

DEVELOPMENT OF ADVANCED CERMET WASTE FORMS

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Abstract

The growing interest in the expansion of nuclear energy in the United States is widely acknowledged. While public support for the expanded use of nuclear power is relatively high, the disposition of the resulting waste remains a significant concern. A Blue Ribbon Commission on America's Nuclear Future has recently been established at the direction of the President to examine options for the permanent disposal of high-level nuclear waste. Waste forms other than glass for high-level-waste (HLW) disposal are expected to be included in this assessment.

The Oak Ridge National Laboratory has been conducting research to develop a cermet waste form for the immobilization of the HLW generated in processing of used nuclear fuel. The cermet waste form will allow emplacement of the high-radioactivity, high decay heat-generating fission products, $^{137}\text{Cs/Ba}$ and $^{90}\text{Sr/Y}$, along with other oxide-forming fission products in a ceramic or oxide form, distributed within a high-thermal-conductivity metallic matrix. The metallic phase will contain those waste components that are amenable to metal formation by simple hydrogen reduction of oxides, as well as the cladding and hardware materials (e.g., Fe, Cr, Ni, and Sn). This cermet waste form (1) will improve the heat transfer characteristics and reduce the centerline temperature and/or allow for increased waste loading and higher density when compared with a glass or ceramic waste form; (2) may result in significant cost benefits through the improvements to the heat transfer from the waste during decay heat storage; and (3) may simplify or eliminate some of the currently proposed upstream separations processes. The successful deployment of such waste forms may also facilitate an option of using the decay heat during an interim storage period for process and facility heating applications.

To date we have demonstrated the production of several cermet materials from simulated waste streams.

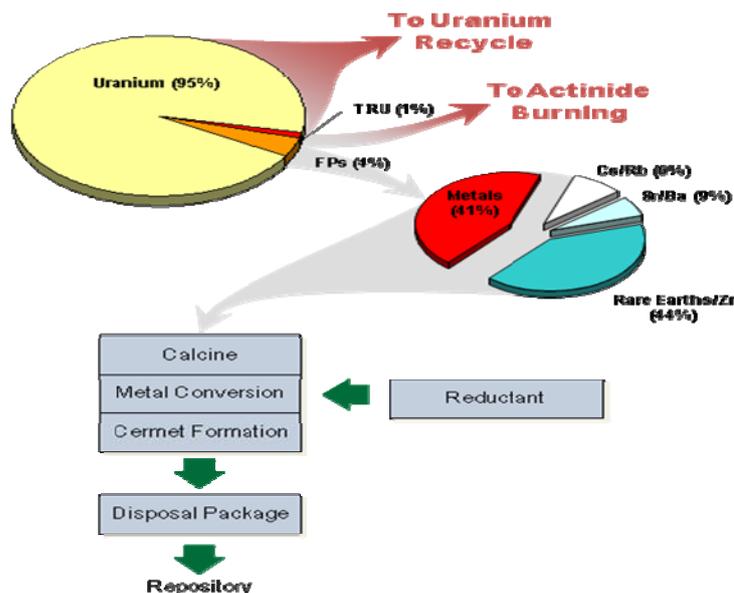
Cermet development

The goal of this research effort is to explore an alternate “cermet” waste form for high-level waste (HLW). A cermet is a composite material that consists of ceramic phases dispersed in a continuous metal phase. This provides an opportunity to take optimal advantage of the properties of both metallic and oxide materials and to tailor, as needed, each phase to improve the performance properties of the waste form. We are seeking to develop a cermet using, to the extent possible, only the intrinsic components of the waste streams to form the ceramic materials to sequester the short-lived, but highly heat generating $^{137}\text{Cs}/\text{Ba}$ and $^{90}\text{Sr}/\text{Y}$ components of used nuclear fuel (UNF) and to form metal alloys that enable isolation of long-lived fission products (FPs) such as ^{99}Tc , noble metal components, transition metals, fuel assembly hardware, and cladding materials. This metal alloy also provides the required heat transport properties to deal with the higher heat generation rates associated with the higher waste loading.

Preparation of surrogate waste materials

As previously noted, a goal of this initiative is to produce a waste form that contains only a minimal amount, if any, of added fresh or unirradiated materials. Examination of the composition of the FPs present in the liquid waste from the processing of UNF appears to indicate that under proper conditions a cermet or cermet-like material could be formed without the use of any additives. As shown in Figure 1, FPs that are separated from the uranium and transuranic products during the processing of UNF comprise a very small fraction of the total mass of the UNF and are roughly evenly divided between those that will remain in the oxide form once calcined and those that are easily reduced from the oxide to a metal form. While this “raffinate-waste-only” cermet may not have all of the desired characteristics, the initial 100% waste loading material provides an opportunity to tailor both the metal and oxide phases of the cermet with the minimal addition of “nonwaste” components to produce a waste form that possesses the advantages of both materials.

Figure 1. Fission products (FPs) from the processing of used fuel.



As a starting point for this effort, we used the composition of the solvent extraction raffinate waste stream from the recently completed Coupled End-to-End (CETE) demonstration [1]. This stream contained the residual FPs following the UREX solvent extraction operations used to remove the U, Pu, Np, and Tc. Americium and curium were subsequently removed from this stream by additional solvent extraction operations. The elemental composition of the UREX raffinate is shown in Table 1. The composition of the noble metal undissolved solids (UDS) that were recovered following the dissolution of the fuel is shown in Table 2.

Table 1. Mass content of the solutions from the processing of Dresden fuel during the first CETE campaign.

Material	CETE Raffinate (g/L)	Surrogate Composition (g/L)
Y	0.0274	—
Zr	0.1997	0.1997
Mo	0.1796	0.1796
Tc	0.0006	—
Ru	0.0132	—
Pd	>0.0002	—
Total Noble Metals (NM)s	0.1935	0.1796
La	0.0817	0.0817
Ce	0.1538	0.1538
Pr	0.0739	0.0739
Nd	0.2683	0.2683
Sm	0.0468	0.0468
Eu	0.0078	0.0078
Gd	0.0097	0.0097
Total Lanthanides	0.6419	0.6419
Cs	0.1215	0.1215
Ba	0.1368	0.1368
Rb	0.0062	0.0062
Sr	0.0384	0.0384
Total High Heat	0.3030	0.3030

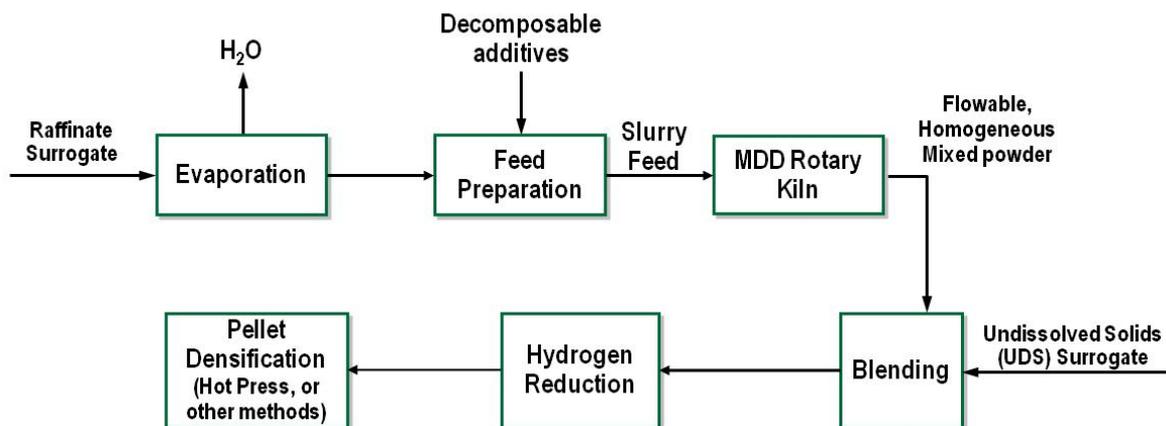
Table 2. Undissolved solids composition.

Element	Weight Fraction
Mo	0.20
Re	0.22
Ru	0.22
Rh	0.06
Pd	0.30

Phase 1 cermet—No additional constituents

The preparation of the cermet waste test material is a multistep process. Figure 2 shows the overall processing steps used to form the cermet from the surrogate raffinate.

Figure 2. Simplified cermet production flowsheet.



For purposes of testing the methods involved and demonstrating the processes, two surrogate waste solutions were prepared. The first was a cerium nitrate solution, and the second was a nitrate solution mixture of nonradioactive stand-ins for the FP elements with concentrations similar to those in the raffinate from the processing of UNFs. To convert the nitrate solutions to a solid oxide form, we utilized a process referred to as Modified Direct Denitration (MDD) [2], under development at Oak Ridge National Laboratory for preparation of mixed actinide oxides. In a continuous-mode operation, the MDD process uses a rotary kiln to thermally decompose nitrates in liquid solution to oxides. The process utilizes the decomposition behavior of some metal/inorganic double-nitrate salts, which do not melt prior to decomposing, to avoid certain processing issues.

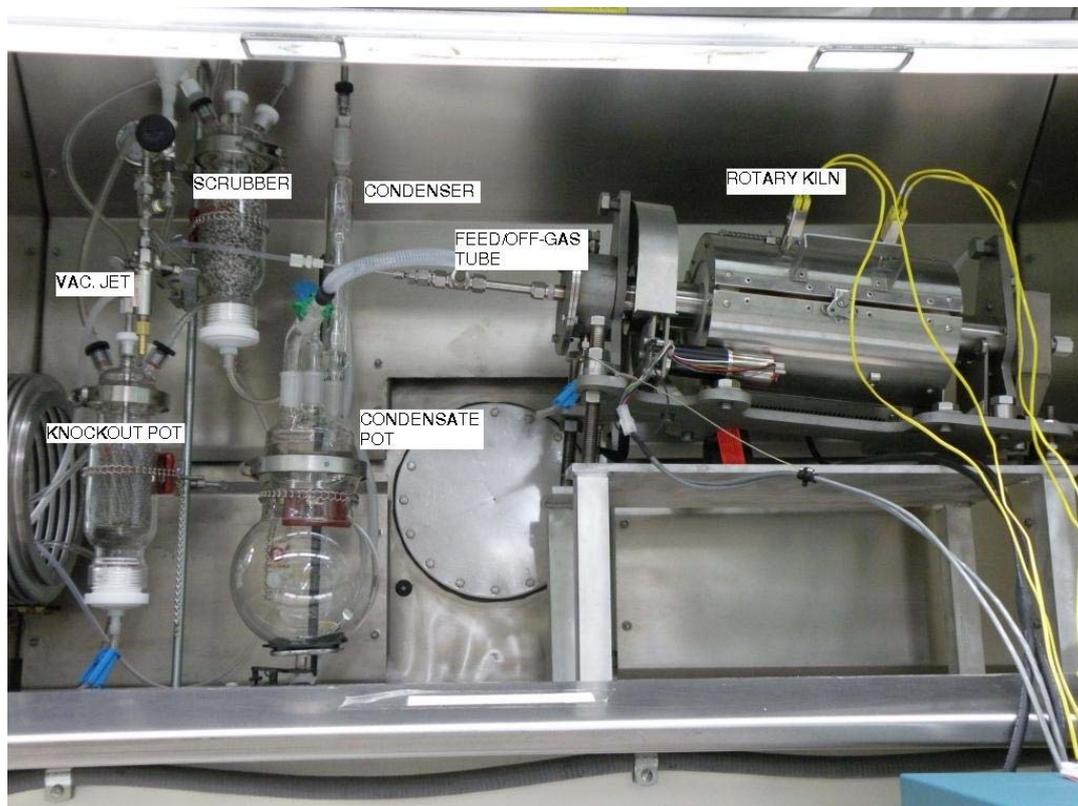
Initially, batch denitrations of the raffinate surrogate and cerium nitrate solutions were conducted to examine the denitration of the raffinate solution. Batch tests provide a good indication of how the material will behave in the rotary kiln used in the continuous MDD process.

Batch denitrations of the raffinate surrogate and cerium nitrate solutions were carried out in stainless steel beakers. The behavior of the cerium with this equipment is well known from earlier MDD cold tests and is the standard for comparison. Ammonium nitrate is added in the MDD process to modify the decomposition reactions and prevent the deleterious formation of a mastic phase during the denitration. One sample of the mixed FP surrogate was denitrated without the addition of ammonium nitrate for comparison of the resulting oxide product powder. Samples of the products are shown in Figure 3. The results were promising and justified proceeding with further testing using continuous process equipment. Figure 4 shows some of the equipment used.

Figure 3. Products from batch denitrations, indicating successful production of oxide powders suitable for cermet processing through processing with addition of ammonium nitrate.



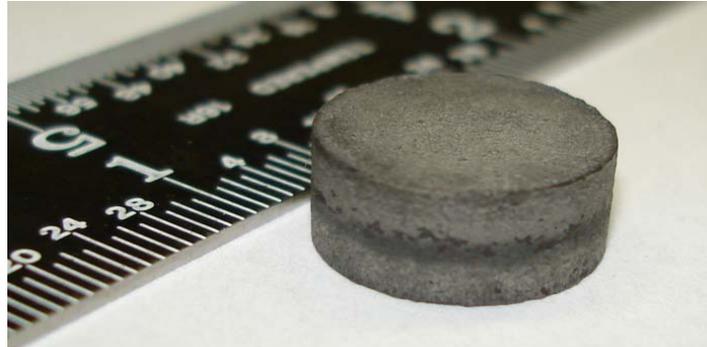
Figure 4. Equipment installed in a fume hood for testing a continuous process.



The calcined products from the MDD process were then blended with a simulant representing the UDS, with a composition as shown in Table 2. The amount of UDS added to the oxide was estimated using the results of ORIGIN calculations, which were confirmed by sampling results from the CETE demonstration. Following blending of the oxide with UDS, the oxide materials were reduced with hydrogen and pressed into pellets.

A cermet pellet was successfully produced (Figure 5) from a sample of the mixed oxides and metals. The material was hot pressed. The resulting cermet material is unique in that it consists completely of representative compositions of waste streams from fuel recycling and contains no additives to tailor either the ceramic or the metal phases. This material is ~30 wt % metal and 70 wt % ceramic. The ratio is reversed from what is desired in that we were trying to produce a cermet of ~70 to 75 wt % metal to provide a continuous metal phase to improve the heat transport properties.

Figure 5. Initial cermet pellet successfully produced from compositions representative of nuclear fuel recycling streams, with no added alloy or ceramic formers.



Phase 2 cermets—Addition of other metal wastes

The largest mass of material that may have to be disposed of as waste from the reprocessing of UNF is the cladding and hardware. As shown in Figure 6, the total mass is ~30% of the mass of the fuel assembly. Within the DOE/NE Fuel Cycle Research and Development Program, work is under way to evaluate the feasibility of recovering and recycling zirconium from the zircaloy cladding. The residual alloying materials (~2% of the zircaloy mass) and the stainless steel hardware would still need to be managed as radioactive waste. Great interest was focused on the potential incorporation of these materials into the cermet waste form described above to boost the metal fraction.

Three metal mixes, prepared as shown in Table 3, were used as the metal feedstock. The differences in the three metal mixes are the presence (or absence) of tin and the form—metal or oxide. While the iron, chrome, and nickel were added to represent stainless steel, they were added as individual metals (i.e., not alloyed). The mass of noble metals the UDS make up was held constant in the final metal–oxide blend and is the same composition as shown in Table 2. In all cases the final mixture was 25 wt % oxide and 75 wt % total metals. These mixes, blended with MDD oxide as described in the Phase 1 cermet work using a Turbula blender, served as pellet feedstock.

Figure 6. Incorporation of additional metal waste streams into the HLW raffinate cermet.

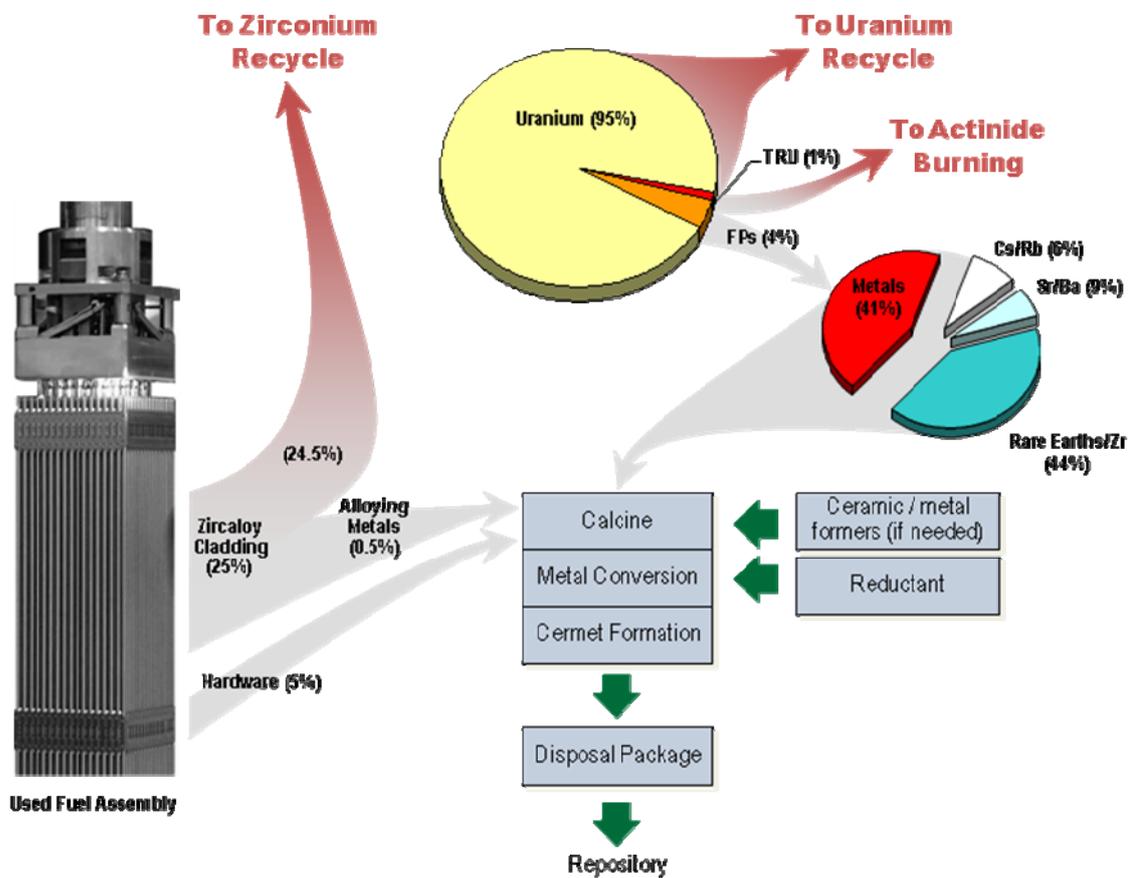


Table 3. Metal mixtures used to simulate hardware waste plus UDS.

	Metal Mix 1 (wt %)	Metal Mix 2 (wt %)	Metal Mix 3 (wt %)
Fe	53.71	60.7	54.82
Cr	16.93	19.1	17.28
Ni	12.04	13.6	12.29
Sn	0	0	9.63
SnO ₂	11.46	0	0
UDS simulant (see Table 2)	5.86	6.60	5.98

A hot pressing technique to produce consistently high density pellets was developed, and ~6.5-g batches of nine formulations were pressed for thermal diffusivity measurement and phase analysis.

Compositions of the nine samples were as follows:

- A Metal Mix 1 + CeO₂
- B Metal Mix 2 + CeO₂
- C Metal Mix 3 + CeO₂
- D Metal Mix 1 + Surrogate Oxides Mix (see Table 1)
- E Metal Mix 2 + Surrogate Oxides Mix
- F Metal Mix 3 + Surrogate Oxides Mix
- G Metal Mix 3
- H Metal Mix 2
- J Surrogate Oxides Mix 3

Pellets were hot-pressed and had densities that were within $\pm 5\%$ of the calculated theoretical density for the materials being used and low-porosity composition. Some of the resulting pellets are seen in Figure 7. The CeO₂ pellets were produced to provide a relatively simple ceramic-phase cermet to use during thermal analysis of the products. The MDD surrogate and metal-mix pellets were also produced to provide materials for comparison with the individual metal and ceramic phases of the cermet samples. With the exception of the MMD oxide pellet, production of test specimens for subsequent analysis was very successful.

Figure 7. Hot-pressed cermet pellets from Phase 2.



Cemet Hot Press Samples	
A	CeO ₂ + Metal Mix
B	CeO ₂ + Metal Mix
E	MDD Surrogate + Metal Mix
J	MDD Surrogate only
H	Metal Mix only

Conclusions

Excellent progress has been made toward the project goals of increasing the waste loading and demonstrating the feasibility of making a waste form with high thermal conductivity and minimal

additives. The initial pellet produced from the surrogate HLW raffinate and UDS had a composition of 30 wt % metal and 70 wt % ceramic and a waste loading of >85 wt %. However, this product lacked the desired continuous metal phase. The addition of waste metals from the hardware and cladding can be used to increase the metal composition to 70 wt % while maintaining a waste loading of >40 wt %. Samples of these high-metal surrogate cermets have been successfully produced.

References

- [1] Jubin, R. T., E. D. Collins, L. K. Felker, B. B. Spencer, E. A. Walker, R. J. Vedder, R. D. Taylor, and J. L. Binder, "CETE R&D at Oak Ridge National Laboratory Supporting Management of Nuclear Waste," Waste Management 2009, Phoenix, Arizona, March 2009.
- [2] Felker, L. K., R. J. Vedder, and E. A. Walker, "Preparation of Mixed Oxides by Modified Direct Denitration," *Proceedings of the American Nuclear Society Winter Meeting 2006*.