WSRC-MS-2002-00736

Treatment of Legacy Materials Using the Melt-Dilute Treatment Technology

by

T. Adams

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

N. Iyer

R. Sindelar

A document prepared for DOE SNF AND FISSILE MATERIALS MANAGEMENT at Charleston, SC, USA from 9/17/2002 - 9/20/2002.

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

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

WSRC-MS-2002-00736

TREATMENT OF LEGACY MATERIALSUSING THE MELT-DILUTE TREATMENT TECHNOLOGY

Thad M. Adams
Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

Natraj C. Iyer
Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

Robert L. Sindelar
Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

ABSTRACT

The Melt-Dilute technology was selected as the preferred technology for the treatment and disposition of aluminum based research and test reactor spent fuel. The melt-dilute (MD) treatment technology has advanced significantly over the past several years and a number of key elements of the treatment technology have been demonstrated including process versatility and modularity. It thus offers the potential to treat many DOE legacy waste streams. This paper reviews the candidate legacy materials and addresses adaptation of the melt-dilute technology to treat DOE legacy waste streams. The legacy materials waste stream includes the following: depleted uranium, high enriched uranium, streams containing organic materials including metallurgical mounts, streams containing small amounts of plutonium etc. The flow sheets for the treatment of these legacy materials have been presented. Specific legacy waste streams studied included metallurgical mounts with uranium, and uranium oxide and/or U-233 packaged in stainless steel containers. Finally, an approach to disposition of the legacy materials using a modular, transportable melt-dilute treatment facility is also presented.

I. BACKGROUND

There are currently various classes of nuclear materials that fall under the oversight of the DOE-Nuclear Materials Stewardship (NMS) Program that have no defined disposition pathway. These materials include off-spec HEU (High Enriched Uranium) metal and oxides, surplus depleted and natural uranium, uranium-233, Pu-238 scrap, miscellaneous Pu-239 scrap, metal, and powder, and various spent nuclear fuel "cats & dogs." Development of well-defined disposition pathways—which may include various stabilization, treatment, or disposition technologies-- is paramount for an effective nuclear materials stewardship program. In order to achieve this goal, the most appropriate technology must be identified to ensure that efficient and effective management of the legacy materials inventory. One approach is to explore/evaluate currently existing stabilization, treatment, and disposal technologies with respect to their ability to handle diverse new/alternate feed streams.

The melt-dilute technology, which is currently in the pilot-scale irradiated demonstration phase, offers the potential to treat and dispose of many of the materials managed under the DOE-NMS program. The melt-dilute technology has been developed at SRS to effect the treatment and ultimate disposition of Al-Based SNF to be returned to SRS from domestic and foreign research and test reactors. The technology development program was in the process of start-up and initial testing of an irradiated pilot-scale facility prior to suspension of the program in by DOE. The irradiated pilot scale facility has been designed to make the most use of commercially available components and technologies. This facility will be capable of handling a single irradiated fuel assembly for treatment. The treatment equipment occupies a footprint approximately 10'x 30'. This facility is in essence a mini-batch, modular melt-dilute system.

An attractive concept would be to adapt the irradiated pilot scale system design concept for the treatment of alternate feed streams using the melt-dilute technology. Such a "mini-batch" system could be turnkey fabricated and installed at any of the end-user sites in need of treatment and disposition of nuclear materials or installed in a tractor trailer to make a mobile treatment system.

<u>The Melt-Dilute Process:</u>

Approximately 20 metric tons heavy metal of aluminum-based spent nuclear fuel (Al-SNF), or approximately 15,000 assemblies from foreign and domestic research reactors, are being consolidated at the Savannah River Site. The melt-dilute treatment has been developed for ultimate disposal of these fuels, most of which contain highly enriched uranium (HEU) (>20% ^{235}U), in the monitored geologic repository (MGR).[i] This alternative for disposition of the Al-SNF was selected as the preferred alternative through the EIS (environmental impact statement) process. The melt-dilute treatment involves melting the SNF in a furnace and diluting with depleted uranium. Figure 2 shows a schematic of the process. Dilution of the SNF to reduce the U235 content of HEU to LEU levels (i.e. <20% enrichment) offers the primary benefit of reducing criticality potential. The product is an isotopically diluted SNF form that can be tailored to optimize the degradation characteristics by addition of aluminum or other elements. Significant benefits are also accrued from the ~70% volume reduction resulting in fewer canisters to be stored and shipped for repository disposal when compared to direct/co-disposal. Melt-dilute treatment also minimizes characterization requirements through erasure of the SNF's history and acquisition of in-process characterization data.

Advantages of diluting the uranium to below 20% ^{235}U 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 process and materials costs. When compared to other dilution methods, the 20% dilution offers the greatest versatility because waste forms containing approximately 5-67 wt% uranium can be produced and stored in less than 400 canisters which compares very favorably to the >1200 canisters required for direct/co-disposal.

The National Research Council in its review of the various non-processing alternatives noted that " all of the technologies necessary to make this system (melt-dilute) functionally successfully have been used in other applications, and it should be a relatively straightforward exercise to bring them together for aluminum spent fuel treatment". The melt-dilute technology development included development of the treatment process and systems technology using both surrogate and irradiated materials testing; and the demonstration of compliance with OCRWM (Office of Civilian Radioactive Waste Management) Waste Acceptance Criteria. The project implementation activities included development of a treatment and storage facility (TSF) to treat, package, and store Al-SNF using the melt-dilute and direct/co-disposal technologies.

Figure 1 presents the flow sheet of the process steps involved in implementing the melt-dilute treatment process. The focus of the technology development was as follows: (i) validation of the laboratory processing studies through a melt-dilute treatment demonstration using full scale irradiated SNF and (ii) development of the engineering and scientific data necessary to support repository qualification of the diluted aluminum SNF form. The process development focused on the issues and challenges related to the technical uncertainty of key technology functions and systems. Table 1 shows a matrix for the functional areas shown in Figure 1 and the associated status of development.

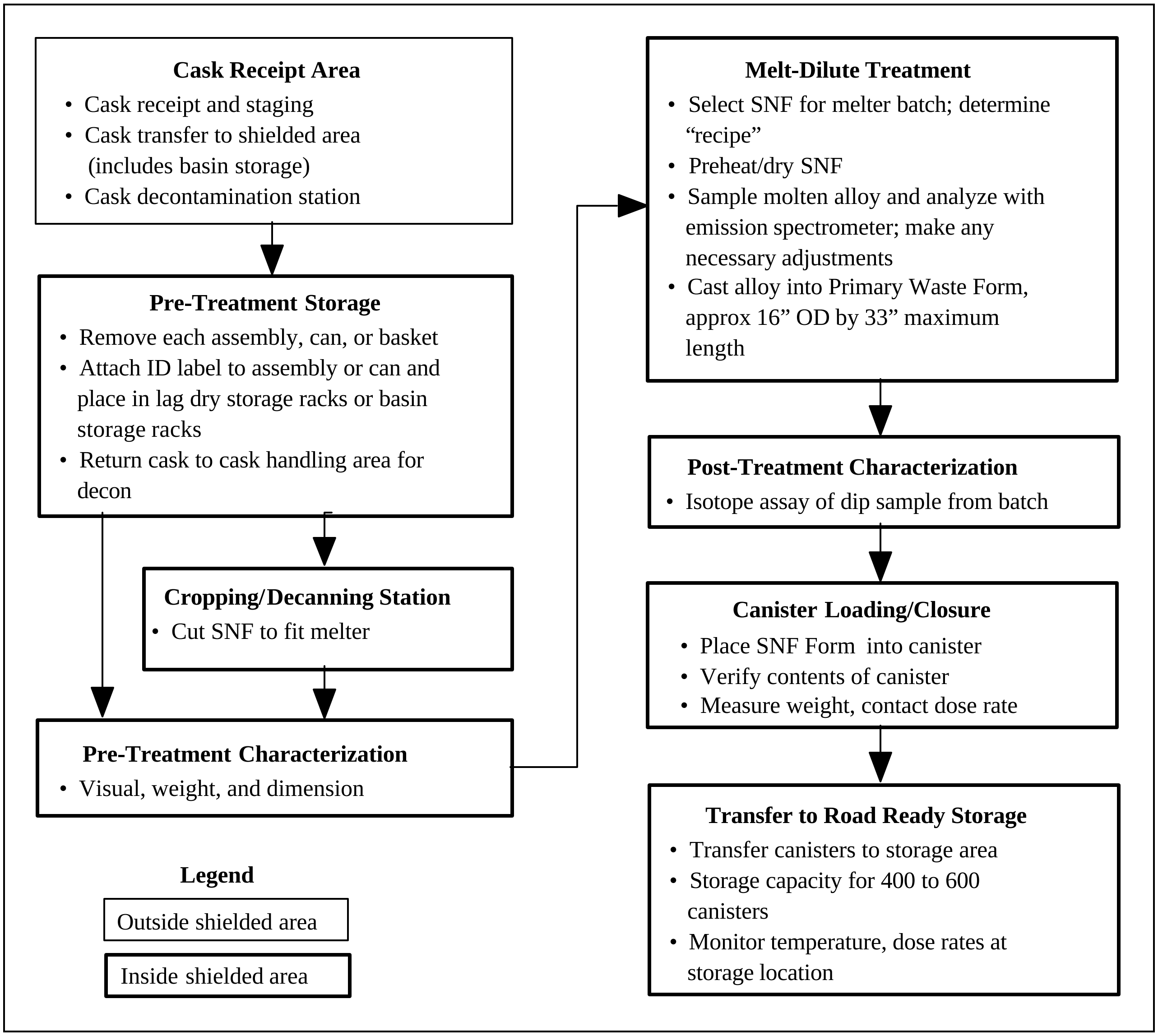

Figure 1. Process Steps in TSF for Melt-Dilute Technology

II. LEGACY MATERIALS STREAMS

Uranium-233—CEUSP

The three basic categories of Uranium-233 include clean ^{233}U, materials from the Consolidated Edison Uranium Solidification Program (CEUSP), and the light-water breeder reactor (LWBR) program. The CEUSP material is a very attractive candidate for the melt-dilute process. This material consists of mostly uranium oxide in stainless steel containers, which is compatible with the current MD process. However, other materials could be processed in this manner provided the package meets metallurgical specifications.

The CEUSP ^{233}U material was created from the irradiation of HEU-thorium fuel in the Indian Point Reactor Unit I. The SNF was reprocessed with the ^{233}U shipped in the form of an uranium-nitrate aqueous solution to ORNL. The solution was put into stainless steel containers and heated to form a monolith of uranium oxide that is physically bound to the container. Cadmium and gadolinium was added to the liquid mixture for criticality control and remains as oxides in the storage container. The CEUSP material is a mixture of approximately 7 wt% ^{233}U, 58 wt% ^{235}U and other uranium isotopes.

The CEUSP material at Oak Ridge National Laboratory is stored in 401 stainless steel canisters. The can dimension is 3.625 inches in outer diameter and is 24.75 inches long. The stainless steel can including the A36 ferro-magnetic cap plate weighs about 5957 grams. There is a total of 1043 kg of uranium with 796 kg ^{235}U and 101 kg ^{233}U that is currently stored and requires treatment.

<u>Pu-Contaminated HEU Parts</u>

Pu-contaminated HEU parts are expected to be shipped from Rocky Flats to SRS—235-F for storage and ultimate disposal. Approximately 300 Pu contaminated parts and 85 Pu/EU composites are anticipated to be shipped and stored in D-22 containers.

<u>Metallurgical Mounts</u>

Metallurgical mounts were generated in the past few decades as part of fuel process development and fuel performance studies. The metallurgical mounts are typically stored in stainless steel containers and in wet storage basins or in various hot cells. The mounts primarily contain organic materials (thermosetting or thermoplastic resins) along with the irradiated Uranium and/or aluminum or stainless steel.

<u>Depleted Uranium and Off-spec HEU</u>

There are approximately 40,000 MTU (metric tons Uranium) of DU (depleted Uranium) and off-spec HEU within the DOE complex. The majority of these materials are located at ORNL and SRS. Much of the ORNL materials is off-spec HEU metal and DU. The majority of the SRS materials are DU metal and oxide. INEEL also has approximately 1700 MTU of de-nitrator oxide that is included in these materials.

III. Proposed FlowSheets

<u>Uranium-233—CEUSP</u>

The process flow diagram for the melt-dilute process is shown schematically in Figure 2. The stainless steel can containing the monolith would first have to be vented to release any pressure build-up during the heating cycle. Commercial 1100 Al and SRS DU or DU oxide (UO_3) could be used for isotopic dilution. The MD process is readily adapted to the treatment of ^{233}U except ffor additional shielding requirements for the eequipment. The operations must be done remotely due to the high level of radioactivity.

<u>Pu-Contaminated HEU and DU and Off-spec HEU:</u>

Treatment of Pu-contaminated HEU and DU/Off-spec HEU using the Melt-Dilute Treatment Technology would require very little adaptation to the base process developed for treatment of Al-based DOE SNF, Figure 3. With respect to Pu-contaminated HEU, the primary issue will be facility modification to minimize facility contamination from Pu. Plutonium will alloy readily with aluminum in the process and will ultimately reside in the intermetallic phases within the microstructure of the Melt-Dilute ingot. The composition of the phases will resemble the following: $(U,Pu)Al_4$ and $(U,Pu)Al_3$.

Excess DU inventory at SRS and DOE complex would be used to effectively dilute enrichment of higher enrichment materials. The ORNL off-spec HEU which is mostly in metal form will be alloyed with aluminum and diluted as was the common practice for 30years during SRS M-area Fuel fabrication operations.

<u>Metallurgical Mounts</u>

The existing melt-dilute process is readily adapted to accommodate the metallurgical mount materials. Analysis of the process flow sheet leads to an additional train to the off-gas system to handle the organic material and a small change in the process cycle to ensure effective off-gas of the organic materials, Figure 4. Conventional off-gas system for the base-line melt-dilute process primarily consists of a multiple stage of zeolite filter bed. The off-gas system for this stream includes a charcoal bed filter to handle the hydro-carbons. These beds have been demonstrated to be very effective for trapping and aerating the hydro-carbons. In addition, the process cycle is refined to include a hold time in the 350 – 500^{o}C range to allow full and effective off-gas of the hydrocarbons. Aluminum additions are made to the melt to the extent necessary to meet the aluminum waste form protocols. The resultant product is an aluminum- based monolith. The microstructure is that of Uranium Aluminide in an aluminum-rich matrix with small amounts of carbon either in solution in the aluminum matrix or partitioned as carbides in the grain boundaries.

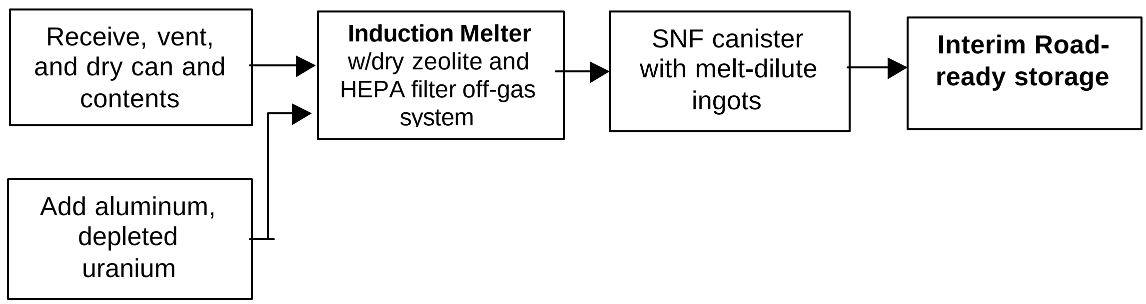

Figure 2. Flow diagram for U233-CEUSP using the Melt-Dilute Treatment Technology

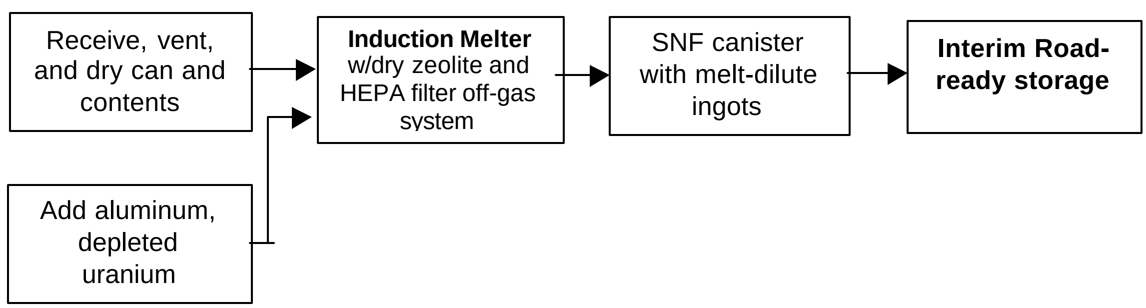

Figure 3. Flow diagram for Pu-contaminated HEU and DU/Off-spec HEU using the Melt-Dilute Treatment Technology

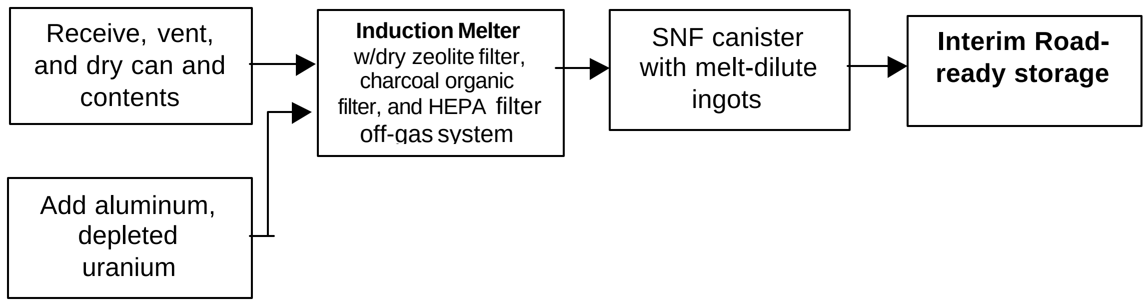

Figure 4. Flow diagram for Metallurgical Mounts using the Melt-Dilute Tretament technology

.

IV Waste Form Qualification

The technical basis for the qualification of the Al-SNF wasteform, obtained through the Melt-Dilute Treatment Technology, for geologic repository disposal has been developed. The technical basis included detailed analysis of criticality, corrosion, and thermal performance with respect to repository acceptance criteria. The basis development involved comprehensive experimentation and analytical calculations to demonstrate compliance.

With respect to the treatment of these legacy materials streams using the melt-dilute technology, it is expected that the resulting wasteforms will be bounded by the experimental data and analytical calculations developed for treatment of the Al-based DOE SNF. Minimal wasteform qualification testing would need to be conducted to wasteform performance.

IV. Implementation Strategy

The SRS has developed the melt-dilute treatment technology through the construction, and start-out testing phase for a pilot-scale irradiated facility. The scale of the pilot facility is ideally sized for the treatment of the aforementioned legacy materials streams. Optimization of the design has lead to two off-gas system options: 1) traditional SRS off-gas deisgn involving a combination of dry zeolite beds and HEPA filters or 2) a closed evacuated self-contained melting system. An effort is underway to optimize the pilot-scale facility design for legacy waste streams in order to facilitate assembly and installation of such units at multiple locations within the DOE complex. Alternatively, a transportable mobile unit is also envisioned for the treatment of legacy waste materials. Such a system will be capable of being readily adapted and modified to meet he requirements in different parts of the country or world, as necessary. A preliminary engineering cost estimate for such a modular system has been developed and the approximate cost for either type system—customer site installed or transportable—is approximately $15,000K.

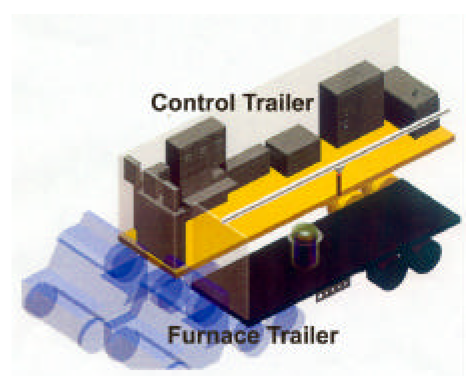

Figure 5. Conceptual Modular, Transportable Melt-Dilute System

V. Summary

An evaluation of the treatment of legacy waste materials using the Melt-Dilute Treatment Technology has been performed. Several legacy materials streams including, Pu-contaminated HEU, U-233, DU/Off-spec HEU, and metallurgical mounts have been assessed. The Melt-Dilite Treatment technolgy has been shown to be a robust, versatile technology capable treating all of the aforementioned legacy materials stream with little adaptation.

A modular "mini-batch" systems approach has been proposed that would either result in installation of a pilot-scale facility at end-user sites or would result in a mobile transportable system that could be temporarily used at end-user sites. This concept is not only amenable to treatment of legacy materials in this country but could be applied in foreign countries as well.

REFERENCES

---

i T. M. Adams, H. B. Peacock, Jr., R. L. Sindelar, N. C. Iyer, W. F. Swift, F. C. Rhode, and H. M. Brook, "Melt-Dilute Treatment Technology for Aluminum-Based Research Reactor Fuel," Proceedings of the ANS-DOE Spent Nuclear Fuel and Fissile Management, pp. 41-45, 2000.