WSRC-MS-2000-00181

Evaluation of Neutron Absorbers for the Melt-Dilute Treatment of Aluminum-Based Spent Fuel

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A document prepared for EMBEDDED TOPICAL MEETING ON DOE SPENT NUCLEAR FUEL AND FISSILE MATERIAL at San Diego, CA, USA from 6/4/2000 - 6/8/2000.

DOE Contract No. **DE-AC09-96SR18500**

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WSRC-MS-2000-00181
MSD-STI-2000-00309

EVALUATION OF NEUTRON ABSORBERS FOR THE MELT-DILUTE TREATMENT OF ALUMINUM-BASED SPENT FUEL

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ABSTRACT

Aluminum-based spent nuclear fuel (Al-SNF) from foreign and domestic research reactors is being consolidated at the Savannah River Site (SRS) for ultimate disposal in the Monitored Geologic Repository (MGR). Most of the aluminum-based fuel material contains highly enriched uranium (HEU) (>20% ^{235}U), which poses a proliferation risk and challenges the preclusion of criticality events for disposal periods exceeding 10,000 years.

The melt-dilute treatment technology developed at SRS consolidates fuel assemblies by a melting/casting process in which depleted uranium is added to reduce enrichment below 20% ^{235}U. Criticality analyses have shown that minor amounts of neutron-absorbing materials are needed to demonstrate criticality control ($k_{eff} < 0.95$) for MD-SNF with 20% ^{235}U enrichment.

A major advantage to the melt-dilute treatment of Al-SNF is that neutron-absorbing materials can be added to the melt. Compatibility of neutron absorbing materials in the MD-SNF form, including their degree of homogeneity and relative solubility, are important to maintain criticality control. A program to demonstrate the compatibility and effectiveness of neutron-absorbing additions to the MD-SNF form has been initiated. This work will provide data on the effect of neutron absorbing material additions on MD-SNF degradation and degradation product formation, microstructure, homogeneity, and criticality potential under repository relevant vapor and aqueous environments. Initial testing includes melt-dilute plus gadolinium, melt-dilute plus hafnium, and melt-dilute plus gadolinium and hafnium. Preliminary results show that the absorbers are metallurgically compatible with the U-Al alloy. Exposure of surrogate melt-dilute alloys to water vapor shows low post-passivation corrosion rates, similar to that of aluminum.

I. INTRODUCTION

Approximately 50 metric tonnes heavy metal of aluminum-based spent nuclear fuel (Al-SNF), or 30,000 assemblies, are being consolidated at the Savannah River Site. The melt-dilute treatment technology is being developed at SRS for ultimate disposal of these fuels, most of which contain highly enriched uranium (HEU) (>20% ^{235}U), in the monitored geologic repository (MGR).[1] This alternative for disposition has been selected as the preferred alternative through the EIS process.[2] The proposed waste package will codispose a canister containing the melt-dilute SNF form with several borosilicate glass logs of DHLW.

One issue in the disposal of SNF is the potential for achieving a criticality event. Analyses of degraded configurations of the MD-SNF form at 20% ^{235}U enrichment[3-4] indicate that the reactivity of some configurations exceeds the limit of $k_{eff} \leq 0.95$.[5] Among the possible methods available to reduce the reactivity of the SNF forms is to control the amount of fissile material disposed of in a single waste package and to integrate neutron absorbers with diluted HEU SNF assemblies through implementation the melt-dilute treatment technology. This paper considers the integration of neutron absorbing materials with the MD-SNF form to reduce the reactivity of the system. Attention is given to the issues associated with the selection and behavior of the MD-SNF form under repository-relevant conditions.

The degradation behavior of the MD-SNF form, including degradation rate and degradation product formation, as well as the behavior of the neutron absorbing materials, including degradation product formation and relative solubility, are important characteristics used to demonstrate MD-SNF/neutron absorber compatibility and long-term criticality control in the repository. A neutron absorber compatibility-testing program is being conducted at SRS to fully characterize

the degradation behavior of the MD-SNF form with neutron absorbing material additions under vapor and aqueous conditions relevant to the proposed repository. Activities include corrosion testing, characterization, and geochemical analysis and modeling.

II. DISCUSSION

Criticality of the Melt-Dilute SNF Form

Criticality control in waste packages for disposal at Yucca Mountain is governed by 10CFR60. It must be demonstrated through analysis that there is no possibility (probability< 10^{-6}) of criticality for 10,000 years following disposal. Failure of containment is generally assumed to occur beginning several thousand years after emplacement. Therefore, both intact and degraded states of the waste package contents must be evaluated.

Neutron absorbing materials are needed to maintain $k_{eff} < 0.95$ in desired packaging configurations of MD-SNF with 20% ^{235}U enrichment loaded in DOE-SNF canisters. Criticality of the MD-SNF loaded in a fully flooded, intact DOE-SNF canister was evaluated using the SCALE family of computer codes.[3] Results for the MD-SNF form at various stages of degradation, at several enrichments, and with various fill levels, indicate that criticality control for the 20%-enriched MD-SNF form can be maintained through implementing a minimum fill level for the DOE-SNF canister.[3]

Analyses of several scenarios for DHLW and MD-SNF form within the waste package have been conducted.[4] These preliminary criticality calculations indicate that the resulting configurations require the addition of neutron absorbing material to maintain criticality control. The results of these calculations indicate that a cylindrical configuration of the degraded MD-SNF form within the intact waste package provide a greater criticality potential than the configurations originally suggested by previous studies.[6]

Neutron Absorber Options and Considerations

Candidate melt-dilute/neutron absorber systems include includes melt-dilute plus gadolinium, melt-dilute plus hafnium, and melt-dilute plus gadolinium and hafnium. These systems have been selected based upon thermal neutron absorption cross-section and upon geochemical considerations. The specific compositions have not been determined; however it is anticipated that less than 1% by weight of neutron-absorbing species in the melt-dilute form will be required to maintain reactivity limits.

Gadolinium has the highest absorption cross section of any element. Gadolinium, however, has very poor corrosion resistance and high solubility. 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 material. In addition, gadolinia provides improved solubility characteristics over gadolinium metal. However, preparing a dispersion of oxides in the MD-SNF form would introduce an undesired complexity to the melt-dilute treatment technology. Therefore gadolinia is not currently being pursued for melt-dilute criticality control.

The phosphate form of gadolinium, gadolinium-phosphate ($GdPO_4$), would provide significant neutron absorbing capacity while exhibiting desirable geochemical characteristics. However, $GdPO_4$ is not commercially available at this time, and achieving a homogeneous dispersion of $GdPO_4$ in the melt-dilute form would introduce complexity in the simple melt-process.

Gadolinium has been selected due to its high neutron absorption cross-section. The solubility of gadolinium metal may become a concern over geologic times as it has the potential for being selectively removed from a waste package while leaving behind fissile uranium. However, gadolinium metal has the potential for forming a less soluble oxide, Gd_2O_3, or even an insoluble phosphate, $GdPO_4$, as the MD-SNF form degrades in expected repository environments.

Hafnium is attractive metallurgically. In its pure form, hafnium is extremely corrosion resistant and is relatively insoluble over a wide pH range. However, the thermal neutron absorption cross-section of hafnium is significantly lower than that of gadolinium. Hafnium has been selected due to its modest neutron absorption cross-section in combination with its relative insolubility. The hafnium loading required to preclude criticality over geologic times in the proposed repository is many times that of gadolinium.

The ideal melt-dilute/neutron absorber system is one that will utilize a combination of gadolinium, for its very large neutron cross-section, and hafnium, for its insolubility. This combination will provide suitable neutron absorption and solubility characteristics to allow for the demonstration of criticality control of the MD-SNF form over geologic times. The final neutron absorber mix requires degradation product species evaluation that is an integral part of the neutron absorber compatibility program at SRS.

Melt-Dilute/Neutron Absorber System Fabrication

The Al-SNF assemblies were originally fabricated using enriched uranium and aluminum alloy, with an aluminum alloy cladding. During reactor service, fission products are produced within the assemblies. The relatively small quantities of fission products by mass, however, are not expected to significantly alter the microstructure of the MD-SNF form from a simply binary mixture of uranium and aluminum. Therefore, the compatibility program at SRS utilizes a surrogate fuel assembly fabricated of depleted-uranium and aluminum to simulate the behavior and characteristics of actual MD-SNF. These surrogate fuel assemblies are melted and alloyed with additional aluminum to obtain a near eutectic composition (~13.2 percent by weight U in Al). Neutron absorber materials are added during the melt-dilute treatment to produce samples used in the compatibility program, as necessary.

Melt-Dilute/Neutron Absorber System Microstructure

The general microstructure of the MD-SNF form is that of a simple binary eutectic. The addition of gadolinium and/or hafnium, in amounts up to a total of three percent by weight, to the MD-SNF form does not substantially alter the microstructure of the form. This general microstructure is presented in Figure 1.

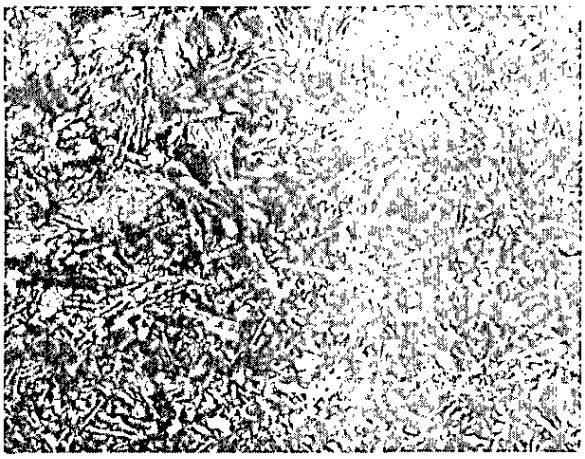

Figure 1 General microstructure of melt-dilute/neutron absorber system (MD plus 3% Gd by weight shown here) (200X).

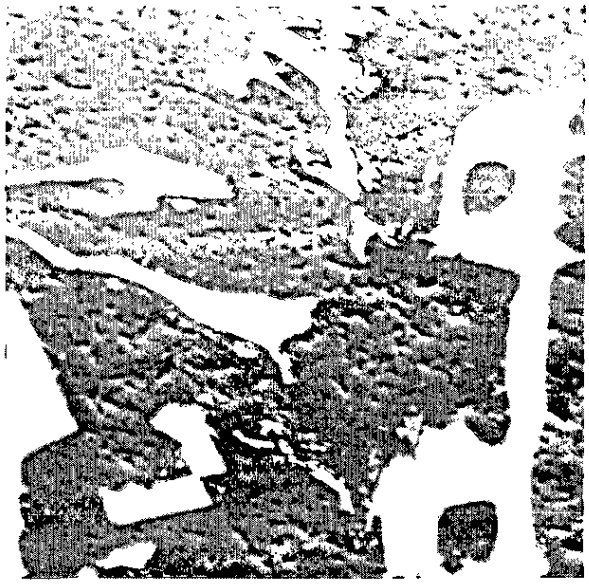

Figure 2 X-Ray photomicrograph of the surrogate MD-SNF form (730X).

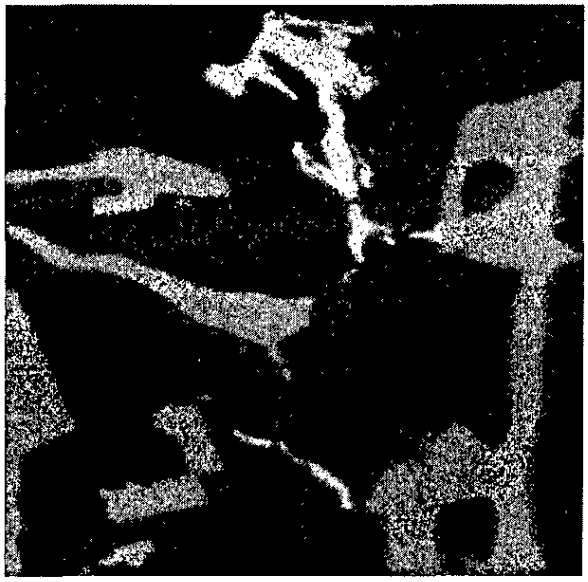

Figure 3 X-Ray map of uranium in the surrogate MD-SNF form (730X).

The microstructure of the melt-dilute form without neutron absorber additions consists of UAl_x phases dispersed in an aluminum matrix. In Figure 2, the UAl_x phases appear as the light phase contrasted to the dark appearance of the Al matrix. Figure 3 presents the x-ray map that indicates the presence of uranium. Higher uranium density leads to lighter appearance in the x-ray map. These figures suggest the presence of two separate uranium-containing phases. The phases are UAl_3 and UAl_4. The UAl_3 phase appears lighter, of the two phases.

The detailed microstructure of the melt-dilute form with an addition of 3% gadolinium by weight is presented in Figure 4-Figure 6.

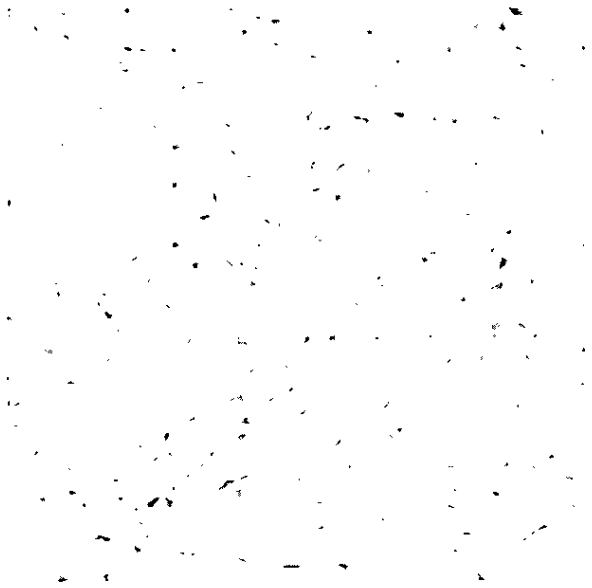

Figure 4 X-Ray photomicrograph of the surrogate MD-SNF form with 3% Gd by weight (750X).

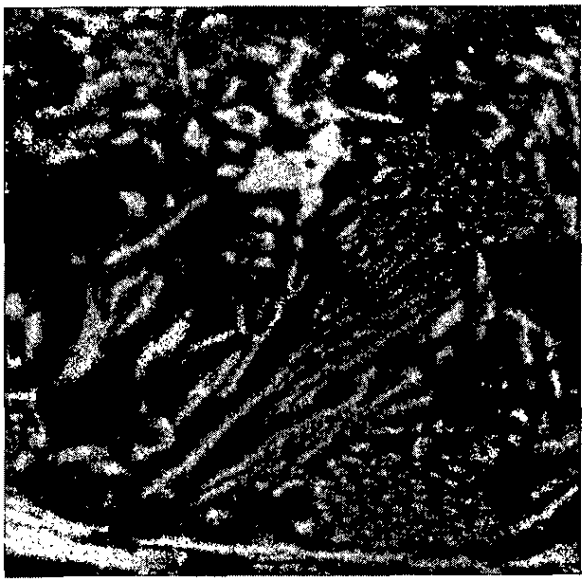

Figure 5 X-Ray map of uranium in the surrogate MD-SNF form with 3% Gd by weight (750X).

A comparison of Figure 4 with Figure 1 shows the microstructures with and without the gadolinium addition are similar. Figure 5 presents the x-ray map that indicates the presence of uranium within the MD-SNF form, while Figure 6 presents the x-ray map indicating gadolinium location. A comparison of these figures shows that the gadolinium added to the melt-dilute form collocates with the uranium present in the UAl_4 phase.

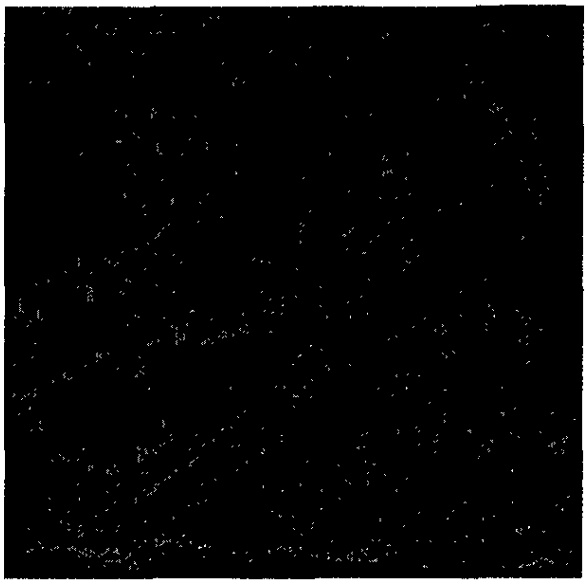

Figure 6 X-Ray map of gadolinium in the surrogate MD-SNF form with 3% Gd by weight (750X).

The microstructure of the melt-dilute form with an addition of 3% hafnium by weight is presented in Figure 7-Figure 11. In Figure 7, the light gray areas are areas of simple binary eutectic microstructure. The dark gray regions are individual grains of an aluminum-hafnium phase (see Figure 11). Unique to the systems containing hafnium is the presence of a new phase, $U_xAl_yHf_z$ as indicated in Figure 8. Higher magnification photos of this phase are provided in Figure 9-Figure 11. Figure 10 presents the x-ray map that indicates the presence of uranium within the MD-SNF form, while Figure 11 presents the x-ray map indicating hafnium location. From these figures along with Figure 8, it is evident that the hafnium added to the melt-dilute form is located in both in the aluminum-hafnium phase and the ternary U-Al-Hf phase. Hafnium does not appear to collocate with the uranium present in the UAl_4 phase, as does gadolinium.

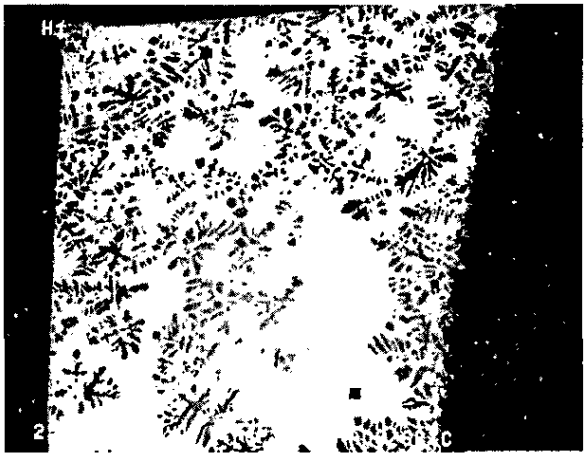

Figure 7 SEM photomicrograph of the surrogate MD-SNF form with 3% Hf by weight (21X)

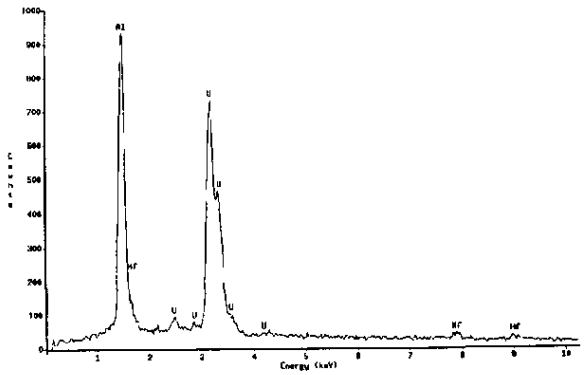

Figure 8 EDS of $U_xAl_yHf_z$ phase (white spots in Figure 7).

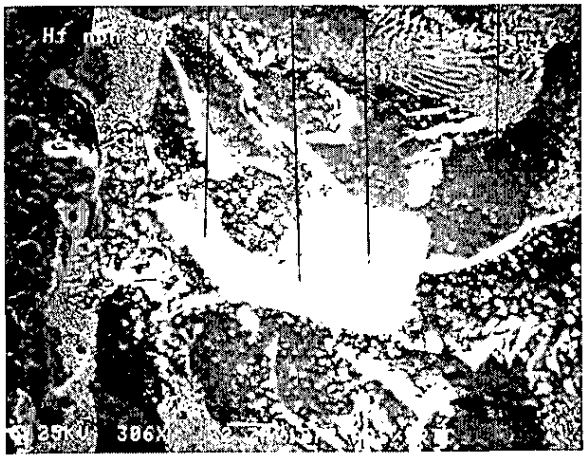

Figure 9 SEM photomicrograph of the surrogate MD-SNF form with 3% Hf by weight (306X)

Figure 10 X-Ray map of uranium in the surrogate MD-SNF form with 3% Hf by weight (306X). (Uranium shows up light.)

Figure 11 X-Ray map of hafnium in the surrogate MD-SNF form with 3% Hf by weight (306X). (Hafnium shows up light.)

The microstructure of the melt-dilute form with an addition of 1.5% gadolinium and 1.5% hafnium by weight is presented in Figure 12-Figure 16. Figure 12 displays the microstructure of this alloy. Figure 13 provides higher magnification to assist in phase identification. Figure 14 presents the x-ray map that indicates the presence of uranium within the MD-SNF form, while Figure 15 presents the x-ray map indicating gadolinium location, and Figure 16 presents the x-ray map indicating hafnium location.

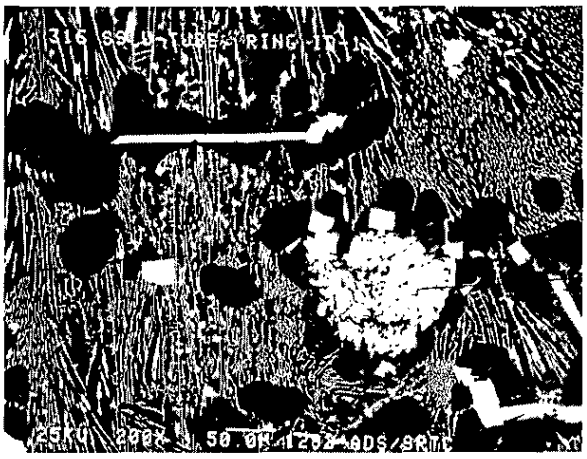

Figure 12 SEM photomicrograph of the surrogate MD-SNF form with 1.5% Gd and 1.5% Hf by weight (200X).

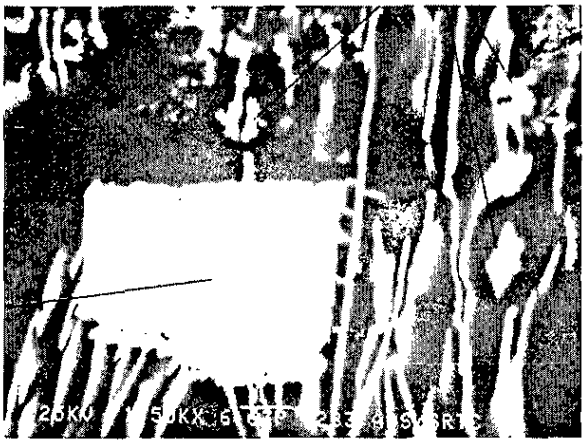

Figure 13 SEM photomicrograph of the surrogate MD-SNF form with 1.5% Gd and 1.5% Hf by weight (1500X).

The microstructure of this system is complicated, with five distinct phases. These phases are: 1) an aluminum phase; 2) an aluminum-hafnium phase; 3) a uranium-aluminum-hafnium phase; 4) a uranium-aluminum-gadolinium phase; and 5) a uranium-aluminum-gadolinium-hafnium phase.

Figure 14 X-Ray map of uranium in the surrogate MD-SNF form with 1.5% Gd and 1.5% Hf by weight (200X).

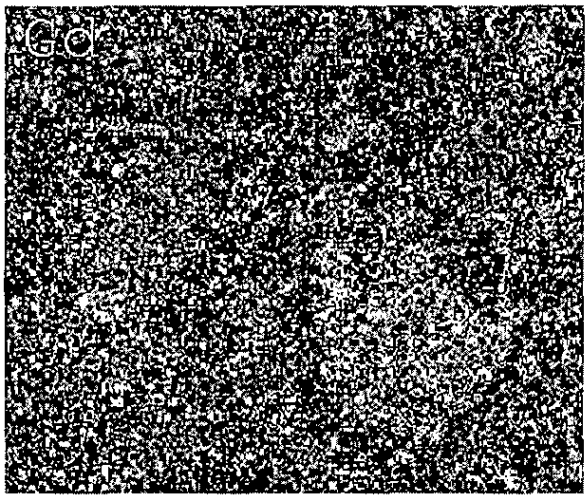

Figure 15 X-Ray map of gadolinium in the surrogate MD-SNF form with 1.5% Gd and 1.5% Hf by weight (200X).

From these figures, it is evident that the gadolinium added to the melt-dilute form collocates with the uranium present in the UAl_4 phase. The hafnium added to the melt-dilute form is generally tied up in aluminum-hafnium and uranium-aluminum-gadolinium-hafnium phases.

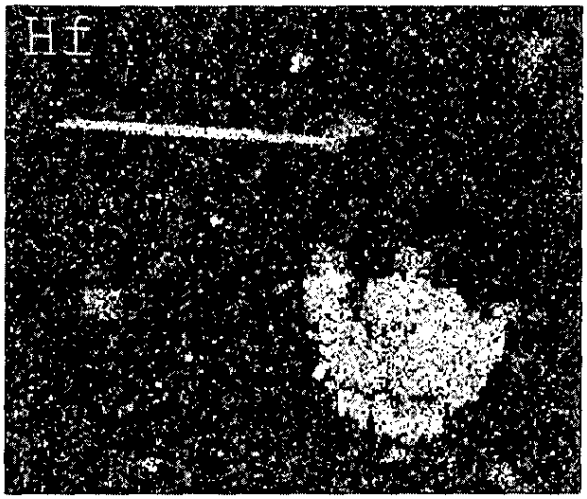

Figure 16 X-Ray map of hafnium in the surrogate MD-SNF form with 1.5% Gd and 1.5% Hf by weight (200X).

The metallurgical evaluation of the surrogate melt-dilute/neutron absorber systems to date provides evidence that the melt-dilute treatment can integrate neutron-absorbing materials into the MD-SNF form uniformly throughout the ingot in U-Al phases. Both neutron-absorbing nuclides currently exhibited desirable alloying characteristics. Gadolinium additions tend to concentrate in the UAl_4 phase that is more corrosion resistant than the bulk MD-SNF form. Therefore, the gadolinium is expected to stay closely associated with fissile uranium in the UAl_4 phase as the MD-SNF form degrades, providing an additional barrier against the solubility facilitated removal of gadolinium from the waste package.

Hafnium additions tend to concentrate with aluminum in an aluminum-hafnium phase or in a uranium-aluminum-gadolinium-hafnium phase. This makes the hafnium more susceptible to corrosion. However, the relative insolubility of hafnium would prevent it from being removed from the waste package. The combination of gadolinium and hafnium for criticality control provides the highest probability for maintaining criticality control of the MD-SNF form.

Corrosion Test Program

An experimental corrosion program is designed to evaluate the degradation behavior of several melt-dilute/neutron absorber systems under repository conditions. The first stages of the program will address the degradation behavior of the melt-dilute/neutron absorber systems, including melt-dilute without neutron absorbers, in a vapor environment. The corrosion rates of each system will be evaluated for exposure duration of up to one year. The materials are being exposed to various water-vapor chemistries and at different temperatures. The current chemistries include synthetic J-13 and condensate water vapor, but will be expanded to include simulated irradiated vapor and chloride chemistries. The current temperatures include 50, 100, and 200°C water vapor for the J-13 chemistry, and 100°C water vapor for the condensate chemistry.

This report presents the current state of experimental testing that is being carried out to determine the degradation properties of the surrogate melt-dilute /neutron absorber systems. These tests include vapor corrosion and aqueous corrosion tests. The tests utilize J-13 and modified J-13 water chemistry to simulate the chemistry effects due to the radiolytic decomposition of water, to the degradation of HLW glass logs, and the infiltration of chlorides into the waste package. Also, galvanic corrosion tests will be conducted in the test program. Aqueous corrosion tests include both static and flow tests as described below.

Static tests will be conducted to measure the following properties/behavior of surrogate melt-dilute/neutron absorber systems: 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 tests to measure the desired properties.

Flow testing will be conducted to determine both the dissolution and corrosion characteristics of surrogate melt-dilute/neutron absorber systems. 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 of surrogate melt-dilute/neutron absorber systems.

It is important to identify the degradation products of the surrogate melt-dilute/neutron absorber systems and the relative solubility of these products at repository relevant oxygen potential and pH values with respect to the fissile constituents of the Al-SNF degradation products. The aqueous corrosion tests will be used to obtain solubility data, and to identify degradation product formation for the surrogate melt-dilute/neutron absorber systems.

The current vapor corrosion experiments include 2-inch x 0.75-inch x 1/8-inch coupons of surrogate melt-dilute/neutron absorber systems. They have been polished to a 600-grit finish and have been given unique

labels. The tests to date include coupons of the melt-dilute plus 3 percent gadolinium by weight for 21 days in simulated J-13 water vapor at 100°C. The results of these tests (see Figure 17) indicate no decrease in corrosion resistance of the MD-SNF form due to the addition of 3% gadolinium by weight.

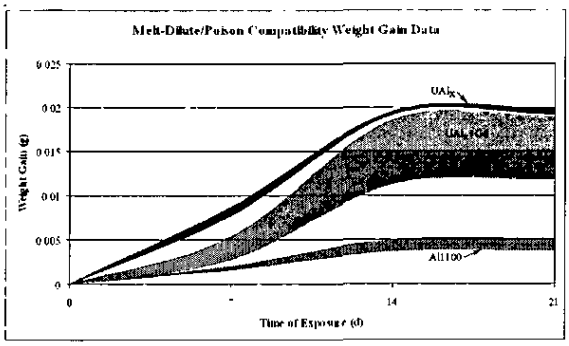

Figure 17 Preliminary surrogate melt-dilute corrosion data.

Additional tests in progress include coupons of the surrogate melt-dilute/neutron absorber systems exposed to simulated J-13 water vapor in vapor corrosion capsules as shown in Figure 18 and Figure 19.

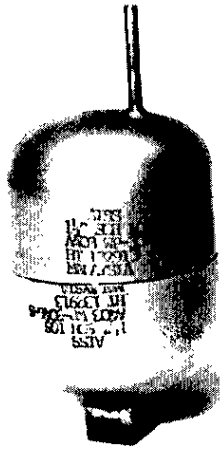

Figure 18 Stainless steel capsule, constructed of two pipe caps.

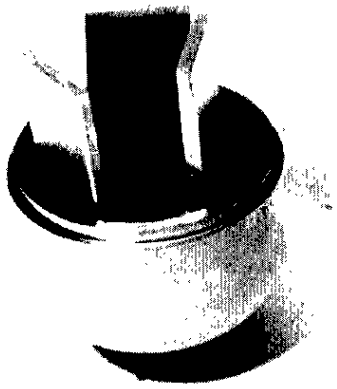

Figure 19 Three corrosion coupons are mounted in each capsule.

The exposure capsules, with their contents have been produced in quintuplicate to allow the periodic removal of samples at five predetermined time intervals. The time intervals being used in this program are 1 week, 1 month, 3 months, 6 months, and 1 year. The results of these tests will be reported upon completion of the vapor corrosion testing.

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