.1 Mechanical Stirring

Mechanical stirring is typically accomplished by using a motor-driven shaft on which is fixed an agitator. Shaft rotational speeds vary depending on the degree of agitation desired but for this application have been fixed at approximately 60 rpm. For use in molten aluminum, a stainless steel shaft is recommended for good resistance to molten attack. In preliminary experiments, the agitator was constructed of plain carbon steel and was formed into a basket to hold the depleted uranium. Observation of the melt agitation revealed that only the central portion of the molten volume was stirred by the mechanical stirrer. In addition, after stirring was complete, the steel basket was almost completely consumed. Future experiments employed a machined graphite agitator with holes drilled to accommodate the uranium additions. This agitator was found to withstand the molten attack but still produced limited agitation of the melt.

5.3.1.3.2 Inductive Stirring

Modern induction furnaces operate at frequencies of 70 to 5000 Hz, allowing high power densities and producing a natural stirring action in the melt. When alternating current is applied to an induction coil, it produces a magnetic field which in turn generates a current flow through the charge material, heating and finally melting it. The amount of energy absorbed by the charge depends on the magnetic field intensity, electrical resistivity of the charge and the operating frequency. A second magnetic field is created by the induced current in the charge. Because these two fields are always in opposite directions, they create a mechanical force that is perpendicular to the lines of flux and cause metal movement or stirring when the charge is liquefied. The mechanical force stays perpendicular to the field only in the center of the coil; on both ends of the coil it changes direction. The metal is pushed away from the coil, moves upward and downward, and flows back. This is referred to as four-quadrant stirring, which aids in alloy and charge absorption and produces a more chemically and thermally homogeneous melt. The stirring is directly determined by the amount of power induced and is inversely proportional to the square root of the frequency. Therefore, the higher the power and the lower the frequency, the more intense the stirring.

Melting bath agitation is caused by the induction coil itself, depending on the power input and the frequency. However, use of this coil to assist in the bath agitation is basically limited to the melt-down period. If it is desired to agitate during the cooldown period, a second system may be used. This involves electromagnetic agitation with an additional coil. This coil is operated at 50 to 60 Hz and will induce stirring with no temperature increase. The melt agitation produced by operation at this frequency also differs somewhat from that at higher frequencies but is very effective in maintaining melt homogeneity.

5.3.1.4 Evaluation of Ternary Constituent Effects

Preliminary studies to identify the potential ternary constituents for the melt-dilute process have been performed. These studies involve an assessment of the possible ternary elements excluding radioactive fission products (the role of fission products will be discussed in subsequent sections). The majority of the stable ternary elemental additions to the melt-dilute alloy result from either intentional alloying additions to the aluminum cladding alloys or from impurities in the uranium used to manufacture the fuel meat. Cladding alloys for typical MTR type fuel elements were manufactured by three countries namely, France, Germany, and the United States. The major alloying additions in the French cladding are magnesium, iron, silicon, and nickel. German and US cladding alloys are based on the standard ASTM designated aluminum alloy. There are only two major alloying additions to 6061 aluminum. These are magnesium and silicon.

Examination of the typical impurities within the uranium metal used to fabricate typical research and test reactor fuel assemblies shows that the highest concentration impurities are carbon, iron and silicon. However, it must be noted that the level of these impurities is on the order of a few hundred ppm which is considerably lower than their concentrations in the cladding alloys.

Ternary constituents have the potential to affect the melt-dilute process in several ways:

- Increase/Decrease in the liquidus temperature of the alloy
- Shift of the phase boundary in the alloy system
- Synergistic chemical effect
- Compound/phase formation or suppression

As a first approach to assessing the potential impact of these ternary constituents, ternary isothermal section phase diagrams such as the one previously provided for the U-Al-Si system should be constructed for the temperature of interest. Construction of these isothermal sections can be performed using the binary phase diagram as a starting point. Isothermal sections for 800-1000 °C for the U-Al-Mg, U-Al-Fe, and U-Al-Ni systems will be developed.

5.3.2 Melt-Dilute Off-gas System Development

Volatilization of fission products and gases will occur during the melt-dilute processing of Al-base DOE SNF. Noble gases such as krypton and xenon will be released immediately upon the melting of the fuel. Fission products such as cesium and tellurium, will volatilize

once the melt temperature reaches the boiling point for these elements. For cesium and tellurium the candidate melt temperature from 800-1500 °C is high enough to cause volatilization. As a result, the design of an off-gas system for the collection of the volatile and semi-volatile fission products is paramount. This section identifies the activity/amounts of these volatile fission products, reports on previous volatilization studies concerning MTR fuels, and offers a preliminary design for a melt-dilute processing technology off-gas system

5.3.2.1 ORIGEN Calculations for Radionuclide Inventory for Material Test Reactor SNF

Calculations of radioactive nuclide inventories for typical Material Test Reactor spent nuclear fuel assemblies are underway. The SAS2 module of the SCALE code package is being used to perform 1-D depletion calculations using a 44 group ENDF-B/V crosssection library. These depletion calculations are a necessary input to the ORIGEN-S code which calculates the activity (Ci) and mass quantities of fission products, actinides, and light elements generated during reactor operation and after shutdown. Several representative MTR type fuel assemblies are being considered in the hopes of providing an upper and lower limit of the expected radioactive nuclide inventories in these types of fuel for input into the design of a fission product recovery system for the melt-dilute project.

Due to the fact that radionuclide inventories at any time after irradiation are a function of fuel burnup, initial enrichment, reactor operating history, and shutdown time, all of these variables must be considered when performing ORIGEN-S calculations for a particular fuel type. In order to begin performing these analyses, scoping calculations have been performed to isolate the relative effects of each of these variables individually (with respect to their effect on radioactive nuclide inventory). For this scoping study the Missouri University Research Reactor fuel was chosen.

5.3.2.1.1 MTR Fuel Assembly Description

Most traditional MTR type fuel assemblies (3" square x 3' tall) are operated in small research and test reactors. These fuel assemblies are highly enriched in the isotope U^{235} (93.5 wt %) however, some are enriched to ~45 wt % and others are as low as ~20 wt %. Typically anywhere from 4 to 20 assemblies are operated in the core at any given time and the initial U^{235} contents of any assembly can range from ~100 g up to ~1000 g. Most of these reactors are operated at relatively low power levels (~1-50 MW) and the average power produced by any given fuel assembly is ~ 1-2 MW.

Some of these reactors are operated in a continuous fashion, while many are routinely started up and shutdown several times a week. Because the specific operating characteristics of any given reactor fuel type can vary widely, one must consider the total burnup a given fuel assembly experiences in terms of total MWd as a key variable which affects radionuclide inventory. In many cases, the total burnup experienced by a given individual fuel assembly from the time it is charged into the core until the time it is discharged (for final storage) is ~200 MWd.

Since many of the MTR fuel assemblies which are scheduled to be received at SRS over the next 30 years can also have a wide range of decay times since discharge from the reactor (3-50 years), ORIGEN-S calculations will consider the following fuel decay times for each fuel analyzed; 0, 3, 5, 10, 25, 50, 100, 500, 1000, 10,000, and 100,000 years respectively.

5.3.2.1.2 Reactor Operating History Study

The first variable to be considered is that of fuel burnup and reactor operating history. For this study, the MURR fuel is chosen due to the somewhat unique operating characteristics of the reactor. The MURR reactor utilized 8 assemblies arranged to form an annular core shape. Each assembly contains ~785 g U^{235} (fresh) and during its lifetime, an assembly can be expected to burn (deplete) ~250 g of U^{235} (~150 MWd of burnup).

To analyze the effects of reactor operating history, several ORIGEN cases were constructed which simulated the MURR reactor operating cycle to vary as follows:

Case #1	Operate @ 10 MW for 5 days, shutdown for 7.5 days	24 cycles
Case #2	Operate @ 10 MW for 10 days, shutdown for 15.0 days	12 cycles
Case #3	Operate @ 10 MW for 20 days, shutdown for 30.0days	6 cycles
Case #4	Operate @ 4 MW for 300 days, no shutdown	1 cycle

The cases were designed such that the total burnup on the fuel is 1200 MWd (full core) or 150 MWd per assembly. Also, the total time from initial reactor startup to fuel discharge is 300 days. Case #1 is the actual reactor operating cycle which the MURR fuel experiences while cases #2 - #4 are contrived to analyze the effects operating history has on radionuclide inventory.

Despite the fact that each ORIGEN run calculates inventories for hundreds of radionuclides, several key species were identified as having the most significance in terms of volatile fission products needed to be evaluated for the design of a recovery system. These radionuclides are Ce¹³⁷, Sr⁹⁰, I¹²⁹, Te^{127m}, Tc⁹⁹, Kr⁸⁵, and Se⁷⁹.

Table 5.12 shows the results of these calculations by comparing the mass inventories for each of these 7 radionuclides as a function of selected times after shutdown for each assumed operating cycle. Several key observations and conclusions which can be drawn from this data involve the relative half-lives of the radionuclides of concern.

Nuclide	Time	Case #1	Case #2	Case #3	Case #4
Cs ¹³⁷	5 уг.	41.6	41.6	41.6	41.7
	100 yr.	4.64	4.64	4.63	4.64
	1.0e+5 yr.	~0	~0	~0	~0
Sr ⁹⁰	5 yr.	22.5	22.5	22.5	22.5
	100 yr.	2.45	2.45	2.45	2.46
	1.0e+5 yr.	~0	~0	~0	~0
I ¹²⁹	5 yr.	5.54	5.31	5.31	5.31
	100 yr.	5.54	5.31	5.31	5.31
	1.0e+5 yr.	5.51	5.29	5.29	5.29
Te ^{127m}	5 yr.	6.20e-07	6.05e-07	5.75e-07	6.26e-07
	100 yr.	· ~0	~0	~0	~0
	1.0e+5 yr.	~0	~0	~0	~0
Tc ⁹⁹	5 yr.	33.0	33.0	34.0	33.0
	100 yr.	33.0	33.0	34.0	33.0
	1.0e+5 yr.	23.8	23.8	24.5	23.8
Kr ⁸⁵	5 yr.	0.873	0.873	0.872	0.874
	100 yr.	1.88e-03	1.87e-03	1.88e-03	1.88e-03
	1.0e+5 yr.	~0	~0	~0	~0
Se ⁷⁹	5 yr.	0.192	0.192	0.192	0.192
	100 yr.	0.192	0.192	0.192	0.192
	1.0e+5 yr.	2.35e-02	2.35e-02	2.35e-02	2.35e-02

Table 5.12.	Masses of	Radionuclides	After	Shutdown	(grams)
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In general, the assumed reactor operating cycle has very little affect on the calculated mass quantities of the radionuclides of concern for this study. Short-lived radionuclides (Te^{127m} , Kr^{85}) are slightly affected by the choice of operating cycles whereas the longer-lived nuclides are not. This observation in fact has some theoretical basis since radionuclides with half-lives on the order of a few years or less will begin to undergo some decay during the time periods of reactor shutdown between cycles whereas the very long-lived nuclides will not (i.e., they will simply accumulate with essentially no decay).

As a result of these calculations, one does not necessarily need to consider the exact reactor operating cycle a particular fuel experienced in order to estimate its radionuclide inventory. Simply considering the total fuel burnup is sufficient. Relaxation of this constraint greatly simplifies the analysis since, for many MTR fuels, sparse data exists concerning the exact operating cycle characteristics.

5.3.2.1.3 MTR Fuel Analysis

Having identified total fuel burnup as a key parameter in determining the radionuclide inventory of a spent fuel assembly, the next series of calculations attempted to simulate

three broad classes of highly enriched (93.5 wt %) MTR fuels in terms of their U^{235} loading and operation in a typical reactor core over several ranges of fuel burnup. The three classes of fuel assemblies are as follows:

- Case A High U²³⁵ Loading, High Burnup Fuel
- Case B Medium U²³⁵ Loading, Medium Burnup Fuel
- Case C Low U²³⁵ Loading, Low Burnup Fuel

The ORIGEN calculations were performed assuming a constant power level while varying the irradiation time. The wt.% U in U-Al values were assumed nominal given the assumed U^{235} loading for each assembly type, as shown in Table 5.13.

Figures 5.22-5.24 show the ORIGEN calculated Cs^{137} fission product inventory for each of the three fuel types as a function of fuel burnup and decay time after shutdown. Similar data exist for the hundreds of ORIGEN calculated radionuclides although only Cs^{137} data is shown here.

In Figure 5.22, the curves for Cs¹³⁷ mass as a function of decay time cover a range of core burnup from 100 MWd (lower curve) to 2000 MWd (upper curve). This corresponds to individual assembly burnup values from 12.5 MWd to 250 MWd.

In Figure 5.23, the curves for Cs¹³⁷ mass as a function of decay time cover a range of core burnup from 10 MWd (lower curve) to 500 MWd (upper curve). This corresponds to individual assembly burnup values from 0.83 MWd to 41.6 MWd.

In Figure 5.24, the curves for Cs¹³⁷ mass as a function of decay time cover a range of core burnup from 1 MWd (lower curve) to 50 MWd (upper curve). This corresponds to individual assembly burnup values from 0.0625 MWd to 3.125 MWd.

5.3.2.1.4 Annular Core Calculations

Another series of ORIGEN calculations are planned for highly enriched, U-Al fuel types which are in the form of involute annular core arrangements. Two notable examples of this type of core are RHF and HFIR. In these reactors, the entire reactor core is simply one (or 2) annular piece(s) containing ~10 kg of U^{235} . These reactors are typically used for isotope production and operate at higher power levels (and have considerably higher burnup) than typical single-element composed MTR reactors. The total radionuclide inventories from these reactors may be 10-100 times greater than those from single MTR assemblies and therefore must be considered separately.

Fuel Type	g U ²³⁵ / assembly	wt %U in U-Al	# Assy. in Core	Core Power Level (MW)	Core Burnup Range (MWd)	
Case A	1000.0	70.0%	8	40.0	100-2000	
Case B	500.0	45.0%	12	10.0	10-500	
Case C	100.0	15.0%	16	1.0	1-50	

 Table 5.13. Parameters for Fuel Burnup Calculations



Figure 5.22. Cs¹³⁷ Mass vs. Decay Time for Various Fuel Burnup for Case A Assembly

5.3.2.2 Analysis of Fission Product Release from MTR-SNF

The melting of reactor fuel and reactor core components and the release of volatile fission products from the molten fuel have been studied extensively because of their importance for severe nuclear reactor accidents. Some of these studies have analyzed the release of fission products from aluminum-clad U-Al fuel, including the measurement of fission product release from irradiated fuel and unirradiated fuel using simulated radioactive elements. Of these studies, many were done on SRS uranium-aluminum alloy fuels similar to the FRR fuels which will be the feed material for the melt-dilute process. A literature review on the release of fission products from the melting of irradiated aluminum-clad,

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Figure 5.23. Cs¹³⁷ Mass vs. Decay Time for Various Fuel Burnup for Case B Assembly



Figure 5.24. Cs¹³⁷ Mass vs. Decay Time for Various Fuel Burnup for Case C Assembly

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uranium-aluminum alloy nuclear fuel has been completed under Subtask 5.3 of the technical task and quality assurance plan. A report entitled "Fission Product Release from Spent Nuclear Fuel During Melting (U)", WSRC-TR-0112, was issued in May 1997 (Reference 5.12).

The objectives of this review were to determine the radioactive species generated during the irradiation of aluminum-clad, uranium alloy research reactor fuels and identify the fission gases and products which would be released from spent nuclear fuel during the melt-dilute process. The information from this survey provides baseline data for design of a furnace and off-gas system to process research reactor fuel prior to shipment to a repository.

In the melt-dilute concept, enough uranium would be added to dilute the uranium enrichment to the desired level. In doing this, the ideal melting point of the diluted uranium-aluminum alloy would be near 850 °C, although stirring constraints could drive this temperature up to 1050 °C or higher. The concern in designing an off-gas system for use with the furnace would be in identifying the elements which would be released from the melt process and the ability to trap them. The review of the literature concentrated on these areas. Parts of this review were previously reported in the April 1997 Status Report, WSRC-TR-97-0085.

5.3.2.2.1 Radionuclide Inventory from Typical Foreign Research Reactor Fuels

Foreign research reactors use a number of different fuel designs (Reference 5.13). These can be grouped into five categories: (1) plate-type, (2) concentric tube-type, (3) pin-type, (4) special-type, (5) rod-type. The first 4 designs are aluminum-based while the fifth is a TRIGA type. The plate and tube types of (1) and (2) are known as MTR fuels. MTR fuels are used in a majority of the foreign research reactors. For the typical plate type design, the fuel assembly has a box-like housing about four feet in length with two outside housing plates and two outside fuel plates. The number of fuel elements in an assembly varies between 6 and 23, and the initial U^{235} content varies between 37 gm and 420 gm per assembly. The average burnup of a discharged SNF assembly varies between 15 and 76% U^{235} . The enrichment of MTR type fuels vary from just below 20 to 93%.

The spent nuclear fuel inventory is directly related to the initial mass of fuel, the level of burnup, and the cooling period (decay time) following discharge from the reactor. The radionuclide generation in an irradiated fuel is a function of reactor power level and the duration of the irradiation process.

5.3.2.2.2 Overview and Analysis of Volatile Fission-Product Release Data from Melted U-Al Reactor Fuels

A perspective overview and analysis of data obtained for the following uranium-aluminum reactor fuels is presented in this review: U-Al_x, U₃O₈-Al, U₃Si-Al, and U₃Si₂-Al (Reference 5.14). The systematic data are limited and come from four basic sources:

noble gas release for U-Al dispersion fuel, fission-product release data for U-Al fuels from ORNL studies, fission product release data from U-Al and U_3O_8 cermet SRS product fuels, (References 5.15-5.16) and silicide fuels from the Japan Atomic Energy Institute (Reference 5.17). The data covers fuel U^{235} burnup of 24, 65, 52, and 62% for heating times ranging from 2 minutes to 60 minutes. The data are correlated to present mathematical formulations for the change in time of release rates of fission products from heated U-Al fuels in various environments.

For noble gases such as krypton, xenon, neon, etc., release for the aluminide fuels occurred in three stages at temperatures well above the boiling point of the gases. The first rapid release was observed at 560 °C, along with some blistering of the fuel plates. The next release coincided with the melting temperature of 6061 Al at 585 °C. The last stage occurred at about 650 °C, corresponding to the eutectic temperature of the uraniumaluminum alloy. Maximum temperature in these tests was 700 °C. Less than 0.1% iodine and cesium were released in these tests. Noble gas release from U-Al, U₃O₈-Al and dispersed U-Al fuels in other experiments was found to be similar. However, noble gas release from silicide fuels was radically different from other fuels as seen in Figure 5.25 which shows a comparison of the various fuels. Significant burnup dependence was seen indicating substantial retention capability in the dispersed uranium silicide grain matrix.

The principal species investigated for all these fuels are the noble gases, iodine, cesium and tellurium. Measurements of the volatile fission products like cesium, iodine, tellurium and the ruthenium (normally considered non-volatile) from all the data bases revealed significant dependencies on the ambient medium, fuel burnup, heating-collection time, and fuel composition. These dependencies were generally:

- (1) oxidizing environments greatly enhanced the release of iodine, cesium, and tellurium, (Figure 5.26 shows the variation of releases with atmospheres and temperatures.),
- (2) the amounts of release increased with burnup, (Figure 5.27 shows variation of volatile specie release with burnup.),
- (3) the rate of release varied substantially with time and temperature. (Figure 5.28 shows the variation of fission product release with temperature for U_xSi_y -Al in air.),
- (4) significant fission-product retention in the fuel matrix was observed at temperatures well above the boiling point of individual species (which indicates the possibility of substantial chemistry effects), and
- (5) smaller amounts of volatile fission products are released from dispersed fuels than from alloy fuel. The reverse was found for the U₃Si₂-Al fuel where significantly higher cesium release fractions were observed from the silicide and aluminum dispersion fuels than from the U-Al fuels.

The review article developed an extensive library of correlations for predicting release rates that may vary with time, ambient environment, temperature, and burnup. There were

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Figure 5.25. Noble Gas Release Variation with U-Al Fuel Type and Burnup

some shortcomings, and all of the data bases were limited to 1027 °C maximum fuel temperature, but the library of information contained in this report and in the reports listed in the bibliography should be useful in helping to predict fission product release during the melt-dilute phase in processing FRR spent nuclear fuels. This review article is considered by many as the single definitive work on the subject of fission product release from uranium-aluminum alloy fuels.

5.3.2.2.3 Fission Product Release Phenomena During Melting Experiments

The phenomena that determine fission product release from a core melting accident in a metal-fueled, heavy water reactor have been described in detail by SRS researchers (Reference 5.18). The article discusses data from the experimental database available at that time. Some of this has already been discussed in this literature review, but the comparisons between the different data are important and are presented again here as deemed appropriate.

The release of fission products from U-Al fuel is extremely low until about 650 °C, at which point some microstructural constituents within the fuel begin melting. As a result, the release of volatile fission products from metal U-Al fuel is dominated by releases from the molten state. The majority of the volatile fission products, except noble gases, are released from liquid pools rather than from the solid fuel during the heat up to melting. In some cases, it has been shown that metallic foams can form as the U-Al alloy softens resulting from the agglomeration of fission gas and other gas bubbles. Test evidence indicates that metallic fuel foams occur with low burnup. One metallic fuel element that failed in the SRS reactors because of localized overheating exhibited the onset of foaming. The foam began to form in the fuel and then expanded to force its way through the



Figure 5.26. Variation of Volatile Fission Product Releases from U-Al Alloy Fuel in Steam, Air, and Helium with Temperature



Figure 5.27. Variation of Volatile Species release from U-Al Alloy Fuel with Burnup

cladding cracks. This phenomena was later verified in fuel foaming experiments conducted by SRTC (Reference 5.19). In these experiments, the initial fuel failure occurred as a result of internal cracking or blistering. This resulted in the immediate failure of the cladding and the release of large amounts of fission product gases and volatiles. Continued heating of the fuel caused the cracks and blisters to swell and Page 5.56 of 5.82



Figure 5.28. Variation of Fission-Product Release with Temperature for U_xSi_y-Al Fuel in Air

resulted in approximately a 30% increase in volume. Rapid and significant foam expansion occurred upon reaching the eutectic temperature. The foam was agitated by physical stirring due to the melting and loss of structural rigidity of the aluminum cladding at a temperature of 667 °C, while foam collapse and the concomitant initiation of a melt flow occurred at temperatures greater than 772 °C. Large fission gas/volatile gas releases have been correlated with the cladding melting at 667 °C. Fission gas release has also been associated with the solidification of foamed Al-U fuel, presumably due to the lower solubility of the solid for these species.

The primary reason for the increased rate of fission products (particularly the noble gases, cesium, and iodine) from U-Al fuels after melting is the increased mass transport in the liquid phase. This is exacerbated by the physical stirring due to melt flows. By contrast, release fractions are found to be small at temperatures below the eutectic temperature unless blisters form on the surface of the cladding. Thus, when modeling fission product release, careful attention must be paid to the changes in state occurring when the melting temperature of any microstructural constituent is reached.

The dominant process by which fission products can be released from the fuel is from formation of molten pools in the reactor vessel or coolant piping. The high power density typical of metallic fuels can lead to rapid superheating of the fuel. This superheat enhances the release rate of the fission products by changing the chemical form of the fission products or directly through increased vapor pressure (Reference 5.18). Molten pool geometry affects the mass transfer and activity coefficient of the fission products. Pool depths could be large and have significant natural circulation patterns in the melt. The natural circulation patterns enhance the fission product release. Nucleation of vapor bubbles can also occur as the pool superheats. The formation of these bubbles causes an increase in the release rate by increasing the mobility of the fission products in the melt. The coalescence of the bubbles can lead to a mechanism that rapidly depletes metallic fission products from the molten pool.

The paper reviews the experimental database of several investigators. The fission product release for solid metal fuel is composed of work from ORNL, Knolls Atomic, Japan, SRS, and others. In 1958 Reynolds (Reference 5.20) measured the release of krypton from 20% burnup uranium-aluminum fuel at temperatures between 605 °C and 695 °C. No release of krypton was measured below the eutectic point of the alloy (646 °C). The conclusion reached was that the aluminum matrix was not permeable to gas diffusion until the matrix melts. Above the eutectic point the evolution of krypton followed the expected time dependence of gas diffusion from spherical particles. Reynolds concluded from his data that the UAl₃ and UAl₄ intermetallic grains release krypton to the aluminum at all temperatures. However, the aluminum matrix is impermeable to krypton diffusion until the matrix becomes molten.

Shibata (Reference 5.17) measured fission product release rates with high burnup metallic fuel plates clad with 6061 aluminum. The results were in general agreement with Reynolds in that these rates were small until the aluminum matrix melted. Characterization of the release was analyzed in three stages: (1) blisters forming on the fuel, (2) 6061 clad melting, (3) fuel eutectic point reached. The data gives the release rates of xenon, iodine, and cesium as a function of temperature. The key result of this work is that the release of fission products from the blistering and from the melting of the eutectic phase should be negligible in comparison to the release that occurs upon melting of the aluminum cladding.

Data obtained from ORNL in the early 1960s on uranium-aluminum fuels are in general agreement with that of Reynolds and Shibata. It includes information as a function of temperature and atmosphere for xenon and krypton, iodine, cesium, and ruthenium. The data also provide information on fission product release rate dependence upon burnup of the fuel. The burnup effects appear to saturate above 3% burnup and there is no longer a burnup dependence upon the release of fission products.

SRS fuel melting studies measured the release rates for noble gases, iodine, cesium, and tellurium in atmospheres of steam air, and argon at temperatures between 700-1100 °C. Atmospheric effects appear to be small on release rates in this data. Both cesium and tellurium are released at a faster rate in these experiments than earlier ORNL studies. The data generally support the previous observations of an impermeable aluminum matrix preventing fission product release until melting of the aluminum matrix. Other SRS studies have shown that metallic foams can form as the U-Al alloy softens and swells resulting from the agglomeration of fission gas and other gas bubbles (Reference 5.19). This is an important release mechanism.

5.3.2.2.4 Fission Product Release from Melt-Refining Operations

Melt refining operations used in the production of the common metallic alloys give us information to understand the release rate of fission product elements and compounds from molten pools (Reference 5.21). This experience has shown that dissolved gases are removed from molten metals through:

- a. vapor evolution by diffusion of the gas to the surface of the melt
- b. vapor evolution by diffusion of the gas to bubbles in the melt,
- c. vapor deposition in the slag or skull by diffusion to the crucible or skull region of the melt.

The evolution of vapors from the melt is strongly influenced by the formation and coalescence of bubbles in the melt. Release rates are greatly increased if bubbles form.

Several of the fission products are insoluble in the melt, and can nucleate in the melt to form vapor nuclei. The melt can also contain suspended uranium-aluminum particulate when its temperature is between the solidus and liquidus points. Based on these considerations, there is a strong possibility that the melts will contain bubbles of nucleated fission products attached to the U-Al particulate in the melt.

Experimental data specific to fission product release from metallic melts are available from the early work on reprocessing metallic uranium by melting and from early ORNL data. The reprocessing work was reported by Argonne National Laboratory in a series of studies in 1991 (References 5.22-5.25). In these experiments the release rates of ruthenium, molybdenum, palladium, rhodium, technetium, antimony, tellurium, yttrium, strontium, cesium, iodine, krypton, and xenon were measured from melts of uranium.

About 99% of the noble gases xenon and krypton were released upon melting of the fuel, with the remainder of the noble gases remaining in solution. The noble gases remaining in solution may then provide heterogeneous nucleation sites for the formation of bubbles in the melt (Reference 5.22).

Iodine acted as a metallic compound in the melt refining experiments (Reference 5.26). Iodine was retained in the melt until a temperature of 1400 °C was reached, after which it was released from the melt. No evidence was found for the evaporation of iodine as free iodine in these melt refining operations. The iodine is these experiments may have been bound with uranium as uranium tri-iodide, or with another fission product element. It should be noted that this result disagrees with other findings and is therefore open to question. UI₃ is probably volatile at these temperatures. Barium and strontium exhibited similar behavior in these experiments (Reference 5.24). Cesium was released by vaporization. Tellurium formed a low vapor pressure compound and was not readily vaporized from the melt (Reference 5.25). The remainder of the fission products, ruthenium, molybdenum, palladium, rhodium, and technetium were retained by the melt with no appreciable vaporization. This indicates that substantial losses of these materials do not occur. There was some diffusion of these materials in the melt because a few percent was found in the slag around crucible walls, but no evaporation from the melt surface was observed.

5.3.2.3 Effects of Ternary Fission Product Reaction on the SNF Form

Release of volatile fission products may occur upon melting of the fuel assemblies in the melt-dilute process. At a melt temperature of 850 °C, seven species were identified as primary concerns in the document WSRC-TR-0112 (U). These seven species were Cs¹³⁷, Rb⁸⁷, Te¹²⁷, H³, Ba¹³⁷, Sr⁹⁰ and I¹²⁹ and were selected based on their boiling points, all of which are less than 1000 °C. Kr⁸⁵ was also identified as a potential off-gas species but since it is a noble gas it was considered to be nonreactive.

As part of the background work for the planned off-gas system for the melt-dilute project a literature review of these off-gas species was conducted to determine if intermediate phases or compounds could be formed that would reduce the quantity of these elements in the off-gas stream. In addition, reactions between the off-gas species and the fuel and cladding material (U and Al) were considered, for a total of nine elements. The binary phase diagrams for these elements were analyzed and a matrix of phases was constructed, shown in Table 5.14. A total of 55 known binary phases was identified, the crystal structures of which will be studied to determine if any site substitution of elements is possible. This work is ongoing and should be finished soon.

Another aspect of this work was to determine the composition of a melt composed of fuel elements after two levels of burnup. ORIGEN calculations were utilized for MTR fuel elements in two conditions: high burnup, denoted as 50% and low burnup, taken to be 30%. The majority of the species from the previous list were included in these calculations, as well as Tc^{99} and Se^{79} . The amount of fission products that would be expected in these fuel cells after hold times varying from 0 to 25 years was also calculated.

The composition of a dilute (20% enriched) U-Al alloy was then calculated based on the ORIGEN results. These alloy compositions are shown in Table 5.15 for two levels of burnup and three hold times. As can be seen in this table, all of the fission products were below 1 wt % of the total alloy content. This would suggest that the majority of these elements were within the solubility limit of the phases in the U-Al system and that compound formation is probably of limited concern.

Additionally, investigations were made concerning the possible influence of stable isotopic off-gas species which might be present in typical MTR assemblies. These investigations show that even for burnup in the range of 50%, the amount of stable fission product species are insignificant. The levels of concentration are not high enough to warrant consideration as ternary alloying elements and should have a negligible effect on phase equilibria during processing.

	Ā	U	Cs.	Rb	Te	3 H	Ba	Sr	I
AI		Various solubility of both elements (see phase diagram); Al4U (6); Al3U (ζ); Al2U (η)	Slight solubility of Cs in Al; no other phases	No phase diagram available but no compounds have been observed	Limited solubility of both elements; A15Te; A12Te3	Limited (~ zero) solubility of H in Al; no other phases	Limited solubility of Ba in Al but 5.4 at% solubility of Al in Ba; Al4Ba; Al2Ba; AlBa; AlBa2 phases	Limited solubility of both elements; Al4Sr Al2Sr, Al2Sr3	No phase diagram available
υ	See Al-U		No phase diagram available	No phase diagram available	Sce Te-U	See H ³ -U	No phase diagram available	No phase diagram available	No phase diagram available
Cı	See Al-Cs	No phase diagram available		Complete immiscibility of both elements	Limited solubility of both elements; Cs2Te; Cs2Te2; Cs5Te4; CsTe; Cs2Te3; Cs2Te5; CsTe5	No phase diagram available; CsH is formed	See Ba-Cs	Complete immiscibility of both elements but no phase diagram given	Limited solubility of both elements; CsI; CsI3; CsI4
Rb	Sce Al-Rb	No phase diagram available	See Cs-Rb		Limited solubility of both elements; Rb2Te; Rb3Te2; Rb5Te4; RbTe; Rb2Te3; Rb2Te5	See H ³ -Rb	See Ba-Rb	Complete immiscibility of both elements but no phase diagram given	See I-Rb
Te	See Al-Te	Limited solubility of both elements; UTe; U3Te4; U3Te3; UTe2; U3Te7; U2Te3; UTe3; UTe5	See Ca-Te	See Rb-Te		No phase diagram available	Sec Ba-Te	See Sr-Te	See I-Te
3 H	See Al-H ³	Limited (~0 to 28 wppm) solubility of H in various U allotropes; α, β, δ, ε -UH ₃	See Cs-H ³	No phase diagram available; RbH is formed	No phase diagram available		See Ba-H ³	43.2 at% solubility of H in β-Sr; 4.3 at.% solubility of H in α- Sr; α and β-SrH2	No phase diagram available; HI may be possible but no reference has been found
Ba	See Al-Ba	No phase diagram available	Complete immiscibility of both elements but no phase diagram given	Complete immiscibility of both elements but no phase diagram given	Limited solubility of both elements; BaTe; Ba2Te3; BaTe2	Large solubility of H in Ba (57 at.% at 950°C); α- BaH ₂ ; β-BaH ₂		Two solid solutions formed; no other phases	Limited solubility of both elements; BaI2
Sr	See Al-Sr	No phase diagram available but no compounds have been observed	See Cs-Sr	See Rb-Sr	Limited solubility of both elements; SrTe; Sr2Te3; SrTe2	See H ³ -Sr	See Ba-Sr		See I-Sr
1	No phase diagram available	No phase diagram available	See Cs-1	Limited solubility of both elements; RbI; RbI3	Limited solubility of both elements; Tel; Tel4	See H ³ -I	See Ba-I	Limited solubility of both elements; SrI ₂	

Table 5.14. Compounds and Alloys of Various Off-gas Species with Uranium and Aluminum
Table 5.15. Percentage of fission products expected in an alloy after processing

0 yrs cooling time 10% U in fuel cell 20% U235 after melt-dilute 93% enrichment Grams Wt % in alloy Grams Wt % in alloy (50% burnup) (50% burnup) Element (30% burnup) (30% burnup) Al 4500.00 77.87 4500.00 73.42 U 1162.50 20.12 1627.50 26.55 Cs 137 47.06 0.81 0.54 0.01 Sr 90 29.81 0.52 0.34 0.01 Te 127 0.067200 0.001163 0.000156 0.000003 Kr 85 1.2067 0.0209 0.0127 0.0002 Tc 99 32.44 0.56 0.40 0.01 Se 79 0.3790 0.0045 0.0001 0.0066 I 129 5,4600 0.0945 0.0628 0.0010 Total 5778.92 6128.86 100.00 100.00

Case 2 Assume:

1

Case 1

Assume:

10 years cooling time 10% U in fuel cell

20% U235 after melt-dilute

93% enrichment				
	Grams	Wt % in alloy	Grams	Wt % in alloy
Element	(50% burnup)	(50% burnup)	(30% burnup)	(30% burnup)
Al	4500.00	78.08	4500.00	73.43
U	1162.50	20.17	1627.50	26.56
Cs 137	37.34	0.65	0.43	0.01
Sr 90	23.29	0.4041	0.2700	0.0044
Te 127	0.000000	0.0000	0.0000	0.0000
Kr 85	0.6300	0.0109	0.0067	0.0001
Tc 99	33.33	0.5783	0.3980	0.0065
Se 79	0.3800	0.0066	0.0045	0.0001
I 129	5.5400	0.0961	0.0634	0.0010
Total	5763.01	100.00	6128.67	100.00

Table 5.15. Percentage of fission products expected in an alloy after processing (cont.)

Case 3

Assume:

25 years cooling time

10% U in fuel cell 93% enrichment 20% U235 after melt-dilute

	Grams	Wt % in alloy	Grams	Wt % in alloy	
Element	(50% burnup)	(50% burnup)	(30% burnup)	(30% burnup)	
Al	4500.00	78.34	4500.00	73.43	
U	1162.50	20.24	1627.50	26.56	
Cs 137	26.36	0.4589	0.3000	0.0049	
Sr 90	16.11	0.2804	0.1830	0.0030	
Te 127	0.000000	0.0000	0.0000	0.0000	
Kr 85	0.2400	0.0042	0.0025	0.0000	
Tc 99	33.33	0.5802	0.3970	0.0065	
Se 79	0.3790	0.0066	0.0045	0.0001	
I 129	5.5400	0.0964	0.0635	0.0010	
Total	5744.46	100.00	6128.45	100.00	

5.3.2.4 Preliminary Off-gas System Requirements

Any furnace design will require an off-gas system to capture volatile fission products. The primary contributor to off-gas radioactivity will be Cs^{137} with smaller amounts of Kr^{85} , Tc^{99} , and I^{129} . This report describes some of the available options for design and operation of the off-gas system. All the methods considered include some means for condensing the Cs and Tc followed by a HEPA filter to remove particulates. An iodine absorption bed may also be required. We are assuming for the present that the Kr will be released to the atmosphere. If it must be trapped, a silver mordenite bed operated at dry ice temperature will be used. Several means for final disposition of fission products removed from the off-gas are being studied.

5.3.2.4.1 Cesium Condenser

The simplest method for removal of cesium from the off-gas stream is to cool it to a temperature below its boiling point and to trap the resulting condensate. This will likely be accomplished by use of a metallic labyrinth or other medium on which cesium can be cooled and condensed. Likely candidates for this medium include stainless steel wool, stainless steel demister, stainless steel foil, glass frit, or raschig rings. Other materials such as zeolite may also be considered. The cesium must be kept above its boiling point until it reaches the condenser to prevent its plating out on the surface of the furnace and off-gas piping.

Cesium metal melts at 28.5 °C and boils at 670 °C. The simplest and most effective method for removal of Cs from a hot gas stream is to cool the gas to a temperature well below cesium's boiling point, condensing out the Cs on a cool surface. The Cs can then be disposed of on the condenser medium or be dissolved in an aqueous wash that can then be disposed of to the HLW tanks. The condenser can be located anywhere that its temperature can be kept below 670 °C. The most likely sites are the furnace lid or a trap immediately adjacent to the furnace.

5.3.2.4.2 Iodine Reactor (if needed)

The H-canyon process utilizes an iodine reactor consisting of a vessel filled with berl saddles on which silver nitrate has been coated (Reference 5.27). This reactor is maintained at a temperature between 180 and 200 °C. Other designs for iodine reactors have been considered, most incorporating a silver-loaded, heated bed. An activated carbon bed is also effective for I_2 removal. Although any one of these methods could be utilized in the melt-dilute off-gas treatment process, the activated carbon bed will probably provide the least expensive option if a temperature of less than about 130 °C can be maintained; otherwise a silver-loaded reactor will have to be used.

5.3.2.4.3 Krypton Absorber (if needed)

The issue of krypton absorption is primarily a regulatory one. Preliminary calculations have shown that the radiation dose at the site boundary from the release of this krypton will not exceed 0.04 mrem/year (Reference 5.28), significantly less than the maximum 3 mrem/year dose permitted by 10 CFR 50, Appendix I. Therefore, for planning purposes it is assumed that any Kr released will be vented to a stack without any attempt at removing it from the off-gas stream. Should it become necessary to remove the Kr, a silver mordenite or hydrogen mordenite bed, operated at dry ice temperature, will be effective (Reference 5.29). The primary difficulty in using the Kr absorber is the necessity to operate it at dry ice temperature with a gas stream originating in a 1000 °C or hotter furnace.

5.3.2.4.4 HEPA Filter

No matter what other treatment processes are used to remove fission products from the off-gas stream, a HEPA filter will be used to remove any remaining particulate matter before the gas is finally released to the atmosphere via a stack. HEPA filters are available that use either a replaceable glass medium or a permanent (cleanable) stainless steel medium.

5.3.2.4.5 Furnace Lid

The lid to the furnace could easily incorporate a condensing medium such as stainless steel wool, mesh, or foil. A heat shield between the medium and the melt pool would prevent overheating of the medium by direct thermal radiation. If necessary, cooling coils could be incorporated in the lid design (Figure 5.29).

If the furnace lid temperature cannot be maintained below 670 °C, then a cesium condenser could be placed in the off-gas line outside the furnace. The line leading up to the condenser would have to be heat traced to prevent condensation of Cs in the vent line. The medium in the condenser could be either stainless steel, glass frit, raschig rings, or a zeolite material.

5.3.2.4.6 Disposition of Spent Medium

There are several possible ways to dispose of the condensed cesium:

In Canister

The spent medium can be placed in a melt canister and sealed in with a batch of diluted fuel solid waste or the spent medium can be sealed in a separate container for disposal as solid waste.

Liquid Waste

Cesium can be removed from a stainless steel or glass medium by dissolution with dilute nitric acid or other suitable solvent. The medium can then be returned to service. Acidic waste can be neutralized and sent to the HLW tanks for eventual disposition in the DWPF.

<u>Glass</u>

If glass frit is used as the condensing medium, it may be possible to send it to the DWPF for direct incorporation into the glass waste form.

5.3.2.5 Off-gas System Design Concepts

A conceptual sketch of a typical off-gas system is shown in Figure 5.29. A cooled lid fits on top of the fuel melting furnace so cesium and other volatile metals will collect mainly on the grid of cooled vanes within the lid. Off-gases exit through a high efficiency metal filter which is commercially available. The concept shown here is based on a bottom pouring melt crucible, with the drain controlled by a plug on the end of a magnetically operated vertical rod. Systems of this type are presently used within the DOE complex for casting uranium metal.

After each run the lid is removed to a wash down station for cleanup while the next charge of fuel is added to the crucible. Cesium and other fission products are removed by a water or acid spray and collected for transfer to the high level waste tanks.

Both vanes and filters would be designed to be remotely replaceable in case of pluggage or excessive buildup of metal. According to a vendor, metal filters of this type can be cleaned by back pressure. The capability to provide back pressure could be built into the off-gas system.

5.3.2.5.1 Development Needed

There are a number of questions that must be addressed before detailed design of the offgas system can begin:

- 1. The temperature profile in the canister and furnace should be measured to determine the feasibility of placing a condenser in or on the furnace lid.
- 2. The ultimate capacity and expected longevity of the condenser medium must be determined.
- 3. Any regulatory restraints on disposition of the spent medium or liquid waste must be addressed.



Figure 5.29. Conceptual Design of Melt-Dilute Off-gas System

- 4. The cesium yield of a melt batch should be estimated. The literature suggests that less than half the cesium present in the fuel assemblies will be evolved in the off-gas stream.
- 5. The detailed design of the off-gas system cannot begin until the volumetric flow rate of off-gas can be specified. The options available for operation of the furnace include:
 - Flow induced by natural convection in a closed system,
 - Flow induced by natural convection in an open system,
 - Flow induced by injection of air or inert gas into the furnace.

Obviously, the total flow of gas will vary greatly between these options.

5.3.2.5.2 Conclusions

While removal of volatile fission products from the off-gas stream exiting the spent fuel furnace is necessary, the means for doing so are readily available and require no scientific or engineering break-through. Some developmental effort will be required to answer the uncertainties listed above under the heading of "Unknowns". Providing answers to these questions can proceed in parallel with design and development of the balance of the furnace system and should not constitute a critical path item in the program.

5.3.3 Small-Scale Apparatus Development

5.3.3.1 Small-Scale Equipment Development

Much of the experimental work for the melt-dilute process is being done by simply melting aluminum metal and adding uranium to bring the concentration to the desired level using a bench-scale apparatus. Once the process parameters have been defined, it will be desirable to demonstrate the process with surrogate assemblies that, to the extent possible, duplicate the dimensions and characteristics of MTR fuel assemblies. To carry out small-scale development in the laboratory, depleted uranium metal will be substituted for enriched uranium in the research and test reactor fuel plates.

5.3.3.2 MTR Assembly

Most MTR fuel assemblies are approximately 3 inch square and 3 feet tall. The aluminum fuel assembly contains rows of flat aluminum-clad plates. The active core or meat section of these plates is produced from powder metallurgical compacts of UAl_x , U_3O_8 , or U_3Si_2 and aluminum powders. The compacts are hot and cold rolled to fabricate plates of the proper size and shape. Individual plates are roll swaged into fuel assembly side plates and combs and end fittings are attached. It is not necessary to use precisely manufactured fuel assemblies for small-scale demonstration tests, but it is necessary that the assembly size and final melt composition approximates actual conditions.

For small-scale test assemblies, simulated plates were produced by casting cylindrical, uranium-aluminum alloy billets of approximately 20 wt % uranium composition. This composition was selected so when the entire assembly is melted the melt composition will be about 10 wt % uranium in aluminum, the approximate composition of a melted spent fuel assembly. The billets were extruded to produce an aluminum clad flat plate. Because of the small size of the laboratory extrusion press, only half width plates could be made; therefore, each assembly element is made up of two of the smaller extruded fuel plates. Also, the assembly contains only nine rows of plates instead of approximately 18 because of the thicker extruded plate dimensions. Figure 5.30 is a photograph of one surrogate assembly with the cover plate removed to expose the extruded elements.

These fuel assemblies will be used to demonstrate the small-scale process equipment using the Thermcraft resistance furnace. The furnace and equipment are described in the next section.

5.3.3.3 Resistance Furnace Design

Induction and resistance type furnaces are being evaluated for the melt-dilute technology. Induction provides a fast heating rate and allows stirring of the melt using the induction coil, whereas resistance furnaces are slow to heat up and require mechanical stirring of the melt. For small scale development, a resistance furnace was purchased and retrofitted for melting MTR type fuel assemblies.



Figure 5.30. Mockup of MTR Fuel Assembly for Small-Scale Testing

An induction melting system consists of the high and low frequency power supply and cooling water for the coil. Two manufacturers of induction equipment are Inductotherm and Ajax Magnethermic. Both companies offer furnaces and power supplies in the size range needed from melting spent fuel elements as part of their standard product line and, in addition, they offer engineered systems for unique applications. However, induction furnaces are more expensive than resistance furnaces and normally require longer lead time for purchase. The primary advantage of an induction melting system is the inherent stirring capability. SRS, in the past, has used induction furnaces for manufacturing uranium-aluminum alloy fuel for the reactors.

5.3.3.4 Small-Scale Furnace System

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Resistance furnaces use heating elements to heat the melt chamber of the furnace. The heating elements are typically ceramic, in many cases silicon carbide. Unlike induction furnaces, a resistance furnace requires mechanical stirring of the melt, and if steel stirrers are used, they can dissolve in the molten aluminum alloy increasing the iron content of the melt. A resistance furnace system basically consists of the furnace and power supply. For initial tests, an off-the-shelf resistance furnace was purchased and retrofitted for mechanical stirring of the melt and off-gas capabilities was added to the system. Stirring is needed in the melt-dilute process to get the depleted uranium in solution and to ensure a homogeneous melt and isotopic dilution in the final casting. Mechanical stirring adds additional equipment and complexity to a melting system. In a radioactive environment, it is especially important to keep the system as simple as possible.

To develop the small scale, melt-dilute furnace, a commercial resistance furnace, Thermcraft Model 38 - 12 - ZV - CR, was purchased and installed in the Materials Laboratory of SRTC. The furnace is capable of providing 12 KW of power and is rated for a maximum temperature of 1500 °C. It is a top loading furnace with enough heated chamber space to melt one full size MTR fuel assembly mock-up.

The resistance furnace has been modified for remote melt-dilute process development. All designs were based on using the 5 ton overhead crane which exists in the laboratory. The modifications allow melting of a MTR fuel assembly and stirring the melt while adding depleted uranium metal remotely.

The furnace and controls have been verified to be completely functional. The controls consist of a thermocouple which monitors the internal furnace temperature and provides input to a temperature controller. The temperature controller drives a SCR power controller which provides the power to the heating elements. A redundant thermocouple provides an input to a high temperature interlock which shuts down power to the power controller in the event that the temperature exceeds the limits set by the operator. This control scheme is very typical of resistance furnaces.

Major components of the furnace system include the crucible assembly, the furnace cover hood, and the pneumatic agitator. In addition, other miscellaneous components were developed to enhance operational efficiency. A brief description of each component follows:

• Crucible Assembly - The crucible assembly is made up of the crucible and a spool piece. The fuel element will melt in the crucible, while the spool piece will hold the crucible in the melt chamber of the furnace. The crucible is made from 6-inch diameter sch. 40 carbon steel pipe with an end plate welded on the bottom. The spool piece is made from stainless steel tubing with a flange on the upper end and a specially designed tab on the lower end. The tab on the spool piece and slots milled in the crucible connect the two. The assembly is placed into the furnace with the overhead

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crane. Locating pins on the top of the furnace position the crucible assembly. The spool piece can be reused with a new crucible but the crucible will be filled with solidified fuel and depleted uranium at the end of each campaign. In other words, the system is currently set up to allow solidification of the alloy in the crucible.

- Furnace Cover Hood A furnace cover was designed to support the agitator and tie into the existing ventilation system. The cover design is based on the existing hood used with bench-scale induction furnace. The cover was strengthened sufficiently to support the commercial agitator (described below). The connection to the ventilation system is through a flexible duct. The furnace cover is placed on the furnace with the overhead crane and, as with the crucible assembly, locating pins on the top of the furnace position it.
- Agitator A Lightning XJAC100 agitator was purchased for mixing the molten fuel assembly and dissolving depleted uranium metal. A 1 hp, 360 rpm air motor powers the agitator. Motor speed is controlled by adjusting a needle valve on the air inlet line. The 1.25 inch diameter shaft cantilevers down from the mounting flange into the crucible. The propeller at the end of the shaft was replaced with a basket which will hold depleted uranium. The agitator is placed onto the furnace cover with the overhead crane. Aligning pins on the furnace cover hood position the agitator.
- Miscellaneous Components In addition to the components described above, several other pieces of equipment were designed and fabricated. These include lifting beams for component handling, a component storing stand, and an insulation stand for inside the furnace.

The modified resistance furnace system for small-scale process development is shown in Figure 5.31. Design of the equipment was completed in May while installation and safety inspections were completed in June. Startup testing began in August.

5.3.3.5 Melt Temperature Measurement

The melt temperature is monitored using a PC based data acquisition system. This system has the capability of monitoring temperature from up to six different type K thermocouples and one type R thermocouple. Initial test runs will be made using thermocouples, but an IR thermometer will be installed later. This device utilizes a fiber optic cable and a focusing lens so the thermocouple sensing element can be removed from the crucible.

5.3.4 Process Functional Requirements

Several melt-dilute methodologies are currently being evaluated. This section describes the preliminary functional requirements for the current best estimate of the process. The design of this facility shall be based on a 40 year service-life. The proposed melting, alloying, and casting technologies are relatively simple. The off-gas confinement, high



Figure 5.31. Schematic of Small-Scale Resistance Furnace

radiation fields, high contamination potential, and remote operation/maintenance are the most significant engineering challenges for this proposed project.

5.3.4.1 Preliminary Functional Performance Requirements

Capacity

The Melt-Dilute facility must be capable of processing the following quantities of SNF shown in Table 5.16.

The SNF types, physical dimensions, and quantities are described in Reference 5.31. There are three categories of aluminum-uranium fuel forms to be processed: 1) approximately 50% are aluminum-uranium alloy fuels, 2) approximately 20% are aluminum-uranium-silicide fuels, and 3) approximately 30% are aluminum-uraniumoxide fuels. This technical report assumes that uranium-silicide and uranium-oxide type SNF can be successfully processed by the Melt-Dilute process described herein.

Primary SNF Form Composition

This technical report assumes that the U^{235} concentration of the SNF will be reduced to 2-20 wt % U^{235} by alloying with depleted uranium and the U-Al alloy composition will be maintained ≤ 67 wt % U-Al by alloying with additional aluminum (if required). Selection of the final Primary Waste Form composition is dependent on the following:

	Involute Assemblies	Other SNF Assemblies
Steady State Rate	4	394
Peak Rate (See note below)	6	442

Table 5.16 - SNF Monthly Processing Rates (Reference 5.30)

Note: Peak SNF throughput values represent the peak rate in any one month but not two consecutive months at this peak rate.

U²³⁵ Dilution:

Dilution of the U^{235} concentration to 20 wt % U^{235} would render the SNF unsuitable for use in weapons, eliminate nuclear proliferation concerns, and reduce the nuclear criticality potential of the primary waste form. Dilution to lower U^{235} concentrations (using additional depleted uranium) would further reduce the criticality potential.

SNF Form Stability (corrosion resistance):

The corrosion resistance of the primary waste form is likely to be dependent on the U-Al alloy composition. Waste form stability will be characterized for a range of U-Al alloy compositions.

Primary SNF Form Composition and Melt Temperature:

To ensure homogeneous blending of the U^{235} in the SNF and the depleted uranium (primarily U^{238}), it is necessary to heat the molten alloy above the liquidus temperature (the lowest temperature at which all constituents are molten and a homogeneous liquid is formed). The liquidus temperatures for U-Al alloys range from 640 °C at relatively low uranium concentrations (13.2 wt % U-Al) to ~1600 °C at high uranium concentrations (67 wt % U-Al). As the uranium concentrations (and melt temperatures) are increased, the molten U-Al would react more vigorously with the atmosphere and refractory crucible materials and a greater fraction of volatile fission products would be released from the melt, making off-gas confinement more difficult. The uranium concentration (and required melt temperatures) could be reduced by the addition of aluminum, if desired.

Primary SNF Form Volume:

Depending on the final primary waste form composition, 250-1200 canisters will be produced (Reference 5.1).

Melting Furnace

In order to avoid having to disassemble the relatively large diameter (17.13 inches, OD), involute, HFIR/RHF assemblies; this technical report assumes that HFIR/RHF assemblies will be processed whole (i.e., no disassembly or subdivision). This will require a furnace

capable of utilizing a crucible with a ~ 20 inch ID and ~ 35 inch depth. The final crucible dimensions are dependent on the primary waste form composition. The long (320 cm) pin-type SNF will be processed whole (i.e., these long assemblies will extend out of the top of the crucible at the start of the melting cycle). To effectively utilize the furnace capacity, this technical report assumes that multiple, smaller non-involute type SNF assemblies (i.e., up to 20 non-involute SNF assemblies containing a total mass of up to 110 kg) will be batched, melted, and processed simultaneously in the furnace. The melt-dilute facility must be capable of processing 110 kg of SNF (e.g., one involute assembly or an equivalent weight of non-involute type SNF assemblies) per 24 hour period.

The furnace(s) and associated equipment should be designed to perform the following sequences:

- 1. The SNF will be added to the crucible and heated until molten. After the SNF has been melted, the temperature will be increased to above the alloy liquidus temperature and stirred.
- 2. A molten alloy sample will be obtained and analyzed to determine the uranium concentration of the molten SNF. These data will be used to confirm the DOE Appendix A data.
- 3. The aluminum (if required) will be added to the crucible, melted, and stirred.
- 4. The depleted uranium will be added, melted, and stirred.
- 5. A second molten alloy sample will be obtained and tested/analyzed to confirm that the final uranium concentration conforms to the Primary Waste Form composition before casting.
- 6. After the alloy composition is confirmed, the molten alloy will be cast into a mold to produce the primary waste form.

Two furnaces shall be provided. Only one furnace at a time will be operated. The other furnace will serve as an installed spare.

To ensure nuclear criticality safety, the presence of moderating materials is restricted inside the melt-dilute hot-cell. If cooling is required, a recirculated coolant system should be utilized to limit the quantity of water that could be released due to a cooling water leak.

The furnaces will be interfaced to a computer-based system to provide visual/audio prompts to operating personnel, to monitor and record the furnace operating parameters, and to perform the calculations described above. Equipment will be provided to measure the temperature of the melt. The temperature monitors will be interfaced to the computer-based system to monitor and record the furnace temperature. The power and Page 5.74 of 5.82

control unit and the coolant system heat exchanger will be located in an area outside and adjacent to the melt-dilute hot-cell.

Final design of the furnace must consider the requirement for off-gas confinement and the ability to add materials to the crucible (i.e., SNF, depleted uranium, aluminum), obtain melt samples, and pour the alloy with the furnace at the operating temperatures.

Furnace Off-gas Confinement

The temperatures (up to 1600 °C) required to melt and alloy the SNF exceeds the boiling point of several radionuclides (i.e., tritium, krypton, iodine, cesium, rubidium) (Reference 5.12). In addition, radioactive particulates are expected to be generated. Therefore, an off-gas confinement system must be provided. The off-gas confinement system will be interfaced with the HVAC system.

This technical report assumes that: 1) the volatized metallic species will be captured by condensing these on cool surfaces (e.g., cesium boils at 671 °C and will condense on surfaces below this temperature), 2) radioactive particulates will be captured on HEPA filters, and 3) the concentrations of tritium, iodine, krypton, and other gaseous radionuclides in the off-gas will not exceed 10 CFR 50, Appendix I requirements (i.e., no confinement required for these radionuclides).

Baffles or other medium, maintained at < 600 °C, will be positioned immediately adjacent to the furnace to condense the volatized metallic species. The baffles (or medium) will be designed such that they can be removed periodically to dispose of the condensed radionuclides. Another function of the baffles is to cool the off-gas stream prior to passing through the downstream HEPA filters. Additional equipment will be required to recover and collect radionuclides from the condenser baffles. This technical report assumes that the condenser baffles will be washed with dilute nitric acid and reused.

Final design of the confinement system must consider and include the ability to add materials to the crucible (i.e., SNF, depleted uranium, aluminum), obtain the melt samples, and pour the alloy while the furnace is at the operating temperature.

Analytical Cell

An analytical cell will be located adjacent to the melt-dilute hot-cell to perform analysis of U-Al alloy melt samples. Work is in progress to identify and develop potential suitable analytical methods for these analyses.

Process Control

Two alloy samples to determine uranium concentrations will be obtained from each melt for process control. The first sample will be obtained after the SNF has been melted. These analyses are hold points in the melt-dilute process and must be completed within 30 minutes each to minimize time that the molten alloy is held at an elevated temperature. Data from the first sample will be used to confirm the DOE Appendix A data. After the depleted uranium and aluminum have been added, a second sample will be obtained to confirm that the desired final uranium concentration has been achieved before casting the primary waste form.

SNF Form Characterization

Additional routine analyses to identify concentrations of other elements and radionuclides in the primary waste form may be required to satisfy other site or regulatory requirements. The thermal load and radiation levels from the as-cast primary waste form will be determined in another portion of the TSS.

Waste Streams

Waste from the melt-dilute hot-cell will consist of solid and liquid wastes described below:

- 1. Used crucibles-- 2 per month
- 2. Used HEPA filters-- 1 set per 3 months
- 3. HLW solution from off-gas condenser media wash -- 50 gallons per month
- 4. Miscellaneous job control wastes --96 ft³ per month

Regulatory Requirements

• SEE Table 5.17 - Federal, State, and WSRC Regulatory Requirements.

Interface Requirements

- 1. Low Level Wastes -- Burial grounds
- 2. High Level Wastes -- HLW waste tanks
- 3. Utilities, Service and Support Facilities
- 4. Utilities (ventilation, electric power, cooling water, air, sanitary sewer, process sewer), service and support facilities (personnel facilities, offices, administration change/lunch rooms, parking, training) will be provided by the TSS facility.

Preferred Furnace Technology

Induction furnace melting is the preferred melting technology. Induction furnace technology provides capability for non-contact induction stirring to ensure homogeneity of the molten alloy. Other melting technologies were considered (e.g., resistance furnace); however, these would require mechanical stirring with direct contact with the molten alloy. Also, induction furnace technology provides capability for rapid heating and more efficient batch processing.

5.3.4.2 Criticality Calculations for Crucibles During Melt-Dilute Operation

The proposed melt-dilute process will involve either induction or resistance furnace heating of spent nuclear fuel assemblies inside a crucible. The assemblies will be melted with some fraction of the volatile fission product gases being released and captured inside a recovery system. Once in a liquid state, depleted uranium (uranium high in U²³⁸ content) will be added to the melted mixture and the overall enrichment of the mixture will be reduced from > 90.0 wt % U²³⁵ down to some value < 20 wt % U²³⁵. This diluting or deenrichment process will allow safe disposal of the uranium with reduced (or eliminated) criticality safety controls on the waste package.

To evaluate the proposed pre-conceptual design of the process in terms of criticality safety would typically require an in-depth study of all the process parameters which can affect neutron subcritical multiplication such as moderation, absorption, fissile mass, temperature, poisons, reflectors, enrichment, etc. However, due to the preliminary nature of this study, only the fissile mass of U^{235} and the potential reflection/moderation conditions associated with the crucible will be considered. Future analyses which evaluate all aspects of the process design must be performed prior to any final design being reached.

For this analysis, an 18 inch ID, 35 inch inner height crucible cavity was modeled with MCNP4A. Inside this cavity, the melted uranium and aluminum contents equivalent to either one or two full High Flux Isotope Reactor cores was modeled. The crucible was assumed to be composed of either graphite or carbon steel with a 22 inch OD and 38 inch outer height. A schematic of the model used for the criticality calculations is shown in Figure 5.32.

Since it is planned for up to one entire HFIR core (or ~15-20 typical MTR fuel assemblies) to be melted at a single time in the crucible, criticality calculations were performed to simulate both normal and credible abnormal conditions of processing. Normal conditions would be one HFIR core being melted with no water reflector inside or outside the crucible. Abnormal conditions would be double batching (2 HFIR cores) of the fissile loading inside the crucible with or without water reflection inside or outside the crucible. Since water cooling systems are used for the induction furnace design, water reflection must be considered a credible scenario. Also, cases were run with steel and graphite reflectors to see the effects of reflection on overall system subcritical reactivity.

The results shown in Table 5.18 illustrate several important points. First, the graphite crucible and the external water region provide a significant amount of neutron reflection to the fissile mass inside the crucible. In the case of the graphite crucible, the increase in subcritical reactivity compared to the steel crucible is ~ 30% $\Delta k/k$ whereas the increase in reactivity due to the external water reflector is ~40% $\Delta k/k$. In both cases, increased neutron reflection from the graphite and the water is responsible for these increases in the calculated k_{eff} values.

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Table 5.17. Minimum Federal, State, and WSRC Regulatory Requirements

Document Number	Title
10 CFR 20	Standards of Protection Against Radiation
10 CFR 21	Reporting of Defects and Noncompliance
10 CFR 26	Fitness for Duty Programs
10 CFR 51	Environmental Protection Regulations for Domestic Licensing and Related
	Regulatory Functions
10 CFR 70	Domestic Licensing of Special Nuclear Material
10 CFR 71	Packaging and Transport of Radioactive Material
10 CFR 72	Licensing Requirements for Interim Storage of SNF and HLW
10 CFR 73	Physical Protection of Plants and Materials
10 CFR 74	Material Control and Accounting of Special Nuclear Material
10 CFR 75	Safeguard on Nuclear Material, Implements US/IAEA
10 CFR 95	Security facility Approval and Safeguarding of National Security Information
	and Restricted data
10 CFR 100	Reactor Site Criteria
10 CFR 708	DOE Contractor Employee Protection Program
10 CFR 1017	Identification and Protection of Unclassified Controlled Nuclear Information
10 CFR 1021	National Environmental Policy Act Implementing Procedures
29 CFR 1910	OSHA
29 CFR 1926	Safety and Health Regulations for Construction
40 CFR 136	Guidelines Establishing Test Procedures for the Analysis of Pollutants
40 CFR 268	Land Disposal Restrictions
40 CFR 300 et seq.	National Oil & Hazard Substance Pollution Contingency Plan
49 CFR 172	Hazardous Materials Tables, Special Provisions, Hazardous Materials
	Communications, Emergency Response Information, & Training Requirements
49 CFR 173	Shippers - General Requirements for Ship and Pack
42 USC 9601 et seq	CERCLA
DOE/RW-0333P	Quality Assurance Requirements and Description
SCDHEC R.61-58	Definitions and General Provisions
SCDHEC R.61-62	South Carolina Air Pollution Control Regulations and Standards
SCDHEC R.61-67	Submissions of Engineering Reports and Environmental Impact Statements
SCDHEC R.61-79.264	South Carolina Hazardous Waste Regulations
thru 270	
SCLRCC R.72-300	South Carolina Stormwater Management and Sediment Reduction Regulation (5/92)
WSRC 1S Manual	Waste Acceptance Criteria
WSRC 19Q Manual	Transportation Safety Manual
WSRC 8Q Manual	Employee Safety Manual
WSRC 3Q Manual	Environmental Compliance Manual
WSRC 6Q Manual	SRS Emergency Plan Emergency Management Program Procedure Manual



Figure 5.32. Model used for Criticality Calculations for Crucibles

A second observation is that double-batching of the fissile material (i.e., ~ 20 kg compared to ~ 10 kg) melted inside the crucible does not significantly increase neutron subcritical multiplication. Due to the fact that no water moderation was assumed intimately mixed within the molten fissile mixture, the system is very undermoderated. This high degree of undermoderation allows significantly larger masses of fissile material to be critically safe than if moderation were present.

A third observation of these results is that the assumption of the molten uranium aluminum mixture occupying the entire active volume of the crucible does not result in a significantly different eigenvalue than if one assumes the material to occupy between 20% and 50% of the crucible active volume (with water occupying the remaining half). Again, due to the fact that water moderator is not assumed to be intimately mixed with the molten uranium aluminum mass, the system is very undermoderated. Figure 5.33 shows a schematic illustration of this.

Conclusions from this small set of scoping calculations can be summarized as follows:

- Up to 20 kg of U²³⁵ can be safely melted inside the crucible provided water intrusion does not result in mixing of water and fissile material.
- Full water reflection around the crucible has a significant effect on subcritical reactivity.
- Graphite crucibles will provide considerably higher neutron reflection than steel crucibles.
- Double batching of the fissile mixture does not result in a significant increase in overall system subcritical reactivity.

Case Description	Approx. U ²³⁵ Mass	Crucible Composition	Water Reflection	Eigenvalue (k _{eff})
1 HFIR core	~10 kg	graphite	none	0.0277
2 HFIR cores	~20 kg	graphite	none	0.0545
1 HFIR core	~10 kg	graphite	full	0.4492
2 HIFIR cores	~20 kg	graphite	full	0.4894
1 HFIR core	~10 kg	steel	full	0.0775
2 HIFIR cores	~20 kg	steel	full	0.1145
1 HFIR core, crucible 50% flooded	~10 kg	graphite	full	0.4830
2 HFIR cores, crucible 50% flooded	~20 kg	graphite	full	0.5594
1 HFIR core crucible 80% flooded*	~10 kg	graphite	full	0.5252
2 HFIR cores, crucible 60% flooded*	~20 kg	graphite	full	0.5888

Table 5.18. Crucible Criticality Calculations

* - actual volume of crucible which would be filled with water once U and Al melted

The overall conclusions of this study indicate that quite a large mass of fissile material (~20 kg) can be safely melted inside the crucible provided accidental water intrusion does not allow the water to intimately mix with the fissile material. Should the water and fissile mixture remain separate at all times within the crucible, even a double-batching event would not result in a critically unsafe condition. Also the benefits of using a steel crucible with a resistance furnace are evident since water intrusion and graphite reflection tend to significantly increase the overall subcritical reactivity.

It should be recognized that even the worst case condition analyzed in this study (doublebatching, full water reflection, flooding of the crucible) still does not result in a critically unsafe condition ($k_{eff} \sim 0.58$). However, since only a few accident scenarios were postulated in this study, it is quite possible that as the design of this system progresses, more severe accident scenarios will be postulated. These accident scenarios might in fact result in unacceptably high values of k_{eff} which in turn would restrict the fissile mass melting limits allowed for the crucible. Consequently, decisions on the type of crucible and type of furnace to be used in this process should incorporate the findings of this study. Failure to at least consider these factors might ultimately result in a final process design which is severely restricted in terms of the amount of fissile material which can be melted in a single batch.



Figure 5.33. Model Used For Criticality Calculations for Crucibles

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6.0 TEST PROTOCOL DEVELOPMENT

The objective of the test protocol task is to develop the individual tests or test sequences required to assess the behavior of Al-SNF. The assessments will focus primarily on the degradation of Al-SNF forms after emplacement in a geologic repository. The protocols established for the various test methods will be peer-reviewed by organizations, such as the American Society for Testing and Materials, and subsequently incorporated into approved guides and/or standards. The application of approved guides and standards to the testing of Al-SNF forms will assume that the data accumulated through the prescribed test methodologies may be used to provide a qualified technical basis for determining

- the corrosion behavior of individual Al-SNF forms,
- the relative performance of the various Al-SNF forms, and
- the anticipated repository performance of the Al-SNF forms, including the effects of potential interactions with the surrounding waste package.

The test protocol development program therefore emphasizes the technical development of the test methods necessary for Al-SNF form assessment and the application of those methods to the evaluation of Al-SNF form suitability.

6.1 TEST PROTOCOL OBJECTIVES

The purpose of the test protocol is to evaluate the suitability of aluminum-based spent nuclear fuel for "road ready" storage and subsequent geologic disposal. To accomplish this purpose, tests are being developed to demonstrate that the presence of the SNF will not adversely impact the repository in terms of the potential environmental consequences. The test protocol will provide techniques to establish the release rate of radionuclides from the SNF and the role of environmental variables and SNF degradation on the release rate.

The performance of the aluminum-based SNF in the repository will significantly differ from that of the commercial nuclear fuels and the high level waste glass. The primary differences are the aluminum-based SNF will have a higher U^{235} enrichment (as high as 93%) and aluminum-based alloys are less stable in aqueous environments than the other waste forms. The test protocol task will quantify the effects of these differences on the performance of the repository.

Previously the objectives of this program were to review established and emerging test methodologies for other waste forms and then to identify which of these methodologies were most applicable to aluminum-based SNF (Reference 6.1). Based on a literature review and preliminary scoping studies, three test methodologies will be investigated further: static, single-pass flow, and electrochemical. The objectives of the further testing will be to: 1) develop standard test methodologies to assess the suitability of aluminum-based SNF for "road ready" and repository storage; 2) evaluate and understand the

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degradation mechanisms which may occur in these environments; and 3) assist in the selection of treatment processes (i.e., melt/dilute options or direct disposal) by providing tests which evaluate the waste forms produced by these processes.

Standardized test methodologies that are approved by organizations such as the American Society for Testing and Materials must follow rigorous formats. A draft test protocol is presented in Appendix I of this report which demonstrates the attributes of an approved standard guide. The standard guide describes a corrosion testing program that will demonstrate specific criteria that are defined in the standard guide. These criteria are related to data required to support the safety analyses and performance assessments of the disposal systems.

The results of the preliminary scoping studies are presented in the following sections. These include results from static and electrochemical tests as well as general outlines of the procedures that will be utilized to validate the methodologies. These results were utilized to direct further test methodology development.

In addition, SRS has initiated contracts with Pacific Northwest National Laboratories to assist in the test protocol development. PNNL has established the single-pass flow cell methodology for application to commercial spent nuclear fuels (Reference 6.2). Their role will be to transfer the test methodology to SRS and also perform tests on actual irradiated aluminum-based SNF for comparison with testing that is performed on unirradiated test material. The plans for their testing and some initial results are presented.

6.2 TEST DEVELOPMENT

The literature review led to the selection of a test methodology which will provide a functional assessment of the Al-SNF. The methodology is a comprehensive approach which includes the sample type, test conditions matrix, and test technique. The reactivity of Al-SNF may increase the effect of corrosion on repository performance more than for other waste forms such as commercial fuels and the DWPF glasses. A wide compositional range of the Al-SNF will exist depending on the actual treatment technology for the Al-SNF. The Al-SNF for the test protocol development are in the range of 10 to 67 wt % U (balance Al) to cover the expected range. The test matrix, that is conditions or variables for these tests, is dependent on and defined by the anticipated repository conditions. This aspect of the test protocol development will assess the characteristics of the Al-SNF for disposal in the repository at times greater than 1000 years. The test methodologies that will be evaluated and modified initially for the test protocol are static immersion, low flow, and electrochemical tests.

6.2.1 Development of Al-SNF Sample

The test protocol must assess the stability and behavior of any aluminum-based SNF. During the development, representative test samples, which cover the range of Al-SNF alternatives, will be tested within the proposed methodology. The configuration of the Al-SNF depends on the treatment technology selected for the Al-SNF. The samples for test protocol will include base materials used in the manufacture of these fuels and prototypical samples of the SNF in the stockpile. These fuels are being characterized within the SNF Characterization Program and test samples will be based on this summation. The dilution of the enriched uranium in SNF by a melt process will produce either a single U-Al composition or range of compositions depending on the developed process. Samples for test protocol will cover the anticipated range of the alloys, microstructures, and surface conditions. The initial development phase for the test protocol is concentrated on Al-SNF processed through a melt/dilute treatment.

The uranium compositional range for the melt/dilute waste forms is 2 - 67 wt %. The actual composition will depend on the chosen dilution for the enriched uranium, process requirements, and stability. The U-Al alloys solidify with different microstructures, which depend on both the composition and process variables. Several compositions were selected for testing because of the particular phases that form in the solidified structure. The selection is best understood by referring to the uranium-aluminum phase diagram which is shown in Figure 6.1. The four alloy compositions are marked in the figure and include 10, 13.2 (eutectic), 25, and 67 (peritectic) wt % U. The description of the sample preparation is given in Section 6.3.1.



Figure 6.1. Uranium-Aluminum Phase Diagram (cast compositions 10, 13.2, 25, and 67 wt % U are shown)

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The solidification of the 10 wt % U-Al alloys from the liquid occurs first by the formation of primary aluminum grains and dendrites followed by eutectic. The eutectic structure is composed of lamellae of aluminum and UAl₄. The cast microstructure consists mostly of aluminum dendrites with eutectic filling the interdendritic regions. A microstructure is shown in Figure 6.2 of the actual test material. The microstructure at the eutectic composition consists of only lamellae of aluminum and UAl₄, as shown in Figure 6.3. The 25 wt % U-Al alloy passes through a phase field during solidification in which UAl₃ particles are the primary phase followed by formation of both UAl₄ particles and the eutectic structure. Figure 6.4 shows the 25 wt % U-Al alloy microstructure for the test material. The last composition is that of the peritectic which at equilibrium should form only UAl₄. This reaction is very sluggish, so the microstructure may actually be composed of UAl₃, UAl₄, and a small amount of eutectic. The test material has not been made.

A composition of 15.9 wt % U-Al was chosen initially also; however, the alloy has been deleted from the matrix. From the phase diagram, this alloy should form UAl₄ particles first and then the remaining liquid would solidify as the eutectic. The microstructure of the cast sample, however, was very similar to that of the eutectic as shown in Figure 6.3. The behavior of this alloy was anticipated to be similar to that of the eutectic composition, so the 15.9 wt % U-Al alloy was removed from the test matrix.

The U-Al alloy samples are to have either a cast or wrought microstructure. Aluminum and uranium material are melted in an induction furnace to produce a cast ingot. The composition of the U-Al alloy and the processing of the casting determines the phases and the microstructural features that are present. The wrought bar is fabricated by heating the ingot and extruding the cast ingot through a 0.75 inch diameter cylindrical die. Once the material cools, the bar is flattened so that the minimum height is approximately 0.5 inch. This rolling procedure introduces approximately 15% cold-work into the material. Coldworking the material changes the morphology and the uniformity of the microstructures within the material as compared to the ingot.

6.2.2 Test Matrix

The compatibility of the Al-SNF with the anticipated repository environments is dictated by the requirements of the performance assessment for the repository. Various assumptions, which become more uncertain for extended times, can be made about the environmental conditions. The environment will change and the Al-SNF will degrade as lifetime in the repository increases. The environmental conditions, which will be based on conservative scenarios, include repository temperature, chemistry of intrusion water, and galvanic couples between the Al-SNF and waste packages. The relationships among these conditions and Al-SNF stability are important for understanding the Al-SNF performance in the repository.

Predictions of the temperature profile for the repository vary depending on the initial model assumptions. At extended times, temperature forecasts are typically below 100 °C



Figure 6.2. Microstructure of Cast Ingot for 10 Wt % U-Al Alloy



Figure 6.3. Microstructure of Cast Ingot for 13.2 Wt % U-Al Alloy



Figure 6.4. Microstructure of Cast Ingot for 25 Wt % U-Al Alloy

at atmospheric pressures. Long term temperatures at this level predicate an aqueous environment around the Al-SNF. The temperature range for test protocol was chosen as 25 to 90 °C. An upper temperature of 90 °C eliminates boiling conditions and also follows test conditions for studies on glass waste forms. The lower temperature of 25 °C, which was also used for studies on other fuel types, provides a wide range for establishing a temperature relationship with Al-SNF degradation.

The chemistry of the water that intrudes the repository will vary depending on the initial source, the pathway of entry, and radiolytic exposure. J-13 well water (J-13), which initiates from a source several miles from the proposed repository site of Yucca Mountain, has been used extensively in numerous studies. For test protocol, the nominal water chemistry is J-13. The other water chemistries for test protocol simulate various scenarios due to interactions with soils and other waste forms.

The glass waste forms are to be a significant portion of the repository stockpile. These waste forms are composed of the high-level radioactive glass and a stainless steel canister in which salts have deposited in the vapor space. Exposure of the water to a breached canister would lead to dissolution of salts and of the glass. The test protocol will simulate this scenario by conducting tests in the following: J-13 with DWPF glass simulants and J-13 with deposited salt simulants.

Radiation will change the water chemistry through decomposition of both the air and water constituents. The breakdown products would tend to acidify the water so J-13 at a

low pH will be used. The water will be acidified by the addition of nitric acid since radiolytic decomposition of air nitrogen produces nitric acid. The acidified J-13 will also model acidification resulting from corrosion. The corrosion products will also alter the chemistry of J-13. Static tests will examine this effect by exposing test samples coupled with both aluminum, simulating the aluminum cladding, and stainless steel, simulating canister materials.

6.2.3 Static Tests

Static tests are being assessed for the test protocol to measure the following properties/behavior of the aluminum-based SNF: selective leaching, dissolution rates, and corrosion. Static tests are commonly used for corrosion studies and are generally referred to as immersion or coupon testing. The American Society for Testing and Measurements has a standard practice for conducting such tests (ASTM G31-72 (reapproved 1985)). Various analysis techniques must be used in conjunction with the test to measure the desired properties.

The procedures and apparatus were developed from ASTM G31-72, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals". The apparatus is shown in Figure 6.5. The test cell is a two-part, 2 L glass vessel. The lower part holds the desired solution in which the samples are immersed. The upper part has three circumferential ports that provide several functions and one center port. The central port holds the support tree for the waste form samples. The three circumferential ports are for access to withdraw solution for chemical analysis and placement of a reflux condenser and thermometer. The cell is placed in a heating mantle which is plugged into a temperature controller that uses the thermometer for monitoring.

The support tree for the sample waste forms is made of glass and holds either an aluminum or stainless steel plate. The tree may be adjusted as necessary for handling the samples. The plates are the coupling electrode to the sample for assessing the impact of galvanic and crevice corrosion. The samples are fastened to the plate with nylon nuts and bolts, which pass through a central hole drilled through opposite sides of the sample. The tree is adjusted at the start of the test so that the plate and samples are completely immersed.

The test samples are sectioned from bulk material of the waste form, either cast or wrought, and uniquely numbered. The samples are cubes with an 0.5 inch length. After cutting, the samples are ground to a 1000 grit finish. The samples are cleaned prior to immersion with ethyl alcohol for removal of any surface contaminants. Each sample is weighed prior to and after exposure, along with dimensional measurements.

Pre-test characterization of samples is necessary to detect changes in structure or chemistry due to corrosion during the test. Initially, the samples are weighed and the dimensions measured to calculate surface area, volume, and density of each sample. X-ray diffraction is performed to determine the relative amounts of phases present. Samples Page 6.8 of 6.36



Figure 6.5. Schematic Diagram of Static Test Apparatus

taken from the same casting are expected to have little sample to sample variation, as confirmed by a verification for each composition. Visual examination of the samples provides information on the macroscopic features of the sample. Photographs are taken of the samples at approximately 4X to document this information. Optical metallography is utilized to reveal the phases in the sample and the homogeneity of the microstructural features. The samples are first etched for 10 seconds with a solution that is 4 parts water, 1 part HF, and 1 part HNO₃. Micrographs of the samples are taken at magnifications between 100X and 250X. Scanning electron microscopy and electron dispersive spectroscopy are performed to characterize the topography of the phases present and to correlate the composition of the phases with their microstructure. The uranium and aluminum content are determined for each melt through ChemcheckTM analysis and inductively coupled plasma emission spectroscopy, respectively.

The coupons and the plate are immersed in one of the J-13 waters at the specified test temperature. The nominal composition and the composition from an analysis of the J-13 water that was utilized in the scoping test are shown in Table 6.1. Three variations of the nominal composition are in the test matrix. The first modification is a low pH J-13, which is made by adding nitric acid to obtain a solution pH of 3. The second modification is J-13 at a high pH (~11) to simulate exposure to DWPF glass. The final modification is J-13 with additional chloride salts (100 ppm CI).

The tests are performed for one month. Coupons are removed from the vessel at intervals of 7, 14, and 28 days to determine any time dependence on the degradation rate. Samples of the solution are also taken every three to four days in order to determine which species are being dissolved. The following analyses may be performed: 1) ICPES for Al, Si, Ca,

Na, B, and Fe, 2) Ion chromatography for Cl⁻, F⁻, NO₃⁻, NO₂⁻, and SO₄⁻² 3) ChemcheckTM for U, 4) Atomic Absorption for Na and K, 5) pH, and 6) conductivity.

After each sample is removed, it is weighed and the corroded samples are analyzed by the following techniques: 1) photographs at approximately 4X for examining the macroscopic surface, 2) micrographs taken on the SEM to examine changes in the microstructural features, 3) EDS to identify the microstructural features with chemical information, and 4) XRD for identifying oxide films on the surface. The disks are visually examined for any significant changes.

Species or environmental	Nominal Concentration	Analyzed Concentration	
variable	(ppm)	(ppm)	
SiO ₂	58	56.2	
HCO3 ⁻	125	125*	
F-	2.2	2.0	
Cl-	6.9	10.5	
NO3 ⁻	9.6	5.0	
SO4=	18.7	17.7	
Al ³⁺	0.012	<0.55	
Fe ²⁺	0.006	<0.064	
Ca ²⁺	12.5	9.7	
Mg ²⁺	1.9	0.92	
K+	5.1	4.9	
Na ⁺	44	45.2	
pH	7.6	8.06	

Table 6.1. Nominal and Scoping Tests Compositions of J-13 Well Water

* - Species was not analyzed. However, bicarbonate was added to the J-13 well water when the solution was prepared.

A post-test analysis of the J-13 water is performed to determine the presence of insoluble particles that remained in the test vessel. The solution is filtered through #40 filter paper. The filter paper is also analyzed with SEM and EDS to identify the insoluble particles that remained.

6.2.4 Flow Tests

Flow testing is being assessed for the test protocol as a method to determine both the dissolution and corrosion characteristics of waste packages containing aluminum-based

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SNF. The release rates of radionuclides from these waste forms are affected by these characteristics. Flow tests had been used previously to study the dissolution response of commercial spent fuel. Flow test parameters included water composition, temperature, flow cell design, and flow rate. These parameters are expected also to effect both the dissolution rate and corrosion Al-SNF.

The basic design of the flow test apparatus, which is shown in Figure 6.6, included a feed water reservoir, a pump for controlled flow, the specimen column or flow cell, and the receipt water reservoir. These flow tests were single-pass at low flow rates so as to maintain the concentration of radionuclides below their solubility limit. The actual flow rate was determined from weight measurements of the receipt water for a set period of time. Chemical analyses of the receipt water was performed to determine radionuclide concentrations and ultimately forward dissolution rates.



Figure 6.6. Schematic Diagram of PNNL Flow Test Apparatus

The flow test for Al-SNF is based on previous studies of other spent fuel. However, some modifications to the flow test were necessary since the reactivity and structure of Al-SNF are different and may impact the release rate. Flow cells, made of Type 316 stainless steel, were obtained from PNNL to fully assess the flow cell characteristics. Several limitations of these cells were identified for Al-SNF. The metallic construction can cause galvanic corrosion with the waste form. The sample and flow pattern cannot be observed prior to or during the tests to ensure complete immersion of the sample. The stainless steel filters inside the cell can also cause galvanic corrosion and contribute to the formation of air pockets.

Several changes were made to the new flow cell to overcome the noted limitations and to accommodate the Al-SNF. The cell is made from a borosilicate glass. The stainless steel filters were removed since monolithic samples are to be evaluated. With the low flow rate, particles or corrosion products will drop to the low point of the cell. The flow cell

has several glass dividers to keep individual samples separated; four samples are planned for each cell. A thermometer port was added for temperature monitoring and control. The water lines are made of borosilicate glass. The dimensions are larger than those for the PNNL cells with an inside diameter and length of 0.50 inch (1.27 cm) and 2.5 inch (6.35 cm), respectively.

An additional constraint on the flow test apparatus is that numerous flow tests (>20) are planned to run simultaneously because of the size of the test matrix. The present lay out with multiple pumps would require a large space and entail the possibility of mechanical failure. Two options were being developed for the apparatus. The first option maintained a precision mechanical pump which delivered flow at a maximum rate of 0.2 ml/min. The feed and receipt reservoirs were of similar design.

The second and chosen option, which is shown in Figure 6.7, is a single-pass, gravitydriven system. The flow initiates from a primary storage reservoir for the J-13 water. The water is pumped into a feed reservoir with an overflow, so that the same pressure head is maintained for the cell. Each reservoir feeds four flow cells through individual metered stopcocks which are used for flow rate control. The water flows through the stopcock into the feed line which inputs to the cell at the bottom. The water discharges from the top of the cell through a U-shaped tube into the receipt reservoir where the flow rate can be monitored with weight measurements and chemical analysis sample can be taken.



Figure 6.7. Schematic Diagram of SRTC Flow Test Apparatus

6.2.5 Electrochemical Tests

The corrosion and stability of the Al-SNF, which may impact the dissolution rate of radionuclides, will also be assessed through accelerated electrochemical testing. The electrochemical technique, an accepted standard test method, identifies and characterizes the modes of corrosion for a given material/environment system. The electrochemical tests that will be used for test protocol development involve controlling a potential applied to a sample and measuring the responding current. The relationship between the current and potential is a function of the active corrosion mechanisms. The electrochemical testing will be followed by metallographical analysis of the sample to characterize both the microstructural dependence of corrosion and the morphological changes from corrosion.

Several electrochemical tests are planned for evaluating U-Al alloys in the various simulated repository environments. The electrochemical tests include linear potentiodynamic polarization, cyclic potentiodynamic polarization, and galvanic current measurements. The test procedures are based on accepted ASTM standards (References 6.3-6.5). Various corrosion data are assessed from each test. The general corrosion rate and the stable corrosion potential are determined from LPP. Operable corrosion mechanisms including pitting susceptibility are assessed from the CPP results. Galvanic current measurements are performed to determine the relative galvanic current between two dissimilar materials. As for the static tests, the galvanic interaction will be measured between the Al-SNF and aluminum and stainless steel.

The equipment and instrumentation for conducting these electrochemical tests are an EG&G Princeton Applied Research Model 273A Potentiostat that is controlled by the EG&G corrosion test software, SoftCorr Model M352. The software will also be used to analyze the data with linear regression, resulting in the calculation of several electrochemical parameters. For LPP and CPP, the sample is polarized from the stable or natural corrosion potential over a potential range of 40 mV and 1 V, respectively. The responding current is measured as a function of potential and is displayed graphically. Galvanic curent measurements are performed without applying a potential. The Al-SNF sample is electrically connected to the other sample through the potentiostat which functions as a zero resistance ammeter.

An electrochemical cell contains the sample or working electrode, a reference electrode for measuring the potential, and an inert counter electrode through which the current flows. The test apparatus is a five-port Pyrex® flask. The counter electrodes are graphite rods, and the reference electrode is silver/silver chloride electrode (Ag/AgCl). The reference electrode is specifically made for high temperature use (i.e., <100 °C). A saturated calomel electrode may be used for some room temperature testing and for verifying the potential of the Ag/AgCl electrode. Gas flow into the cell is controlled through a bubbler. A condenser retrofits onto the bubbler for refluxing of the heater solution. The heating is performed with a ThermoWatchTM heating mantle which along with a thermometer provides temperature control.

6.3 PRELIMINARY RESULTS

6.3.1 Test Material Preparation

A series of four U-Al alloys, 10, 13.2 (eutectic), 15.9, and 25 wt % uranium, were casted initially providing the material with which the corrosion samples will be made. As stated previously, the 15.9 wt % U-Al alloy has been dropped from the test matrix. The cast ingots will be archived. The 67 wt % U-Al alloy will be cast in the future.

For each alloy, a measured quantity of aluminum (Type 1100) was melted in a graphite crucible by means of an induction furnace, similar to the technique used for melt-dilute development. With the melt at 800 °C, depleted uranium was added in sufficient quantity to achieve the desired composition. For the 25 wt % U-Al alloy, the melt temperature was higher at 1000 °C. The melt was induction stirred to promote homogeneity, and a dip sample taken for subsequent compositional analysis. The alloy was cast into carbon steel molds of two sizes: 2-3/4 inch diameter by 1-1/2 inch deep and 2-3/4 inch diameter by 3 inch deep. Casting in the larger mold was facilitated by use of a carbon steel pour cup of approximately the same size. Approximately 12 total ingots were produced--eight of the smaller size and four of the larger size.

A vertical cross-section of a large and small ingot from each alloy was cut and mounted to assess microstructural uniformity. Metallographic review indicated a fairly uniform structure throughout the cross-section of each ingot. Additionally, expected phases associated with specific composition of each alloy were observed. Figures 6.2, 6.3, and 6.4 are photo-micrographs of the 10, 13.2, and 25 wt % U-Al alloys, respectively.

Wrought materials were produced from the cast ingots by hot extrusion and cold rolling. Two of the larger billets from each alloy were heated to 450 °C and prepared for extrusion by coating with colloidal graphite and tin oil. The billets were pressed through a die producing a 3/4 inch round rod approximately 3 feet in length. The bars, having been cooled to ambient temperature in still air, were flat rolled to produce a dimension of approximately 1/2 inch between flats. Cold work introduced into the bars, based on reduction in cross-sectional area, is estimated to be 15%.

Test samples are being cut. The smaller cast ingots, which are not rolled, are sectioned by EDM to cut the individual samples. The rolled wrought samples are to be milled to remove the rounded edges and sawed with a diamond blade.

6.3.2 Preliminary Results of Scoping Static Tests

For the preliminary tests, dip samples from a casting melt were utilized to fabricate samples. These samples will closely resemble the cast ingots. Nine dip samples were taken from casting melt #97-18 (produced by melt-dilute program) to fabricate test samples. The melt was intended to have a uranium composition of approximately 30 wt %. Sections from three of the dip samples were submitted for chemical analysis. The

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analytical analysis showed the uranium composition ranged between 23.6-28.3 wt %, which is approximately the desired composition.

XRD was performed on sections of all nine samples. The XRD pattern from sample 7 is shown in Figure 6.8. The three phases were identified as aluminum, UAl₄, and UAl₃. In most cases the relative strength of the peak heights suggested that qualitatively the amounts of UAl₄ and UAl₃ were the same. There were some instances in which the UAl₄ peak was much stronger than the UAl₃ peak. The greater relative amount of UAl₄ may have occurred due to the melt temperature decreasing slightly. Metallography was performed on sectioned slices of dip samples 1, 4, and 9. Examples of primary aluminum, eutectic, UAl₄, and UAl₃ were observed on each sample. Finally each of the sectioned slices was examined by SEM and EDS. The UAl₃ tended to be larger and more block-like and contained traces of silicon. The UAl₄ on the other hand had a diamond-like shape and contained traces of iron. Micrographs of each microstructural feature are shown in Figure 6.9.



Figure 6.8. X-Ray Diffraction Pattern for 25 wt % U-Al Alloy which Displays the UAl₄, UAl₃, and Aluminum Phases

Cubes, 0.5 inch on edge, were sectioned from the dip samples for the tests. The central hole was drilled and the samples were polished to a 1000 grit finish. The samples were cleaned with ethyl alcohol and weighed. The pre-test weights are shown in Table 6.2.


Figure 6.9. Microstructural Features Observed on 25 wt % U-Al Alloy: a) UAl₃ and b) UAl₄ and Eutectic

Vessel	Sample ID	Time (days)	Pre-Test	Post-Test	Difference
	_		Weight (g)	Weight (g)	(g)
	97-18-1	7	4.0481	4.0561	0.0080
1	97-18-2	14	3.4783	3.4884	0.0101
	97-18-3	28	2.5020	2.5239	0.0219
	97-18-4	7	3.6258	3.6342	0.0084
2	97-18-5	14	2.9271	2.9301	0.0030
	97-18-6	28	4.7934	4.8113	0.0179
	97-18-7	7	4.0229	4.0318	0.0089
3	97-18-8	14	5.8220	5.8200	-0.0020
	97-18-9	28	4.5732	4.6020	0.0288

Table 6.2.	Pre-test and Post-test Sample	e Weights for	Preliminary	Static	Test
	Samr	oles			

Visual observations of the samples were recorded by photographs taken at approximately 4X. As shown in Figure 6.10, all the samples exhibited a significant amount of porosity.

The preliminary tests were conducted in glass vessels placed in a heating mantle. All vessels contained approximately 2.5 liters of solution and were maintained at a temperature of 90 °C. Vessel #1 contained cubes #1 to 3 which were attached to a disk fabricated from 1100 aluminum and were immersed in J-13 well water. Vessel #2 contained cubes #4 to 6 which were attached to a disk fabricated from 304L stainless steel and were also immersed in J-13 well water. Vessel #3 contained cubes #7 to 9 which were attached to a disk fabricated from 1100 aluminum. Prior to immersing the cubes and disk, 15 g of DWPF glass obtained from the cold runs was added to J-13 well water. The glass had been ground to a size between 100 to 200 mesh. The result was a solution with a higher pH. For future tests, a simulant of J-13 with the pH adjusted to 11 will be utilized.

The solution was allowed to stand for 7 days which is equivalent to the 7 day leach test performed to qualify the glass waste form. After 7 days the cubes and the disk were immersed in the solution. A test vessel which contained approximately 2.5 liters of J-13 well water with no samples or disk was utilized as a blank.

The samples were removed at intervals of 7, 14, and 28 days. Visually the samples had very different appearances (see Figure 6.11). Cubes that had been immersed in vessel #1 had a dull, matted aluminum appearance. Spots of white, powdery corrosion product were evident, although no gross degradation was observed. Cubes that had been immersed in vessel #2 on the other hand were covered by a black oxide film on the sides which were exposed to the water. The side which was in contact with the disk had a dull, matted aluminum appearance. Spots and streaks of the white powdery corrosion product



Figure 6.10. Example of Porosity Observed on Static Test Samples

were observed, although no gross degradation was observed. Cubes that had been immersed in vessel #3 had a shiny metallic appearance on the sides which were exposed to the water. The side which was in contact with the disk again had a dull, matted aluminum appearance. Corrosion products were not observed on the shiny sides of the cubes, and no gross degradation was observed.

In spite of the different appearance, similar weight changes were observed for the cubes at each of the time intervals (see Table 6.2). These small weight losses correlated with the limited amount of gross degradation that was observed on the cubes. The general trend of increasing weight with time indicated that an oxide film was forming. If it is assumed that the oxide film is primarily boehmite (Al_2O_3 • H_2O) the thickness of the films can be calculated to range between 5 µm after 1 week to 20 µm after 4 weeks (Reference 6.1). An oxide film was detectable through XRD.

The corroded samples were examined by SEM to study changes in the microstructural features. All samples revealed similar changes in their microstructural features. Pits were not observed on the primary aluminum phase. However, in each case there were indications that the aluminum had been preferentially corroded with respect to the U-Al alloy phases. As expected, the aluminum was anodic with respect to the alloy phases. Figure 6.12 shows that, for the eutectic, the aluminum has been etched leaving strands of the U-Al phase in relief. The alloy phase was identified by EDS to be UAl₄. The diamond-like UAl₄ particles were relatively untouched as grinding marks were evident, as shown in Figure 6.12. However, the aluminum, surrounding and in the center of the particle, was etched leaving the particle in relief. In most cases, the UAl₃ particles remained intact. However, there were instances where the particle had cracked and





(c) Figure 6.11. Post-test Photographs of 25 wt % U-Al Alloy removed from: a) Vessel #1, b) Vessel #2, and c) Vessel #3.



Figure 6.12. Post-test Micrographs of 25 wt % U-Al Alloy Showing Preferential Attack of Aluminum Phase around an UAL Particle and within the Eutectic

spalled leaving a crater approximately 100 to 200 μ m in diameter, as shown in Figure 6.13. Examples of these features were seen on both the creviced and exposed sides of the cube. The number of these features increased with time. Inside the crater the main components were identified to be Si, Ca, Al, and O. This degradation of the particle appears to have been caused by pressure from beneath the particle, possibly by oxide film formation or hydrogen gas formation.

The solutions from the vessels were filtered after the tests to determine the presence of insolubles. A section of the filter paper was examined by SEM. The filter papers revealed similar insoluble compounds. Most of the insoluble particles were either aluminum oxides, silica, or calcium. However, several particles of UAl_3 were also observed. These particles may be some of the particles which had spalled from the surface.

Water samples were collected from the vessels every three to four days to determine the dissolution rate of uranium and any other changes in water chemistry during the degradation process. These samples are currently being analyzed to determine the amount of uranium that dissolves in the water and the effect of the degradation process on the water chemistry.



Figure 6.13. Post-test Micrographs of 25 wt % U-Al Alloy Showing Cracking and Spalling of the UAl₃ Phase

6.3.3 PNNL Single-Pass Flow Tests

Single-pass flow tests on aluminum-based SNF and unirradiated fuel specimens were initiated at PNNL according to an approved task plan (Reference 6.6). The purposes of these tests were: 1) to compare dissolution rate results obtained from tests on spent commercial nuclear fuels with those obtained for aluminum-based SNF, and 2) to determine if irradiation effects the dissolution rate of the aluminum-based SNF.

Spent fuel from four different fuel materials will be tested. These fuels will include a casting of U-Al from a Mk 22 and three fuels processed by powder metallurgy for research reactors. These processed fuels are dispersions of uranium oxide, uranium silicide, and uranium aluminide in an aluminum matrix. The fuel materials were prepared and characterized by Argonne National Laboratory (Reference 6.7). Each of the fuel types will be tested in the following three test solutions:

- 0.02 molar sodium bicarbonate, pH = 8, 25 °C; supply water sparged with air containing appropriate CO₂ concentration to maintain pH at 8.
- Simulated J-13 well water, pH~8, 25°C; supply water exposed to air, but not sparged.
- Dilute nitric acid, pH=3, 25 °C; supply water sparged with CO₂-free air.

Water from each flow cell will be sampled one to three times per week and analyzed for uranium. Each test will be conducted until a steady state dissolution rate persists for a few weeks. The tests will be initiated in October and are expected to be completed in three to six months.

The unirradiated fuel specimens were prepared from depleted uranium at SRS. The material was a cast alloy similar to the Mk 22 and contained 19 wt % U. The specimens were tested in the same environments described above. These tests were initiated in August and completed in September. The uranium concentration was highest in the nitric acid solution, while the J-13 produced the lowest steady-state concentration. Areal fractions of the U-Al particles are being determined by metallography so that the area normalized dissolution rates may be calculated. Tests on the unirradiated samples will be duplicated at SRS to confirm the results.

6.3.4 Electrochemical Tests on U-Al Alloys in J-13 Well Water

Corrosion testing was performed on U-Al alloys with nominal compositions of 10, 25, 30, and 50 wt % depleted uranium. This testing initially was part of subtask 3.5, "Corrosion Studies", of the Melt/Dilute Technology Development Program and is now part of SNF Performance and Test Protocol. The test objective was to characterize the stability of these alloys for long-term storage in a geologic repository. The corrosion tests consisted of electrochemical potential monitoring to determine alloy stability in aqueous environments, linear potentiodynamic polarization to determine a general corrosion rate, and cyclic potentiodynamic polarization to assess pitting susceptibility. The results indicated that the corrosion behavior in J-13 well water for the alloys were dependent on the composition and morphology. The electrochemical potentials, which stabilized within several hours for all alloys, became increasingly electronegative with increasing uranium content. The general corrosion rates for the 0-30 wt % U-Al alloys were similar to that for aluminum alloys. The maximum pitting potential was reached at a uranium content of 10 wt %, indicating that this alloy composition was the most resistant to pitting.

Electrochemical Tests

The stability of U-Al alloys was evaluated through three accelerated corrosion tests: electrochemical (corrosion) potential monitoring to assess alloy stability, LPP to determine a general corrosion rate, and CPP to assess pitting susceptibility. The equipment and test cells were similar to those described in Section 6.2.5. Several differences were the use of a saturated calomel reference electrode, testing at 30 °C, and no galvanic current measurements. The test procedure consisted of performing EPM after sample immersion, followed by LPP and CPP. Each sample was tested twice with this series of tests. For the first series, the potential monitoring was conducted for 24 hours. The potentials were found to stabilize within approximately three hours, so EPM in the second test series was conducted until the sample potential was no longer changing.

The tests were performed in standard five-port Pyrex® corrosion cells. The cell electrodes consisted of the working electrode, which was the U-Al alloy sample, graphite

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rod counter electrodes, and a reference electrode which was a saturated calomel electrode. All reported potentials are based on this reference. A low flow of air was blown into the test solution through a gas bubbler. The cell was placed in a heating mantle which, along with a thermometer, provided temperature control.

The test solution was a J-13 well water composition which was similar to that for the static test. The actual test solutions, before and after testing, were analyzed for chemical composition. The nominal composition and the ranges of analyzed values for the pretest solutions are given in Table 6.3. The average solution pH and conductivity were 7.7 (7.4 to 8.2) and 267 (233 to 300) µS/cm, respectively. For most of the constituents, the ranges of concentrations bracketed the nominal values. The carbonate concentrations could not be analyzed because the solutions were not sufficiently alkaline. The chloride concentrations were well above the nominal value. The source of the additional chloride, however, has not been identified. The chloride concentration was lower in post-test solutions, in some cases by greater than 50%. The cause of this fluctuation has not been identified. Silic acid, in powdered form, was used to obtain the necessary silicon concentration. During the first tests for each alloy, excess silic acid was used to make up the solution, which settled out during the test. For the second series, the nominal value was used. The higher end of the range reported in Table 6.3 reflects the first test series, while the lower end is indicative of the second series. This difference in solution composition was not found to affect the results.

	Nominal	Actual		Nominal	Actual	
<u>Constituent</u>	<u>(ppm)</u>	(<u>ppm)</u>	Constituent	<u>(ppm)</u>	<u>(ppm)</u>	
Calcium	13	5-12	Chloride	7.1	30-68	
Potassium	5.3	5-10	Fluoride	2.3	1.9-3	
Magnesium	1.9	0.7-1.1	Nitrate	8.1	5.7-9	
Sodium	44	38-57	Sulfate	18	5.5-21	
Silicon	33	35-87	Carbonate	120	ND	

Table 6.3. Composition of J-13 Well Water for Electrochemical Testing

Sample Characterization

The U-Al alloys were produced in the laboratory from a supply of bulk aluminum ingots and depleted uranium. The initial materials were melted in an induction furnace at temperatures between 800 and 1400 °C. The alloys were cast into 0.75-inch diameter steel dip samplers and either slow cooled in air or water quenched. Thin (0.125-inch) disks were sliced from the cast cylinder. Each disk was uniquely numbered with #1 starting from the bottom of the dip sampler. The disk were placed into epoxy mounts with copper wires attached. These wires were used for making the electrical connections for the tests and were attached to each sample using a conductive epoxy. The surface of each sample was finished on 800 grit silicon carbide paper before corrosion testing. For comparison, several commercial aluminum alloys and depleted uranium were also tested with the same series of electrochemical techniques. The aluminum alloys were 1100, 5052, and 6061. The test samples (0.75 in \times 0.75 in \times 0.125 in) were cut from larger coupons that were distributed by Metal Samples. Depleted uranium was taken from material used for making the alloys. Both the uranium and aluminum alloys were mounted similarly as the U-Al alloys.

Prior to corrosion testing, the samples were prepared metallographically for microstructural characterization. The samples were polished and etched with a nitric/hydrofluoric acid mixture to reveal the microstructure. The samples were examined with both light and electron microscopy. The microstructures varied with alloy composition and cooling rate. The 10 wt % U-Al alloy with slow cooling, which is shown in Figure 6.14(a), consisted of primary aluminum dendrites with the U-Al eutectic filling the interdendritic spaces. The black areas in the photograph are voids created by gas porosity. The microstructure changed significantly when quenched as shown in Figure 6.15(a), forming a fine dispersion of eutectic within an aluminum matrix.

The slow cooled 30 wt % U-Al alloy, as shown in Figure 6.16(a), had UAl₃ particles surrounded by a matrix of eutectic, although some aluminum dendrites were also present. The structure was slightly finer with faster cooling as shown in Figure 6.17(a). The 50 wt % U-Al alloy, as shown in Figure 6.18(a), was highly variable including both dendritic and irregular shaped structures. The microstructure consisted of the intermetallics and the eutectic, along with uranium and aluminum. All these samples contained pores that resulted from the casting as shown in Figure 6.19.

The microstructures of the aluminum alloys were fine grained and similar in appearance to the quenched 10 wt % U-Al alloy shown in Figure 6.15(a). The depleted uranium sample had a larger grain size with numerous small pores. Figure 6.20 is a photomicrograph of this sample prior to testing. The characterization of the 25 wt % U-Al alloy was discussed with the results for the static test.

Test Results

The tests results were analyzed for specific electrochemical parameters that were used to assess the stability of the U-Al alloys. Table 6.4 shows these parameters for each test technique. The trend of E_{∞} over time is an indication of the alloy stability. Figure 6.21 shows a plot for the 10 wt % U-Al sample. Most of the samples reacted similarly after immersion into J-13 water. For all the alloys, the corrosion potential was initially more electronegative than the steady state value, ca. -0.800 V. During the first few hours, the potential rose to the steady state value and remained at this value. This initial change in potential was probably due to the formation of a thin oxide on the sample surface. The potentials had short-term fluctuations of approximately 0.030 V during this period.

<u>Test</u>	Parameter	Abbreviation
EPM	Open-circuit potential	E_{oc}
LPP	Potential at zero current	E _{I=0}
	Polarization resistance	R _P
CPP	Corrosion potential	Ecorr
	Pitting potential	\mathbf{E}_{pit}
	Anodic Tafel slope	B _A
	Cathodic Tafel slope	Bc

Table 6.4. Parameters Measured From Electrochemical Tests

 R_P is the slope of the potential-current plot at $E_{i=0}$, which is shown in Figure 6.22 for a 10 wt % U-Al alloy. R_P was used to calculate the general corrosion rate for the samples. Figure 6.23 shows a typical polarization curve for U-Al alloys calculated from CPP values. The electrochemical parameters for CPP are shown in the figure. E_{corr} is the potential at which the current changes from anodic to cathodic. E_{corr} , $E_{i=0}$, and E_{oc} values should be similar if the electrochemical tests are not altering the sample. The Tafel slopes, B_A and B_C , were used to calculate the corrosion rate, as will be discussed later. Tafel slopes are generally measured using slightly different polarization conditions than those used for CPP; however, to simplify testing these slopes were calculated from the CPP data. E_{pit} is measured at the point where the anodic current starts to increase by at least an order of magnitude. The hysteresis in the polarization curve is also an indication of pitting. The hysteresis results from a larger current generated during the reverse scan (downward arrow), which is associated with the pits, than the forward scan current (upward arrow), which is associated with the passive oxide. If pitting does not occur, the reverse and forward scan are similar and the curve does not show a hysteresis.

The electrochemical parameters for each sample varied between the duplicate runs of each test. The results are shown in Table 6.5 for the U-Al alloys, along with average values for the aluminum and depleted uranium samples. The potentials, E_{corr} , $E_{I=0}$, and E_{∞} , varied over a wide range from -0.219 to -0.568 V, although most values were in the range of -0.350 to -0.400 V. For each sample test, these potentials were consistent, usually differing by less than 20 mV. The sample reproducibility for E_{pit} was not as consistent as the other potentials, typically varying by more than 50 mV. Surface condition of the sample can have a significant effect on the measurement of E_{pit} . R_P measurements were consistent for each sample, but ranged over a couple of orders of magnitude for all the alloys (6 to 300 kohms). The Tafel slopes were quite variable but are dependent on the conditions in both the sample and the solution.

The general corrosion rate (CR) was calculated with R_p and the Tafel slopes by the following equation:

$$CR (mpy) = \frac{0.13 (B_{A}) (B_{C}) (EW)}{(A)(d)(2.3(B_{A},B_{C}))R_{P}}$$
(1)

where EW is the equivalent weight, A is the surface area, and d is the alloy density. The corrosion rate was calculated from an adjusted R_P value because the solution resistance was high. The adjusted R_P was calculated by subtracting the solution resistance from the measured R_P . Since the Tafel slope data was variable for the U-Al alloys, an average value of all the test results was used. For the commercial aluminum alloys and uranium metal, the Tafel slope for each sample was consistent and was not averaged. For U-Al alloys, the values for EW and d of aluminum were used because from microstructural examination the aluminum was found to have corroded, therefore, d = 2.7 g/cm³ and EW = 8.99. For uranium, d = 18.7 g/cm³ and EW = 59.5. The area of the sample was the measured value prior to the start of each test.

	E _{oc}	Rp	E (I=0)	Ecorr	E_{pit}	BA	Bc
Sample 3 1	(V, SCE)	(Kohms)	(V. SCE)	(V, SCE)	(V. SCE)	(V/decade)	(V/decade)
-							
50 slow	-0.381	76.67	-0.382	-0.385	-0.141	0.367	0.181
	-0.395	48.28	-0.389	-0.394	-0.02	0.383	0.489
50 slow	-0.34	6.053	-0.354	-0.424	-0.4	0.163	0.324
	-0.41	15.7	-0.403	-0.406	-0.4	0.106	0.073
10 slow	-0.358	16.93	-0.365	-0.355	0.05	ND	ND
	-0.34	1 9.6	-0.333	-0.32	-0.28	0.082	0.137
10 quench	-0.385	43.97	-0.385	-0.389	-0.04	0.193	0.145
	-0.379	77.8	-0.372	-0.371	0.04	0.428	0.193
10 quench	-0.31	66.88	-0.316	-0.362	-0.07	0.229	0.157
	-0.378	112.5	-0.373	-0.364	-0.115	0.298	0.218
30 slow-	-0.267	287.4	-0.219	-0.22	-0,143	0.064	0.049
	-0.568	101.9	-0.565	-0.553	-0.15	0.362	0.49
30 slow	-0.401	115.9	-0.402	-0.406	0.08	0.219	0.102
	-0.395	113.4	-0.483	-0.49	-0.175	0.27	0.194
30 quench	-0.311	248	-0.311	-0.315	-0.235	0.143	0.081
	-0.355	112.6	-0.35	-0.341	-0.168	0.216	0.214
30 quench	-0.377	205.1	-0.372	-0.375	-0.235	0.225	0.099
	-0.385	110	-0.364	-0.362	-0.125	0.456	0.346
25 slow	-0.466	63	-0.466	-0.466	-0.300	0.216	0.207
	-0.487	55	-0.489	-0.487	-0.225	0.198	0.135
Al		52		-0.360	-0.206	0.125	0.170
U		6.2		-0.481		0.299	0.427

Table 6.5. Electrochemical Parameters For U-Al Samples

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The average values for each composition are shown in Figure 6.24 for the corrosion and pitting potentials and the corrosion rate. Each of these corrosion parameters have a compositional dependence which is discussed below.

Corrosion Potential

The corrosion test results showed that the stability of the U-Al alloys as measured by E_{oc} or E_{corr} varied slightly with the alloy composition. The corrosion potential became more electronegative with increasing uranium content. The 10 and 30 wt % U-Al alloys had potentials more typical of the commercial aluminum alloys 1100, 6061, and 5052. The similarity of these different materials is associated with the aluminum oxidation that occurred on all the samples. The 25 and 50 wt % U-Al alloys had more electronegative potentials similar to the depleted uranium sample. The 25 wt % U-Al alloy was made at a different time than the other samples and appears to have more intermetallic particles similar to the 50 wt % U-Al alloy. The variability of the commercial aluminum alloys and the depleted uranium was not as large as that of the U-Al alloys.

Pitting Potential

 E_{pit} , which is a measure of pitting susceptibility, was also found to be a function of alloy composition. As shown in Figure 6.24, a maximum occurred at the 10 wt % U-Al alloy. The microstructural changes that occurred with composition and processing affected the pitting process. The 10 wt % U-Al alloy had a uniform distribution of the eutectic, especially the quenched samples which did not have large dendrites. The uniform distribution of UAl₄ could have enhanced the surface oxidation and formation of a protective oxide layer.

The 30 wt % U-Al alloy had large UAl₃ particles which could act as efficient cathodic sites, disrupt a uniform oxide on the surface, and induce pitting corrosion of the surrounding aluminum. The distribution of UAl₃ was nonuniform. The 50 wt % U-Al sample did not have a defined E_{pit} value, but still pitted during the experiment. E_{pit} was assumed to be similar to E_{corr} since the sample showed no passive behavior.

The E_{pit} potential for aluminum alloys varied over a larger range than expected, which was primarily from the 6061 sample. This difference may be an anomaly of the sample. The variability was similar to that of the U-Al alloys. The commercial aluminum alloys appear to be more susceptible to pitting than the 10 wt % U-Al alloy since E_{pit} is more electronegative. This difference may be due to the difference in oxide formation. Depleted uranium did not pit and corroded by general corrosion.

Corrosion Rate

The corrosion rate and R_p had a greater dependence on the alloy composition than the potentials. Similar to both potentials, the changes were attributed to both the uranium content, i.e. phases present in the alloy, as well as the morphology. In Figure 6.24, the corrosion rate was constant for the 0 to 30 wt % U-Al alloys and increased for the 30 to 100 wt % U-Al alloys. The maximum rate occurred for the uranium sample. The slight

variation in rate from 0-30 wt % uranium was not considered significant because of the data variability. At the low uranium content, the general corrosion rate could be controlled primarily by the aluminum phase, which has a protective oxide layer. Microstructural characteriztion after testing (Figures 6.14-6.18(b)) showed that for the alloys the aluminum phase had corroded preferentially to the intermetallics that were present.

The corrosion resistance of the 10 wt % U-Al alloy may also be affected by the cooling rate, although the 30 wt % U-Al alloy was not. This difference again may be a manifestation of the microstructure. The cooling rate dramatically changed the microstructure of the 10 wt % U-Al alloy as shown in Figures 6.14(a) and 6.15(a), but only had a slight effect on the 30 wt % alloy as shown in Figures 6.16(a) and 6.17(a). However, only one slow cooled sample was tested so the effect of cooling rate needs further study.

The corrosion rates for the U-Al alloys are less than 1 mpy which is generally accepted as excellent corrosion resistance. The corrosion rates, except for the 50 wt % alloys, are similar to those for the commercial aluminum alloys.

After the first test, the samples were examined in an SEM. Figures 6.14(b) to 6.18(b) show the photomicrographs for each alloy after corrosion testing. The corrosion morphologies of these samples were similar. The aluminum phase corroded preferentially to U-Al phases present in the alloy. Oxides were detected on most samples as shown in Figure 6.15(b).



Figure 6.14. Microstructure of Slow Cooled 10 wt % U-Al Alloy before (a) and after (b) Corrosion Testing

1. - A \$



Figure 6.15. Microstructure of Quenched 10 wt % U-Al Alloy before (a) and after (b) Corrosion Testing

e-

3.11



Figure 6.16. Microstructure of Slow Cooled 30 wt % U-Al Alloy before (a) and after (b) Corrosion Testing



Figure 6.17. Microstructure of Quenched 30 wt % U-Al Alloy before (a) and after (b) Corrosion Testing



Figure 6.18. Microstructure of Slow Cooled 50 wt % U-Al Alloy before (a) and after (b) Corrosion Testing



Figure 6.19. Macrograph of As-Cast 30 wt % U-Al Alloy Displaying Casting Voids



Figure 6.20. Photomicrograph of Depleted Uranium Metal

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Figure 6.21. Typical Potential-Time Curve for U-Al Alloys



Figure 6.22. Typical Linear Polarization Curve for U-Al Alloys



Figure 6.23. Typical Cyclic Polarization Curve for U-Al Alloys



Figure 6.24. Average Values of Electrochemical Parameters as a Function of Aluminum Content

6.4 **REFERENCES**

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7.0 SNF CHARACTERIZATION PROGRAM

7.1 SUMMARY

The focus of the characterization program has been to review, interpret, and apply existing regulations and requirements for both interim dry storage and proposed geologic repository disposal to identify those that involve physical or chemical characterization. Pretreatment characterization requirements applicable to aluminum-based spent nuclear fuel forms have been identified.

From the existing regulations and criteria, pretreatment characterization requirements for the fuels to be received and processed at SRS within the Transfer & Storage Services facility have been developed. For the purposes of this program, the use of the term "pretreatment" is intended to refer to those activities performed prior to the treatment process necessary to place the fuel forms into a "road-ready" package. The two primary optional forms for disposal of Al-SNF, direct and melt-dilute, were evaluated to determine process-specific characterization requirements. Such requirements are expected to be used as input for the selection of a preferred alternative technology for the disposition of Al-SNF.

While each of the two optional forms for disposal of Al-SNF offers individual attributes and/or advantages, the scope and degree of pretreatment characterization requirements for each option may be a significant factor in the down-selection process. Pretreatment characterization requirements, however, are based on repository acceptance criteria which are currently under development and may be subject to change. In addition, the nature and scope of pretreatment characterization requirements for each disposition option are highly dependent upon the validity and acceptability of existing fuel data and operating history, with the direct disposal option currently deemed the more dependent of the two options.

The two primary deliverables for this program are the Pretreatment Characterization Requirements report, issued September 1997 (Reference 7.1), and the SNF Characterization Data Review, due to be issued December 1997.

7.2 PURPOSE/SCOPE

The primary purpose of the characterization program is to establish pretreatment characterization requirements with technical basis to enable storage and disposal of Al-SNF forms. These requirements would then be met as part of the demonstration that the Al-SNF forms are acceptable for disposal into the proposed geologic repository.

The scope of this program applies to DOE Al-SNF to be received at SRS for disposition, primarily the foreign research reactor and domestic research reactor fuels of the MTR

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type. Regulatory requirements and subsequent pretreatment characterization requirements outlined in this summary report are those believed to be the most pertinent for Al-SNF disposition, but should not be considered as an all-inclusive set of requirements to be met within the TSS facility. This report does not intend to address issues and requirements pertaining to the routine receipt, transportation, and handling the fuels. The primary scope of this document is limited to the characterization requirements directly pertinent to the Al-SNF before treatment and placement into a "road-ready" canister within the TSS facility.

7.3 DRIVERS FOR CHARACTERIZATION

7.3.1 Overview

For the purposes of the characterization task, the use of the term "characterization" has been limited to those activities performed to determine or ascertain the fuel properties necessary to meet requirements. Determination of behavioral characteristics of the Al-SNF form, such as corrosion resistance, pyrophoricity, criticality response, etc., is covered under separate tasks.

In order to assess the degree of pretreatment characterization necessary to meet both interim dry storage and geologic repository storage requirements, a review of the current regulations and preliminary data needs deemed pertinent to DOE-owned aluminum SNF was performed. Preliminary data needs and system requirements documents for DOE SNF were reviewed along with applicable CFR sections and DOE Orders. A summary of the regulations and requirements that were reviewed is provided in Reference 7.1, along with specific excerpts and brief interpretations.

A list of the major laws governing the possession, use, storage, and disposition of hazardous materials including DOE SNF is given here in chronological order for reference. These high-level governing documents are generic by nature and were therefore not critically reviewed.

- The Atomic Energy Act of 1954 (AEA) outlines the safety, operation, and licensing of nuclear facilities and activities involved in the management of source, special nuclear and byproduct materials.
- The Clean Air Act of 1963 (CAA) details regulatory standards for all toxic and/or hazardous air pollutants under the National Emission Standards for Hazardous Air Pollutants, for which 40 CFR 61 is the primary EPA interpretation and DOE Order 5400.5 is the guideline for DOE activities.
- The National Environmental Policy Act of 1969 (NEPA, Public Law 91-190) mandates that Federal plans, functions, programs, and resources must be used to achieve six general goals, including the assurance of "safe, healthful, productive, and aesthetically and culturally pleasurable surroundings" for all Americans.

- The Resource Conservation and Recovery Act of 1976 (RCRA, Public Law 94-580) regulates waste that meets two criteria: i) "solid waste"; and ii) it must exhibit certain hazardous characteristics (as interpreted from 40 CFR Part 261).
- The Clean Water Act (Federal Water Pollution Control Act Amendments of 1977, FWPCA) regulates the quality of surface water, drinking water, and its sources.
- The Nuclear Waste Policy Act of 1982 (NWPA, Public Law 97-425) succeeds the AEA and provides environmental protection standards for management and disposal of HLW, SNF, and TRU and specifies the requirements for site characterization and licensing of a federal HLW repository.
- The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA, Public Law 96-510) and the Superfund Amendments and Reauthorization Act of 1986 (SARA) and subsequent amendments both establish a remediation and response program for past hazardous substance activities.
- The Federal Facilities Compliance Act (FFCA) of 1992 mandates the development of plans and capabilities for the treatment of mixed wastes at each DOE site where mixed wastes are either generated or stored.

Primary interpretation of these governing laws is given in the CFR. DOE orders are supplementary to the CFR and are written for specific application to DOE tasks. Documents were critiqued from the standpoint of determining the applicability of individual requirements to the storage and disposition of DOE-owned SNF, with specific focus on the applicability to aluminum-base fuels.

By nature, these documents are subject to interpretation, and therefore, the level of applicability to Al-SNF may be subject to interpretation as well. Without firmly established data needs and requirements, however, the Site disposition process must move forward by assuming data needs and requirements from existing documents and governing regulations. The applicability of such regulations and requirements to Al-SNF is therefore being assumed by SRTC/MTS and does not necessarily reflect the interpretation held by other agencies.

The regulations and requirements deemed the most pertinent and applicable to the pretreatment characterization of Al-SNF are summarized in Table 3.1 of Reference 7.1. The majority of the regulations most applicable to the pretreatment characterization and qualification of the Al-SNF form for repository disposal are under the jurisdiction of 10 CFR, Part 60, "Disposal of High-Level Radioactive Wastes in Geologic Repositories", and 10 CFR, Part 72, "Licensing Requirements for the Independent Storage of Spent Nuclear Fuel and High-Level Radioactive Waste". Specific excerpts from these regulations and requirements are discussed and interpreted in Reference 7.1, with a complete list of the regulations, data needs, and requirements documents reviewed.

Subsequent to the issuance of Reference 7.1, the OCRWM issued revision 0 of the waste acceptance criteria which are the repository requirements for disposal (Reference 7.2). That document incorporates all previous preliminary versions of waste acceptance criteria and repository performance requirements into a single document. The WAC has not been reviewed for characterization needs. Hereafter in the characterization task, the WAC

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should be used as the primary reference for requirements, with items identified as "TBD" to be addressed on a case-by-case basis as necessary.

7.3.2 Impact Upon Characterization Needs

The impact of the federal regulations and requirements upon pretreatment characterization requirements relative to the form of the Al SNF was assessed. As previously noted, many of the regulations and requirements affect not only pre-treatment but post-treatment characterization requirements and form qualification activities as well. Due to the nature of repository acceptance criteria, however, those requirements applicable to the post-treatment characterization of the final form and package are perceived as being applicable regardless of the disposition option selected.

Canisters filled with the direct form (intact assemblies) or the melt-dilute form (melted and cast fuel compositions) will be subject to a similar if not identical degree of postcharacterization requirements such as radiation level monitoring, thermal load determination, and radionuclide release monitoring. Therefore, only the impact upon general characterization requirements will be discussed here; pretreatment characterization requirements for each disposition option are discussed in later sections. A summary of the impact of high-level requirements and regulations upon characterization and/or form qualification activities is provided in Table 3.2 of Reference 7.1.

7.4 PRETREATMENT CHARACTERIZATION REQUIREMENTS

7.4.1 General

One of the major obstacles to the development and final selection of an approved alternate technology for the disposition of DOE-owned Al-clad spent nuclear fuels is the lack of clear definition of the requirements for repository acceptance of the fuels. Although the National SNF Program is currently developing guidelines for SNF custodians to follow in the preparation of fuels for repository acceptance, these guidelines are preliminary in nature and are currently lacking in adequate detail as to the approved test techniques, methodologies, repository conditions, and acceptable accuracy/precision levels for form assessment.

This obstacle is amplified by the fact that the fuel property data and operation history of the fuels to be provided by SNF custodians may be inaccurate, lacking in detail, or in some extreme cases, non-existent. This is anticipated to be more of an issue with FRR fuels than for DRR fuels, but may also be an issue for some of the older DRR fuels as well. Characterization for these fuels is therefore anticipated to be required to a greater extent, if only for documentation purposes.

Although the validity of data (Appendix A-type) provided by SNF custodians is currently unknown or is at least considered subjective, this issue may be negotiated between the OCRWM, NRC, and fuel custodians. Until a definitive official decision or agreement is

made by the respective authoritative agencies, however, the pretreatment characterization requirements for either the direct disposal or Melt-dilution disposition options cannot be clearly defined and are heavily dependent upon the nature of such an agreement.

7.4.2 Direct Disposal

Acceptable Data

Under the direct disposal disposition option, fuels are to be received, placed into interim dry storage, dried to eliminate free liquids, and then packaged and stored in a "roadready" configuration suitable for acceptance into the geologic repository. In order to minimize the degree and scope of pre-treatment characterization activities necessary to achieve this "road-ready" state, the assumption could be made that the Appendix A data package to be provided by the SNF custodians is valid and meets the quality assurance requirements with regard to accuracy, precision, and documentation. Based on review of several Appendix A packages, complete and consistent isotopic data is not expected for all fuels.

Under this scenario, the majority of characterization activities would be limited to that of documentation evaluation, possible SIP tests to determine cladding breaches, and monitoring for radiation for environmental and safety considerations. If burnup data and fabrication details such as original fissile content and U^{235} enrichment are accepted as valid, then thermal load and criticality calculations could be made relatively easily through the use of validated computer codes (ORIGEN-S). Visual examination should still be performed to assess the corrosion condition of the fuel, using conventional high-resolution photographic and video surveillance equipment used for radiation service and/or fuel management activities.

From accepted burn-up data (U^{235} "burned" during the fission process over the service life of the fuel) and original enrichment ($\% U^{235}$ of the total uranium content), isotopic inventory of the fuel would require no separate validation or confirmation technique. This would eliminate the need for gamma spectroscopy scanning equipment or radiochemical techniques. Essentially, fuels could be received, visually examined, put through the drying/treatment process, and packaged into the desired configuration meeting thermal load and criticality limits. The packaged canister would then still be subject to external monitoring for radionuclide release, radiation level, and thermal output per packaging and storage requirements.

Although this scenario is considered to be an ideal case, it is perceived that complete acceptance of the fuel historical and operational data per the submitted Appendix A package without some degree of data validation or qualification is unlikely to be approved by the NRC and does not adequately address the anticipated characterization needs of the TSS facility. A summary of pretreatment characterization requirements for aluminum DOE SNF under the acceptance of existing fuel data (Appendix A-type) is provided in Reference 7.1.

Suspect Data/Validation Tests

As previously discussed, total or complete acceptance of the Appendix A data package and other operational or historical data accompanying fuel shipments is considered to be an ideal case. Appendix A packages are acceptable for shipping requirements but are not expected to meet 0333P QA requirements for storage, handling, and disposition activities. In the more realistic case, the validity or accuracy of Appendix A-type data and operational history may be questionable for many of the FRR fuels and possibly some of the older DRR fuels as well. This may be due to the lack of material control and accountability over the years as well as possible variation in documentation practices between participating nations and facilities. For some of the fuels, the data may not even exist and can only be obtained through characterization upon receipt.

Therefore, in order to ensure the safety of the TSS facility, personnel, and the surrounding environment, as well as the acceptability of fuels for repository disposition, some degree of validation or confirmatory characterization activities are believed to be necessary for the majority of fuels to be received. Although this may involve only one or two primary characterization techniques or activities, the impact upon facility and process design, development, and operation must be considered.

Most of the inherent fuel properties such as thermal load, isotopic inventory, radiation level, etc., are direct functions of fuel enrichment ($\%U^{235}$), fuel burnup, and fuel composition. The determination of these properties must be performed to at least a minimal degree in order to confirm the validity of the data package or to fill in necessary information gaps. From burnup determination and U²³⁵ measurements, the use of ORIGEN-S codes to calculate/verify isotopic inventory could be performed, with the same data used to confirm criticality, thermal load, and/or radiation level calculations. The key unknown parameters for such evaluations are the accuracy and precision required, as well as the range or number of total measurements needed per assembly. For the case of invalid, suspect, or missing data, specific pretreatment characterization requirements for the direct disposal process are provided in Reference 7.1.

7.4.3 Melt-Dilution

7.4.3.1 Overview

Although the primary advantage of the melt-dilution alternate technology option is the ability to alter and control the final composition of the form, thus reducing criticality and proliferation concerns as well as possibly enhancing resistance to environmental degradation, a secondary benefit is the possible reduction in pre-treatment characterization activities to be performed. In the melt-dilution process, the SNF assembly is to be melted, mixed with depleted uranium, aluminum, and/or neutron poisons if desired, and then cast into a crucible or mold. The mold may be an intermediate container or may possibly be the final canister itself, depending upon process requirements yet to be defined. Therefore, because the SNF form is being altered to such an extent, the process may be considered to be inherently independent upon the fuel fabrication and operation history.

For the melt-dilution process, the key parameters for process control are the total uranium content and the $\% U^{235}$ which are used as input for melt composition calculations to determine the relative amounts of depleted uranium, aluminum, and/or poisons to be added in order to achieve the final target composition. These parameters may be determined from review of the fuel data package (Appendix A-type) or may be determined through analytical measurement in the melt during processing. Although acceptance of Appendix A data would be beneficial, determination of these parameters during actual processing may be preferred in order to obtain a more accurate value for the homogeneous form. Therefore, the melt-dilution process essentially eliminates the need to know the in-depth history of the fuel.

7.4.3.2 Process Characterization Requirements

In comparison to the direct disposal approach to SNF disposition, the melt-dilution option results in a completely different form which may exhibit superior properties in terms of corrosion resistance, leachability, etc. Due to the difference in processing and the nature of the resulting form, pre-treatment characterization requirements for the melt-dilution option are not only different from those for direct disposal, but are considered to be significantly less in scope and cost on a per unit basis.

SNF assemblies (MTR-type) are to be placed into a furnace (final design to be determined), melted and mixed with depleted uranium and/or aluminum to alter the final composition, and then cast into a mold or crucible. Although final compositions have not been formally selected, the program is currently focusing on the selection of a 20% (or less) U^{235} composition to reduce criticality concerns associated with higher enriched fuels. Depending upon the final composition selected, melt temperatures, furnace design, crucible material selection, and off-gas systems will be affected. Assemblies are assumed to be melted and processed one at a time, filling approximately 80% of the canister volume.

In order to process the material and to ensure that the final form is consistent and within the target composition range, some degree of pre- and post-treatment characterization will need to be performed. Because the form is being altered and produced into a consistent form, however, post-treatment characterization requirements for process validation may be different and more limited in scope than those for direct disposal. Following treatment (i.e., melting and casting), the canistered form will be expected to meet the same posttreatment characterization requirements such as radiation level and thermal output for repository acceptance as those fuels processed under the direct disposal option.

From the total U and % U^{235} data, a source term using ORIGEN-S or similar validated computer code may be employed to produce the isotopic inventory of the pre-treated fuel. Upon melting however, some isotopes and reactive species may be driven off during the melting and mixing process, thus altering the isotopic inventory of the final product. If, however, the target form composition is less than or equal to 20% U^{235} , the form may not necessarily have to conform to the stricter standards that apply to HEU fuel materials Page 7.8 of 7.18

 $(>20\% U^{235})$ such as material accountability. While the probability of criticality is greatly reduced, some degree of criticality controls will remain necessary. Specific requirements are outlined in Reference 7.1.

7.4.4 Disposition Option Comparison

In order to aid in the down-selection of the two alternative disposition options, a comparison of the two options was made. The down-selection process should be made based on three primary factors: 1) cost evaluation of disposition option, 2) evaluation of safety/proliferation factors, and 3) acceptability of the respective forms into the geologic repository. An accurate overall comparison between the two options does not appear to be feasible at this point in time due to the following reasons:

- A) A significant part of the overall cost of the direct disposal option may be the pretreatment characterization requirements and data acquisition activities, which are heavily dependent upon the acceptability and validity of the fuel data package (Appendix A-type). This issue has not been formally resolved, and may require evaluation on a case-by-case basis. Baseline data validation tests could be performed, however, to confirm the accuracy of the data package, with the capability to perform additional characterization as needed pending baseline data results.
- B) The repository acceptability and performance of the primary form generated by the two disposition options have not been fully established. Although DOE SNF comprises a relatively small portion of the total waste inventory to be disposed within the geologic repository, with Al-clad SNF an even smaller amount of the total DOE SNF inventory, issues such as leachability or durability of the form, pyrophoricity (not perceived as an issue for the aluminum fuels), corrosion resistance, and criticality factors have not been completely and formally resolved for HEU fuels.

Therefore, the only comparison made within the scope of this program is that of pretreatment characterization requirements. The most significant difference between the two disposition options from a characterization standpoint are therefore in the type and degree of characterization activities performed during the pretreatment phase of disposition. The other primary design difference between the two options affecting overall facility and process costs are the furnace design, operating costs, and the costs associated with design, construction, and compliance activities for the off-gas system. The complexity of the off-gas system in the melt-dilution process is also dependent upon the final composition selected which will determine melt temperatures and the range of radionuclides to be released.

The primary, if not only, advantage of the direct disposal option lies in its simplicity. The receiving, inspection, handling, assembly scanning, dewatering, and canister packaging activities to be performed are all relatively straightforward and are expected to deviate only slightly from current basin storage and transfer operations with the exception of characterization activities. Most of the characterization activities are expected to be

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performed within a single characterization station or cell, with some to be performed at later stages and during "road-ready" storage. The primary drawback from a characterization point of view is that because the fuels are to be dispositioned "as-is", with only free liquids and/or organic materials removed from the fuel assembly, extensive characterization may be required on an individual basis depending upon resolution and acceptance of the Appendix A data package and accompanying documentation. This will undoubtedly require assessment of the fuels" "acceptability" on a case-by-case basis, which will involve a significantly greater amount of engineering time and support.

The primary advantage of the melt-dilution process, however, is that if the target composition can be shown through experimental, analytical, or computational means to consistently exhibit characteristics far below prescribed limits, the need for post-treatment characterization on a per-canister or per-melt/ form basis may be reduced. This may significantly reduce the need for post-treatment characterization, monitoring, and documentary activities before the material is emplaced within the repository. A product consistency or validation program could then be established similar to that for the DWPF process, in which only periodic samples are analyzed for confirmation of compositional and process control.

Per 10 CFR 73, Physical Protection of Plants and Materials, the licensee is exempt from 10 CFR 26 and subparts 10 CFR 73.20, 73.25, 73.26, 73.27, 73.45, 73.46, 73.70, and 73.72 for special nuclear material having U^{235} content less than 20%, <u>or</u> for materials exhibiting a gamma radiation dose rate of greater than 100 rem/hour at 1 meter from the unshielded canister. These requirements are primarily for physical protection and security of special nuclear materials of strategic significance. Therefore, if the final melt composition under the melt-dilution option is less than 20% U^{235} , the form is interpreted as being exempt from these requirements regardless of radiation dose rate. Material containing less than 20% U^{235} is still, however, covered by subpart 73.37, Requirements for Physical Protection of Irradiated Reactor Fuel in Transit.

It should be made clear, however, that although the melt-dilution process essentially "erases" the fuel assembly history and thereby creates a new form, the final waste package must meet the same criteria as that obtained from the direct disposal option in order to enter the repository. While form stability may be enhanced, similar characterization of the form may have to be performed during the post-treatment and interim storage period to establish that the waste package meets such criteria as thermal load, radiation level, IAEA safeguards/security traceability and/or accountability requirements, fissile species, etc.

Therefore, while pretreatment characterization requirements for both disposition options may differ, overall characterization requirements of the form and final waste package may be very similar in terms of scope, nature, and overall cost. Post-treatment waste package characterization, however, may be minimized through product consistency tests (PCT) similar to that developed for the DWPF HLW glass product. Thus, selection of disposition option should not be based solely upon pretreatment characterization requirements, but rather a complete evaluation of all factors. A simplified comparison of pretreatment characterization requirements for the two primary disposition options is shown in Table 7.1.

Table 7.1 Comparison of Pretreatment Characterization Requirements (Direct Disposal vs Melt-Dilution)

Melt-Dilution

- Appendix A validation not required
- Fuel to be visually inspected and examined per QA requirements (if applicable)
- Fuels to be dried per safety requirements to prevent possible violent reactions (if applicable)
- In-melt/pre-melt characterization:
 - total uranium
 - U²³⁵ content/% U²³⁵
 - Isotopic inventory (ORIGEN)
 - composition
- Off-gas system/product inventory
- Post-treatment Characterization of Canistered SNF (monitoring of radiation levels, thermal output, radionuclide release, etc.)

Review Appendix A data package; validation may be required

Direct Disposal

- Fuel to be visually inspected and examined per QA requirements
- Radiation levels (gamma/neutron) to be determined (measured or calculated)
- Determine thermal output (calculation based on ORIGEN, Appendix A, gamma scan or measured).
- Determine radionuclide inventory based on ORIGEN from Appendix A data or confirm with gamma spectroscopy or alternative technique (U²³⁵ content) and fabrication records.
- Fuel assemblies/elements to be weighed per accuracy requirements
- Canister emplacement/drying process
- Drying process validation (gas pressure, canister weight, system pressure, etc.)
- Post-treatment Characterization of Canistered SNF (monitoring of radiation levels, thermal output, radionuclide release, etc.)

7.4.5 Facility Design Considerations

7.4.5.1 General

As previously discussed, the primary difference between the two disposition options in terms of characterization is the degree of pretreatment or "in-process" characterization required to ensure that the Al-SNF form is accepted for geologic disposition. Post-treatment characterization requirements for the as-processed form to be contained in the "road-ready" package and stored until repository acceptance are perceived as similar if not equivalent between the two options. Through control over form composition during the melt-dilution process, some post-treatment characterization requirements such as radiation level monitoring or thermal load may be reduced due to the dilution of U²³⁵ within each canister/package, but are not expected to be completely eliminated.

For both options, determination and/or verification of total uranium, %U²³⁵, burnup, thermal output, isotopic inventory/fissile species, radiation level, and free liquid content are necessary to meet requirements for interim storage and repository acceptance of Alclad SNF. The amount of actual characterization performed on a per-assembly or perelement basis in the direct disposal option, however, is highly dependent upon the validity and acceptability of the fuel data and operating history (Appendix A data package). Therefore, because the validity of the fuel data package has not been formally resolved, and the repository acceptance criteria has not been finalized, preliminary facility designs should include or account for a higher degree of characterization activities for this option.

Regardless of disposition technology (direct disposal vs melt-dilution), characterization activities are perceived as being performed within a separate analytical cell (characterization cell or system) complete with remote handling, inspection, and analytical and characterization capabilities. This cell could be on the front end of the facility process to be used upon fuel receipt/drying, or could be more centralized to accommodate both pre- and post-treatment characterization, such as for the melt-dilution process in which pre- and post-characterization activities will be very similar.

With the need for a separate characterization analytical cell perceived as being common to both disposition options, the true difference in operating cost and throughput will be the degree of characterization performed per assembly or per element, rather than physical or equipment considerations. Therefore, the overall design of the facility should not be significantly impacted by the disposition option selected from a characterization standpoint, but operating/labor costs associated with a higher rate of characterization activities per assembly, assembly handling, etc. may be significantly different. The higher per unit characterization costs of direct disposal should be carefully considered and compared to the costs associated with furnace and off-gas system operation and maintenance over the lifetime of the melt-dilution process.

The effects of variation in fuel construction and element geometry may also influence the specific characterization technique and should be carefully considered when performing technology selection and facility design activities. This is especially true for the direct

disposal option in which the form is to be characterized in its original, unmodified form. Characterization to be performed in the melt for the Melt-dilution option may require different characterization techniques and equipment, but is expected to be less in scope due to homogeneity and volume reduction.

7.4.5.2 Direct Disposal

In direct disposal, the form is essentially unchanged with the exception of drying treatment to eliminate free liquids. Therefore, characterization must be performed upon either intact assemblies or individual elements, depending upon the nature of the analysis and the sensitivity of the technique to fuel geometry and variation in element properties within a particular assembly.

Depending upon the validity of the Appendix A data package, characterization of a particular assembly may range from that of visual inspection only (Interim Storage Acceptance Criteria), to full assembly gamma spectroscopy scans, calorimetry, neutron detection, metallography, radiochemical analysis, etc. Throughput and associated facility costs are directly dependent upon the validity of the Appendix A data and therefore, the per-assembly characterization needs. The best compromise may be to design the facility in order to accommodate all perceived characterization needs within the Characterization Cell, with a range of throughput factored in depending upon Appendix A validity. Specific pretreatment characterization capabilities within the TSS facility for the direct disposal option are provided in Reference 7.1.

7.4.5.3 Melt-Dilution

For the melt-dilution process, however, characterization of the melt (total uranium, $\% U^{235}$, melt composition, density, homogeneity, etc.) could be performed from grab samples obtained during melting and transferred to the characterization cell or possibly within the furnace containment area itself. This may reduce the need for additional handling and inspection technologies associated with a separate characterization cell.

The majority of pretreatment characterization activities may be consolidated into only a few to be performed in the melt, with most of the post-treatment characterization requirements being similar to those for direct disposal. In addition to the off-gas system and associated equipment, facility design considerations for the melt-dilution option are provided in Reference 7.1, and are summarized here:

- 1) The characterization station or system for the melt-dilution option should have the capability to perform video surveillance and remote inspection of fuel assemblies as they are removed from shipping casks (similar if not equal to that required for direct disposal).
- 2) The overall weight of the fuel assemblies should be characterized or determined prior to treatment, with dimensions measured as well.
- 3) Furnace design to accommodate multiple sampling ports and characterization activities.

- 4) Melt assembly, stir for appropriate time to homogenize material; determine total uranium and U²³⁵ content via glow discharge emission spectroscopy, induction-coupled plasma emission spectroscopy, gamma spectroscopy, radiochemistry, or other appropriate technology. Compositional analysis and density to be determined if needed.
- 5) Characterization station should be capable of performing post-treatment (after melting/casting) characterization of cast SNF material to validate process and melt composition calculations (may involve same techniques as before or other more appropriate techniques for solid material evaluation).
- 6) Based upon U²³⁵ content, radiation levels, thermal loads, and radionuclide inventory may be determined, with inventory of evaporated radionuclides in the off-gas system monitored for comparison.
- 7) As for Direct disposal, the characterization system should have the capability to perform metallographic examination of the as-cast form, if only on a random sampling basis to confirm product consistency or to verify improbability of pyrophoric behavior.
- Product consistency test to include but not be limited to: density, determination of total uranium and U²³⁵ content, metallographic examination, compositional analysis via SEM/EDX, glow-discharge emission spectroscopy, or other applicable technique.

7.5 SNF CHARACTERIZATION DATA REVIEW

7.5.1 Purpose/Scope

The purpose of the characterization data review is to provide an in-depth cross-section of existing fuels that are to be dispositioned through the TSS facility. Some of these fuels are already in storage at SRS, while others are to be transferred at later dates. The primary focus of this task is to review and evaluate existing characterization data as it pertains to the inherent properties of the fuel (burnup, isotopics, enrichment, fissile species, etc.) and to compare that data to the assumed requirements for characterization of the fuels. This is being done to establish whether or not the existing data provided by SNF custodians is adequate for acceptance, or if additional confirmatory tests are required.

The scope of the data review is limited to the Al-clad fuels to be dispositioned in the TSS facility and does not at the present time include metallic fuels such as Hanford N-fuels or Fort St. Vrain fuels. The scope of this data review has changed over the course of the last fiscal year and is now primarily focused upon the review and determination of inherent fuel properties as a function of fuel burn-up and/or enrichment values. Although the melt-dilution process will alter the fuel structure and final form, the direct disposal process and any long-term interim dry storage program can benefit from the knowledge provided.

7.5.2 Review Content

The characterization data review or manual will basically consist of review of existing databases and reports on select fuels and fuel types, with specific information on the effect of burn-up and enrichment upon inherent fuel properties to be assimilated.

Although specific fuels have not been finally selected, a minimum of one fuel type for the classes or categories of fuels shown below shall be included:

- High burnup, low enrichment (20% or less)
- High burnup, high enrichment (up to 93%)
- Low burnup, low enrichment (20% or less)
- Low burnup, high enrichment (up to 93%)

For each category of fuels, one representative type shall be identified, with all pertinent information from origin, fabrication records, Appendix A data package, and existing databases to be reviewed and compared to the existing and/or assumed requirements for characterization in the TSS facility.

Properties to be assimilated shall include but not be limited to: microstructure of fuel meat/cladding as a function of burn-up and enrichment, cladding/meat composition, oxide layer thickness/composition, and review of Appendix A-type data (burnup, BOL/EOL U^{235} content, isotopic inventory based on ORIGEN-S or other approved computer codes, facility origin, discharge history, etc.

7.5.3 Status/Path Forward

Due to changing nature and scope of the characterization data review, the majority of progress made thus far has been to review the existing fuel databases for either research programs or inventory tracking purposes, including but not limited to the Matos database (ANL), SFSD site database, and the National Program inventory database. Some characterization of fuel types has been performed at ANL as part of specific tasks for the direct disposal and melt-dilution programs, with that information to be provided for the characterization data manual. Large-scale experimental characterization of individual fuel types has not been performed to date in order to minimize costs of hot cell activities. Until the validity of Appendix A data packages submitted with the fuels has been established or negotiated with NRC and OCRWM, in-depth characterization of each fuel type will not be performed.

The path forward for the remainder of CY97 is to complete the review of existing data/databases with regard to inherent fuel properties as a function of burnup, enrichment, etc. A cross-section of specific fuels under certain categories will be provided, with a correlation or comparison made between existing data, the validity of that data, and the existing and/or assumed requirements for SNF characterization and disposition. In addition, the results of characterization activities performed to date at ANL will be provided. The development and/or consolidation of this information will provide
fundamental technical information for both the direct disposal and melt-dilution process options, with the direct disposal method being more heavily dependent upon inherent microstructural characteristics of the unaltered or "as-received" fuels.

7.6 CONCLUSIONS/RECOMMENDATIONS

Based upon review of the regulations deemed pertinent to the pretreatment characterization of Al-SNF for interim storage and repository disposition, the following conclusions are drawn:

- Pretreatment characterization requirements for the melt-dilution disposition option are perceived as being considerably less than those for fuels dispositioned under the direct disposal option. The magnitude of the difference between the two options is heavily dependent upon the acceptability of the Appendix A data package to reviewed prior to or upon fuel receipt. As the acceptability of such data increases, the pretreatment characterization requirements for the fuels will be reduced. A graded approach to Appendix A acceptance may be necessary for FRR fuels and older DRR fuels.
- The majority of pretreatment characterization for the melt-dilution option can be performed in the molten state or from dip samples rather than from significant handling and manipulation of intact assemblies. This will increase characterization efficiency and reduce the need for space in order to accommodate movement of large-scale characterization activities and sample transport.
- Post-treatment characterization of canistered SNF produced from either disposition option is considered to be similar in scope and nature to ensure repository acceptance of the final form. Some of the post-treatment characterization requirements such as the determination of radiation dose rates and thermal loads at the time of repository acceptance of the final form will most likely have to be physically verified, but may be resolved through calculations based upon either Appendix A data, routine monitoring, or from previous characterization.

Depending upon the relative performance characteristics of the final form(s) generated under the respective disposition options, some requirements may be reduced if not eliminated. Specific issues such as the establishment of pyrophoric behavior may be addressed in the Test Protocol program or through a product consistency test that will require no additional characterization or verification following treatment.

• Down-selection of the primary alternate treatment technology for the disposition of aluminum SNF is expected to be based on many factors including but not limited to: process safety evaluation, non-proliferation concerns, environmental impact, economic impact, operating costs, and acceptability of the final form for

the proposed geologic repository. The scope and economic impact of pretreatment characterization should be considered in the evaluation, but may be relatively less significant in terms of the overall down-selection process.

Additional recommendations from a fuel characterization viewpoint are provided for reference:

- Sensitivity analyses should be performed by authoritative agencies upon fuel properties such as burn-up, enrichment, isotopic analysis, radiation levels, and thermal output to determine the degree of accuracy and precision necessary for fuel characterization as well as the respective impact upon repository performance. This issue must be completely resolved through official discussion and negotiation with the OCRWM (RW) and NRC in order to properly assess the pretreatment characterization needs of the TSS facility, particularly for the direct disposal option.
- Depending upon which disposition option is selected as the primary alternate treatment technology, in-depth evaluation and/or characterization of bounding or representative fuels may or may not be necessary. Under the melt-dilute option, the condition of the fuel will be altered and the "history" will be essentially eliminated; thus extensive characterization and investigation into fuels in the asreceived condition may not provide significant additional information. For direct disposal, however, evaluation of fuels to be received is deemed significantly more important in order to establish the technical basis for addressing individual fuel characteristics and requirements for storage and/or repository acceptance.
- SFS in conjunction with SRTC, DOE, RW and the NRC should resolve the issue of Appendix A data acceptability and/or the establishment of confirmatory or validation tests to be performed, particularly for the direct disposal option.
- Clarification of the applicability of DOE/IAEA accountability and tracking requirements is needed to determine the appropriate requirements for fuels to be dispositioned. For fuels containing less than 20% U²³⁵, such as those that may be generated under the melt-dilute process, accountability requirements may be reduced if not eliminated. In addition, the accountability of radionuclides to be removed in the off-gas system should be investigated. This may affect the requirements for radionuclide inventory at the time of acceptance, particularly for forms generated under the melt-dilution option.
- The determination of items such as parameter measurement techniques, precision/accuracy levels, acceptable corrosion rates, and/or repository conditions identified in many current documents as "TBD" should be resolved at the national SNF program level in order to provide more definitive guidance for SNF custodians and operation of the TSS facility. Specific characterization activities, techniques, etc. cannot be properly defined at the Site level for the TSS facility until such clarification is made. Until specific requirements are defined, the use of

commercially-available resolution limits and equipment parameters should be adequate for cost-estimates and planning purposes.

The SNF characterization data review is deemed more important for direct disposal/interim storage options and activities; detailed information on the metallurgical condition and history of the fuels is considered to be less significant for the melt-dilution process during which the metallurgical condition and history of the fuel is essentially erased or altered.

7.7 **REFERENCES**

- 7.1 T. E. Skidmore. Pretreatment Characterization Requirements for the Disposition of U.S. DOE Aluminum SNF. WSRC-TR-97-00290 (September 1997).
- 7.2 M. S. Abashian. *Mined Geologic Disposal System Waste Acceptance Criteria*. B0000000-0171704600-00095 REV00 (September 1997).

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APPENDIX I

STANDARD GUIDE FOR CORROSION TESTING OF ALUMINUM-BASED SPENT NUCLEAR FUEL IN SUPPORT OF GEOLOGIC REPOSITORY STORAGE

1.0 Scope

1.1 This standard guide describes corrosion testing of Al-SNF in support of geologic repository disposal (per the requirements in 10 CFR 60). The testing described in this document is designed to provide the data required for analyses of the chemical stability and anticipated behavior of Al-SNF. Extended interim storage and transportation of the spent fuel will precede geologic disposal; therefore, reference is also made to the requirements for extended interim storage (per 10 CFR 72) and transportation (per 10 CFR 71). The analyses that will be based on the developed data are necessary to support the safety analyses reports (SARs) and performance assessments (PAs) for disposal systems.

1.2 SNF that is not reprocessed must be placed in a secure interim storage facility as a step toward transportation to, and disposal in, a geologic repository. Placement in the interim storage facility may include direct placement of the irradiated fuel and/or treatment of the fuel prior to placement. The Al-SNF may be required to be ready for geologic disposal or "road ready", prior to placement in extended interim storage. Interim storage facilities, in the United States, handle fuel from civilian commercial power reactors, defense nuclear materials production reactors, and research reactors. The research reactors include both foreign and domestic reactors. The aluminum-based fuels in the spent fuel inventory in the US are primarily from defense and foreign and domestic research reactors and include several different fuel forms and levels of U²³⁵ enrichment.

1.3 Knowledge of the corrosion behavior of Al-SNF is required to assure safety and to support licensing and/or other approval activities necessary for disposal in a geologic repository. The response of the Al-SNF to exposure environments must be established for configuration safety analyses, criticality analyses, performance assessments, and other analyses required to assess the storage, treatment, transportation, and disposal of SNF. The test protocols described in this standard guide are designed to establish material responses to relevant disposal conditions.

1.4 The majority of the Al-SNF are aluminum clad, aluminum-uranium alloys. The aluminum-uranium alloy typically consists of uranium aluminide particles dispersed in an aluminum matrix. Other aluminum-based fuels include dispersions of uranium oxide, uranium silicide or uranium carbide particles in an aluminum matrix. These particles, including the aluminides, are generally cathodic to the aluminum matrix. Selective leaching of the aluminum in the exposure environment may provide a mechanism for

redistribution and relocation of the uranium rich particles. The potential for redistribution will depend on the nature of the aluminum corrosion processes and the size, shape, distribution, and relative reactivity of the uranium rich particles. (Interpretation of test data will be an understanding the material behavior and the design and configuration of the waste package.) Test samples must be selected and evaluated to assure that particle morphology is representative of the waste form.

1.5 The use of the data obtained by the testing described in this standard guide will require that the samples mimic the condition of the aluminum SNF at some future time. The use of ASTM Standard Practice C1174 concerning the accelerated testing of waste package materials is recommended for guidance concerning the accelerated testing of the Al-SNF. The selection of samples and any "artificial aging" of selected samples for testing purposes must be carefully evaluated to assure that condition of the samples tested duplicates sample conditions anticipated in the distant future.

2.0 Referenced Documents

2.1 10 CFR 60, US Code of Federal Regulations Section 10, Part 60, Disposal of High Level Radioactive Wastes in Geologic Repositories;

2.2 10 CFR 72, US Code of Federal Regulations Section 10, Part 72, Licensing Requirements for the Independent Storage of Spent Nuclear Fuel and High-Level Radioactive Waste;

2.3 10 CFR 71, US Code of Federal Regulations Section 10, Part 71, Packaging and Transport of Radioactive Materials;

2.4 40 CFR 191, US Code of Federal Regulations Title 40, Part 191, Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes;

2.5 ASTM C1174-91, Standard Practice for Prediction of the Long-Term Behavior of Waste Package Materials Including Waste Forms Used in the Geologic Disposal of High Level Nuclear Waste.

3.0 Significance and Use

3.1 Disposition of aluminum-based SNF will involve: removal from the existing storage or transfer facility; characterization and/or treatment; creation of a waste package that includes the SNF and its contained and packaging materials; placement of the waste package in a safe and environmentally sound interim storage facility; removal from the interim storage facility; transport to the repository; placement in the repository; repository closure; and geologic storage.

3.2 Al-SNF displays physical and chemical characteristics that differ significantly from the characteristics of commercial nuclear fuels and from high level radioactive waste glasses. The impact of this difference to repository performance must be evaluated and understood.

3.3 The US Nuclear Regulatory Commission has licensing authority over the interim dry storage, transportation, and repository placement of both spent nuclear fuels and highlevel radioactive waste under the requirements established by 10 CFR Parts 60, 71 and 72. These requirements outline specific information needs that must be established through the test protocol developed in this Standard Guide. The information needs include:

- a) a knowledge of the solubility, leaching, oxidation/reduction reactions, and corrosion of the Al-SNF constituents in/by the repository environment (dry air, moist air, J-13 water, and modified J-13 water), (10 CFR 60.135);
- b) a knowledge of the effects of radiolysis and temperature on the oxidation, corrosion, and leaching behavior, (10 CFR 60.135);
- c) a knowledge of the temperature dependence of the solubility of Al-SNF constituents, oxidation and corrosion products, (10 CFR 60.135);
- d) laboratory experiments that provide information about time dependence of the internal condition of the waste package, (10 CFR 60.143);
- e) demonstrations that, in spite of the electrochemical differences between the Al-SNF and the candidate packaging materials, there are no significant galvanic reactions (10 CFR 71.43) and/or that the effects of the electrical contact between the Al-SNF and the packaging materials on a), b), c) and d) are understood (10 CFR 60.135);
- f) assurance that the spent fuel can be received, handled, packaged, stored, and retrieved without undue risks (10 CFR 72.3) and/or that the condition of the Al-SNF upon repository is known to the point that a), b), c) and d) can be evaluated (10 CFR 60.135);
- g) confirmation that any degradation of the Al-SNF during interim storage will not pose operational safety problems with respect to its removal from storage (10 CFR 72.123) and/or does not compromise the evaluation of a), b), c) and d) (10 CFR 60.135).

3.4 Exposure conditions over the time frame covered by the geologic disposition period will include dry, moist, and wet environments. Waste form behavior under each of these conditions must be assessed by the evaluation program.

4.0 Terminology

4.1 Definitions: Terms used in this Standard Guide are defined in the ASTM Standard C1174-91, by common usage, by Webster's New World Dictionary and/or as described in Section 4.2.

4.2 Description of Terms Specific to the Standard Guide

4.2.1 AI-SNF - irradiated nuclear fuel or target elements and/or assemblies that are clad in aluminum or aluminum alloys and/or contain significant quantities of aluminum as a core material.

4.2.2 Interim storage facility - any facility designed to store SNF for at least twenty years and which meets the intent of the requirements of an Interim Spent Fuel Installation or a Monitored Retrievable Storage facility as described in 10 CFR 72.

4.2.3 Artificial aging - any short time treatment which is designed to duplicate or simulate the material/property changes that normally occur after prolonged exposure.

4.2.4 Performance assessment - An analysis that identifies the processes and events that might effect the performance of a disposal system, examines the effects of those processes and events on the performance of the disposal system and estimates the cumulative releases of radionuclides caused by the processes and events.

4.2.5 Safety analysis - an analysis to determine the risk, to the public health and safety, associated with the storage, treatment, transportation, and disposal of aluminum- based SNF.

5.0 Information Needs for Geologic Disposal

5.1 Tests of the Al-SNF should provide data pertinent to the following: a) oxidation of waste form constituents; b) corrosion of Al-SNF constituents; c) dissolution of constituents, oxidation products, and corrosion products; and d) selective leaching of constituents. Selected tests should establish the data necessary to predict:

- a) the solubility of Al-SNF constituents, oxidation products and corrosion products in J-13 and modified J-13 water,
- b) the temperature dependence of Al-SNF constituent solubility in J-13 and modified J-13 water,
- c) the effect of radiolysis on constituent solubility,

- d) the corrosion rate and/or relative corrosion rates of the various constituents in the Al-SNF, and
- e) the effect of the size, shape, distribution, and volume fraction of the uranium rich particles on corrosion and oxidation behavior.

5.2 The data collected from tests described in Section 5.1 should provide sufficient information to establish empirical relationships and basic equations that correlate:

- a) corrosion rates with anticipated repository conditions,
- b) the solubility of Al-SNF constituents, including corrosion and oxidation products, with the temperature and chemistry of the water that may surround the Al-SNF after a canister breach in the repository, and
- c) the tendency for selective leaching constituents in the anticipated repository environments.

5.3 The data from the tests described Section 5.1 and relationships described in Section 5.2 should provide sufficient information to calculate the release rate of radionuclides from the aluminum SNF stored in the repository.

5.4 The data or information described in Section 6.1 should provide the necessary particle size and leach rate information to model the potential for a criticality due to the redistribution of uranium rich particles.

6.0 Relationship of Aluminum-based Waste Forms to Other Waste Forms

6.1. The aluminum SNF differ from commercial spent fuels and high level waste glasses in several respects, including homogeneity, reactivity, and galvanic interactions.

6.2. The core of the aluminum SNF is a dispersion of uranium rich particles in a matrix of relatively pure aluminum. Virtually all the uranium in the fuel will be contained in the microscopic, uranium rich particles.

6.3. The aluminum matrix is more chemically reactive than the uranium particle, thus, the particles may be cathodic to the aluminum matrix. Corrosion of the particle matrix composite may result in selective leaching of the aluminum; thus releasing the particles to the surrounding environment.

6.4. The tendency for selective leaching should depend on the characteristics of any surface films that are present on the Al-SNF and on the extent to which the Al-SNF is galvanically coupled to waste package and/or over pack materials. The position of

aluminum in the electromotive series is such that, among the common structural metals, only magnesium and beryllium are more reactive.

6.5. Al-SNF treatments such as a melt-dilute process, may alter the typical morphology of the uranium rich particles, the nature of the surface films and even remove a substantial fraction of the fission products. The treated Al-SNF, however, will remain chemically active, relative to commercial spent fuels, high level waste glasses and the structural materials for the waste package. This difference in chemical activity or corrosion potential provides an additional driving force for galvanic corrosion and selective leaching if the aluminum-based waste form is in electrical contact with any of the less active materials that may be contained in the waste package.

6.6. The corrosion resistance of aluminum and aluminum-based alloys is largely due to the presence of a protective oxide film and any understanding of aluminum corrosion necessarily incorporates an understanding of oxide film behavior.

6.7. The nature and characteristics of the oxide will evolve during repository exposure and the effects of this evolution on subsequent corrosion processes must be considered in the evaluation of Al-SNF behavior, particularly with regard to the tendency for release of microscopic uranium-rich particles by selective leaching.

6.8. Determination of the roles of microstructural heterogeneities, oxide and/or other surface films, galvanic coupling and selective leaching processes on the nature and rate of release of radionuclides to the repository environment requires the application of multiple test methodologies.

7.0 Summary of Test Methods

7.1 This Standard Guide addresses the requirements of tests to establish the corrosion behavior of Al-SNF in support of the geologic repository disposal of this material. The tests necessary to provide the required information include:

7.1.1 Tests to determine the susceptibility of the Al-SNF to selective leaching and to characterize the resulting release of microscopic uranium-rich particles to the repository environment.

7.1.2 Test to establish the forward dissolution rates of the various microstructural constituents in a Al-SNF exposed to actual or simulated ground water.

7.1.3 Tests to establish the effects of galvanic coupling on corrosion rates, corrosion products, and the release of radionuclides to the repository environment.

7.1.4 Tests to establish the effects of Al-SNF condition (nature and characteristics of surface films and deposits) on corrosion rates, corrosion products, and the release of radionuclides to the repository environment.

7.2 The tests summarized in sections 7.1.1 through 7.1.4 should include provisions to measure the effect of temperature on the corrosion processes.

7.3 The tests summarized in sections 7.1.1 through 7.1.4 should include provisions to establish the effects of ground water chemistry on the corrosion processes.

8.0 Selection of Test Samples

8.1 Representative samples of the waste form should be selected for testing. The waste form will not be a homogeneous, isotropic medium; therefore, the selection of representative samples should include provisions to establish the microstructure and surface condition of the waste form.

8.2 The position of the aluminum-based waste form material in the electromotive series will virtually assure that electrical contact with waste package materials and/or other waste forms co-disposed with the aluminum-based waste form will cause the aluminum-based waste form to act as a sacrificial anode. Test samples should be selected to reflect this potential for galvanic corrosion.

8.3

9.0 Test Methods

10.0 Use of Test Data

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