Waste Management Research by the U.S. Department of Energy Office of Nuclear Energy - 11564

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ABSTRACT

The U.S. Department of Energy, Office of Nuclear Energy is evaluating options for disposition of commercial used nuclear fuel (UNF). Research is being performed to develop transformational technologies that may be employed as part of a sustainable nuclear fuel cycle. The program is aimed at developing a broad set of options that will enable future decision-makers to make informed decisions about how best to manage UNF.

R&D activities include a focus on recycling of used fuel components, waste form development for byproducts of UNF separations and advanced nuclear fuel fabrication, long-term UNF storage, and development of improved understanding of waste form performance in a range of potential disposal environments. The research approach includes closely-coupled theory, experimentation, and modeling. This paper summarizes the waste management research goals and approaches of the Fuel Cycle Technology Program. Recent technical highlights from these programs are also discussed.

BACKGROUND

For several decades, the United States has been pursuing site selection, characterization, and licensing of a geologic repository for permanent disposal of UNF and high-level nuclear waste (HLW). These efforts culminated in submittal of a DOE license application to the Nuclear Regulatory Commission (NRC) in 2008. In parallel with the national repository program efforts, the DOE has also conducted an advanced fuel cycle research and development program (currently Fuel Cycle Technology [FCT], preceded by the Global Nuclear Energy Partnership [GNEP] and Advanced Fuel Cycle Initiative [AFCI]). The fuel cycle program is intended to inform future fuel cycle options in an expanding domestic and global nuclear energy enterprise.

The current Administration has made a decision not to proceed with the Yucca Mountain repository and pursue other approaches to UNF and nuclear waste management. One key Administration action was to form the Blue Ribbon Commission (BRC) on America's Nuclear Energy Future. The BRC was appointed by the Administration and charged to "…conduct a comprehensive review of policies for managing the back end of the nuclear fuel cycle. The Commission will provide advice and make recommendations on issues including alternatives for the storage, processing, and disposal of civilian and defense spent nuclear fuel and nuclear waste…"[1] The BRC will deliver their recommendations 24 months after appointment (January 2012).

In anticipation of the BRC's recommendations and the termination of the Yucca Mountain Project, DOE has incorporated the repository science efforts of the Office of Civilian Radioactive Waste Management (OCRWM) into the Office of Nuclear Energy (NE). This resulted in a broader scope for the FCT program, which now includes research activities related to storage, transportation, and disposal of UNF and HLW. This new focus, coupled with the traditional foci in advanced fuels, separations and processing, waste forms, and safeguards, allows DOE-NE to develop a comprehensive program to inform

fuel cycle options for current and future UNF and nuclear waste inventories as part of an expanding nuclear energy enterprise.

DOE-NE has prepared a Roadmap, recently delivered to Congress, that describes the options and the associated R&D required to inform future fuel cycle policy decisions.[2] The fuel cycle options can be grouped into three general categories: Open, Closed, and Modified Open. In open fuel cycles, UNF is disposed of without treatment. In closed fuel cycles, the UNF is processed to recycle those components valuable for energy generation and important to waste disposal. Modified open fuel cycles (MOC) span the range between open and closed. In these fuel cycles, some UNF is ultimately disposed of, but fissile material resources are more effectively used. Examples of MOC's include continuous limited separations, discontinuous thorough separations, advanced breed/burn concepts, and use of ultra-high burnup fuels. MOC concepts may be used individually or in combinations.

RECYCLING AND REUSE

Some of the compelling reasons to recycle UNF are the ability to transmute potential weapons usable materials, recover materials with high energy value, and reduce the impact of actinides on repository performance. In addition, reuse of UNF components has the potential to reduce the amount of highly radioactive waste requiring disposal in a cost effective manner.

Many options have been studied, world-wide, for the reuse of uranium. Recycled uranium (RU) is typically between 0.8 and 1.3% U-235 and contains between 0.3 and 0.7% U-236. This level of enrichment is significantly above natural. The presence of U-236 would require 0.22 to 0.30 units of additional U-235 enrichment per unit of initial U-236 in the reactor fuel (e.g. 4.6% U-235 in place of 4.5%). Four primary options for reuse are being considered [3]: 1) reenrichment plus blending for reuse in light water reactors, 2) directly burn UNF in CANDU reactors (up to ~3000 MTU/yr in existing Canadian reactors)(may require some blending), 3) use in fast reactors as breeding stock, 4) mix with other fissile materials (e.g., MOX fuel).

The other general category of recyclable material is cladding. U.S. commercial UNF is generally clad by Zircaloy. The Zircaloy cladding makes up roughly 25% of the fuel assembly mass and pure Zr is a highly valuable metal. Methods for separating the Zr from recoil atoms, tritium, and most activation products are being developed by ORNL. One such method has shown, in principle, to have the capacity to removal high purity Zr that contains only a small fraction (0.01 to 0.03 wt%) of Zr-93. There may also be ppm levels of Nb-94 in the product. Both radionuclides are β emitters with low activity[3]. Due to these low levels of soft β in the final product, recycled Zr could be used in nuclear applications such as new cladding, reactor materials of construction, waste packages, and/or waste forms.

A lot of attention has been focused on the possible reuse of noble metals from UNF. Specifically, Pd, Rh, Ag, and Ru metals are in significant concentrations in the UNF and are of high value in commercial markets. These metals account for 0.26% of typical UNF and are produced by the U.S. nuclear power industry at roughly 10 MT/yr. At current market values, this material is worth nearly $130k/MTIHM or $336M/y. Roughly 16% of the Pd is made up of the radioactive isotope Pd-107, which emits a soft β-particle with a 6.5×10^6 y half-life. Collins et al. conclude that this small amount of radioactivity should not hinder the industrial use of these metals.[3]

Other, high-value, components of UNF are also being considered for reuse (lanthanides, noble gases, stainless steel hardware, and heat generating components [Cs, Sr]) but will not be discussed in detail here.

ENGINEERED WASTE FORMS

Concurrent with the evaluation of potential materials reuse, engineered waste forms are being developed for the remaining waste components. Waste form development is undertaken in a general fashion – independent of fuel processing flowsheet. However, to define the likely compositions and forms of the waste to be immobilized, two generalized process assumptions were made:

1. electrochemical (pyrochemical) processing of fuels leading to hulls and undissolved metals including each UNF component more noble than U, an alkali halide salt containing all UNF components less noble than U, and noble gases;

2. aqueous processing in nitric acid solution with the possibility to separate the streams including undissolved solids (dissolver fines), soluble Tc fraction, lanthanides with TRU contamination, combined fission products (high-level waste [HLW] raffinate), and gaseous fission/activation products (H-3, I, Xe, Kr, C-14)

Waste forms are being developed to immobilize the key individual or combined waste streams.

Iodine

One of the most challenging aspects of recycling in the U.S. is disposition of I-129. This isotope has a half-life of 1.57×10^7 y and tends to be highly soluble and therefore mobile in many disposal environments. Current U.S. regulations require that less than 5 mCi/GWye of I-129 be released to the environment for the entire fuel cycle by all vectors. Roughly 95% of the iodine is released in the aqueous process during the dissolution step.[4] Most of the focus on iodine waste form development has been on combined capture and immobilization. One mature option is sorption of iodine onto silver impregnated mordenite (AgZ).[4] The mordenite could then be hot pressed into a sodalite waste form [5], encapsulated into a low-temperature glass [6], embedded in a cement [7], or eluted from the mordenite and separated by a number of means. Alternatives to this AgZ option is the use of ultra-high surface area aerogels [8], including silica aerogel functionalized with zero valent Ag and chalcogenide glass aerogels with a high affinity and solubility of halides.[9] The aerogel concept includes capture of the iodine followed by thermally collapsing into durable waste forms. The low-melting glass encapsulation and aerogels are recent and significant developments.

Krypton

Whereas currently operating recycling facilities do not capture Kr, current U.S. regulations require that Kr be captured if the fuel is cooled for less that roughly 30 years from reactor discharge. The exact timing depends on the amount of burnup and the electric energy extracted from the fuel. Historically, many processes have been proposed for Kr removal, including cryogenic distillation, membrane separations, ion sputtering, selective adsorption on charcoal or zeolites, and a combination of cryogenic trapping and molecular adsorption. More recently the project began developing metal organic frameworks (MOF) to capture Kr from gas streams and Xe at room temperature.[9]

With a half-life of 10.7 y, Kr-85 decays relatively quickly, and would require a shorter-lived waste form. However, even low chemical durability waste forms are difficult to fabricate with noble gases. Compressed gas cylinder storage of Kr, until sufficient decay occurs, raises certain safety concerns. The application of MOF's as a storage media will significantly reduce storage pressures (for equal volume) and will minimize the impacts of Rb ingrowth on corrosion. For a significant increase in storage density, a high durability waste form was developed – SiC with embedded Kr.[9]

Tritium

Tritium has a relatively short half-life (12.3 y). If it is cleanly separated (e.g., without significant concentrations of other radionuclides), it will not require a waste form with long-term chemical durability. One option would be a low water content, cement-based form. The key in waste management is the clean separation of H-3 from I-129. Only small fractions of the I-129 to this stream may cause the waste to require immobilization for long times.

Undissolved Solids and Technetium

In typical aqueous process flowsheets one of the first processes is the dissolution of fuel in nitric acid. This dissolution is not complete and leaves an undissolved solids (UDS) fraction, which is rich in Pd, Ru, Rh, Mo, Zr, Tc, and O. Roughly two thirds of the Tc is dissolved into solution and would be separated from the uranyl nitrate stream as a pertechnetate ion.[10] Two primary options are considered for these Tc bearing wastes: 1) incorporate into the glass waste form or 2) form a separate waste form specifically aimed at immobilizing Tc. In the first option the noble metals (Pd, Ru, Rh) may significantly limit the loading of HLW in glass. However, addition to the glass reduces the number of processes required to treat the waste and number of waste forms with very long lived radionuclides requiring qualification.

Distinct waste forms for Tc allow for waste forms targeted at effectively immobilizing this radionuclide that is expected to significantly affect repository performance in many different disposal environments. Three primary waste forms have been developed by the program for immobilization of these Tc-bearing materials.

1. An iron based alloy that contains the UDS, reduced soluble fraction of the technetium, and potentially the soluble fraction of the noble metals and stainless steel fuel assembly hardware. This waste form strives to maintain Tc in the immobile reduced state Tc^0. Relatively low processing temperatures (<1600°C) are required to form this alloy.[11] (This is the only of the three waste forms that is being developed for the electrochemical UDS.)

2. The Epsilon-metal phase, which makes up a large fraction of the undissolved solids, would make an outstanding waste form. This waste form would incorporate the UDS, the soluble fraction of Tc, and the soluble fractions of the noble metals.[12] There are natural analogs that attest to the durability of this phase. Natural reactors operating in Gabon, Africa produced epsilon metals. The decayed Tc-99 was found to migrate less than one meter in roughly 2 billion years.[13] That fact combined with the fact that they survive the boiling nitric acid solution despite the very high surface area attest to the high chemical durability.

3. The third waste form developed by the program for immobilization of UDS, soluble Tc, soluble noble metals, and potentially lanthanide fission products was a pyrochlore oxide ceramic – $(Zr,Nb,Mo,Tc,Ru,Rh,Pd)_2Ln_2O_7$.[14] This waste form immobilizes Tc in the immobile Tc^{4+} state and displays relatively high chemical durability that is independent of disposal environment.

HLW Raffinate

A cost-benefit analysis was performed to evaluate the value of separating the HLW raffinate into constituent streams.[15] It was concluded, that aside from the noble metals, there was not a strong cost driver to further segregate the HLW. In the case of noble metals, there was a case for treating them separately under some circumstances.

Vitrification is the Best Demonstrated Available Technology (BDAT) for HLW raffinate in the U.S. and also the international standard treatment method.[16] While vitrification into a borosilicate glass is the reference process, the program is investing in the next generation waste forms for HLW with potential benefits over vitrification. Two such forms are:

1. Glass ceramics may allow for significantly higher waste loading than possible in typical borosilicate glasses. There are three primary limitations to the loading of HLW in glass: i) decay heat, ii) solubility of waste components (e.g., MoO_3), and iii) noble metals. Glass ceramics could allow for higher heat as the crystalline portions may be much more thermally stable. They also are expected to tolerate significantly higher concentrations of components that are sparsely soluble in the glass melt. The noble metals limit would depend on the processing methods, but, will not be more restrictive for glass ceramics. Crum et al.[17] demonstrated durable, potentially radiation resistant glass ceramics that can be processed in existing melter technologies containing roughly double the waste loading of typical glasses. Figure 1 shows graphically the potential for waste loading increases.
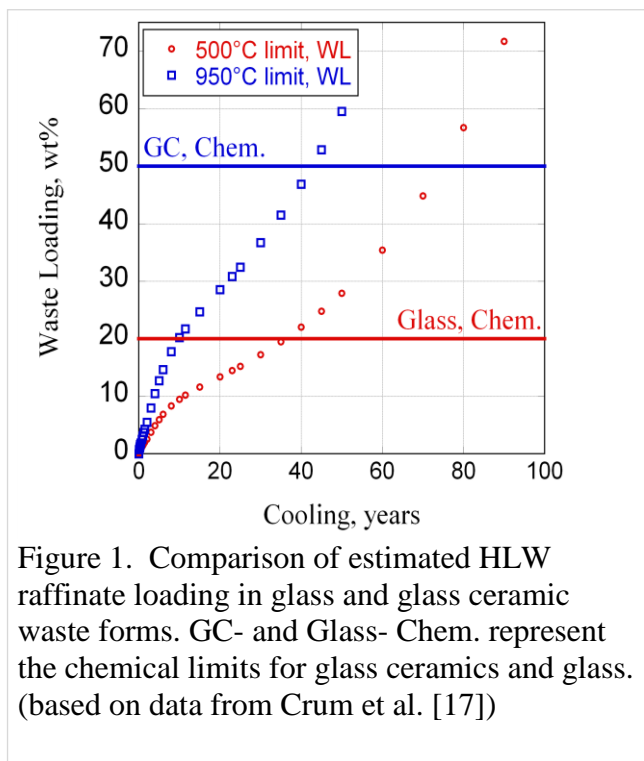

Figure 1. Comparison of estimated HLW raffinate loading in glass and glass ceramic waste forms. GC- and Glass- Chem. represent the chemical limits for glass ceramics and glass. (based on data from Crum et al. [17])

2. Crystalline ceramic waste forms show promise for high loading and high chemical durability. Billings et al.[18] have begun development of mixed phase titanate ceramics. These forms are similar to the synthetic rock (synroc) materials. Development of these types of waste forms began in the 1950's; the term synroc was coined by Ringwood et al. in 1979 when the most concerted waste form development and testing on these forms began.[19] The current work aims at extending this work to FCT program waste stream estimates and expanding the processing methods to melting and crystallizing and spark plasma sintering.

Spent Salt

Electrochemical spent salt is an alkali-chloride containing lanthanide, alkali, alkaline-earth, and halide fission products and trace transuranics. The reference waste form for the experimental breeder reactor-II (EBR-II) spent salt is a glass bonded sodalite.[20] The loading of salt in this waste form is roughly 7.5 wt% due to the high chlorine plus the sodium required to form sodalite. Two advanced waste forms are being developed that simultaneously incorporate the alkali-halides at higher loading and show high chemical durability.

1. Tellurite glasses have relatively high alkali-chloride solubility's, based on literature data. Riley et al. have fabricated a series of these glasses to determine the solubility for the mixed waste composition and have begun durability testing.[21] They found that a $PbO\text{-}TeO_2$ glass could incorporate at least 10 wt% of the spent salt (the highest concentration attempted) while maintaining good durability as measured by the product consistency test. Accounting for the density difference between the EBRII baseline and the $PbO\text{-}TeO_2$ glass a volumetric loading increase of more than 3× may be possible.

2. Sintered sodalite mineral formed by a sol-gel process will have comparable properties to the EBR-II baseline waste form with roughly double the loading. The methods of fabrication and densification were developed and proof-of-principle tests were performed by Riley et al.[21]

STORAGE AND DISPOSAL

In addition to the development of advanced waste forms and processes, the program is developing credible strategies for managing radioactive wastes from nuclear fuel-cycles in order to provide acceptable disposition paths for all wastes regardless of transmutation system technology, fuel reprocessing scheme(s), and/or the selected fuel cycle. These disposition paths will involve the storing and transporting of radioactive materials and the disposal of radioactive wastes. The disposal of radioactive waste of all classifications (low-, intermediate-, high-level waste, and UNF) has been investigated world-wide since the inception of nuclear energy. In the U.S., deployment of near-surface disposal facilities for low-level waste (LLW) and geologic disposal of defense-related transuranic wastes (TRU) have been successfully implemented. However, the capacity for disposing of LLW is limited, [22] potential disposal paths for Greater Than Class C wastes (GTCC, which is essentially intermediate level waste) have yet to be identified, and the disposal of UNF and HLW has not been demonstrated. Geologic repositories have experienced challenges throughout the world.[23]

Waste Forms Performance over Geologic Timescales

The first barrier to the release of radionuclides into the environment is the waste form. In addition to the protection from release to the environment due to contact with water, waste forms also protect the environment during storage, transportation, and handling before permanent disposal. They also offer significantly improved performance during repository intrusion scenarios, as opposed to containerized waste without robust waste forms. However, the performance of UNF and HLW waste forms over time scales as long as a million years is still uncertain. The program is applying a method of closely-coupled theory, experiment, and modeling to significantly reduce the uncertainty in waste form performance and to develop international consensus on the mechanisms that determine release rates from waste forms in a variety of different geologic environments.

The primary focus for waste form performance evaluations is on borosilicate glass, UNF, and iron-based alloy waste forms. Certain aspects of glass corrosion are well established by theory and experiment. The behavior of glass exposed to water, in a closed (or slow-flowing) system, takes the general form shown in Figure 2. The process(es) responsible for the residual rate and the time and effects of renewal are not well understood. A European Union sponsored study evaluated the current data and models and concluded that both reaction affinity and mass transport processes play a role in determining the residual rate to some degree.[24] An international program has since begun to develop the understanding of the relative importance of these processes in determining the residual rate of glass corrosion, which is primarily responsible for the release of radionuclides to the environment over vary long time scales.
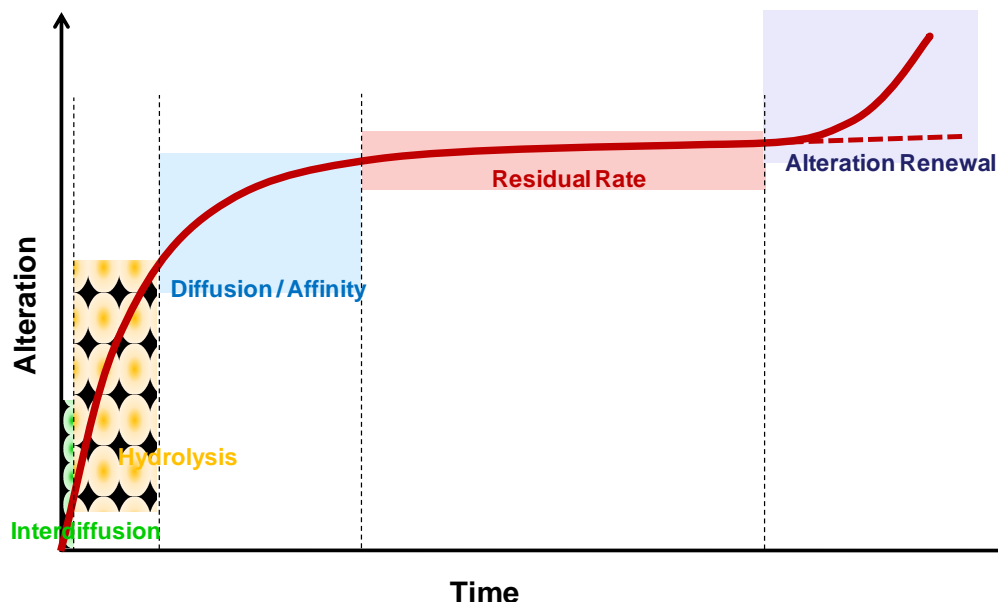
Figure 2. Schematic of glass alteration as a function of time in a closed system

UNF corrosion over geologic timescales is likewise uncertain. Irradiated fuel is marked by an initial, near instantaneous, release of radionuclides (called instantaneous release fraction, IRF), followed by bulk corrosion of UO_2 by oxidative corrosion.[25] The oxidative corrosion rate depends strongly on the generation of oxidizing species in solution contacting the fuel in the presence of epsilon metal phase and high radiation fields. These critical aspects of the corrosion require irradiated fuel to be used in corrosion testing rather than unirradiated UO_2, significantly increasing the cost and difficulty of study. The program will perform the necessary testing to understand the reaction rates of UNF in a variety of environments to support repository performance models.

Iron based alloy corrosion studies are currently focused on development of alloys with sufficient long-term corrosion resistance and fabricability to be a suitable waste form.[26] To develop such a waste form, the kinetics of radionuclide release must be understood.[27] These latter models are being used to develop reactive transport models for the prediction of repository performance.

Generic Disposal System Environment (GDSE) Modeling

Generic repository models are being developed to help evaluate the potential impacts of disposal on waste form development. These models are in two general classifications: 1) coupled reactive transport models for near-field performance and 2) far-field fate and transport models. These models are being developed for four general repository environments: tuff, granite, salt, and clay. The near-field models treat multi-physics in a fully coupled fashion, including chemical reaction and solubility, aqueous transport, and material movement (geomechanics) in the case of salt. These models could also be next-generation models in support of repository performance evaluation. One key aspect of the models includes the extension of reactive transport models to very small grid size (nanometer scale). This helps to evaluate the relative impact of mass transport and affinity impacts on the long term corrosion of glass.

SUMMARY

The FCT program is investing in the development of technologies to support waste management for a range of different fuel cycle options. These investments include the development of technologies to reuse UNF components, development of advanced waste forms and waste processes, and the development of next-generation repository performance models. These developments will ensure that the sustainable benefits of recycling can be achieved by disposing waste byproducts in engineered forms that have been developed from a science-based approach for reliable, long term performance in the waste repository

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