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Melt-Dilute Treatment of Spent Nuclear Fuel Assemblies from Research and Test Reactors

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Abstract

The Savannah River Site is the U.S. Department of Energy's preferred site for return and treatment of all aluminum-base, spent, research and test reactor fuel assemblies. There are over 20,000 spent fuel assemblies now stored in different countries around the world, and by 2035 many will be returned to SRS for treatment and interim storage, in preparation for disposal in a geologic repository.

The early fuel assemblies for research and test reactors were made using aluminum clad plates that were fabricated from highly enriched (93%) uranium-aluminum alloy. Later, powder metallurgical fabrication methods were developed to produce plate fuels with higher uranium contents using either uranium aluminide, uranium oxide or uranium silicide powders mixed with aluminum. Silicide fuel elements generally are fabricated with low enriched uranium containing less than 20% ^{235}U. Following irradiation, the spent fuel assemblies are discharged from the reactor, and most assemblies have been stored in under-water pools, some since the early 1950's.

A number of disposition options including direct/co-disposal and melt-dilute treatment were evaluated recently. The melt-dilute technique was identified as the preferred method for treatment of aluminum-base spent fuel. The technique consists of melting the spent fuel assembly and adding depleted uranium to the melt for isotopic dilution to <20% ^{235}U. Aluminum is added, if necessary, to produce a predetermined alloy composition. Additionally, neutron poisons may be added to the melt where they form solid solution phases or compounds with uranium and/or aluminum. Lowering the enrichment reduces both criticality and proliferation concerns for storage. Consolidation by melting also reduces the number of storage canisters.

Laboratory and small-scale process demonstration using irradiated fuel is underway. Tests of the off gas absorption system have been initiated using both surrogate and irradiated RERTR mini fuel plates. An experimental L-Area facility (LEF) is planned to validate induction furnace operations, remote handling, and the off gas system for trapping volatile elements under plant operating conditions. Results from laboratory tests and the small-scale process studies are discussed.

Introduction

The U.S. Department of Energy (DOE) is consolidating at the Savannah River Site (SRS) both foreign and domestic spent research and test reactor fuel assemblies that originated in the United States. These transferred assemblies are presently stored on site in water basins until a treatment and interim storage facility is available. The DOE through SRS has evaluated direct/co-disposal and melt-dilute technologies and has identified Melt-Dilute Treatment Technology (MD) as the preferred alternative for ultimate disposal of spent nuclear fuel in the Draft Environmental Impact Statement(1). The record of decision on spent fuel management is expected late this calendar year.

During the next 30-40 years, SRS will receive and store approximately 28 metric tons of heavy metal (MTHM) from spent nuclear fuel. This material may be treated and dry stored at SRS in a "road ready" canister until a geologic repository is available. About three quarters of the fuel by volume is in the form of high-enriched uranium (HEU) and could present criticality control issues during storage that are not inherent to low enriched (LEU) fuel disposition. The melt-dilute option will reduce the alloy isotopic enrichment to < 20% by diluting the material with depleted uranium thereby reducing concerns over criticality and proliferation. This method also decreases SNF volume by about 70% while producing a robust waste form for long term storage.

Early research and test reactor fuels were manufactured using cast aluminum-uranium alloy containing highly enriched uranium (93% ^{235}U). Fuel plates of MTR type were clad with aluminum alloys and bonded to the meat section by hot and cold rolling methods. Later, powder metallurgical techniques were developed for fuel meat fabrication using either blended UAl_x or U_3O_8 and aluminum powders. Finally, to increase uranium fuel density, aluminum silicide fuels were developed in the 70-80's, and are now used to make low enriched uranium fuel elements for research and test reactors. After irradiation many fuel assemblies have been stored at reactor sites in under-water fuel basins (some as long as 30 years after discharge from the reactor).

Process Description

The melt-dilute (MD) process for treatment of spent fuel has been under development at SRS for several years. The flow diagram for this process is shown in Figure 1. Initially, the spent fuel assembly is loaded into a crucible/liner arrangement placed in a commercial induction furnace. Depleted uranium is added to lower the isotopic content, and aluminum to adjust the final composition. The melt is stirred by induction stirring to accomplish the isotopic dilution. In the case of oxide based fuels, the charge is held at temperature to allow for reduction of this oxide by aluminum or other additions. After this, the melt is sampled to insure compositional consistency. Finally, the alloy is furnace cooled in the crucible to produce an ingot for storage. During the entire process the gases released from the melt are treated through an off-gas system designed to trap radionuclides and volatile fission products.

The melt-dilute process development has included bench-scale studies using surrogate and irradiated spent fuel. In addition, small-scale studies using MTR equivalent surrogate spent fuel materials (using depleted uranium alloys) was also conducted to evaluate the off-gas system concepts to trap volatile fission products released from spent fuel assemblies during the melt and dilute process. Currently, a small-scale facility capable of demonstrating and validating the melt-dilute process using single irradiated MTR elements is being designed and assembled in the L-Reactor Area at SRS. This facility is referred to as the L-Area experimental facility (LEF). The DOE has considerable experience in the melting of aluminum-uranium fuel materials and limited experience in the melting of irradiated spent fuel. The melt-dilute process operations differ from aluminum-uranium casting primarily in the radiation field and the volatility of some fission products associated with spent fuels. These factors necessitate the development of remote operations (i.e., stirring and sampling) and of the off-gas system. The off-gas system consists of zeolite adsorption beds for the adsorption of volatile fission products and HEPA filters to ensure the entrapment of condensed particles. The melt-dilute system consisting of an induction furnace and off gas adsorption beds are contained inside a steel enclosure that is located inside a shielded concrete facility. All operations are conducted remotely from a control room using an overhead crane and a hardened camera system.

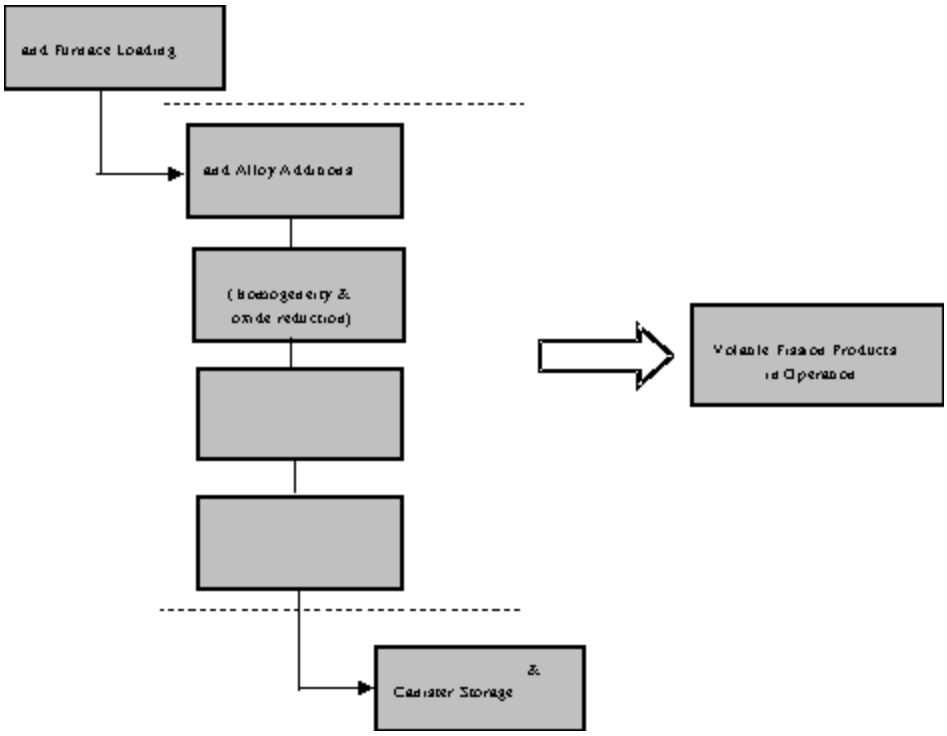

Figure 1. Melt-Dilute Process Flow Diagram

Before fuel loading, the stainless steel top of the furnace enclosure is removed. The spent fuel assembly, removed from the transportation cask, is placed in a consumable aluminum basket. The basket including the spent fuel is put inside the crucible/liner. Depleted uranium for isotopic dilution (<20%) and aluminum for compositional control (13.2 wt% Al-U alloy) are added to the crucible/liner before startup. The amount added is based on initial calculations. The off-gas system including the absorption bed is then located on top of the crucible and the furnace enclosure top replaced.

The melt-dilute process cycle is approximately 6 hours including the approximate 1 hour it takes to completely melt and dilute one MTR assembly, induction stirring and melt-sampling. The temperature of the eutectic composition is the lowest liquidus temperature (646 °C) in the binary uranium-aluminum system but the process is expected to operate at 850 ± 50 °C. This will provide sufficient super heat to adequately dissolve the uranium diluent and minimize volatilization of some fission products. The cooling time needed to reach the solidus temperature is approximately 5 hours. Once solidified the ingot and carbon steel liner is removed from the furnace and stored in a storage canister.

Experimental

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 cast U-Al, and Al-UAl_x, Al-U_3Si_2, and Al-U_3O_8 powder metallurgy research test reactor fuel assemblies. These investigations have been centered on binary uranium-aluminum alloys with compositions at or near the eutectic (13.2 wt % U) but have included ternary additions to simulate processing of silicide and oxide fuel assemblies. Development of ternary isothermal sections for the U-Al-Si using the standard Gibbs triangulation technique and fundamental thermodynamic calculations assessing the possible reaction paths in the U-Al-O system have been performed. Additionally, fundamental dissolution kinetic experiments have been conducted using depleted U_3O_8 and U_3Si/U_3Si_2 samples and molten aluminum. The microstructures of dip samples as well as sections from the cast form were characterized using light optical microscopy, X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy. Additionally, chemical analysis was performed using ICPES.

Additional melting experiments were performed at ANL-East using irradiated SNF coupons. The test specimens used in this test consisted of 1.25" x 0.5" x 0.06" strips of UAl_x fuel with Al-2Mg cladding. The original loading of the entire fuel assembly from which these strips were sectioned was 1.7 gU/cc with a beginning of life enrichment of 44.9%. The average burnup of this assembly was 74%. For this test, the irradiated SNF coupons were placed in a graphite crucible and heated in the test assembly at 850°C for 1 hour.

Results and Discussion

Metallurgy

U-Al Fuels and Alloys: Many MTR and other research reactor fuel elements were originally fabricated using highly enriched uranium (93 wt% 235U) 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 235U remaining in the fuel assembly. For isotopic dilution, depleted uranium metal (0.02 wt% 235U) is added to the melt to reduce the enrichment of the uranium to about 20 wt% 235U or less. When depleted uranium metal is added the primary phases present in the melt and in the final microstructure of the casting are affected. According to the phase diagram in Figure 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 UAl_3 or UAl_4 become thermodynamically stable and begin to precipitate from the liquid solution. For this reason, additional aluminum is added to maintain the composition at, or near, the eutectic composition. This prevents gravity segregation from occurring at the process temperature of 850°C. In Figure 3a and b, photomicrographs illustrate the difference in microstructure obtained after processing UAl_x with the melt and dilute process.

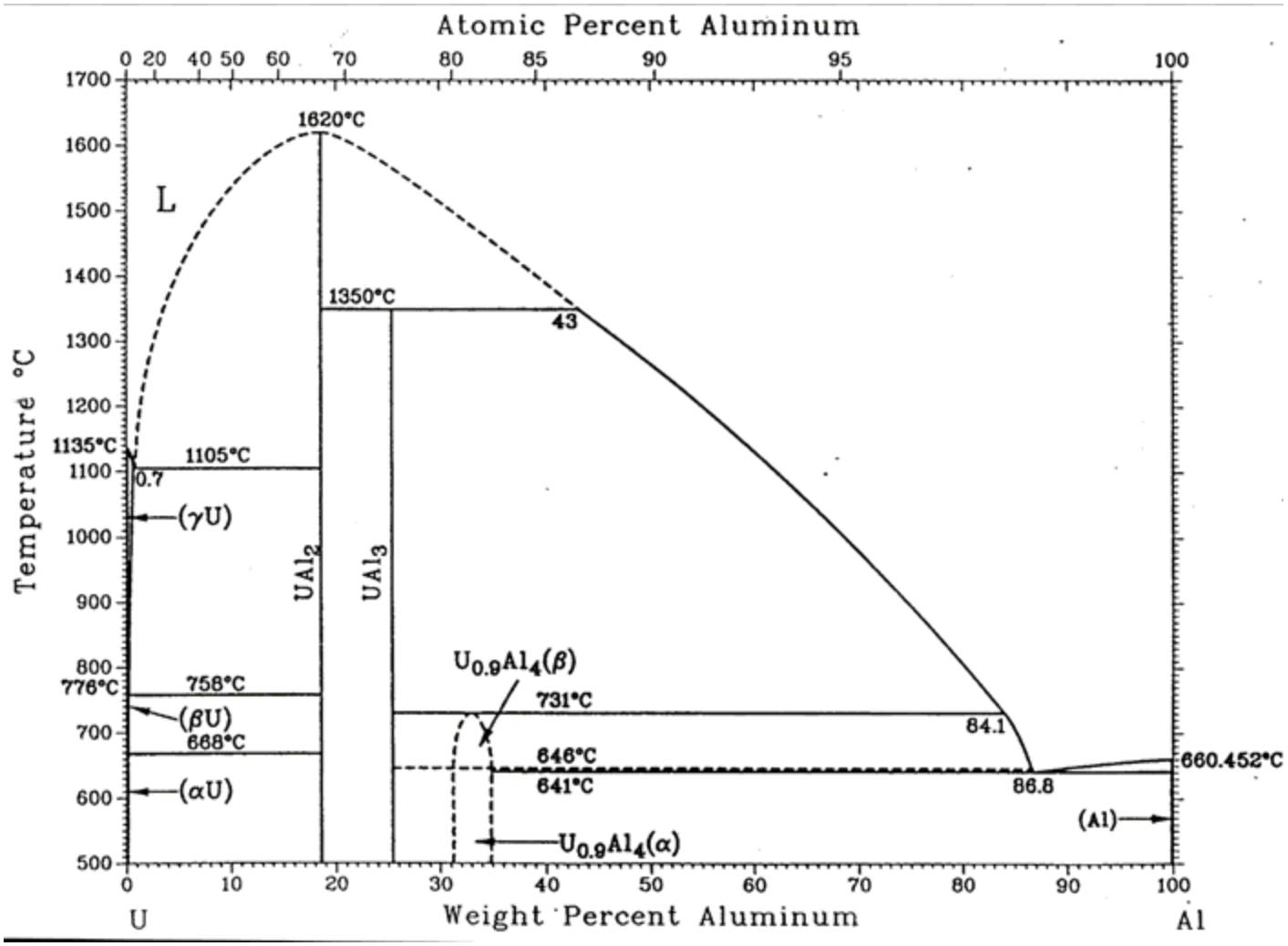

Figure 2 Binary Equilibrium Uranium-Aluminum Phase Diagram(2)

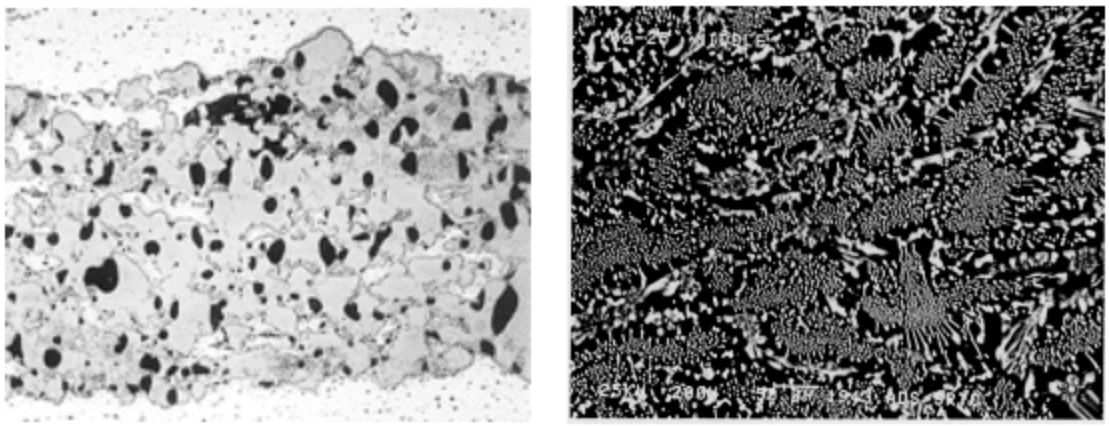

Figure 3 Photomicrograph of typical irradiated UAl_X fuel plate (a) and a backscattered electron micrograph of a simulated fuel plate after the melt and dilute process (b).

U-Al-Si Fuels and Alloys: Fuels based on the U-Si system have been developed by the Reduced Enrichment Research and Test Reactor program operated by Argonne National Laboratory, which has worked for the past 15

years to develop low enriched (<20%) uranium alloy fuel for use in research and test reactors. Examination of the U-Si binary equilibrium phase diagram shows two compounds possessing high atomic uranium fraction: U_3Si and U_3Si_2. Research and test reactor fuels using these two compounds have been manufactured as fuel core composites consisting of powder metallurgy blends of Al powder and the individual uranium-silicide compounds. They are expected to be approximately 20% of the fuel inventory to be treated by the melt-dilute process(3). Consolidation is of prime importance for these fuels because they are fabricated using LEU and no isotopic dilution is required for most assemblies.

The aluminum-uranium-silicon ternary phase diagram was developed using the Gibbs triangulation method and experimental data. Isothermal sections were studied to determine the liquid phase region at the expected fuel composition. At 800°C a significantly large liquid phase region exists at the aluminum rich end of the ternary phase diagram as shown in Figure 4. Thus, treatment of these fuels should be similar to the uranium-aluminum alloy fuels and similar process operating parameters are expected. In Figure 5, a typical photomicrograph of the fuel core from a silicide fuel assembly (a) shows interaction between the uranium-silicide intermetallic and the Al matrix. The new phase formed is the $U(Al,Si)_3$ which is the one of the equilibrium phases for this mixture[3]. Also included in this figure is a photomicrograph showing the resultant microstructure of a melt and dilute processed silicide fuel assembly (b).

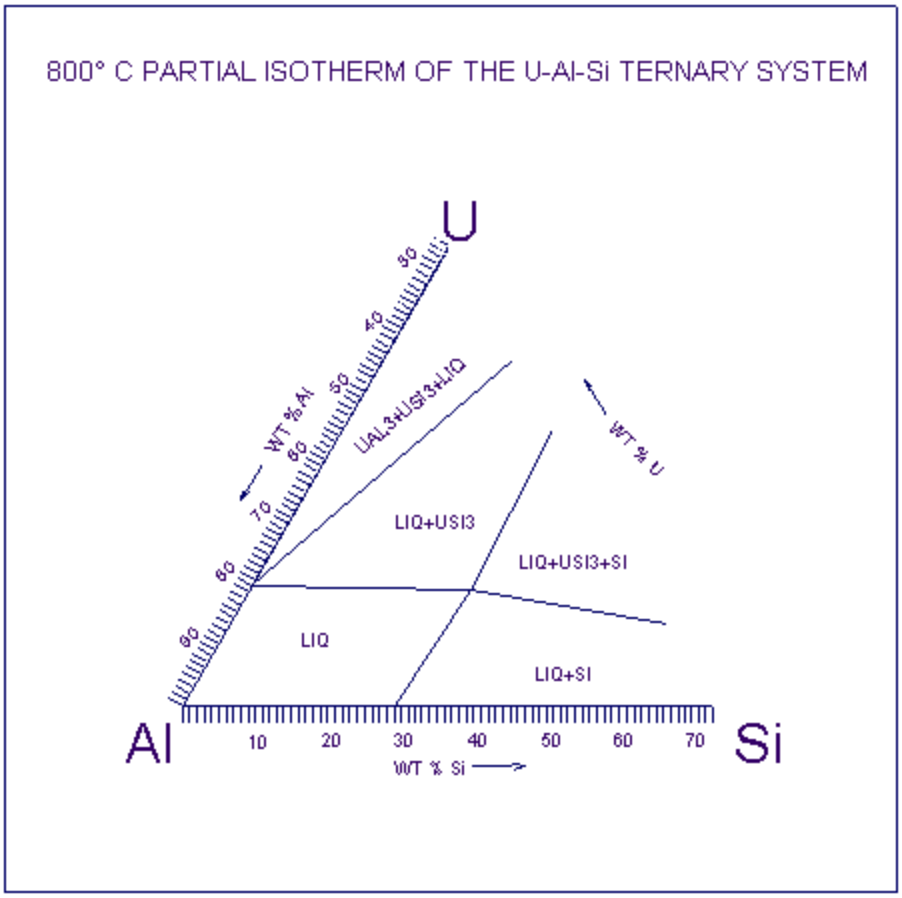

Figure 4 Aluminum-Rich Corner of the Aluminum-Uranium-Silicon isothermal section of the ternary phase diagram at 800 ºC.

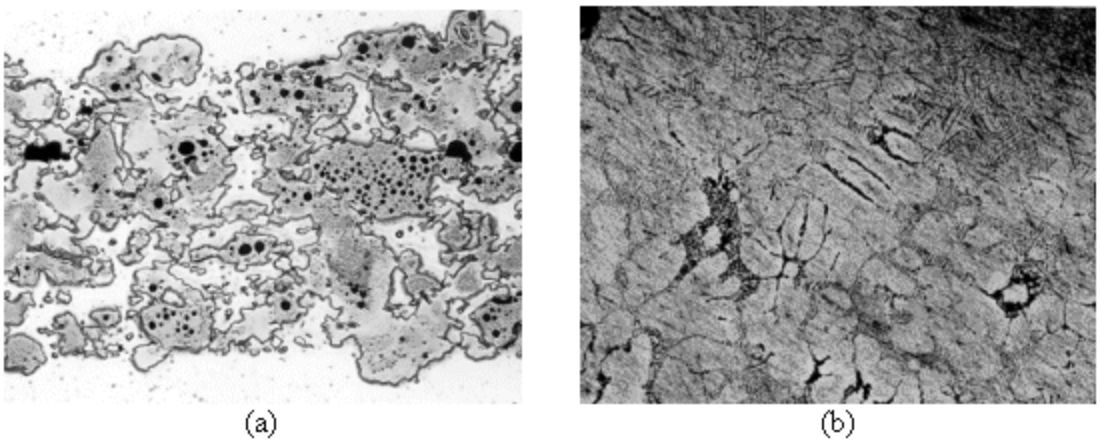

Figure 5 Photomicrograph of typical irradiated U_3Si_2 fuel plate (a) and a micrograph of a simulated fuel plate after the melt and dilute process (b).

Oxide Fuels and Alloys: Like the silicide fuels the uranium oxide fuel particles react with the aluminum matrix while in service as is evident from Figure 6a. However, the extent of the reaction in the oxide is much greater than in the silicide fuels. At 850°C, thermodynamic calculations indicate that the reaction between uranium oxide and aluminum is favorable. Unfortunately, the reaction kinetics are relatively slow at this temperature. For example, Figure 6b is a micrograph of an oxide fuel element simulation after the melt at 850°C for 3 hrs. Large particles of partially reduced UO_2 are still present. It is expected that the slow reaction kinetics are a result of the formation of a stable aluminum oxide layer at the particle-liquid interface. However, the addition of small amounts of calcium to the melt greatly increases the reaction rate making the processing time similar to U-Al alloy fuel. In Figure 6c, the resulting microstructure of a similar test with small additions of calcium (i.e., ~5%) shows complete reduction of the uranium oxide at 850°C in less than 1 hour.

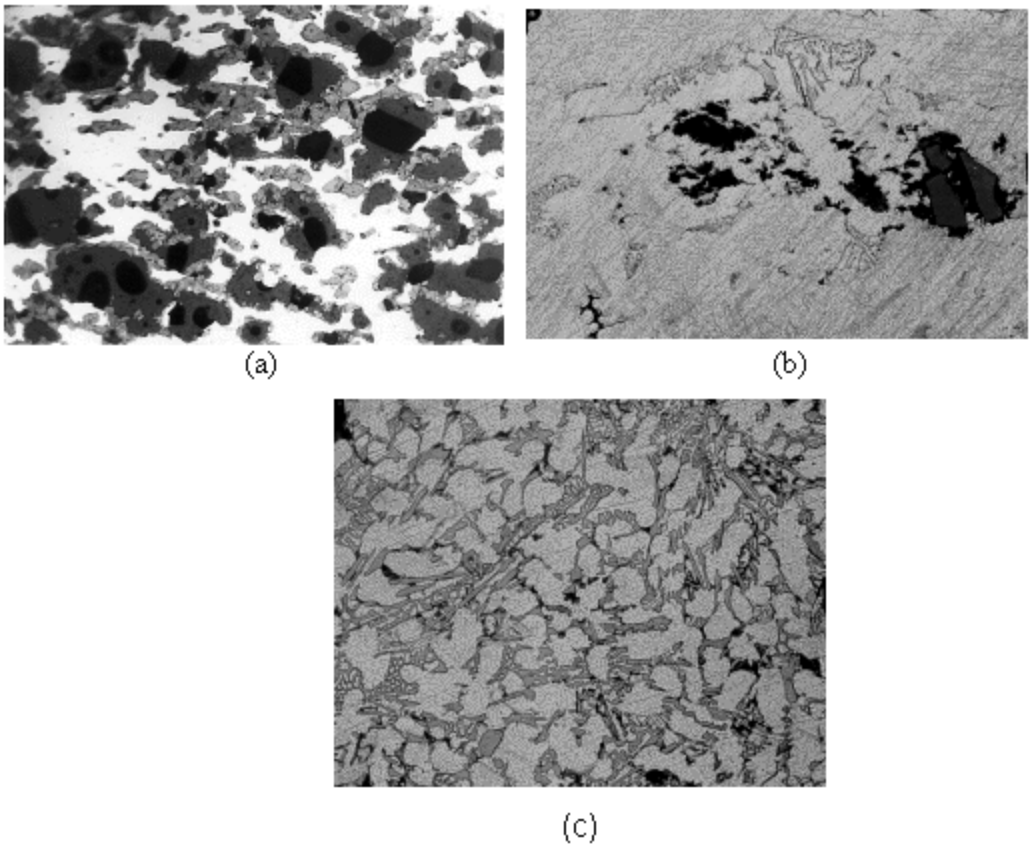

Figure 6 Photomicrograph of typical irradiated Al + U_3O_8 fuel plate (a) a micrograph of a simulated fuel plate after 3hrs at 850ºC (b)
and a simulated fuel plate after the melt and dilute process with small additions of calcium(c).

Off Gas Treatment Studies

A critical technology element in the development of the melt-dilute process is the development of an off-gas system. The volatilization of radioactive fission products during the melting stage of the process constitutes the off-gas. The challenge for the melt-dilute treatment process is to capture these volatile fission products and radionuclides. With this in mind an analytical and experimental program has been undertaken to assess the volatility and capture of species under the melt-dilute operating conditions.

Thermodynamic calculations were performed for uranium-aluminum fuels to determine elements that may be released when melting. Types and quantities of fission products and radionuclides were calculated for a 250 MWd MTR assembly after 5 years cooling using the Origin-S computer code. Based on an ideal solution model, elemental vapor pressures, and an air flow rate through the system of 1 scfm, it was determined that the fission product of most concern was cesium. Other elements remained in the melt either because they had a low vapor pressure or because they formed compounds within the melt having low vapor pressures. Gaseous fission products, such as I, Kr, and tritium will be completely released during melting however, preliminary calculations show that for both on-site and off-site individuals the effective dose equivalents do not exceed regulatory limits..

Actual fission product release experiments have been conducted within the DOE complex with respect to research and test reactor safety and core melt-down scenarios [3-7]. These experiments clearly showed that noble gases and cesium vapors are released from Al-based fuels. Two major outcomes from these sets of experiments are as follows:

1. Cesium releases from Uranium aluminide and silicide fuels are less than 20% up to **1000°C** when heated in air for time from 30-60 minutes.[3,4,6,7]
2. "As shown, much of the iodine release occurs over a relatively short duration and over a wide range of temperatures, whereas this is not the case for cesium...."[7]

Throughout these experiments the release of cesium has been shown to be a nonlinear function of burnup, atmosphere, temperature, and fuel composition.[7]

Additionally, because of the published variability of cesium release data and testing conditions two sets of fission product release tests have been performed at SRTC and ANL-East. The SRTC tests employed non-radioactive fission product surrogates in full-scale melt-dilute melts and the ANL-East test used bench-scale irradiated SNF coupons. These ANL tests using RERTR mini-fuel plate sections were done in the Alpha-Gamma Hot Cells at ANL East. These tests were carried out using conditions that closely mock up the melt-dilute process. Plate samples (~5 gram size) were placed into a graphite crucible and heated at 850 °C for 1 hour with a 1 scfm air flow rate through the crucible and zeolite bed. The purpose of the tests was to determine fission product release, to verify thermodynamic calculations, and to determine the effectiveness of a zeolite sorption bed in capturing volatized fission products. A water scrubber was used to capture any volatile fission products that may break-through the zeolite bed.

After heating the crucible, piping and zeolite bed were gamma scanned, and the scrubber solution was analyzed for fission product activity of elements that might escape the sorption bed. A typical gamma spectrum from the crucible and absorber bed is shown in Figure 7.

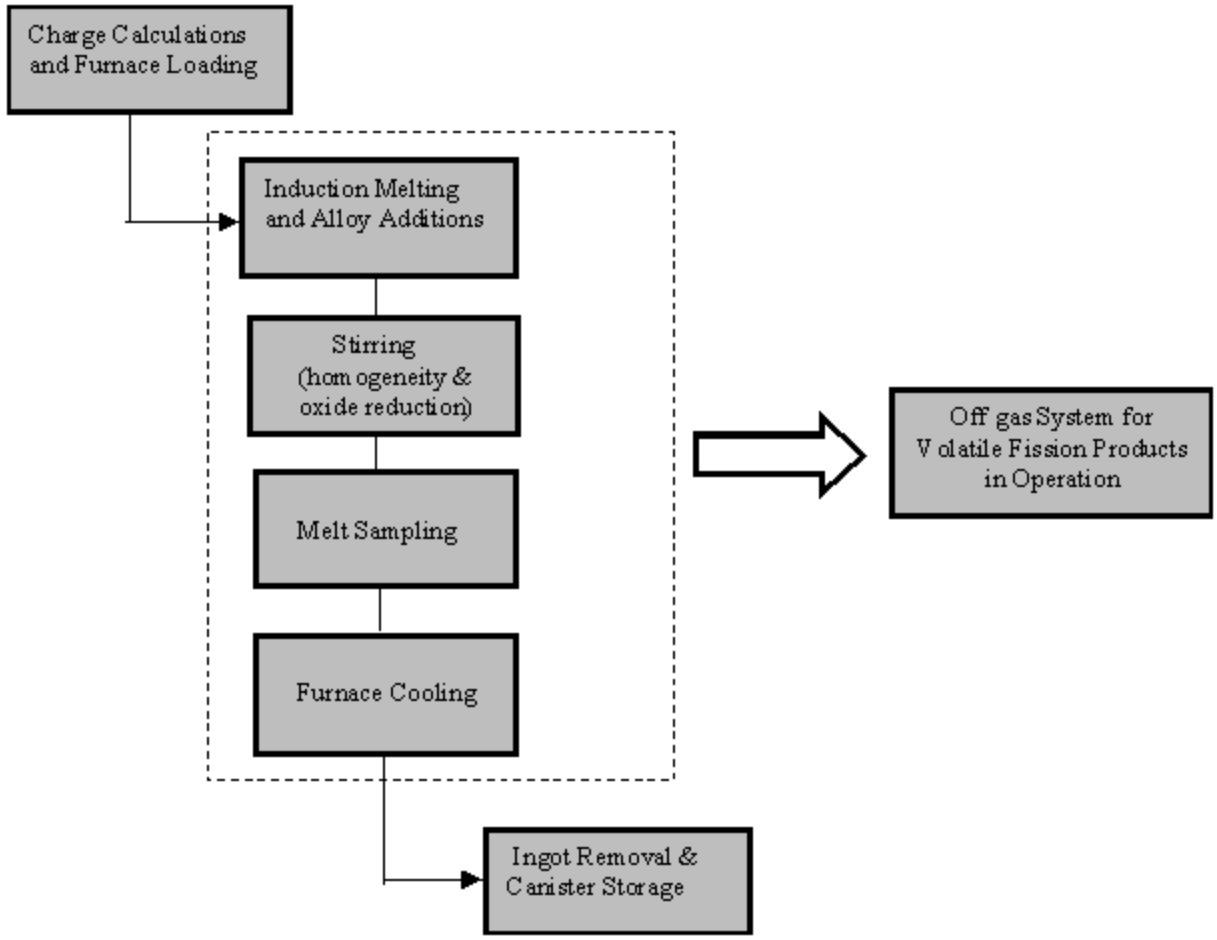

Figure 7 ANL Results from RERTR Fuel Melt Experiment.

When the cell background is subtracted from the gross activity, as shown by the lower curve in the figure, it was found that 78% ^{137}Cs remained in the solidified ingot. Of the fraction released, 16% was located at the bottom few centimeters of the zeolite bed, and 6% plated out on the stainless steel tubing leading from the crucible to the sorption bed. No other volatile elements were detected on the bed, and no activity was found in the wet scrubber solution; therefore, complete sorption of volatile cesium occurred on the bed. At 850°C, 22% of the cesium was released from the melt in this study.

The analytical and experimental tests conducted at both SRTC and ANL, have identified cesium as the melt constituent of most concern with respect to volatilization. Experimental tests using both cesium surrogates and radioactive cesium have confirmed previous data by Hoe[8] and Wolkoff[9] that zeolite 4A is an effective cesium trap, and as a result a preliminary off-gas system concept has been developed employing dry zeolite 4A adsorber beds as the primary cesium trapping medium. Validation of this off-gas concept will occur during full-scale irradiated testing in the proposed L-Area Experimental Facility.

L-Area Experimental Facility Off Gas System Concepts

Design of the off-gas system for the LEF pilot-scale facility is based on experimental results obtained from laboratory tests and from the ANL study of irradiated samples. The system layout is shown in Figure 8. The induction furnace as well as the primary and secondary adsorber beds is located inside a steel enclosure (confinement space). There is a negative pressure differential between the room, enclosure and furnace crucible, so any air leakage is into the crucible and is exhausted through the off gas HEPA system. Also, inside the enclosure is the secondary absorption bed which serves as a backup in the event breakthrough occurs during melting. From the secondary bed, the off gas is directed through a dual bank of HEPA filters to remove particulate particles. After passing through the system, the off-gas is discharged to the stack. Nobel gases

released are expected to be within current regulatory guidelines, but if not, gases such as iodine and krypton can be captured using charcoal and low temperature silver mordenite beds,[10] respectively.

Initially, six assemblies will be melted for evaluation; the need for additional tests will be determined after analysis of the data from the first six tests. The initial six assemblies will range from an aluminum-depleted uranium surrogate assembly for equipment and process checkout to assemblies with increasing burnup to 50%. Since, each assembly will have a higher burnup the level of Cs-137 will increase with each test. The purpose of these tests is to evaluate current process parameters and off-gas system design. Data obtained will include absorber bed performance and efficiency, dilution composition, and crucible/liner performance. The design of the off-gas system for the full-scale irradiated fuel assembly facility will be based on data obtained from the bench-scale and full-scale surrogates tests as well as the bench-scale irradiated SNF coupon test.

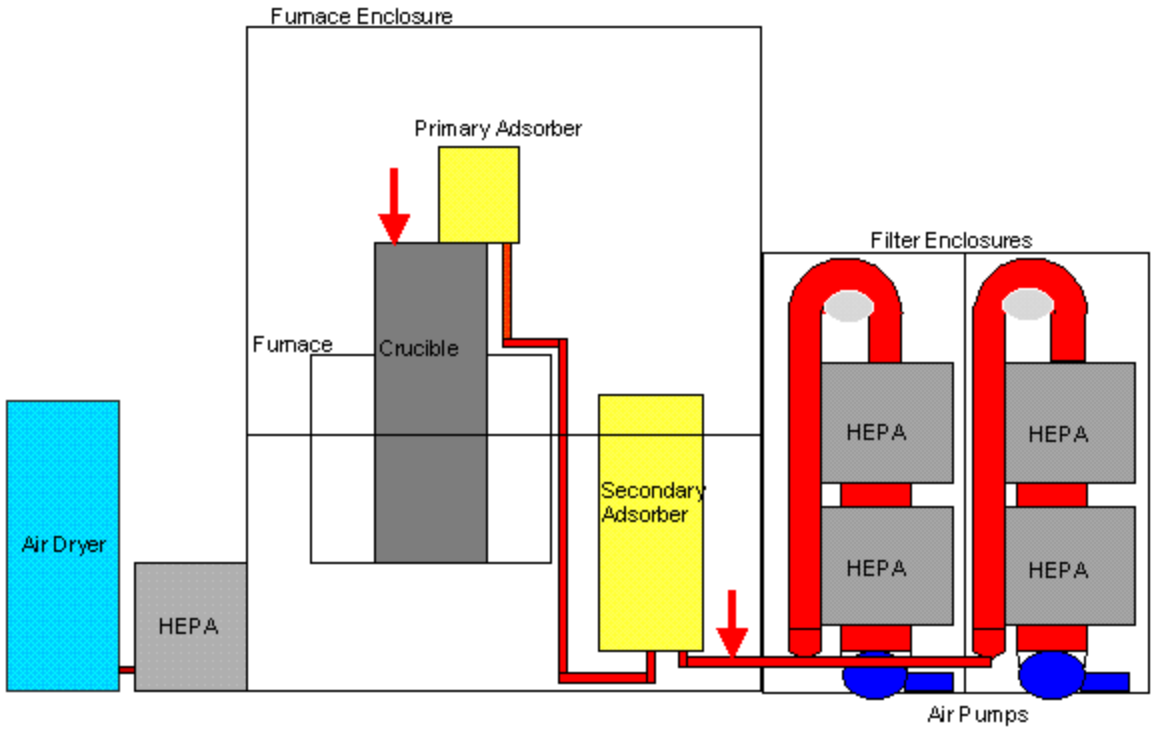

Figure 8 Melt-Dilute Off-gas system Flow Diagram for the LEF Facility.

Conclusions

Preliminary investigations using both surrogate and irradiated SNF coupons have been conducted at SRTC and ANL to validate the melt-dilute treatment technology process and off-gas development. Through bench-scale and full-scale surrogate testing, the melt-dilute treatment technology has been shown to effectively treat all of the Al-based research and test reactor fuel types. Furthermore, with regard to the off-gas system development studies, experiments conducted at SRTC and ANL with surrogate and irradiated materials have shown that zeolite 4A is an effective medium for trapping gaseous cesium vapors. Finally, validation of these experiments will be demonstrated in a full-scale irradiated melt-dilute facility to be constructed in L-Area at SRS.

Acknowledgment:

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