

## Development of Advanced Cermet Waste Forms – 11116

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### ABSTRACT

The development of high-level waste (HLW) disposal options that minimize repository use and maximize efficiency and public safety is critical to the resurgence of nuclear energy in this country. Oak Ridge National Laboratory has been working to develop an advanced cermet waste form for the storage and disposal of HLWs arising from the processing of used nuclear fuel.

Cermets are composed of ceramic phases dispersed in continuous metal matrices. This composition provides an opportunity to tailor the primary phases to take advantage of the properties of both metallic and ceramic materials. This paper describes experimental and modeling efforts to fabricate and characterize cermet materials containing high mass fractions of fission product and other used fuel waste components. 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 advantage of the properties of both metallic and oxide materials and to tailor, as needed, each phase to improve the performance of the waste form. 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 glass or ceramic waste forms; (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.

To the extent possible, our effort is focused on developing a cermet using only the intrinsic components of the waste streams to form the ceramic materials to sequester the short-lived, but highly heat generating <sup>137</sup>Cs/Ba and <sup>90</sup>Sr/Y components of used nuclear fuel (UNF) and to form metal alloys that enable isolation of long-lived fission products (FPs) such as <sup>99</sup>Tc, noble metal components, transition metals, fuel assembly hardware, and cladding materials. While this “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.

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## PREPARATION OF SURROGATE WASTE MATERIALS

We used the composition of the solvent extraction raffinate waste stream from the recently completed Coupled End-to-End (CETE) demonstration as a starting point for this effort [1]. This aqueous stream contained the residual FPs from the solvent extraction process that recovered 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 raffinate is shown in Table I. The 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. In addition to the raffinate waste stream, we included the noble metal undissolved solids (UDS) that were recovered following the dissolution of the fuel. The UDS composition is shown in Table II.

Table I. Mass Content of the Solutions from the Processing of Dresden Fuel during the First CETE Campaign

Material	CETE raffinate (g/L)	Target liquid waste 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	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 II. Undissolved Solids Composition

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

The preparation of the cermet waste test material is a multistep process. Figure 1 shows the overall processing steps used to form the cermet from the surrogate liquid waste stream. We utilized a process referred to as Modified Direct Denitration (MDD) to convert the nitrate solutions to a solid oxide form [2]. This process is 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 the resulting metal/inorganic double-nitrate salts, which do not melt prior to decomposing, to optimize processing and product properties. The materials added to implement the MDD process ultimately decompose to gaseous products and do not add to the final waste form.

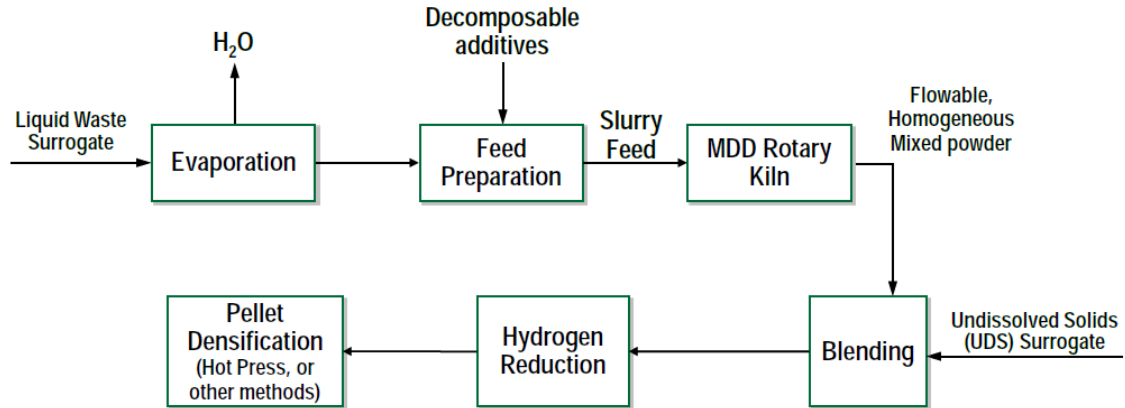


Fig. 1. Simplified cermet production flowsheet.

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.

Batch denitrations of the raffinate surrogate and cerium nitrate solutions were carried out in stainless steel beakers. Batch tests provide a good indication of how the raffinate material will behave in the rotary kiln used in the continuous MDD process. The behavior of the cerium with the MDD equipment is well known from earlier cold tests and is the standard for comparison. An inorganic salt is added in the MDD process to modify the decomposition reactions and prevent the deleterious formation of a mastic phase during the denitration. The results were promising and justified proceeding with further testing using continuous process equipment [3].

The calcined products from the MDD process were then blended with a simulant representing the UDS, with a composition as shown in Table II. Following blending of the oxide with UDS, the oxide materials were reduced with hydrogen and pressed into pellets. The resulting cermet material is unique in that it consists completely of representative compositions of waste streams from fuel recycling and contains no additives that remain in the waste to tailor either the ceramic or the metal phases. This material is ~30 wt % metal and 70 wt % ceramic. However, the ratio is reversed from what is desired to produce a continuous metal phase.

Ultimately we would like to produce a cermet of ~70 to 75 wt % metal to improve the heat transport properties. To this end, we began looking for other “waste” metals from the UNF. The largest mass of material that may have to be disposed of as waste from the reprocessing of UNF is the cladding and hardware. This mass is ~30% of the total mass of the fuel assembly. Work is currently under way, sponsored by the DOE/NE Fuel Cycle Research and Development Program,

to evaluate the feasibility of recovering and recycling zirconium from the zircaloy cladding [4]. The residual alloying materials from this process (~2% of the zircaloy mass) and the stainless steel hardware would still need to be managed as radioactive waste. The second phase of our efforts focused on the potential incorporation of these materials into the cermet waste form to increase the metal fraction.

Three metal mixes, prepared as shown in Table III, were used as the metal feedstock. The differences in these mixes are the presence (or absence) of tin and the form—metal or oxide. While the Fe, Cr, and Ni were added to represent stainless steel, they were added as individual metals (i.e., not alloyed). The mass of noble metals in the UDS makeup was held constant in the final metal/oxide blend and is the same composition shown in Table II. In all cases the final mixture was 25 wt % oxide and 75 wt % total metals. A hot-pressing technique was developed that consistently produced high-density pellets. Nine formulations were pressed for thermal diffusivity measurement and phase analysis. Compositions of the nine samples were as follows:

- A Metal Mix 1 + CeO<sub>2</sub>
- B Metal Mix 2 + CeO<sub>2</sub>
- C Metal Mix 3 + CeO<sub>2</sub>
- D Metal Mix 1 + Surrogate Oxides Mix (see Table I)
- 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 Only

The CeO<sub>2</sub> pellets (samples A–C) were produced to provide a relatively simple ceramic-phase cermet to use during thermal analysis of the products. The MDD surrogate (samples D–F) and metal-mix pellets (samples G and H) were produced to provide materials for comparison with the individual metal and ceramic phases of the cermet samples. With the exception of the MDD oxide pellet (sample J), which fractured during pressing, production of test specimens for subsequent analysis was very successful.

Table III. 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 <sub>2</sub>	11.46	0	0
UDS simulant (see Table II)	5.86	6.60	5.98

Characterization of the resulting cermets was conducted by a number of different methods, including scanning electron microscopy (SEM), for identification of the phases present and laser flash thermal analysis to determine the thermal diffusivity or thermal conductivity.

## OBSERVATIONS OF CERMET PELLETS

### Iron and Chromium Separation

The X-ray mapping revealed that the simulant powders combined to represent the stainless steel components did not alloy during the hot pressing. This behavior was initially attributed to the fact that each of the components of the stainless steel simulant was added as a separate metal powder. To validate this assumption, a pellet was produced using 304L stainless steel powder in place of the blend of Fe, Cr, and Ni. Similar separation of the iron and chromium phases was observed, as shown in Fig. 2.

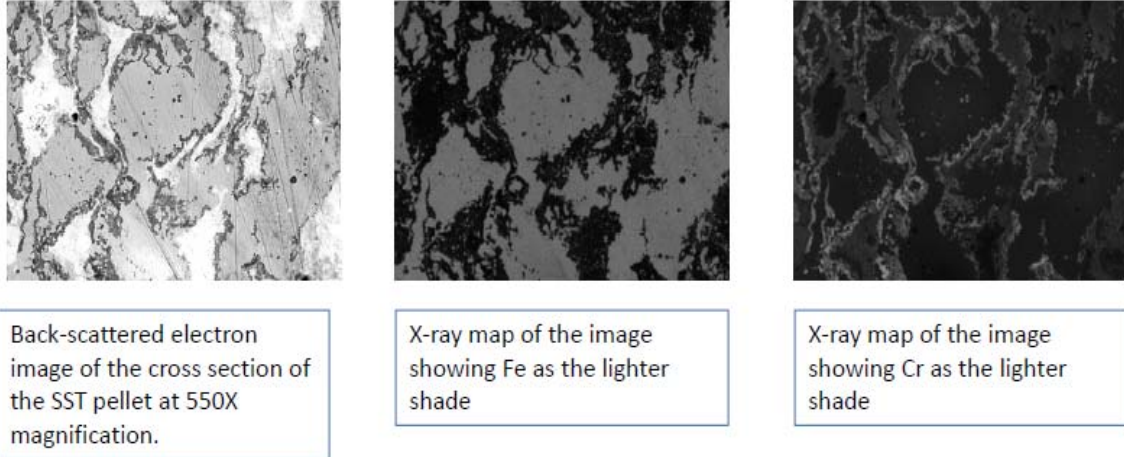


Fig. 2. Iron/chromium phase separation observed in cermet pellet produced using 304L stainless steel powder in place of the blend of Fe, Cr, and Ni.

### Cesium

Some pellets that had been exposed to air after being cut and polished showed elevated concentrations of cesium on the polished surface. This finding is thought to be the result of the hydroxide that formed when cesium reacted with moisture in the air; however, this speculation has not been confirmed analytically. The elevated concentrations are not surprising, because no efforts have been made in these samples to promote the formation of more-stable cesium compounds within the cermets. This activity is planned as part of the next phase of the development effort.

### Strontium

During the attempts to hot press the oxide components without any metals, significant amounts of strontium were visually observed as a white powder escaping from the die, an identification later confirmed by X-ray fluorescence. This strontium release was not observed during the pressing of the 75% metal–25% oxide combinations.

### Tin

Tin metal in the proportions of Metal Mix 3 appears to stay in the pellet. Higher concentrations of tin readily wick from the hot-pressing die and weep from cold-pressed pellets during sintering.

## CERMET MICRO-HEAT-TRANSFER ANALYSIS: THERMAL CONDUCTIVITY

Cermets are inhomogeneous by design, which significantly complicates the prediction of basic heat generation and heat transport properties. The goal of the microstructure thermal analysis is to aid in the understanding of the heterogeneous heat generation and heat conduction to evaluate the overall thermal performance of the waste form. Heat transport properties are actually “effective” quantities. This thermal analysis/simulation will be critical to understanding the experimental results from the thermal flash technique employed to measure the thermal conductivity of the cermet samples.

The micro-heat-transfer analysis begins with the identification of the various phases in the SEM images, followed by the assignment of diffusivities or thermal conductivities to the individual phases, and finally the calculation of the point-wise temperature on the inhomogeneous domain. (The last process allows the effective thermal conductivity and/or diffusivity to be determined.) Several techniques of image processing were developed and integrated to determine the cermet microdomains in the SEM images. Ultimately we settled on the identification of the four “primary” phases (metal, oxide, a finely dispersed metal/oxide phase, and a “void” area).

In the phase-identification process, the distributions of individual constituents were identified by SEM elemental mapping and sharp lines of demarcation were determined by edge-sharpening algorithms. Figure 3 shows this process for the iron, chromium, and oxygen constituents. From the elemental maps it was determined that iron was located predominantly in zones that constitute 47% of the area ( $\varphi_{Fe}$ ), as shown in white, while chromium was present in only 9% of the area ( $\varphi_{Cr}$ ).

This approach was repeated for the remaining 18 elements. The original SEM image shown in Fig. 3 was then reduced to four discrete phases with sharp lines of demarcation using an overlay technique. The images in Fig. 3 represent an area that is  $230 \times 180 \mu\text{m}$ . The results are shown in the lower-right side of Fig. 3, and the results of the composite phase analysis are summarized in Table IV. In Fig. 3, the white area is associated with a metal phase containing Fe, Cr, Ni, Pd, Ru, Re, Rh, Gd, and Eu. This makes up 49% of the area. Of particular importance is the oxygen map, which was helpful in resolving metal and oxide locations. The light-gray area in Fig. 3 is the oxide phase containing Nd, Zr, Mo, Ce, O, Ba, Cs, La, Sm, Sr, and Rb. This phase makes up 33% of the area. The dark-gray area, which composes 16% of the area, is identified as a finely dispersed metal/oxide mixture. Approximately 2% of the area was either a void area or could not otherwise be assigned in view of the combined uncertainty in the original elemental map data and the image-processing algorithm.

The conclusions drawn from this effort are as follows: (1) segmenting the images is a tractable problem if SEM elemental maps are used; (2) a relatively automated element-by-element build-up process was successfully implemented; and (3) identification of the oxide and metal phases is a nontrivial task. Once the phases were identified, the microthermal analysis was done in two stages.

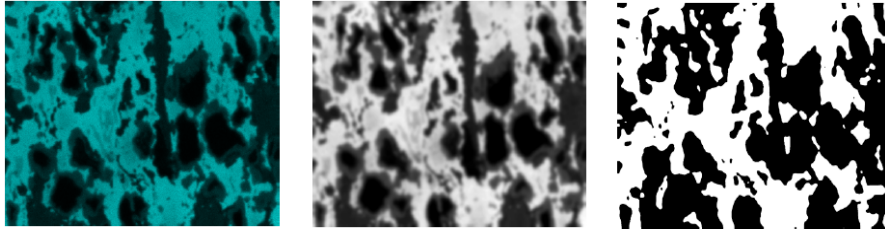
*Stage 1:* The material was assumed to be orthotropic. (Heat was applied in two orthogonal directions, axial and radial, while insulation was applied on the opposite boundaries of the sample.) Thus, the thermal conductivity tensor had only two nonzero components in the Cartesian coordinate system. Therefore, radial and axial directions were assumed to be the principal directions. The computed temperature fields and the resulting conductivities in the radial and axial directions are shown in Fig. 4.

*Stage 2:* The material was assumed to be anisotropic. Here a temperature was applied just as in the Stage 1. However, the insulated boundary condition was relaxed to allow heat flux on all

boundaries. We computed the principal directions of heat conduction and the thermal conductivities for the full tensor. The computed principal directions (eigenvectors of the conductivity tensor) were very close to the radial and axial directions. Therefore, the material was “nearly” orthotropic: that is, it was characterized by two principal thermal conductivity values, and these principal values were associated with directions that were nearly aligned with the radial and axial directions of the cermet pellet.

➤ **Fe phase (color/bright/white)**

$$\phi_{\text{Fe}} = 0.47$$



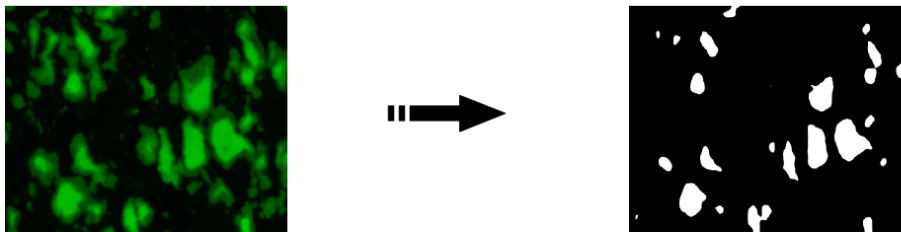
original

smoothed

Step 1: filtering     $\Rightarrow$     Step 2: anisotropic smoothing     $\Rightarrow$     Step 3: threshold segmentation

➤ **Cr phase (color/bright/white)**

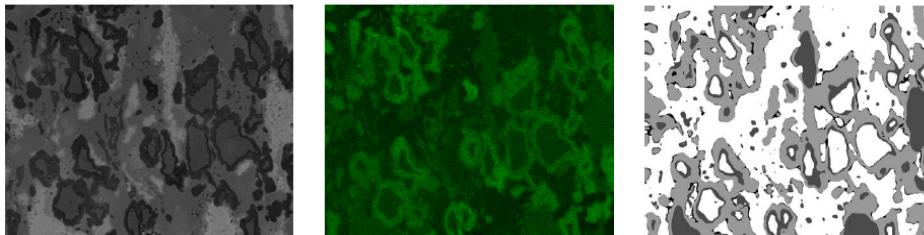
$$\phi_{\text{Cr}} = 0.09$$



original

segmented

➤ **Oxygen distribution aids final segmentation**



Original SEM

Oxygen distribution

Final segmentation

Fig. 3. Elemental distribution determination of Fe, Cr, and O in cermet sample E. The horizontal direction is aligned with the axis of the pellet, and the vertical direction is aligned with the radial direction.

Microthermal simulations were performed at various subsample sizes to investigate length-scale dependence of the effective thermal conductivities. Lengths of 150  $\mu\text{m}$  are required to reach a length-independent effective conductivity for this particular point in the pellet. It was further determined that the material is nearly orthotropic at sufficiently large length scale and that the principal directions for heat conduction aligned with the radial and axial directions. The radial conduction was predicted to be  $\sim 30\%$  higher than that in the axial direction: that is, the thermal conductivity is 21.8 W/m K in the axial direction and 29.0 W/m K in the radial direction. Finally, the simple volume-average calculation was made for estimating an effective thermal conductivity based on the assigned phase values and area fractions in Table 4 while ignoring the thermal behavior of the inhomogeneous material. This estimate of 49.0 W/m K systematically overpredicts heat conduction for any subsample size above 50  $\mu\text{m}$ .

Table IV. Results of Phase Identification for Cermet Sample E and Assignment of Thermal Conductivities<sup>a</sup>

Phase	Components	Area fraction	Thermal conductivity ( $k$ ) (W/m K)
Metal mix (white)	Fe, Cr, Ni, Pd, Ru, Re, Rh, Gd, Eu	0.49	81.7
Oxide mix (light gray)	Nd, Zr, Mo, Ce, O, Ba, Cs, La, Sm, Sr, Rb	0.33	5.85
Metal/oxide mix (dark gray)	Ni/oxides	0.16	43.8
Void/unclaimed (black)	Ar (assumed)	0.02	0.018
<b>Area-averaged conductivity</b>			<b>49.0</b>

<sup>a</sup>Refer to Fig. 4 for images of Sample E. Thermal conductivities are based on estimates of the element constituents of each phase.

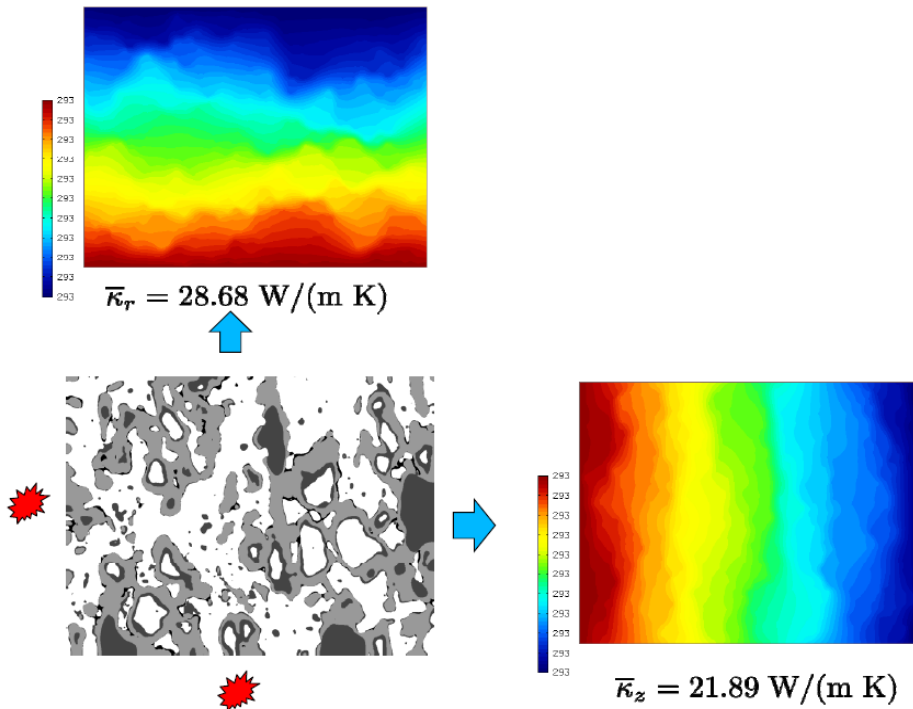


Fig. 4. Simulated heat transfer in cermet sample E based on phase segmentation.



## CONCLUSIONS

Significant progress has been made in the development of a high-level cermet waste form. We have demonstrated that a cermet material could be formed from only the simulated liquid HLW and simulated UDS. A critical demonstration was the successful use of only the intrinsic components of the waste from the aqueous separations of the UNF, as well as the waste from the hardware components and proposed recovery and recycling of the zircaloy fuel cladding materials, to form a high-metal-content cermet. Significantly, this cermet is ~100% waste: that is, with the exception of oxygen, no nonwaste constituents have been added. We have developed and refined methods and tools needed to guide the preparation and tailoring of the cermet waste forms and to model the resulting materials so that we can project their performance in terms of thermodynamics and heat transfer. To date, we have accomplished the following:

- Produced the first cermet pellet from the simulated liquid waste from aqueous UNF reprocessing without the use of additives to tailor the ceramic or metal phases
- Produced a cermet pellet from the simulated liquid waste from aqueous UNF reprocessing plus the residual simulated waste resulting from the proposed recycle of the UNF zircaloy cladding materials and fuel assembly hardware—again, without the use of additives to tailor the ceramic or metal phases
- Characterized the resulting cermets by different methods including SEM and laser flash thermal analysis
- Created a thermal transport simulation method, based on SEM microscopic data, for prediction of effective thermal conductivity and identification of principal directions of heat conduction for the waste form for ultimate comparison with laser flash data
- Through combined simulation and experimental characterization, identified anisotropy in the samples analyzed. (Cermet material analyzed appears to be orthotropic with higher radial conductivity.)

Much future work remains to be completed. This includes the continued characterization of the resulting ceramic and metal phases, determination of the waste form durability through leach testing as well as other mechanical tests, and optimization of the cermet phases to improve both the mechanical and chemical durability as required. The most important demonstration remains one with actual waste materials.

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