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Chemical Pre-Treatment of Used Fuel for Long-Term Storage^a

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Abstract

Repository programs throughout the world have been slowed by the need for increased local public involvement in the siting and licensing process. The result has been an increase in the dry storage of used fuel at reactor sites and the potential that such storage may be extended for many decades, even centuries. While there are sound technical reasons to believe that dry storage can be conducted safely, there are increasing concerns that the ultimate transfer to either a future repository or a centralized separations plant may result in fractured cladding and serious handling issues, including criticality concerns. These concerns would be increased for higher burn-up fuels. Currently, various chemical pre-treatment processes under R&D for application to commercial used oxide fuel have been investigated at the laboratory scale as methods to simplify and increase the safety of the remaining stages of conventional solvent extraction processing. This includes advanced decladding methods and various oxidation/reduction processes designed to release volatile and semi-volatile fission products, produce finely divided uranium oxide powder, and ameliorate the subsequent nitric acid dissolution step. The paper examines the potential for combining several chemical and physical pre-treatment steps to minimize long-term concerns about safe transport of used fuel, possibly providing another option for future nuclear waste management. Laboratory data from both cold and hot testing will provide the basis for the evaluation. An example of a potential pre-treatment process includes shearing, advanced voloxidation and off-gas treatment, the possible mixing of the resulting uranium oxide with a secondary oxide, and densification and recanning in nitric acid-soluble storage containers for extended time periods. Chemical decladding may be feasible to replace shearing. Zirconium recycle may also be feasible, significantly reducing high level waste quantities. Both analytic and experimental data will be applied to the examination of this potential fuel cycle option.

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1. Introduction

In the United States, use of dry cask storage at nuclear power reactor sites is increasing. Currently, approximately 23% of all commercial used fuel assemblies are in dry storage, with that percentage increasing each year. The current U. S. policy for the management of used nuclear fuels (UNF), as described in the Nuclear Waste Policy Act of 1982 (NWPA), as amended, is based on the open fuel cycle, with untreated used fuel storage followed by disposal. Between 1982 and 1987, there was a significant effort to site and license a Monitored Retrievable Storage facility at the former Clinch River Breeder reactor site in Tennessee. After that effort was ended in 1987 by an amendment of the 1982 act, there was a follow-on effort to site a centralized storage facility at a volunteered location. That effort also failed. As a consequence, essentially all U. S. UNF storage is at the originating reactors, primarily using storage pools with older fuel gradually relocated to dry storage facilities.

The withdrawal of the license application for the Yucca Mountain repository means that on-site storage will be the only available nuclear fuel management option in the United States for many years. The Blue Ribbon Commission on America's Nuclear Future has recommended one or more centralized UNF storage facilities as soon as possible, particularly for the relocation of UNF from shutdown power reactors. Depending on whether and how soon the U. S. Congress modifies the NWPA, such an option may become available in the future. In any case, the possibility exists that thousands of metric tons of UNF may be kept in dry storage facilities in the United States for many decades, even centuries.

Commercial UNF from existing power reactors in the United States has zirconium alloy cladding tubes covering stacked cylindrical pellets of ceramic oxide fuel in rod-type arrangements. The fuel cladding is susceptible to failure during long-term storage, and the most susceptible will be, in general, the oldest fuel. Previous systems studies [1] have shown that if a decision is made to relocate UNF from reactor sites to a centralized storage facility, and to perform pre-treatment, as described in this paper, to rectify the potential for cladding failure during storage, a multi-decade time period will be required to design, construct, and license the transportation, surface storage, and pretreatment facilities at the centralized storage site. This facility or facilities must have the capacity to process the 2500–3000 MT/year of UNF being generated. The age of the oldest fuel is now ~ 40 years; by the time transportation and pre-treatment can be started, the fuel will be 50–60 years old. Operating in the mode of oldest-fuel-first at a rate equal to UNF generation, the age of fuel treated and stored will remain ~ 50 years during the life of the facility. During the aging process, significant radioactive decay of the short- and intermediate-lived radionuclide components will occur, with some beneficial effects. These benefits will include reduced radiation levels and less volatile emissions from stored UNF. However, a detriment will be that enhanced physical safeguards will be required because the penetrating radiation barrier previously provided by 30-year half-life ^{137}Cs , will have decreased exponentially with time.

2. Potential UNF cladding degradation during long-term storage

In the transfer of used fuel from under water storage at reactor sites to dry casks, the storage canister and its necessary shielding are placed in the storage canal, and the fuel is transferred into the canister. The canister is then sealed, removed from the canal, the water around the used fuel is removed by vacuum drying, and the canister is prepared for long-term storage by repeated back-filling with an inert gas, helium. The canister can then be placed either in a vertical concrete or metal-shielded cask, or horizontally in concrete cylindrical structures.

Dry cask storage of commercial UNF relies on passive cooling. That is, there is no supplemental forced cooling system to remove the decay heat. Instead, decay heat is removed by natural circulation of outside air

over the sealed canister containing the used fuel that is protected from outside moisture by the contained helium under pressure. However, the initial drying process may be incomplete or the helium gas may gradually gain moisture through inleakage over an extended time period, so some moisture may eventually be in contact with the fuel cladding. Used fuel cladding already contains hydrides from external exposure to high-temperature water during nuclear power generation and from internal exposure to the fission product tritium. Those hydrides and more produced from moisture during extended storage can result in hydrogen embrittlement, reducing Zircaloy ductility and increasing the probability of cladding failure.

The formation of a stable oxide layer on the external cladding surface necessarily means that some of the produced hydrogen will diffuse into the metal. A certain amount is soluble, but beyond that amount, zirconium hydride will precipitate. Under high stress and temperature, as may be experienced during fuel drying before dry storage, the crystalline orientation of precipitated zirconium may be modified and lead to metal embrittlement and potential cladding failure. This is expected to increase with fuel burn-up. Although commercial fuel rods that have been dry-stored for decades are available for study, fuel rods exceeding 50,000 megawatt days per tonne with long storage histories are not generally available for detailed examination.

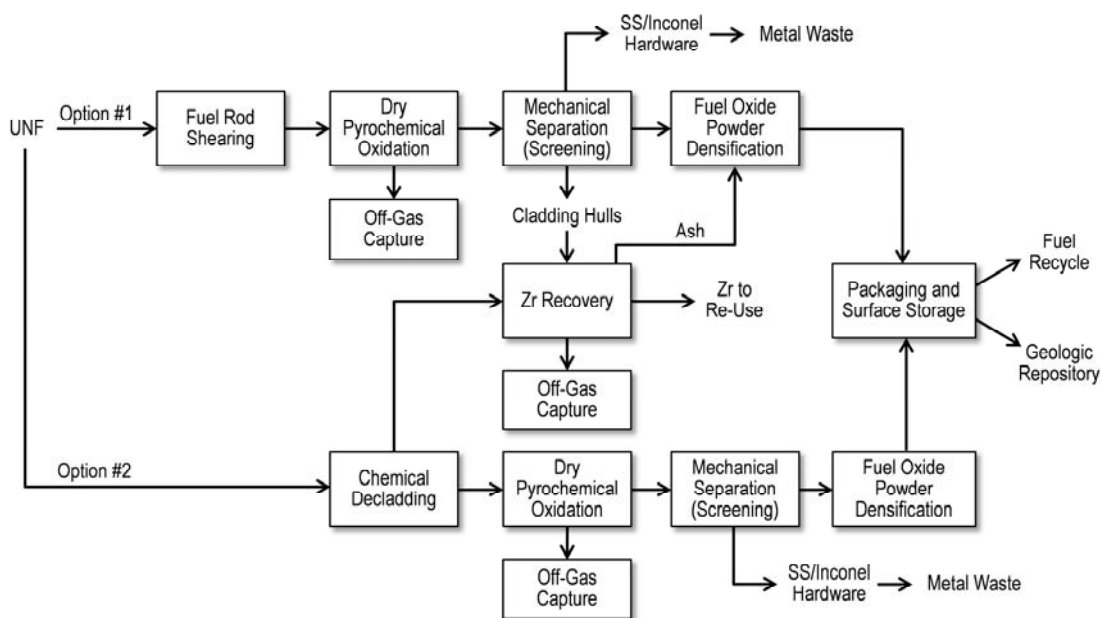


Fig. 1. Pre-treatment options.

The hydride content of the cladding of high-burn-up UNF may exceed 1000 ppm at 70,000 megawatt days per tonne, compared with approximately 200 ppm at 35,000 megawatt days per tonne. Due to swelling of the fuel pellets at high burn-up, internal stress on the cladding may also increase with burn-up. When in the future, UNF is moved from individual reactor storage sites to a centralized storage location and/or from central storage to a repository or recycle facility, cladding failures could present serious problems. Such problems include increased criticality hazards, potential localized overheating, and, if canisters must be opened before final disposal, atmosphere-borne contamination issues. Repackaging activities may also be difficult. Further, if future fuel reprocessing is carried using technologies similar to those currently in use, brittle cladding may make a “chop-and-leach” head-end treatment extremely difficult.

3. Alternate pretreatment options

Currently, several UNF pre-treatment technologies are being studied at the U.S. Department of Energy national laboratories with potential to simplify and increase the safety of subsequent storage or chemical recycle processes. They are alternate decladding methods, oxidation of exposed fuel following either conventional shearing or chemical decladding, and the collection and stabilization of released volatile radionuclides. Chemical decladding or later chemical treatment of sheared cladding hulls could enable zirconium recycle. Although not yet under experimental study, densification of uranium oxide would be required before storage. Alternate pre-treatment steps are shown in Fig. 1.

A brief description of each of the major process steps follows.

One option is to use fuel shearing (whole-bundle or single-pin shearing) followed by a dry chemical oxidation to release all or part of the volatile fission product elements, with subsequent densification and packaging of the remaining UNF for long-term storage. In addition to the release of volatile fission products, dry oxidation has the added benefit of converting ceramic UO_2 to finely divided U_3O_8 or UO_3 powder, making the physical separation of the oxide from the cladding relatively straightforward. The voloxidation process that has received the most experimental study has been carried out at 480 to 600°C in the presence of oxygen or air. Under these conditions, the reaction of UO_2 to form U_3O_8 is rapid. The oxidation of the pellets results in the expansion and restructuring of the grain-level crystallites, accompanied by a crumbling of the monolithic fuel pellets to a fine powder with 99% of the resulting particles reduced to $< 20 \mu\text{m}$ and the bulk density to $\sim 2.2 \text{ g/mL}$. The conversion of the UO_2 to finely divided U_3O_8 or UO_3 powder releases the used fuel from the cladding and helps promote the volatilization of fission gases.

Tritium present in elemental and oxide forms diffuses to the surface of the fuel pellets or particles, encountering oxygen which converts the hydrogen gas to steam before it is carried away with the process gas stream [2]. Experimental studies have shown that greater than 99% of the tritium in the fuel pellets is released by voloxidation. However, for Zirconium alloy-clad fuels, the cladding itself may contain 40–50% of the tritium, which will not be released during voloxidation [3]. Smaller percentages of other gaseous fission products are released using what might be termed conventional voloxidation (using air or oxygen). For example, approximately half of the ^{14}C , perhaps 50% of the xenon and krypton, and about 1% of the iodine in the fuel are released by conventional voloxidation. More vigorous oxidants such as ozone and nitrogen dioxide, offer promise of greater removal of gaseous fission products. Preliminary cold testing of nitrogen dioxide has resulted in nearly quantitative removal of iodine. The extent of the further release of krypton and ^{14}C during voloxidation using the more vigorous oxidants has not been measured but is also expected to be well over 80%. Advanced voloxidation with these alternate reactants (e.g., ozone, steam, nitrogen dioxide, etc.) also has the potential of releasing a number of the semi-volatile components that must be addressed in the off-gas treatment systems.

Current research is investigating the technical and economic feasibility of zirconium recycle [4]. Zirconium alloy cladding makes up approximately 25% of the weight of the high-level waste represented by non-recycled used fuel. Several volatility processes are under consideration as potential zirconium recovery methods. Absent isotope enrichment, recycle zirconium would contain ^{93}Zr , a 1.5 million-year half-life, soft beta-emitting radioisotope. Its use would require segregation of “nuclear zirconium” from its non-radioactive counterpart and a license for its commercial applications. However, the current market for zirconium use in the nuclear industry is sufficiently large that zirconium recycle is worthy of consideration. As noted previously, the cladding may contain up to 50% of the total fission product tritium. During the processing of the cladding for recycle, the

complete release of this tritium would be expected. The same is true of the case for the optional chemical decladding of the fuel.

A potentially simplified option is to use chemical decladding as the initial step, replacing the shearing, as illustrated in Figure 1. Tests have shown that the ceramic oxide fuel pellets are not reactive with the chlorine or hydrogen chloride reagent used to convert the zirconium metal in the cladding to volatile zirconium tetrachloride. In this case, dry oxidation treatment would likely still be required to remove volatile fission products from the fuel.

The remote densification of the U_3O_8 or UO_3 produced by the various oxidants used in voloxidation will present serious engineering issues. The traditional voloxidation process is followed by acid dissolution, which permits repeated washing of the cladding hulls for the essentially complete separation of oxide and metal. Performing the same separation dry will present significant engineering difficulties, particularly with atmosphere-borne particulates. Dry pressing of powder to form UO_2 pellets is an awkward process when performed in a glove box. In addition to that the complications of remote operations and maintenance and the potential to adjust the valence of the uranium for long-term storage the proof of its technical feasibility will be quite challenging. For heat-transfer purposes, it may also be necessary to dilute the uranium oxide powder with an inert diluent such as magnesia. Clearly, the development of an effective remote consolidation process will be one of the most challenging steps in the entire pre-treatment process.

The final stage in the process will involve canning the densified uranium oxide for long-term storage. Rugged metallic containers can be used with predictable performance under a variety of external conditions, including alternate repository environments. Their design would include plenums within which further gaseous emissions can be readily accommodated. Metal or alloy selection that would facilitate future recycle will also be a consideration in the development of the overall process.

4. Radioactive off-gas management

Recent studies on the capture requirements for the volatile radionuclides from the processing of UNF based on current US regulations indicate that > 99.9% of the iodine must be captured; tritium capture would be required for fuels with less than ~60 years of cooling and krypton capture would be required for fuels younger than 30 years. Depending on the dose contribution to the maximum exposed individual allocated to the volatile radionuclides, ^{14}C capture could also be required for higher burn-up fuels [5].

Depending on the process(es) selected for chemical pretreatment and the extent of treatment, the off-gas system could be somewhat simpler than that needed for a commercial reprocessing facility. First, this is envisioned as using only non-aqueous process(es), which will eliminate the concerns of the need to treat large volumes of water or gas streams containing large quantities of water. The limited number of process steps and air in-leakage points will result in an off-gas stream(s) with higher concentrations of the volatile radionuclides than in conventional reprocessing. These two factors will result in potentially smaller systems. The use of an inert environment in the process cell may also simplify the recovery of krypton from shorter-cooled fuels by eliminating the need to remove oxygen from the gas stream prior to the cryogenic recovery step.

Conceptually, the primary off-gas treatment system would first capture the semi-volatile species that may be released during the voloxidation process particulate removal and recycle. This would be followed by HEPA filtration. Tritium would be captured as tritiated water using molecular sieves. Iodine would be recovered on silver mordenite or an alternate sorbent currently under development. If required, ^{14}C could be recovered by

caustic scrubbing. Finally, depending on the age of the fuel being processed, krypton recovery would be accomplished by either a cryogenic process or on a solid sorbent material.

The off-gas treatment for the zirconium recovery operations would focus on capture and recycle of the reactive gases, tritium recovery, and particulate removal.

The off-gas system design for the advanced dry head-end processes should also include operations to allow for the recycle of the reactant gases to avoid the generation of large waste streams. These recycle operations, coupled with the removal of the volatile radionuclides from the reactant gas streams, remain to be demonstrated. For example, tritium must be removed from the large quantities of iodine or chlorine gas that may be recovered and reused in the zirconium recycle step. Similarly, the advanced voloxidation process introduces oxidants such as NO₂ at significant levels in the off-gas stream which should be separated and recycled, but the tritium, iodine, and potentially krypton must be captured from this more complex gaseous mixture.

5. Summary

Long-term storage of UNF in the United States is the probable result of current U.S. nuclear waste management policies. Significant changes in the chemical and physical characteristics of UNF can occur during decades of storage time, including the increasing susceptibility to failure of the zirconium alloy cladding. Options exist for transfer to a centralized storage site or sites where pre-treatment operations can be performed to alleviate problems that could occur in long-term storage.

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