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Enabling MgO-Pyrochlore Actinide Immobilization and Reduction with Retrievable Storage

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INTRODUCTION

The Department of Energy has consolidated the storage of surplus non-pit Plutonium Special Nuclear Material (SNM) at Savannah River Site (SRS) per DOE-STD-3013-2012. In the Surplus Plutonium Disposition Supplemental Environmental Impact Statement (SPD Supplemental EIS), DOE analyzed the potential environmental impacts of reasonable alternatives to disposition plutonium from pits as well as reasonable alternatives for approximately 5 metric tons of non-pit plutonium that cannot be sent to the MOX facility at SRS. The most recent DOE Report[1] looked at all plutonium disposition options that could potentially provide a more cost effective approach to dispose of at least 34 MT of US surplus weapon-grade plutonium to meet international commitments using existing facilities at Los Alamos National Laboratory (LANL) and SRS to the greatest extent possible. All of the non-MOX options may require further development and/or analysis (e.g., technology development, discussions with Russia, modification of federal legislation) during a standby period. A ceramic process was one of the immobilization processes discussed produced by mixing plutonium with oxide precursor chemicals (e.g., including pyrochlore and neutron absorbers such as gadolinium), forming a mixed powder which is sintered in a furnace. The ceramic product is placed in stainless steel cans, sealed, leak tested, assayed, and transferred out of the immobilization facility to a suitable Federal Storage Facility until a geologic repository is available.

CURRENT SRS SNM NON-MOXABLE DISPOSAL METHOD

The consolidation of plutonium from across the DOE Complex including Rocky Flats to the SRS K-Area nuclear material storage facility has increased the amount of surplus non-pit SNM to 12.8 metric tons in 3013 containers. Current methods for SNM immobilization and long term storage of Non-MOXable SNM from SRS and Nuclear Facilities across the DOE Complex are significantly limited in the amount of SNM that can be disposed of at the WIPP.

SRS Disposal Method for surplus SNM at WIPP

One disposal option considered by DOE for the non-pit plutonium at SRS was to establish and operate a capability to prepare and package non-pit plutonium for disposal as transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP) provided that the material meets the WIPP waste acceptance criteria. A 55 gallon drum is limited to a maximum of 0.5 wt% SNM and less than 200 fissile gram equivalents (FGE) per the Nuclear Criticality Safety Evaluation (NCSE) for Contact-Handled Transuranic Waste at the WIPP, WIPP-016, Rev. 0. The less than 200 grams of FGE is downblended in a mixture of materials that makes the SNM very difficult to recover in a nitric acid solution. Rocky Flats used a mixture of materials including iron and a dry concrete mixture to reduce the plutonium content to less than 10 wt% in the drum for transport of SNM from Rocky Flats to SRS for storage. This method gets the SNM mass down below the WIPP requirements, provides a safeguard determination, and places the material in a pipe overpack 9975 certified Type B package for shipment to WIPP. SRS uses the 9975[2] packaging for movement and storage of SNM, primarily plutonium and uranium metals and oxides. In the Feasibility Study for the Disposition of about 2.5 MT of the 5 MT total surplus non-pit Pu from Rocky Flats, the 3013 containers in K-Area were to be processed for final disposal at the WIPP. The 2.5 MT of Pu that requires processing and packaging for WIPP also contains 0.7 MT of fissile uranium (U-235) which is equivalent to 0.45 MT FGE Pu-239. About 175 FGE Pu-239 is mixed with iron and cement materials in each 9975 package and is ready to go after WIPP is reopened by DOE, the shipment has been evaluated by WIPP as acceptable for shipment, and it is determined to be suitable for permanent immobilization. The 2.5 MT of SNM will require about 16,000 to 17,000 9975 packages to disposition this amount of surplus material to WIPP.

South Carolina law requires that DOE be fined $1 million/day up to $100 million/yr for every day past 12/31/15 for which DOE has not removed one MT of Pu (1000 kg) from South Carolina. The K Area processing area for these containers and the number of 9975 containers is limited. At a rate of one 9975 container per day, less than 250 of the 9975 would be processed per WIPP requirements. It is extremely unlikely that the South Carolina law will be complied with using the current method limited to less than 200 FGE per container.

The current method does not reduce the amount of SNM. It only disperses the SNM in a larger volume

which consumes more valuable space in an already half filled WIPP. This is also not an efficient method to utilize 9975 container space for the storage of SNM and takes up valuable space in limited Federal Storage facilities. This method does not reduce radiotoxicity or the amount of the SNM bound for permanent immobilization.

The logical solution is to increase the loading of SNM FGE in each container using an alternate approved dry blend material method to permanently immobilize the SNM suitable for WIPP disposal. DOE has successfully increased SNM loading in drums by ORNL in 2003 for NpO_2 storage, handling and transport[3]. The increased loading provided for the shipment of up to 6 kg of $^{237}NpO_2$ per 9975 container moved from SRS to Y-12 National Security Complex. Recently, SRNS initiated a Nuclear Criticality Safety Evaluation (NCSE) for the safe on-site transport of up to 5 kg of PuO_2[4] in 9975 packaging to include the AFS-2 Program to feed the MOX plant.. A suitable permanent waste form is defined by IAEA as waste in its physical and chemical form after treatment and/or conditioning (resulting in a solid product) prior to packaging. The immobilization of High Level waste including SNM is achieved by its atomic-scale incorporation into the structure of a suitable matrix (typically glass, a GCM, or a crystalline ceramic (also sometimes referred to as a mineral analog waste form) so that radionuclides are incorporated into a durable structure. The waste form is a component of the waste package which can be grouped into ten classes per Jantzen, C. M., et.al.[5]:

- Single-phase (homogenous) glasses
- multi-phase glass composite materials (GCMs; heterogeneous glasses)
- single-phase crystalline ceramic/mineral analogs
- multi-phase crystalline ceramic/mineral assemblages
- bitumen
- metals
- cements
- geopolymers and organic polymers
- hydroceramics
- ceramicretes

Waste forms can be produced using thermal technologies such as Cold Pressing and Sintering of crystalline ceramics to yield higher waste loadings and minimum disposal volume. Ceramic waste forms can be single phase, e.g. PuO_2, or single-phase solid solutions like $(U,Pu,Th)O_2$. Typically multiphase ceramics are formulated so that each radionuclide can substitute on a given host lattice in the various phases. Of great importance when relying on the long range order (size and coordination of the crystallographic site which will act as host to a given radionuclide or its decay product upon transmutation) is that the crystal-chemical substitutions must be electrically balanced. When a monovalent cation transmutes to a divalent cation, the substitutions must be coupled to retain the electrical balance of the host phase without destroying the integrity of the phase: the lattice site must be of suitable size and bond coordination to accept the transmutated nuclide. One complex oxide with a crystalline ceramic phase of particular interest capable of hosting radionuclides are Pyrochlores. Pyrochlores are a derivative of the fluorite structure type, $A_2B_2O_7$, where the A-site contains large cations (U, Pu, Th, and lanthanides) and the B-site contains smaller, higher valence cations (Zr, Nd, Gd).

An alternate approved method for the onsite and offsite transport of Non-MOXable SNM greater than 200 FGE quantity of SNM per container that can be permanently immobilized is feasible using MgO-Pyrochlores.

SRNL Alternate method Concept for loading 9975 containers for Storage and/or immobilization

Savannah River National Laboratory (SRNL) proposes to utilize a Low-Temperature Vitrified waste form for accelerating SNM storage with accountability per the DOE-STD-1194-2011 and add a limit of about 4 kg FGE per container of plutonium and other fissionable isotopes (SNM) with sufficient poisons such as gadolinium oxide that can be applied to storage at SRS, WIPP or other suitable future Federal Storage locations like Waste Control Specialist, WCS, in 9975 packages. The alternate waste form for immobilization of SNM will use microencapsulation to capture SNM bound in a solid sintered matrix of MgO-Pyrochlore. This waste form could reduce the cycle time for removal from SRS of one MT of non-MOXable Pu to 55 weeks, as compared to between 2.5-5.6 years using the present method limited to 200 FGE per container.

SRNL proposes to develop a process to sinter SNM in a MgO-pyrochlore ($A_2B_2O_7$) inert matrix as a future SNM waste form using a method developed and tested as an inert matrix form (IM) described by Yates, Nino, et. al. during experiments in the Advanced Test Reactor (ATR)[6]. Additional research on the low-temperature sintering method must be completed to ensure the dispersal and microencapsulation of the SNM material can be verified. Sintering or powder processing can be carried out to produce a suitable waste form at temperatures well below the normal melting point of glass. Sintering is an alternative to manufacturing glass waste forms by melting at high temperatures >1000 C such as that used by SRS at DWPF. Sintering temperatures for micron-sized glass or mineral particles can be accomplished in the temperature range of 500 to 700 C. The general progression in sintering is from bulk powder, less dense collection of particles that are physically touching, towards a final densified, interconnected network of fused particles into a

more monolithic form. Such sintering that includes trace particles for immobilization would result in microencapsulation of the particles within the mineral or glass form. Some porosity remains in the fully sintered product and some research has examined the combined mechanical pressing with sintering to achieve near theoretical density, i.e., removal of nearly all porosity. While physical separation methods could be used to separate and recover waste components from the initial powder mixes used for sintering, more aggressive dissolution methods involving strong acids and bases at elevated temperatures would be required to recover SNM from the fully sintered product. One obvious advantage using sintered glass or mineral forms for encapsulation of PuO_2 relative to hydrated inorganics like cement or geopolymers is the lack of water present, i.e., no radiolytic hydrogen is expected. Areas that could be investigated by SRNL for the use of sintered glass or mineral form for microencapsulation of PuO_2 include the following:

- Evaluate mixing of dry powders developed by Nino to incorporate PuO_2 (using HfO_2 as a surrogate) from 3013 containers into micron-sized powders.
- Perform analyses on low-temperature sintered waste forms containing HfO_2 surrogate to ensure even and homogeneous distribution of Hf throughout the matrix.
- Scaleup of the sintered waste form to support SC production needs.

Magnesium oxide (MgO) utilized in a pyrochlore has many properties desired for an IMF such as high thermal conductivity, high melting point, low neutron absorption cross section, and good radiation tolerance. It has been demonstrated in ATR cycle 144A experiments with MgO-$Nd_2Zr_2O_7$ in target positions at temperatures of 300 C and 700 C and a fast neutron fluence of 10^{25} n/m^2 that a multiphase composite approach could yield sufficient hydration resistance for use of MgO in LWRs; e.g. MgO-$Nd_2Zr_2O_7$ in a mass proportion of 7:3. Up to 8 wt% SNM and trace amounts of minor actinides such as AmO_2 can be added to inert matrix as described by Ewing, et. al.[7] to form an inert IMF.

Flexibility and Retrievability of SRNL Concept SNM 9975 Package Media

There are over 500 synthetic compositions, including actinides, with the pyrochlore structure, and natural pyrochlores are also abundant in highly evolved rock types, such as pegmatites and carbonatites. A number of compositions with thorium and uranium, as well as transuranium elements (e.g., Cm and Pu), have been synthesized and natural compositions may contain up to 30 wt% UO_2 and 9 wt% ThO_2. Thus, it is not surprising that pyrochlore structure-types were present as an actinide-bearing phase in the earliest nuclear waste for formulations. The successful disposition of SNM including plutonium and substantial quantities of minor actinides such as Np, Am, and Cm has an important impact on the geologic disposal of high-level radioactive waste. Significant interest has been expressed toward the use of the isometric pyrochlore structure for the immobilization of actinides. Most of the interest focused on titanate-pyrochlore because of its chemical durability; however, these compositions experience a radiation-induced transition from crystalline-to-aperiodic state due to radiation damage from the alpha-decay of actinides. Depending on the actinide concentration, the titanate pyrochlore will become amorphous in less than 1000 years of storage. Systematic ion beam irradiations of a variety of pyrochlore compositions has revealed that many zirconate pyrochlores do not become amorphous, but remain crystalline even to very high doses, greater than 100 displacements per atom. Systematic experimental studies of actinide-doped and ion beam-irradiated pyrochlore, analysis of natural U- and Th-bearing pyrochlore, and simulations of the energetics of the disordering process now provide a detailed understanding of the structural and chemical controls on the response of pyrochlore to radiation. These results provide a solid basis for predicting the behavior and durability of pyrochlore used to immobilize SNM plutonium and minor actinides. The SNM MgO-Pyrochlore IMF pellets produced at SRS can be put in a 9975 in the configuration subcritical and placed into Federal Storage facilities with sufficient safeguards. The ability to retrieve stored actinide material is comparable to the French plan to retrieve spent fuel from their repository if mistakes occur such as the release of radiation from WIPP. Retrieval capability of 9975 containers from Federal Storage for repository disposal or material reconfiguration into targets for LWR transmutation to reduce actinide inventory by transmutation and fission to reduce radiotoxicity is a practical alternative to reduce heat load ultimately in geological repositories.

Transmutation of SNM in SRNL Concept SNM Drum Media to Reduce SNM Mass and Radiotoxicity

An approach for reducing the actinide burden of nuclear waste including SNM while utilizing their energetic value is by using a mixed oxide (MOX) or an inert matrix fuel (IMF) for the transmutation of waste in light water reactors (LWRs). An IMF consists of a non-fertile inert matrix (IM) that supports a fissile phase (Pu and/or minor actinides) for efficient transmutation. These fertile-free fuels have a distinctive advantage in that they allow a much greater degree of reduction of the transuranic (TRU) elements than can be achieved by using MOX fuels. Heterogeneous recycling is considered a superior option for minor actinides like americium and

curium. It involves loading the minor actinide containing pyrochlore pellets into separate, distinct fuel assemblies, often referred to as "target assemblies" or "target assemblies". These can be positioned in the core in such a way as to optimize burnup of the minor actinide content, and they may also be retained for a longer dwell time than the conventional fuel to maximize burnup. This increased flexibility in loading is more suitable for americium and curium. In addition, heterogeneous recycling allows the manufacture of the target assemblies to be carried out independently of the manufacture of the bulk fuel, and thus the stringent shielding and containment measures only need to be applied to a relatively small throughput[8]. With heterogeneous recycling, the irradiated target assemblies would be encapsulated for geological disposal, with no further processing required. Multiple recycling has the potential to achieve very low residual levels of radiotoxicity and decay heat. The 9975 packaged SNM IMF reconfigured into Zircaloy clad targets can be evaluated for irradiation in target positions at the ATR or other government thermal reactors thereby eventually reducing the SNM concentrations and weapons grade isotopics through fission and transmutation. The inert matrix material pellets produced should exhibit equal or better properties than conventional fuel. The sintered pellets produced initially would be evaluated after irradiation to determine their suitability for long term storage and eventual direct geologic disposal as is.

Thermal Reactor fuel configuration with SRNL SNM media in targets for Transmutation

The chemical, neutronic, thermophysical and radiation tolerant properties of MgO-$Nd_2Zr_2O_7$ are expected to make it an excellent candidate matrix material with ^{241}Am added for the transmutation of SNM in reactor targets. Although some material has been included in test reactor assemblies, they have not been inserted as targets in commercial reactors to date. Because the global inventory of Pu grows at a rate of 70-90 MT per year, there is presently a keen interest in developing IMFs. The addition of minor actinides including Am, which is a byproduct of MOX fuel, to the IMF fuel pellet will reduce the falling gradient of the reactivity curve. Yates, et. al. have discussed several compositions of MgO-$Nd_2Zr_2O_7$ from the point of view of the k-effective value. They showed that because of larger thermal absorption cross-section of Nd, as compared to that of Mg, the best ratio of $Nd_2Zr_2O_7$ to MgO was 3:7 in order to provide enough end-of-life (EOL) reactivity for the case of 8 wt% weapons-grade PuO_2 incorporated into the pyrochlore. Importantly, it is shown that the MgO-pyrochlore can maintain the eigenvalue at EOL despite the existence of lanthanides. Since the less negative Doppler coefficient of IMF suggests the need for a UO_2/IMF mixed core, it is necessary to optimize the pin layout in IMF assemblies by taking into account the exchange of thermal neutron flux from neighboring UO_2 assemblies. Am is an ideal material in this system because of its dependent absorption reactivity throughout the whole burn-up period and its relatively small reactivity loss at EOL.

Currently, commercial power reactors operate on once-through or open cycle, with the spent nuclear fuel eventually destined for long-term storage in a geologic repository. The SNM material that is non-MOXable presents a proliferation risk, limits the repository capacity and is a major contributor to the long-term toxicity and dose from the repository, methods and systems are needed to reduce the amount of TRU that will eventually require long-term storage. Jon Carmack, et. al. have studied the option of burning the TRU in commercial light water reactors (LWRs)[9] in conjuction with the Advanced Fuel Cycle Initiative Light water Reactor transmutation fuel development program. Fuel forms under consideration included MOX and IMF. Fertile-free IMF offers several advantages relative to MOX, principally it provides a means for reducing the TRU in the fuel cycle by burning the fissile isotopes and transmuting the minor actinides while producing no new TRU elements from fertile isotopes. A four-bundle, neutronic, thermal-hydraulic, and transient analyses of proposed IMF in comparison with the results of similar analyses for reference UOX fuel bundles. The Advanced Fuel Cycle Initiative Light Water Reactor (AFCI LWR) transmutation fuel development program irradiation test, designated LWR-2, in the Advanced Test Reactor is to test both MOX and IMF. The AFCI LWR transmutation program is to develop a fuel composition that fulfills the following general criteria:

- The fuel must produce the same power as a standard uranium oxide (UOX) fuel in a light water reactor.
- The fuel composition must target destruction of actinide species (Pu, Am, and Np) and emphasize proliferation resistant forms.
- The fuel must perform these functions without greatly increasing the fissile material loading (which affects fuel cycle cost) in the overall nuclear fuel cycle, and should be within the existing safety envelope of commercial LWRs.
- The fuel consumption must allow for extraction and processing to recover the heavy metal for possible further destruction (via recycling into LWRs) or treatment for ultimate burial in a geological repository.

To provide for flexibility in the incorporation of plutonium/actinide bearing fuels in pressurized and boiling water reactors, a variety of MOX and IMF compositions are being proposed for inclusion in the planned AFCI irradiation experiment, LWR-2. Chang

and Ryskamp proposed IMF pins interspersed in standard LWR UO_2 fuel bundles to achieve burnup and destruction of Pu SNM material without negatively affecting operational characteristics of LWR operation. Due to the fission efficiency of reactor-grade plutonium the use of burnable poisons will likely be required to control excess reactivity throughout the fuel life, control the power distribution within an acceptable range, and provide additional Doppler feedback in IMF compositions. The reference core for the analysis was a typical 4-loop Westinghouse PWR with a thermal power of 3400 MW and 193 17 x 17 fuel assemblies. The reference fuel is low entriched (<5wt%) ^{235}U, uranium oxide capable of achieving an 18-month cycle, and a typical fuel management strategy with 3-batches, and once through then out with geological repository storage for the discharged spent nuclear fuel. Results suggested that mixed cores of IMF and UOX assemblies are the most likely implementation approach in order to keep an existing LWR such as Kewaunee within its licensed safety envelope. The results of the neutronic performance analysis show that there is no significant difference in the system criticality due to the matrix materials considered assuming an 18 month operating cycle. The reactivity coefficient and control rod worth show that soluble boron worth of IMF is lower (very similar to MOX case) than for UOX standard fuel. Mixed UOX/IMF cores may be required to ensure that the reactor remains within its operational and safety envelope. TRU recycling in thermal reactors could have a role to play as a technology demonstrator for more advanced minor actinide recycling schemes that might follow. The major benefit of beginning minor actinide recycling with SNM in existing thermal reactors is that it would remove the long-lived radiotoxic nuclides from the fission product waste.

Suitability of SRNL SNM Targets for Direct Repository Permanent Immobilization after Irradiation

If testing is positive, the novel concept of producing an IMF waste form that can be stored as is, retrieved if wanted for future energy use, and geologically discarded without further processing will become a viable disposition alternative for SNM. In the event that the used IMF is utilized for direct disposal in a geologic repository, high corrosion resistance under the conditions of the geologic repository is also desirable. Materials such as pyrochlores ($A_2B_2O_7$) have been proposed as a candidate IMF as it meets some or all of the geologic repository requirements. The SNM minor actinide irradiated target fuels will be treated differently compared to the driver fuel, possibly with a higher decay heat output and higher neutron activities. The target fuel might require a different regime for fuel pool cooling and different arrangements for transport. Whether the target fuel is intended for geological disposal or reprocessing and recycling, there will be completely different requirements to those of the thermal reactor driver fuel. SNM with minor actinide burning in LWRs leads to significant reductions in the decay heat load in the geological disposal facility. Actinide burning is beneficial because the decay heat load generally limits the capacity of a geological disposal site.

Conclusion

The SRS disposal method for non-MOXable SNM will not meet the SC law and will exceed the storage capacity of Federal Storage Facilities available. SRNL proposes to use a novel pyrochlore waste form suitable for geological repository disposal, a form that can be irradiated to produce energy, reduce SNM inventory and reduce long term heat load in the geological repository disposal unit.

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