RELEASE BEHAVIOR OF NEPTUNIUM, PLUTONIUM, URANIUM AND TECHNETIUM FROM THE METALLIC WASTE FORM FROM THE ELECTROMETALLURGICAL TREATMENT PROCESS

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ABSTRACT

The metallic waste form, currently under development at Argonne National Laboratory, is subjected to immersion tests using simulated ground water at 90 °C to determine the extent of material released to solution. This waste form is an alloy consisting of stainless steel with 15 wt% zirconium and acts as a host for the immobilization of radionuclides that remain with the spent fuel cladding hulls following their treatment using an electrometallurgical treatment process. The results presented here are from 14, 34 and 90-day immersion tests. These tests show that the release of uranium is considerably higher than that of all other major elements present (Fe, Cr, Ni, Zr), but that release of all constituents is comparable to or lower than that for borosilicate glass.

INTRODUCTION

Argonne National Laboratory is developing an electrometallurgical treatment for spent metallic fuel from the Experimental Breeder Reactor II [1]. A product of this treatment process is a metallic waste form that incorporates the stainless steel cladding hulls, zirconium from the fuel and the fission products that are noble to the process, i.e., Tc, Ru, Pd, Rh, Ag. The nominal composition of this waste form is stainless steel/ 15 wt% zirconium/ 1-4 wt% noble metal fission products/< 11 wt% uranium. The process used to produce the metallic waste form ingots from the cladding hulls is straightforward. Spent fuel is chopped into small segments and placed into an electrorefiner where the fuel is anodically dissolved into a molten salt electrolyte. The hulls, after being removed from the electrorefiner, are introduced to a furnace where the adhering salt from the electrorefiner is distilled off. The hulls are then placed into a crucible and, if necessary, small amounts of trim chemicals are added, such as zirconium or stainless steel, to adjust the composition to match the target range. The casting takes place at 1650 °C with a 2 hour hold. The finished product is an ingot approximately 40 cm in diameter and 10-15 cm thick. The behavior of actinides, specifically, U, Pu, and Np, and also Tc is evaluated using a standardized leach test modeled after ASTM C1220 [2]. The behavior of these radionuclides is of interest in a geologic repository setting.

The relatively simple test employed here will not yield sufficient information to effectively model the performance of the metallic waste form in a geologic repository. It will yield, within the limitations of the test conditions used, the relative release behavior of the various elements that make up this multi-phase waste form. This information can then be used to revise the existing model [3]. Readers interested in a discussion of the current corrosion model for the metallic waste form are encouraged to read ref. [3].

The metallic waste form (MWF) is a two phase structure of Fe_2Zr intermetallic and an iron solid solution phase, see figure 1. The intermetallic phase acts as a host for the actinides and some of the technetium [4,5]. The presence of different poly-types of intermetallic has been reported [5]. An earlier effort yielded preliminary information regarding the behavior of uranium and technetium in long-term immersion tests [6]. The relative release behavior of matrix elements and radionuclides (U, Pu, Np, Tc) from this waste form has not been reported previously and is the intent of this paper.

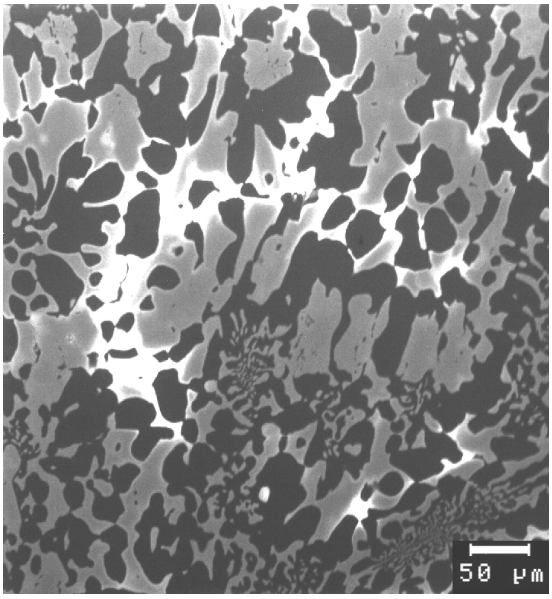


Figure 1. A Backscattered Electron Image of the Metallic Waste Form. The dark contrast areas are iron solid solution phase, the medium contrast area is the intermetallic area and the light contrast area is the actinide rich intermetallic area.

EXPERIMENTAL

Samples from several small scale ingots of surrogate MWF were prepared using a slow speed saw (Buehler Co.) and polished to a smooth, uniform surface finish. The composition of the samples by weight is: SS/15 Zr/6 Pu, SS/15 Zr/2 Np, SS/15 Zr/6 Pu/2 Np, SS/15 Zr/11 U/0.6 Ru/0.3 Tc and SS/15 Zr/2U/1 Tc/1 Ru/1 Rh/1 Nb/1 Ag (The nomenclature indicates the weight percent of each component with the balance being stainless steel). The leach test employed is modeled after the ASTM C1220 test developed and commonly employed for glass waste forms [2]. The surface area to volume of leachant ratio (S/V) used here was 40 m^{-1} with a test temperature of 90°C. The duration of the test was 14, 34 and 90 days. The test vessels were PTFE material. When the test was terminated the sample was removed and the leachate decanted into an analysis container. A volume of acid strip (2 volume % HNO_3) equal to the original volume of the leachant used was added to the vessel and it was re-sealed and placed into the oven at 90 °C for 18 hours. The vessel was then removed and that solution submitted for analysis.

An inductively coupled plasma mass spectrometer (ICP-MS) was used for the elemental analysis of all solutions from the test. The results for both the leachate analysis and the acid strip analysis are combined to give a value for the amount of material released during the test. The normalized mass loss (NML) was calculated for each element of interest (Fe, Cr, Ni, Zr, Pu, Np, U, Tc). The formula for calculating this quantity is given in eqn. (1).

(1) $NML(i) = (C_i \times V)/(S \times f_i)$

Where C_i is the concentration of the i^{th} element in solution, V is the volume of the solution, S is the surface area of the sample being tested and f_i is the mass fraction of that element in the solid sample.

The leachant used for the test was a simulated ground water (SJ-13) made with small additions of chemicals to demineralized water. Table I below contains the list of chemicals used to produce the simulated ground water.

Table I. The Chemical Composition of the Simulated Ground Water used for the Immersion Experiment.

Compound Added	Concentration (mg/L)
$NaHCO_3$	180
$KHCO_3$	14
$CaCl_2 \cdot 2H_2O$	14
$Ca(NO_3)_2 \cdot 4H_2O$	19
$CaSO_4 \cdot 2H_2O$	20
$MgSO_4 \cdot 7H_2O$	18
$SiO_2 \cdot H_2O$	84

RESULTS AND DISCUSSION

The intent of the test whose results are reported here was multi-fold. The standard high-level waste form for disposal into the Yucca Mountain repository is borosilicate glass [7]. All other waste foms are considered by the repository to be “non-standard”. A comparison between the non-standard waste forms, such as the metallic waste form, and borosilicate glass is required to establish whether or not they will perform as well as glass to retain radionuclides in the repository. This comparison must involve the results of models since that is the established manner to compare waste form behavior over the time span of interest to the repository (10,000 years). Comparison of individual test results for relatively short-term tests, such as those reported on here, is considered indicative, but insufficient to predict long-term behavior. Therefore the test results presented here for the metallic waste form provide two important pieces of information: 1) results that can be compared directly to those of borosilicate glass and 2) results that can be used to refine an existing corrosion model for the MWF. While it is certainly true that the corrosion mechanisms of borosilicate glass and the metallic waste form are different (congruent dissolution vs. metallic oxidation) the net result of radionuclide release to the

repository is the same. The radionuclides of greatest interest to the repository are those that exhibit the highest toxicity to humans [8]. For the MWF that includes Np and Tc. The release behavior of U and Pu is also of interest. To obtain information on the behavior of these radionuclides and the MWF for reasons discussed above several surrogate alloys were prepared and tested.

The target base composition for the MWF is stainless steel with 15 wt% zirconium (SS/15 Zr). To that base composition Np, Tc, U and Pu were added to obtain alloys for testing. The levels of the various radionuclides are in some cases exaggerated to aid in detection of released species (Pu and Np), although the levels of U and Tc employed are close to those anticipated in the actual MWF produced from irradiated cladding hulls.

The test employed is modeled after the ASTM C1220-98, MCC-1, which was originally intended for glass waste forms. The surface area of sample to volume of leachate was modified to 40 m^{-1} from 10 m^{-1} to make the solutions more concentrated for analysis. Earlier tests of a similar nature had indicated that the waste form was very robust and thus released very little material to solution [6]. Three duration tests (14, 34, 90 days) were performed with either triplicate or duplicate samples being utilized. The precision of the results presented here varied depending on the element but the one sigma precision was typically ±40% (percent relative standard deviation). The elements monitored in the test solution and the acid strip were: Fe, Cr, Ni, Zr, Pu, Np, U and Tc.

The normalized mass loss (NML) for each test is presented in figure 2 A-C. Several observations can be made upon examining the figure:

1) All elements are not released in a congruent fashion to the solution from the waste form. Cr and Zr are released in smaller quantities than any other element. U is released in much larger quantities than any other element.

2) Of the base alloy constituents (Fe, Ni, Cr, Zr), Fe is released in the greatest quantity.

3) The various dopants (U, Tc, Pu, Np) do not affect the release behavior of the base constituents (Fe, Cr, Ni, Zr) as these values appear relatively constant for the various alloys tested at each duration employed.

4) The elemental concentrations for all species determined here was less than 1 ppm in the test solution and the acid strip and thus not limited by solubility concerns.

5) No precipitates were observed in the test vessels.

6) The NML for Fe, approximately 5E-2 g/m^2 effectively bounds the release of all the elements released with the exception of uranium. The uranium NML is observed to be as high as 8E-1 g/m^2.

A comparison of NML for borosilicate waste glasses with those reported here for the metallic waste form can now be performed. This comparison will use values for simulated waste glasses

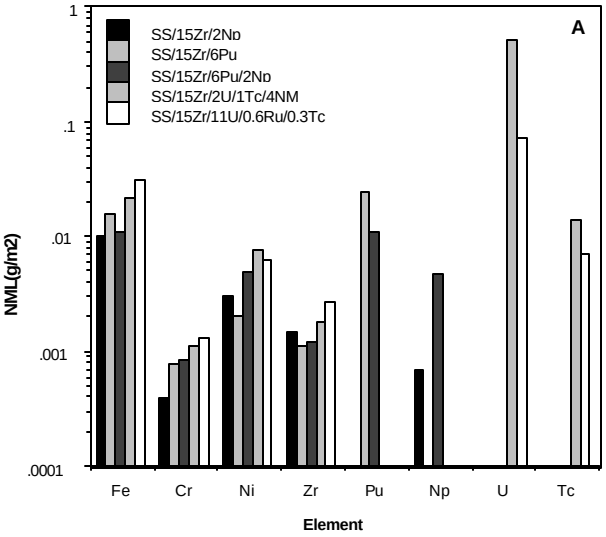
tested under similar but not identical conditions. The test temperature for the waste glass was 90°C, which is the same as that employed here. The S/V ratio was 10 m^{-1} , 40 m^{-1} was used for the MWF tests, and the duration is 28 days with a leachant of demineralized water. The duration of 28 days is similar to 34 days and that set of results will be used for the comparison. Simulated ground water should provide a more aggressive leachant than de-mineralized water. The values from ref.[2] are for three simulated waste glasses (ARM-1, PNL-76-68 and UK-209) and the elements analyzed for were B, Cs, Si and Sr. Table II contains the values from these three glasses.

Table II. MCC-1 Results of Several Simulated Waste Glasses from ref. [2]. Also included for comparison are selected results from the 34 day test on the samples of SS/15Zr/2U/1Tc/4NM.

NML (g/m^2)/Glass	ARM-1	PNL-76-68	UK-209	MWF
B	12.2	36.05	10.52	Fe-(2E-2)
Cs	8.23	27.75	9.54	Tc-(1.3E-4)
Si	9.33	23.91	9.54	Cr-(1E-3)
Sr	5.40	1.85	5.37	U-(2.8E-1)

As can be clearly seen, from Table II, the release from the metallic waste form is mush less than that for typical waste glasses. The difference is large enough to out-weigh any small variations in the test parameters.

The release of uranium at a higher level compared to the other constituents of the waste form is perplexing. The disposition of the uranium in the waste form has been studied in some detail by Keiser et al. [5] using scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS) and to a much lesser degree with transmission electron microscopy (TEM) and neutron diffraction. SEM/EDS was used to determine the elemental make-up of the alloy at the microstructural level, whereas TEM and neutron diffraction yielded information regarding the crystalline phases present. Uranium is known to reside in the intermetallic phase of the waste form, see Fig. 1. This phase also hosts the Np and Pu and some of the Tc [4,5]. The primary host phase for the Tc is the iron solid solution. Although uranium, neptunium and plutonium are contained in the intermetallic phase, their concentrations in that phase vary widely without explanation. For example, the concentration of the uranium in the intermetallic phase(s) has been shown to vary from 1.7 to 19.3 wt% U for the alloy containing 11 wt% U and from 3 to 12.2 wt% in the alloy containing 2 wt% U. Examination of the alloys containing Pu and Np has shown a similar tendency for these actinides to concentrate in the same regions as uranium. TEM and neutron diffraction were applied to alloys containing Tc and U but not to alloys containing Np and Pu. TEM analysis is currently underway for these alloys and may yield information that indicates a microstructural answer to explain these results [9].


A
SS/15Zr/2Nb
SS/15Zr/6Pu
SS/15Zr/6Pu/2Nb
SS/15Zr/2U/1Tc/4NM
SS/15Zr/11U/0.6Ru/0.3Tc
NML(g/m2)
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Fe
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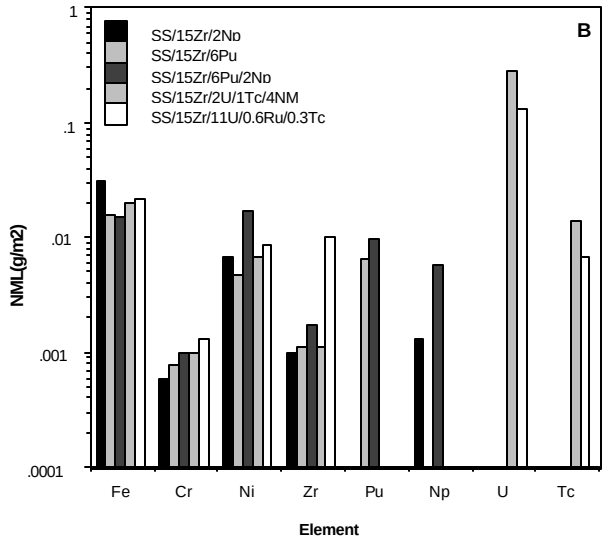
B
SS/15Zr/2Nb
SS/15Zr/6Pu
SS/15Zr/6Pu/2Nb
SS/15Zr/2U/1Tc/4NM
SS/15Zr/11U/0.6Ru/0.3Tc
NML(g/m2)
1
.1
.01
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Fe
Cr
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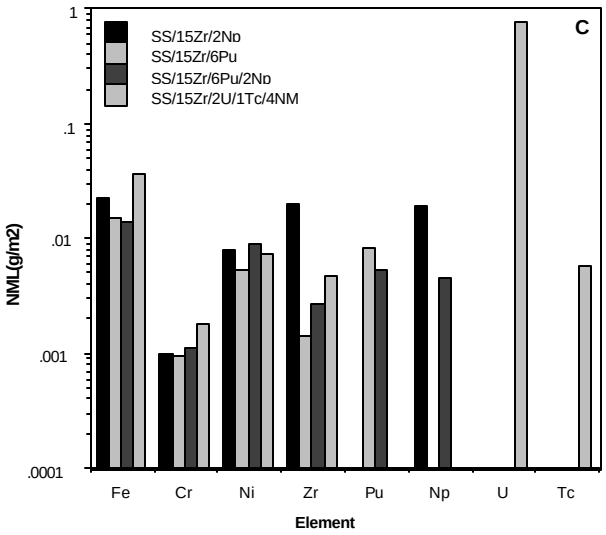

Figure 2. Results from Immersion Tests on Doped Metallic Waste Forms Samples. The test parameters were: S/V (40 m-1), T (90°C), SJ-13 water leachant, and duration A (14 days), B (34 days) and C (90 days).

CONCLUSIONS

Several samples of base composition SS/15 Zr doped with Tc, U, Np and Pu were subjected to static immersion tests with simulated ground water at 90 °C for 14, 34 and 90 days. The relative release characteristics were obtained. The release of iron was noted to bound all other elements with the exception of uranium. The iron release was typically 5E-2 g/m^2 or less while uranium was observed to be 8E-1 g/m^2 or less. In contrast, the NML of matrix constituents for borosilicate glass, the standard high-level waste form for the repository, is >1 g/m^2 under similar test conditions [2]. The anomalous behavior of uranium is most likely due to the formation of a minor phase or phases with differing release characteristics from the bulk. Additional experimental work is underway to establish the validity of this theory.

The results presented here achieve the two primary goals for this work: 1) a comparison of test results between the non-standard metallic waste form and borosilicate glass and 2) they provide a basis to revise the existing MWF corrosion model [3].

ACKNOWLEDGMENTS

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