

**MONITORING THE CONSISTENCY OF THE METALLIC WASTE FORM DERIVED
FROM ELECTROMETALLURGICAL PROCESSING**

by

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ABSTRACT

A metallic waste form alloy that consists primarily of stainless steel and zirconium is being developed by Argonne National Laboratory to contain metallic waste constituents that are residual from an electrometallurgical treatment process for spent nuclear fuel. An approach for monitoring the consistency of metallic waste forms (MWFs) is developed based on consideration of the intent of regulatory requirements, production method, measured physical and chemical properties of the MWF, and analytical capabilities. It is recommended that the Zr content of the MWF be measured and tracked to monitor consistency because the Zr content: (1) provides a measure of the amount of the $Zr(Fe,Ni,Cr)_{2+x}$ intermetallic phase, which sequesters the majority of radionuclides in the MWF and affects its physical robustness and (2) indicates that the desired Fe-Zr eutectic was obtained, which provides a direct indicator that the appropriate process conditions (time, temperature) were employed. It is recommended that the Zr content be measured by chemical analyses of drill shavings taken from the MWF products.

INTRODUCTION

Argonne National Laboratory has developed an electrometallurgical treatment (EMT) for conditioning sodium-bonded, spent nuclear fuel for disposal. This process uses an electrorefiner that is filled with LiCl-KCl molten salt electrolyte heated to 500°C. Chopped fuel segments are placed into baskets that serve as the anode for the EMT process. Radionuclides and other fuel components are electrolytically dissolved in the molten salt. Some elements in the fuel or cladding hulls are not dissolved during the EMT process; these are referred to as being noble with respect to the process. Uranium is deposited onto a cathode mandrel, while other radionuclides remain

either dissolved in the salt electrolyte or with the cladding hulls. A uranium product is produced from the material deposited on the cathode, and the ceramic waste form (CWF) and metal waste form (MWF) are produced from waste in the salt and anode baskets, respectively. The uranium recovered from the electrorefiner is down-blended to an enrichment below 20%. The CWF is a glass-bonded sodalite that contains fission products and actinides from the salt. The MWF is a stainless steel (SS)- zirconium (Zr) alloy comprised of the cladding hulls, noble metal fission products and actinides left at the anode, along with added Zr.

The consistency of the ceramic and metal waste forms must be monitored to ensure that acceptable waste forms are produced that can be disposed of in a geologic repository. According to the DOE Office of Civilian Radioactive Waste Management System (OCRWMS) Waste Acceptance System Requirements Document (WA-SRD) [1], the objective of monitoring product consistency is to ensure that the physical and chemical properties of each waste form satisfy acceptance criteria for disposal. The same test used for high-level waste (HLW) glasses, namely, the Product Consistency Test (PCT), will likely be proposed to DOE for monitoring the consistency of the CWF. Use of the PCT is recommended for the CWF because of the similarities in the physical nature and corrosion mechanisms of the CWF and HLW glass. The PCT is not feasible for the MWF because (1) the physical characteristics of the MWF make the preparation of finely divided samples used in the PCT impractical, (2) the corrosion mechanism of the MWF is significantly different from that of glass, and (3) application of the PCT to the MWF results in solutions that are too dilute to be analyzed reliably. Therefore, a different approach for monitoring the consistency has been developed to be applied to the MWF.

The objectives of monitoring product consistency and possible approaches for developing a product consistency test for the MWF are discussed in this paper. We first discuss the intent of the current product consistency requirements and the methods currently employed for measuring the product consistency of non-metallic waste forms. We then describe the characteristics of the MWF that have been measured to qualify the waste form for disposal in a repository and how they could be used to monitor product consistency. Finally, the specific characteristic to be measured for product consistency purposes will be recommended, along with how this characteristic can be measured.

DESCRIPTION AND CURRENT APPLICATION OF PRODUCT CONSISTENCY

As mentioned above, product consistency is monitored to ensure that the physical and chemical properties of each waste form meet acceptance requirements for disposal. In this context, consistent does not mean all waste forms will be identical. Rather, it means the physical and chemical properties of the waste forms will consistently be within the ranges defined for the intended (acceptable) product. The requirement of product consistency in the WA-SRD applies waste forms that result from a treatment process, such as vitrification. Product consistency requirements are not specified for commercial or U.S. government-owned spent nuclear fuel. The need to monitor consistency is especially important for waste forms such as high-level radioactive waste glasses that will have a wide range of composition variations. While the consistency of the MWF products will need to be addressed for qualification, the expectation that the composition of the metallic waste stream will remain essentially constant can be used to simplify the tracking of consistency of MWF products.

Before considering what would be appropriate and adequate product consistency methods for the MWF, it is instructive to evaluate the role that product consistency serves for high-level glass waste forms. This will also provide insight into the role of product consistency in the OCRWMS program. Of the various waste forms to be disposed in the repository, the need for product consistency is probably the greatest for HLW glasses. This is because of the wide range of waste glass compositions that will result from immobilization of various tank wastes at DOE facilities at the Savannah River, West Valley, Hanford, and Idaho sites. The compositions of different batches of glasses made at each site will

also vary because of significant variations in the waste compositions in the different tanks and even within an individual tank. Waste from one or more tanks will be mixed in a blending tank prior to vitrification to maximize waste loading. Vitrification of a particular waste stream feed is done by identifying a composition within a pre-determined composition envelope that is compatible with the waste stream composition and then blending the waste stream with added chemicals to achieve a glass melt with that targeted composition. The tank where the blending is performed is a quality assurance hold point in the vitrification process. The blended waste is not fed to the melter until chemical analysis verifies that the composition of the blended waste stream is within the acceptable composition envelope. The composition envelope identifies a range of glass compositions that meet processing requirements and waste acceptance criteria. The product consistency requirement for borosilicate glass waste forms, given in Section 4.2.3.1H of the WA-SRD, [1] states:

- “1. The Producer shall demonstrate control of waste form production by comparing production samples or process control information, separately or in combination to the Environmental Assessment benchmark glass using the Product Consistency Test or equivalent.
- 2 For acceptance, the mean concentrations of lithium, sodium, and boron in the leachate, after normalization for the concentrations in the glass, shall be less than those of the benchmark glass.”

The intent of this requirement is to ensure a consistent glass product by controlling the vitrification process. High-level waste glass producers meet this requirement with a combination of chemical analysis data from the final blending tank (process control information) and a statistical sampling plan that subjects samples of the glass to the Product Consistency Test. The requirement identifies the Environmental Assessment (EA) glass as a benchmark glass for chemical durability. The benchmark is used to ensure that the spectrum of waste glasses produced is bounded so that design of the waste packages for the repository can proceed with confidence, and the reactivity of waste glass and water is bounded so that conservative but realistic assessments of the engineered barrier system performance can be made. “Consistency is

necessary to reflect consideration for the waste package designs.” [2]

The crux of the product consistency requirement is the need to demonstrate control of production. Use of the Product Consistency Test and comparison with the EA glass is the recommended method (but not necessarily the required method) for demonstrating control of the vitrification process for HLW glasses. Reliance can be (and is) also placed on production records. Although comparison of the PCT response of the HLW glass with that of the EA glass provides a measure of the relative chemical durability of the HLW glass, that measure is relevant solely to product consistency and comparison of a potentially wide range of HLW glass compositions. It is not necessarily relevant to the actual chemical durability of the HLW glasses in the disposal system.

We do not plan to use the EA glass or any other standard material as a benchmark or standard for monitoring the consistency of MWF products. There is no need for a standard because, unlike the case of HLW glasses, the release of radionuclides is not sensitive to the composition of the MWF products within the processing range. The MWF will be monitored to ensure that all products are made within the specified processing range. As a part of qualification, we will show that the MWF is more chemically durable than both HLW glasses and the EA glass.

Possible Application of the Product Consistency Test to MWF

The ASTM C 1285 product consistency test has been applied to the MWF. Although the MWF is not amenable to crushing to isolate the -100 +200 mesh size fraction, tests similar to PCT were conducted using that size fraction of micromilled saw and drill shavings of MWF. [3] The microstructure of the filings and shavings were both shown to be consistent with the bulk microstructure. The repeatability of tests with MWF was poorer than that for tests with HLW glass. This was probably due to the higher analytical uncertainty for analysis of the very dilute test solutions.

Although it has been demonstrated that the PCT can be conducted with the MWF, it is not a practical method for tracking the consistency of the MWF products. It is unlikely that the PCT will be sufficiently sensitive to variations in the composition of the MWF to identify products with off-specification compositions. In addition, since the MWF and the EA glass have no major elements in common, the

measure of relative chemical durability provided by the PCT can at best be determined only indirectly.

There is a precedent for using a method other than the PCT to track the consistency of a waste form product. The DOE Fissile Materials Disposition Program (DOE/FMD) is developing the immobilized plutonium waste form (IPWF) for disposal of surplus and waste weapons plutonium. Although the product consistency requirement for the IPWF has not yet been specified, a place for one is reserved in Section 4.2.3.1.M(2) of the WA-SRD. The significance is that a placeholder exists for a method other than the method specified for HLW glass. The DOE/FMD program is currently evaluating the use of phase identification (by X-ray diffraction) and density to monitor IPWF product consistency [4]. These measures do not provide an indication of the chemical durability of the IPWF nor do they have any relationship with the EA glass. That the DOE/FMD program obtained agreement on an approach for qualification other than the PCT justifies consideration of physical rather than chemical characteristics to track the product consistency for the MWF. Our intent is to follow the approach taken to qualify the IPWF and leverage insight gained and agreements made within DOE based on similarities of these heterogeneous (multi-phase) waste forms, though not necessarily using the same testing or analysis methods. However, the DOE/FMD program has recently suspended testing operations in response to a budget cut, so further progress towards qualification of the IPWF is not expected until after OCRWM submits the license application for the disposal system. Our goal is to have provisions for the CWF and MWF included by DOE in the license application.

PRODUCTION, CHARACTERIZATION, AND TESTING OF THE METAL WASTE FORM

Production

The MWF is used to immobilize the metallic waste stream generated during electrometallurgical treatment in a waste form that is suitable for disposal in the federal high-level waste repository. The metal waste stream includes cladding hulls, fuel components and fission products that are not oxidized during treatment, as well as small amounts of residual salt. As a part of the treatment process, the residual salt waste that remains in the metallic waste stream will be distilled and removed as the metal waste form is melted and cast.

The metal waste stream will be placed in a crucible with added zirconium metal and depleted uranium and melted in an induction furnace to consolidate it into a monolithic, disk-shaped ingot 14 to 16 inches in diameter and 2 to 5 inches thick. The ingots will be placed in steel containers for later loading into a waste package canister.

Characterization

Depleted uranium and zirconium will be blended with the metal waste streams to produce MWFs with a consistent gross composition, phase assemblage, and microstructure. The composition and microstructure of the MWF is affected primarily by the mass ratio of stainless steel fuel cladding, which comprises about 98 mass % of the metal waste stream inventory, and Zr from the driver fuel. The blanket fuel cladding is Type 304L stainless steel and the driver fuel cladding includes Types 316, D9, and HT9 stainless steels. Additionally, the cladding or furnace environment introduces Fe, Cr, Ni, Mo, Mn, Co, Cu, V, and Si, and trace amounts of Sn, C, and S to the metal waste stream.

The control limits on the concentrations ranges are 0 - 11 mass % U and 5 - 20 mass % Zr, and the target concentrations are 10 mass % U and 15 mass % Zr. The upper limit to the range of U is based on criticality limits, which requires that the U-235 content be below 20 mass%. Depleted U will be added to the MWF charge to meet this requirement. The target of 10 mass% U (total in the MWF) accounts for the anticipated enrichment level in the waste stream and the depleted U that is added. However, the actual enrichment in the metallic waste stream will dictate the amount of depleted uranium that will be added and the total U content of the MWF. The range of Zr was selected to ensure all MWF ingots had the same phase assemblage and a generally consistent microstructure. The low end of the Zr range provides slightly more Zr than is needed to sequester noble metal fission products to account for the possibility of localized regions having lower than average Zr contents. The high end of the Zr range ensures that MWFs will contain an adequate portion of the stainless steel phase to ensure physical integrity. Compositions of some MWF ingots cast from actual irradiated cladding are listed in Table 1. Ingots 05, 06, and 07 were cast with driver fuel cladding, and ingot 08 was cast from blanket cladding.

Table 1. Chemical Analyses Results* for CD Samples From MWF Ingots CFMW05, CFMW06, CFMW07, and CFMW08.

Analyte	Units	Driver Fuel Cladding			Blanket Fuel Clad
		05	06	07	08
Total U	wt. %	9.34	2.36	0.93	4.96
Zr	wt. %	14.13	10.60	16.41	13.5
Fe	wt. %	45.00	61.88	57.34	61.3
Cr	wt. %	11.57	13.72	11.61	16.1
Ni	wt. %	7.48	11.73	13.21	8.6
Mo	wt. %	1.54	2.39	2.57	0.18
Mn	wt. %	1.05	1.69	1.75	1.2
Cd	ppm	110	ND***	18	ND
Y	ppm	23	4	68	45
Pd	wt. %	0.08	0.11	0.12	ND
Tc	wt. %	0.11	0.32	0.31	ND
Ru	wt. %	0.17	0.66	0.62	ND
Mn54	ppb	228	8.2	154	4.0
Co57	ppb	ND	ND	ND	ND
Co60	ppb	383	191	457	2851
Nb95	ppb	ND	ND	ND	ND
Ru106	ppb	3123	420	2999	26.1
Sb125	ppb	3212	2356	5600	31.1
Cs137	ppb	1425	44	ND	ND
Ce144	ppb	8.5	ND	5.2	ND
U234	% of U	0.65	0.67	0.54	0.05
U235	% of U	58.02	61.01	47.61	4.70
U236	% of U	2.12	2.11	1.55	0.16
U238	% of U	39.22	36.21	50.30	95.1
Np237	ppm	499	9	10	9
Total Pu	ppm	32	7	4	82

* Compositions are averages of multiple samples, where the agreement was good between the various samples (i.e., low standard deviations); the highest errors are associated with the Fe concentrations. ** ND: Not Detected (below detection limits); (Other elements looked for and not detected include: Li, K, Na, Nd, Ce, Zr95, Cs134, Eu154, Rh106, Eu155, and Ta182)

The amounts of U and Zr that are added will be weighed. Driver fuel is a U-10% Zr alloy, whereas blanket fuel is primarily U metal. For driver fuel, some Zr is left behind with the cladding after electrorefining.

Negligible Zr is left with the blanket cladding. Some U is left with both driver fuel and blanket fuel cladding.

Chemical analyses will be performed on a small number of cladding hulls taken from individual batches to determine the amounts of U and Zr left with the cladding hulls. This information will be used to determine the amounts of U and Zr that must be added. It is anticipated that the amounts of driver and blanket fuel cladding mixed for a batch will be adjusted to optimize the U content of the mixture rather than the Zr content. Production records generated during these measurements will be used in conjunction with a statistical sampling plan to verify the consistency of the MWF product. Based on casting experience to date, it is anticipated that the Zr concentration in each ingot of MWF can be controlled to within 1 wt% of the 15 wt% target.

Microstructure

The microstructure of the MWF has been investigated over a range of Zr contents from 0 to 90%. [5] The main phases observed in the alloy are the Fe solid solution phases ferrite (α -Fe) and austenite (γ -Fe), as well as the Laves intermetallic, $Zr(Fe,Cr,Ni)_{2+x}$. For MWF ingots with 5-20 wt% Zr, a eutectic microstructure is observed. This microstructure is observed no matter which cladding (HT9, 304SS, 316SS, or D9) is added to the waste form. Changing the type of cladding only affects the Cr, Ni, and Fe concentrations of the various phases, but not the types of phases that are present. The relative proportion of $Zr(Fe,Cr,Ni)_{2+x}$ increases with increasing zirconium content until ~42 wt% Zr, when the alloy is ~100% intermetallic.

The intermetallic phases are the primary hosts for radionuclides and noble metal fission products. In MWFs with no Zr, a complex mixture of stainless steel phases and phases rich in noble metals is formed. The presence of Zr results in the formation of the phase, $Zr(Fe,Cr,Ni)_{2+x}$, which sequesters noble metals and results in a simple microstructure. Although the chemical and physical durabilities of MWFs made with low Zr contents (or without Zr) may be acceptable for disposal, maintaining the same phase assemblages in all MWFs will simplify meeting the requirement to identify the phase assemblage specified in the WA-SRD. [WA-SRD-1999, Section 4.2.3.1.E.1]. Although this specification is written for HLW glass, it will likely also be a requirement for heterogeneous waste forms such as the MWF. This expectation is based on the fact that the WA-SRD

requires the Producer report the chemical and phase projection for the IPWF. [1]

Testing

Various mechanical properties of the MWF have been measured. Tensile, compression, impact, and microhardness tests have all been performed on alloys with a range of Zr contents. The major conclusions derived from these tests are listed as follows:

1. SS-15Zr alloys fail before yielding during the tensile tests; the failure stress (~270 MPa) is comparable to the yield strength for Type 316 stainless steel (SS316).
2. In compression, the yield strength increases and the failure strains decrease with increasing zirconium content. This occurs because the $Zr(Fe,Cr,Ni)_{2+x}$ content of the alloy increases with zirconium content.
3. The alloys fail in a brittle manner during Charpy V-notched impact tests and show little deformation.
4. The average microhardness of the as-cast SS-15Zr alloy is almost twice that of SS316. The hardness of the $Zr(Fe,Cr,Ni)_{2+x}$ intermetallic is more than three times that of SS316.

The thermophysical properties of MWF alloys with 5, 15, and 20 wt% Zr have been measured, including the density, the specific heat, the coefficient of thermal expansion, the thermal diffusivity, and the thermal conductivity at temperatures up to 900°C. The room temperature density of the SS-Zr alloys tested varied from 7.56 to 7.9 g/cm³. In general, alloy density decreased with increasing zirconium content, since the amount of $Zr(Fe,Cr,Ni)_{2+x}$ was increasing. This is because $Zr(Fe,Cr,Ni)_{2+x}$ has a lower density than stainless steel (7.45 versus 7.9). The addition of noble metal fission products (e.g., Nb, Pd, Ru, etc.) increases the density of alloys. The specific heat for the alloys with the three different Zr contents varied from ~0.45 J/gm-K to 0.7 J/gm-K as the temperature was increased from room temperature to ~1000°C. A peak in the curves was observed at 550°C due to a magnetic transition in the ferrite present in the alloys. Not much difference in thermal expansion was observed for SS-15Zr and SS-20Zr alloys. From 100°C to 900°C, the thermal expansion increased from $\sim 1.0 \times 10^{-5} K^{-1}$ to $\sim 1.2 \times 10^{-5} K^{-1}$. For the SS-5Zr alloy the values ranged from $\sim 1.4 \times 10^{-5} K^{-1}$ to $\sim 1.7 \times 10^{-5} K^{-1}$ for the same range in temperatures. The

measured thermal diffusivity for the SS-Zr alloys increased from $\sim 0.035 \text{ cm}^2/\text{s}$ to $\sim 0.055 \text{ cm}^2/\text{s}$ for temperatures increased from room temperature (RT) to $\sim 900^\circ\text{C}$. The thermal conductivity of the alloys increased from $\sim 0.12 \text{ W/cm-K}$ to $\sim 0.22 \text{ W/cm-K}$ as the temperature was increased from room temperature to $\sim 600^\circ\text{C}$.

Based on the physical property tests described above, it is evident that the MWF has density, thermal conductivity, coefficient of thermal expansion, and specific heat values that are comparable with those of SS316. The high thermal conductivity implies that the SS-Zr waste form alloys are capable of containing a significant quantity of radioactive (heat-generating) isotopes while maintaining a relatively even temperature distribution.

The chemical durability of the MWF has been measured using a variety of testing methods. These methods include static immersion, pulsed flow, electrochemical, and vapor hydration tests.

The static immersion test is based on Materials Characterization Center static leach test procedure (MCC-1). This test procedure was originally developed to evaluate the relative chemical durability of various waste forms and has recently been standardized by ASTM as method C1220 [6]. The MCC-1 test was itself based on tests used to study the weathering of rocks and minerals. The test involves immersing a monolithic sample in a static solution for an extended duration, at a fixed temperature. The MCC-1 tests with the MWF were conducted in simulated J-13 well water as well as other solutions. Changes in specimen mass and solution composition are evaluated after completion of a particular test. Sample surfaces are also examined using metallographic analysis to determine what types of corrosion products may have formed. It has been found that MWF alloys are very corrosion resistant both in simulated J-13 well water and deionized water. The corrosion behavior of the MWF is similar over the anticipated range of zirconium (5 to 20 wt%) and noble metal contents (0 to 4 wt%). The normalized losses of sample constituents in simulated J-13 and deionized water solutions are similar. [7] Although testing at 200°C increases alloy corrosion, the normalized losses are only marginally higher than those obtained from the 90°C tests.

The MWF has also been tested in static solutions using drill shavings of MWF, as mentioned earlier.

Test method ASTM C 1285, in which crushed samples are reacted in a static solution (e.g., deionized water) at a fixed test temperature (e.g., 90°C), was employed for testing the MWF. The extent of reaction of the MWF was too low for reliable measurement in these tests.

The pulsed-flow immersion test is similar to the static immersion test in that it involves exposing a monolithic sample to a fixed-temperature static solution for an extended time period. The main difference for the pulsed-flow test is that periodically some of the test solution is removed for analysis and replaced with fresh solution. The test provides a measure of elemental release into solution as a function of time. It was observed that the Tc and U releases from the metal samples were small (the normalized release rates based on Tc and U were both less than $0.005 \text{ g/m}^2\text{d}$). Uranium release rates were greater than those of Tc. Release rates for Tc were unaffected by minor variations in the alloy noble metal content. Uranium release rates were similar for alloys that contain 5, 15, and 20 wt% Zr. The Tc and U releases from the metal alloys occur slower than the U and Tc release from simulated high-level waste glass. [8]

The polarization resistance method [9] was used to measure the corrosion behavior of various alloy samples. These tests were conducted at several temperatures using a corrosion cell filled with distilled water or simulated J-13 well water adjusted to various values of pH. A potential was applied to the immersed MWF sample and the resulting current was measured using a potentiostat. Corrosion rates were calculated from the results of tests with MWF samples in different solutions and at different temperatures. The measured rates are accurate to within an order of magnitude of the true corrosion rates. These rates were consistent with the low corrosion rates observed for the MWF in the immersion tests. The alloys were corrosion-resistant even under highly aggressive test conditions, such as in pH=2 solution. The test results show that the MWF alloy exhibits corrosion resistance similar to that of candidate waste disposal container materials, such as Alloy C-22.

In the vapor hydration test (VHT) monolithic test samples are exposed to water vapor at high temperatures. This test method is used as an accelerated test to measure the chemical durability of glass waste forms. It has also been employed as a corrosion test for the MWF. The test is conducted by

suspending a disk-shaped monolith by a Teflon thread in a sealed stainless steel container that also contains a small pool of deionized water beneath the specimen. The sealed vessel is heated to the test temperature (typically 200°C for test with the MWF), causing the water to vaporize and create a saturated vapor environment. The amount of water added to the vessel is carefully controlled to prevent fluid dripping from the specimen. This keeps the dissolution products on the surface of the sample in a thin film of water, which becomes highly concentrated. Surface layers form as residual layers of leached material or precipitated alteration phases. The thickness of the surface reaction layer is measured at the conclusion of the test, and the amounts and natures of the secondary phases that form are identified. It was observed that the corrosion behavior of the MWF is similar to that of stainless steel in this test environment, and only a thin oxide layer is formed. The typical layer thickness formed during 182-day tests at 100°C was in the range of 0.1 μm to 0.5 μm for various MWF samples.

POSSIBLE ATTRIBUTES OF MWF FOR USE IN MEASURING PRODUCT CONSISTENCY

As described above, many of the physical and chemical properties of the MWF have been measured using small-scale samples. In order to track product consistency during production mode, a selected attribute of the MWF must be measured on large-scale ingots, on samples from large-scale ingots, or on a smaller ingot made in a similar fashion. The attribute should be one that has or reflects an impact on a physical, chemical, or radiological property that affects the performance of the MWF in the disposal system. A range of acceptable values for each of these properties will be identified in the waste form production specifications for the MWF. The product consistency test must be able to determine when a MWF product lies outside the range of acceptability.

In terms of physical properties, no obvious MWF attribute is available for measuring product consistency. The MWF is not required to have load-bearing capacity when inside a storage canister. The handling properties of the waste form will be important only during the manufacturing and packaging at the time of production. It is important that the waste form is never so brittle that it will fall apart during handling. Based on the measurements discussed above, the MWF has more than adequate physical properties. The only way these properties would be affected is if the Zr content of the waste form was too high, since

the physical robustness of the MWF has been shown to decrease once the MWF is comprised entirely of the Zr intermetallic phase. This occurs at Zr contents around 40 wt%. Restricting the Zr content to below 20 mass% will ensure that the MWF is physically robust.

The chemical durability of the MWF depends on the chemical durabilities of the steel and Zr intermetallic phases. The corrosion of these phases occurs mostly independently, and there is negligible feedback effect of constituents dissolved in the solution contacting the MWF. We expect that the least durable phase in the MWF will be used to bound the release of all radionuclides for performance assessment. In the case of the MWF, the radionuclides are more soluble than the primary components of the phases in which they are contained. Therefore, their release can be measured directly. This is in contrast to HLW glass and the CWF, for which the release of a nonradioactive matrix component (e.g., B or Si) is used as an upper bound for the release of radionuclides. Evidence to date suggests that U is the most soluble and readily released radionuclide in the MWF. The U is contained in the Zr intermetallic phase. Therefore, the release rate of U will likely be used as an upper bound for all radionuclides in the MWF for performance assessment purposes.

The requirement in the WA-SRD regarding the radionuclide inventory addresses the inventory for an individual canister. The distribution of radionuclides between phases must be known to meet requirements in section 4.2.3.1, subsections E and F, of the WA-SRD [1], and to identify what phases bound the release of radionuclides for modeling purposes.

USING THE ZR-CONTENT AS A MEASURE OF MWF PRODUCT CONSISTENCY

It may not be necessary to measure the concentrations of all components in the MWF. Determination of the U- and Zr-contents or only the Zr-content may be sufficient to assure processing was adequately controlled. The U-content is not expected to significantly affect the chemical or physical durability of the MWF, but the Zr-content is. This is because the Zr-content is crucial to the formation of the $Zr(Fe,Cr,Ni)_{2+x}$ intermetallic phase. Since the U in the MWF will be low-enrichment (<20% U-235) U, the U-content will not have a strong impact on the radiological properties of the MWF. Although the Zr-

content will not affect the radiological properties directly, it will affect the disposition of most radionuclides in the MWF and the rate at which they may be released. Therefore, the Zr-content is one of the most important aspects of the MWF because it impacts the chemical, physical, and radiological properties. Verification that the Zr-content of the MWF is within the process range provides the best measure of product consistency.

If the Zr concentration for a particular ingot is known to be within the range of 5 to 20 wt%, then the ingot will have a eutectic microstructure with two primary phases, viz. an Fe solid solution phase and a Zr intermetallic phase. This is based on the investigations described above that studied the SS-Zr system with varying Zr concentrations. Once the microstructure of the ingot is known to be eutectic and to consist of these two primary phases, then the chemical and physical properties of the ingot can be inferred, based on the testing described above for SS-Zr samples with varying compositions. As a result, once the microstructure of all of the ingots has been determined to be eutectic with $Zr(Fe,Cr,Ni)_{2+x}$ and Fe solid solution phase as the two primary phases then knowledge of the limited property ranges for that microstructure ensures that the WA-SRD requirement that “the physical and chemical properties of a waste form qualified for disposal are consistent for every waste package” will be met.

METHODS FOR MONITORING THE MWF COMPOSITION OR ZR CONTENT

A variety of approaches have been evaluated for measuring the Zr content of an ingot. These include X-ray fluorescence, hardness measurements, density measurements, X-ray diffraction (XRD), chemical analysis, measurement of the ferrite content, and general microstructural analysis. Each of these approaches is discussed in terms of its possible usefulness for measuring the Zr content of the final MWF product.

To perform some of these measurements, a small sample must be generated from a large ingot. Samples can be generated either when the alloy is still molten or after it has solidified. When the alloy is molten, a process known as injection-casting can be used to generate pin-samples; a specially equipped furnace is required for this process. Injection-cast samples can then be examined in the hot cell or transferred into the laboratory for analysis. For sampling solidified, large-scale ingots, drilling has

been employed to produce small shavings, and core-drilling has been used to generate cylindrical samples. These samples can then be handled like the injection-cast samples.

X-ray Fluorescence

X-ray fluorescence can be used to measure the Zr content of an as-cast MWF. However, it yields only the concentration of Zr near the surface because of the limited penetration depth (and escape depth) of X-rays. Surface slag would need to be removed and it would be necessary to demonstrate that the measured surface concentration is representative of the bulk composition. Although this can be done easily using small laboratory-scale samples, implementation as an in-cell technique would be difficult. For X-ray fluorescence to be a viable technique, the influence of a surface slag and possible contamination of the MWF by the casting crucible would need to be evaluated or minimized by sample preparation. In addition, the uniformity of the Zr concentration across the surface of the MWF and its relationship with the bulk distribution would need to be evaluated.

Hardness

The hardness of the MWF ingot can be measured. A correlation between hardness and Zr content is expected because the Zr intermetallic phases are much harder than the stainless steel phase(s). To prove the viability of this technique, it would need to be demonstrated that hardness is sufficiently sensitive to Zr concentration to be used diagnostically. Hardness could also be sensitive to other variations in the MWF composition, such as variations in the Mo content. Finally, unless a cross section of the MWF product is obtained (which may be impractical), hardness measurements would only determine the hardness of the MWF surface. The relationship of surface hardness to the bulk of the product would need to be evaluated.

Density

Analyses were conducted to determine if the density of an MWF product ingot is related to its Zr content. The densities of laboratory samples of SS-Zr alloys with different Zr contents have been measured. Helium pycnometry has been employed to provide a suitable volume measurement system that overcomes uncertainties introduced by the presence of shrinkage voids or other casting artifacts. Measurement of the densities of laboratory-scale MWF samples indicates the density is not sufficiently sensitive to Zr content for monitoring product consistency.

In situ X-ray Diffraction

X-ray diffraction measurements can be made *in situ* using the MWF itself or using a specimen cut or drilled from the bulk. The response will be sensitive to the near surface structure because of the shallow penetration depth of X-rays. As was the case for X-ray fluorescence, the surface slag would need to be removed prior to analysis and the surface structure may not be representative of the bulk MWF. In order for this technique to be useful, experimental verification using a range of surrogate MWF compositions would be needed to relate the XRD response to the $Zr(Fe,Cr,Ni)_{2+x}$ content of the MWF. Sampling to provide material from the interior of the MWF for X-ray diffraction analysis would require drilling or sectioning.

Microstructural Examination

Examination of the microstructure of an MWF ingot would provide a measure of the amount of intermetallic phases present in the ingot and the chemical composition could be measured using X-ray emission spectroscopy. However, acquisition of a specimen for examination would likely require even greater effort than that for chemical analysis, X-ray diffraction, or X-ray fluorescence. This is because care would be required to avoid altering the microstructure as the specimen is removed from the MWF, and sample preparation for subsequent analysis would be arduous and time consuming.

Chemical Analysis

Chemical analysis of the MWF ingots would provide a direct measurement of the Zr concentration (and other components). This approach requires drilling or cutting into the ingot to obtain an analytical sample, which could be in the form of a small section or a collection of drill shavings. For this technique to be useful, the effects of surface slag would need to be determined or minimized. In general, the slag layers that have been observed on the top surface of MWF ingots are only a few microns thick. An investigation has been performed to compare the compositions of drill shavings and core-drills for samples taken from the top, middle, and bottom of cross-sections of three SS-Zr alloy ingots. Additionally, a drill was used to produce shavings that could be used for chemical analysis. The drill shavings came from the bottom surface of the ingot to avoid the slag layer that is present on the top of the ingot. To avoid any surface contamination that may be present on the bottom of the ingot, a one-half inch hole was drilled into the ingot before shavings were collected for chemical

analysis. No statistically significant differences were observed between the measured elemental composition of the turning samples and the samples obtained from the top, middle, and bottom regions of each ingot. Therefore, chemical analysis of drill shavings will be representative of the bulk MWF.

FINAL RECOMMENDATIONS

The intent of the Product Consistency requirement in the WA-SRD is to ensure that the production of waste forms was adequately controlled so that the chemical, physical, and radiological properties of all waste forms will meet qualification requirements. In the case of HLW glasses, the wide range of glass compositions requires verification that the glass composition matches the target composition and that the glass has an acceptable chemical durability. The compositions of MWF products will not vary significantly and process control can be demonstrated almost entirely using production records. The PCT used to track the consistency of HLW glasses is not considered to be an appropriate test for tracking the consistency of the MWF because of the low solubilities of the major components in the MWF and the difficulty of sample preparation.

It is recommended that the Zr-content be tracked as a measure of product consistency and process control. The Zr-content will be measured intermittently in the cladding hull feed stream to confirm values predicted by computer models. The amount of added Zr can be used to calculate the minimum Zr-content in the MWF. The lower Zr limit (5 mass%) ensures that there is a sufficient volume of the $Zr(Fe,Cr,Ni)_{2+x}$ intermetallic phase to sequester the radionuclides. This is important to meet the requirement of phase identification as well as chemical durability. Drill shavings can be taken for each ingot to provide a check of the Zr content. Chemical analyses can be performed on the shavings to provide a very accurate measurement of the MWF composition, which can be related to the microstructure. This in turn tells us the physical, chemical, and radiological properties of the produced waste forms are as intended. Coupled with the data base for MWF samples evaluated during waste form development, chemical analysis will provide sufficient information to ensure that the physical, chemical, and microstructural properties of the MWF are acceptable and to monitor product consistency.

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MONITORING THE CONSISTENCY OF THE METALLIC WASTE FORM DERIVED FROM ELECTROMETALLURGICAL PROCESSING

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ABSTRACT

A metallic waste form alloy that consists primarily of stainless steel and zirconium is being developed by Argonne National Laboratory to contain metallic waste constituents that are residual from an electrometallurgical treatment process for spent nuclear fuel. An approach for monitoring the consistency of metallic waste forms (MWFs) is developed based on consideration of the intent of regulatory requirements, production method, measured physical and chemical properties of the MWF, and analytical capabilities. It is recommended that the Zr content of the MWF be measured and tracked to monitor consistency because the Zr content: (1) provides a measure of the amount of the $Zr(Fe,Ni,Cr)_{2+x}$ intermetallic phase, which sequesters the majority of radionuclides in the MWF and affects its physical robustness and (2) indicates that the desired Fe-Zr eutectic was obtained, which provides a direct indicator that the appropriate process conditions (time, temperature) were employed. It is recommended that the Zr content be measured by chemical analyses of drill shavings taken from the MWF products.

INTRODUCTION

Argonne National Laboratory has developed an electrometallurgical treatment (EMT) for conditioning sodium-bonded, spent nuclear fuel for disposal. This process uses an electrorefiner that is filled with LiCl-KCl molten salt electrolyte heated to 500°C. Chopped fuel segments are placed into baskets that serve as the anode for the EMT process. Radionuclides and other fuel components are electrolytically dissolved in the molten salt. Some elements in the fuel or cladding hulls are not dissolved during the EMT process; these are referred to as being noble with respect to the process. Uranium is deposited onto a cathode mandrel, while other radionuclides remain

either dissolved in the salt electrolyte or with the cladding hulls. A uranium product is produced from the material deposited on the cathode, and the ceramic waste form (CWF) and metal waste form (MWF) are produced from waste in the salt and anode baskets, respectively. The uranium recovered from the electrorefiner is down-blended to an enrichment below 20%. The CWF is a glass-bonded sodalite that contains fission products and actinides from the salt. The MWF is a stainless steel (SS)- zirconium (Zr) alloy comprised of the cladding hulls, noble metal fission products and actinides left at the anode, along with added Zr.

The consistency of the ceramic and metal waste forms must be monitored to ensure that acceptable waste forms are produced that can be disposed of in a geologic repository. According to the DOE Office of Civilian Radioactive Waste Management System (OCRWMS) Waste Acceptance System Requirements Document (WA-SRD) [1], the objective of monitoring product consistency is to ensure that the physical and chemical properties of each waste form satisfy acceptance criteria for disposal. The same test used for high-level waste (HLW) glasses, namely, the Product Consistency Test (PCT), will likely be proposed to DOE for monitoring the consistency of the CWF. Use of the PCT is recommended for the CWF because of the similarities in the physical nature and corrosion mechanisms of the CWF and HLW glass. The PCT is not feasible for the MWF because (1) the physical characteristics of the MWF make the preparation of finely divided samples used in the PCT impractical, (2) the corrosion mechanism of the MWF is significantly different from that of glass, and (3) application of the PCT to the MWF results in solutions that are too dilute to be analyzed reliably. Therefore, a different approach for monitoring the consistency has been developed to be applied to the MWF.

The objectives of monitoring product consistency and possible approaches for developing a product consistency test for the MWF are discussed in this paper. We first discuss the intent of the current product consistency requirements and the methods currently employed for measuring the product consistency of non-metallic waste forms. We then describe the characteristics of the MWF that have been measured to qualify the waste form for disposal in a repository and how they could be used to monitor product consistency. Finally, the specific characteristic to be measured for product consistency purposes will be recommended, along with how this characteristic can be measured.

DESCRIPTION AND CURRENT APPLICATION OF PRODUCT CONSISTENCY

As mentioned above, product consistency is monitored to ensure that the physical and chemical properties of each waste form meet acceptance requirements for disposal. In this context, consistent does not mean all waste forms will be identical. Rather, it means the physical and chemical properties of the waste forms will consistently be within the ranges defined for the intended (acceptable) product. The requirement of product consistency in the WA-SRD applies waste forms that result from a treatment process, such as vitrification. Product consistency requirements are not specified for commercial or U.S. government-owned spent nuclear fuel. The need to monitor consistency is especially important for waste forms such as high-level radioactive waste glasses that will have a wide range of composition variations. While the consistency of the MWF products will need to be addressed for qualification, the expectation that the composition of the metallic waste stream will remain essentially constant can be used to simplify the tracking of consistency of MWF products.

Before considering what would be appropriate and adequate product consistency methods for the MWF, it is instructive to evaluate the role that product consistency serves for high-level glass waste forms. This will also provide insight into the role of product consistency in the OCRWMS program. Of the various waste forms to be disposed in the repository, the need for product consistency is probably the greatest for HLW glasses. This is because of the wide range of waste glass compositions that will result from immobilization of various tank wastes at DOE facilities at the Savannah River, West Valley, Hanford, and Idaho sites. The compositions of different batches of glasses made at each site will

also vary because of significant variations in the waste compositions in the different tanks and even within an individual tank. Waste from one or more tanks will be mixed in a blending tank prior to vitrification to maximize waste loading. Vitrification of a particular waste stream feed is done by identifying a composition within a pre-determined composition envelope that is compatible with the waste stream composition and then blending the waste stream with added chemicals to achieve a glass melt with that targeted composition. The tank where the blending is performed is a quality assurance hold point in the vitrification process. The blended waste is not fed to the melter until chemical analysis verifies that the composition of the blended waste stream is within the acceptable composition envelope. The composition envelope identifies a range of glass compositions that meet processing requirements and waste acceptance criteria. The product consistency requirement for borosilicate glass waste forms, given in Section 4.2.3.1H of the WA-SRD, [1] states:

- “1. The Producer shall demonstrate control of waste form production by comparing production samples or process control information, separately or in combination to the Environmental Assessment benchmark glass using the Product Consistency Test or equivalent.

- 3 For acceptance, the mean concentrations of lithium, sodium, and boron in the leachate, after normalization for the concentrations in the glass, shall be less than those of the benchmark glass.”

The intent of this requirement is to ensure a consistent glass product by controlling the vitrification process. High-level waste glass producers meet this requirement with a combination of chemical analysis data from the final blending tank (process control information) and a statistical sampling plan that subjects samples of the glass to the Product Consistency Test. The requirement identifies the Environmental Assessment (EA) glass as a benchmark glass for chemical durability. The benchmark is used to ensure that the spectrum of waste glasses produced is bounded so that design of the waste packages for the repository can proceed with confidence, and the reactivity of waste glass and water is bounded so that conservative but realistic assessments of the engineered barrier system performance can be made. “Consistency is

necessary to reflect consideration for the waste package designs.” [2]

The crux of the product consistency requirement is the need to demonstrate control of production. Use of the Product Consistency Test and comparison with the EA glass is the recommended method (but not necessarily the required method) for demonstrating control of the vitrification process for HLW glasses. Reliance can be (and is) also placed on production records. Although comparison of the PCT response of the HLW glass with that of the EA glass provides a measure of the relative chemical durability of the HLW glass, that measure is relevant solely to product consistency and comparison of a potentially wide range of HLW glass compositions. It is not necessarily relevant to the actual chemical durability of the HLW glasses in the disposal system.

We do not plan to use the EA glass or any other standard material as a benchmark or standard for monitoring the consistency of MWF products. There is no need for a standard because, unlike the case of HLW glasses, the release of radionuclides is not sensitive to the composition of the MWF products within the processing range. The MWF will be monitored to ensure that all products are made within the specified processing range. As a part of qualification, we will show that the MWF is more chemically durable than both HLW glasses and the EA glass.

Possible Application of the Product Consistency Test to MWF

The ASTM C 1285 product consistency test has been applied to the MWF. Although the MWF is not amenable to crushing to isolate the -100 +200 mesh size fraction, tests similar to PCT were conducted using that size fraction of micromilled saw and drill shavings of MWF. [3] The microstructure of the filings and shavings were both shown to be consistent with the bulk microstructure. The repeatability of tests with MWF was poorer than that for tests with HLW glass. This was probably due to the higher analytical uncertainty for analysis of the very dilute test solutions.

Although it has been demonstrated that the PCT can be conducted with the MWF, it is not a practical method for tracking the consistency of the MWF products. It is unlikely that the PCT will be sufficiently sensitive to variations in the composition of the MWF to identify products with off-specification compositions. In addition, since the MWF and the EA glass have no major elements in common, the

measure of relative chemical durability provided by the PCT can at best be determined only indirectly.

There is a precedent for using a method other than the PCT to track the consistency of a waste form product. The DOE Fissile Materials Disposition Program (DOE/FMD) is developing the immobilized plutonium waste form (IPWF) for disposal of surplus and waste weapons plutonium. Although the product consistency requirement for the IPWF has not yet been specified, a place for one is reserved in Section 4.2.3.1.M(2) of the WA-SRD. The significance is that a placeholder exists for a method other than the method specified for HLW glass. The DOE/FMD program is currently evaluating the use of phase identification (by X-ray diffraction) and density to monitor IPWF product consistency [4]. These measures do not provide an indication of the chemical durability of the IPWF nor do they have any relationship with the EA glass. That the DOE/FMD program obtained agreement on an approach for qualification other than the PCT justifies consideration of physical rather than chemical characteristics to track the product consistency for the MWF. Our intent is to follow the approach taken to qualify the IPWF and leverage insight gained and agreements made within DOE based on similarities of these heterogeneous (multi-phase) waste forms, though not necessarily using the same testing or analysis methods. However, the DOE/FMD program has recently suspended testing operations in response to a budget cut, so further progress towards qualification of the IPWF is not expected until after OCRWM submits the license application for the disposal system. Our goal is to have provisions for the CWF and MWF included by DOE in the license application.

PRODUCTION, CHARACTERIZATION, AND TESTING OF THE METAL WASTE FORM

Production

The MWF is used to immobilize the metallic waste stream generated during electrometallurgical treatment in a waste form that is suitable for disposal in the federal high-level waste repository. The metal waste stream includes cladding hulls, fuel components and fission products that are not oxidized during treatment, as well as small amounts of residual salt. As a part of the treatment process, the residual salt waste that remains in the metallic waste stream will be distilled and removed as the metal waste form is melted and cast.

The metal waste stream will be placed in a crucible with added zirconium metal and depleted uranium and melted in an induction furnace to consolidate it into a monolithic, disk-shaped ingot 14 to 16 inches in diameter and 2 to 5 inches thick. The ingots will be placed in steel containers for later loading into a waste package canister.

Characterization

Depleted uranium and zirconium will be blended with the metal waste streams to produce MWFs with a consistent gross composition, phase assemblage, and microstructure. The composition and microstructure of the MWF is affected primarily by the mass ratio of stainless steel fuel cladding, which comprises about 98 mass % of the metal waste stream inventory, and Zr from the driver fuel. The blanket fuel cladding is Type 304L stainless steel and the driver fuel cladding includes Types 316, D9, and HT9 stainless steels. Additionally, the cladding or furnace environment introduces Fe, Cr, Ni, Mo, Mn, Co, Cu, V, and Si, and trace amounts of Sn, C, and S to the metal waste stream.

The control limits on the concentrations ranges are 0 - 11 mass % U and 5 - 20 mass % Zr, and the target concentrations are 10 mass % U and 15 mass % Zr. The upper limit to the range of U is based on criticality limits, which requires that the U-235 content be below 20 mass%. Depleted U will be added to the MWF charge to meet this requirement. The target of 10 mass% U (total in the MWF) accounts for the anticipated enrichment level in the waste stream and the depleted U that is added. However, the actual enrichment in the metallic waste stream will dictate the amount of depleted uranium that will be added and the total U content of the MWF. The range of Zr was selected to ensure all MWF ingots had the same phase assemblage and a generally consistent microstructure. The low end of the Zr range provides slightly more Zr than is needed to sequester noble metal fission products to account for the possibility of localized regions having lower than average Zr contents. The high end of the Zr range ensures that MWFs will contain an adequate portion of the stainless steel phase to ensure physical integrity. Compositions of some MWF ingots cast from actual irradiated cladding are listed in Table 1. Ingots 05, 06, and 07 were cast with driver fuel cladding, and ingot 08 was cast from blanket cladding.

Table 1. Chemical Analyses Results* for CD Samples From MWF Ingots CFMW05, CFMW06, CFMW07, and CFMW08.

Analyte	Units	Driver Fuel Cladding			Blanket Fuel Clad
		05	06	07	08
Total U	wt. %	9.34	2.36	0.93	4.96
Zr	wt. %	14.13	10.60	16.41	13.5
Fe	wt. %	45.00	61.88	57.34	61.3
Cr	wt. %	11.57	13.72	11.61	16.1
Ni	wt. %	7.48	11.73	13.21	8.6
Mo	wt. %	1.54	2.39	2.57	0.18
Mn	wt. %	1.05	1.69	1.75	1.2
Cd	ppm	110	ND***	18	ND
Y	ppm	23	4	68	45
Pd	wt. %	0.08	0.11	0.12	ND
Tc	wt. %	0.11	0.32	0.31	ND
Ru	wt. %	0.17	0.66	0.62	ND
Mn54	ppb	228	8.2	154	4.0
Co57	ppb	ND	ND	ND	ND
Co60	ppb	383	191	457	2851
Nb95	ppb	ND	ND	ND	ND
Ru106	ppb	3123	420	2999	26.1
Sb125	ppb	3212	2356	5600	31.1
Cs137	ppb	1425	44	ND	ND
Ce144	ppb	8.5	ND	5.2	ND
U234	% of U	0.65	0.67	0.54	0.05
U235	% of U	58.02	61.01	47.61	4.70
U236	% of U	2.12	2.11	1.55	0.16
U238	% of U	39.22	36.21	50.30	95.1
Np237	ppm	499	9	10	9
Total Pu	ppm	32	7	4	82

* Compositions are averages of multiple samples, where the agreement was good between the various samples (i.e., low standard deviations); the highest errors are associated with the Fe concentrations. ** ND: Not Detected (below detection limits); (Other elements looked for and not detected include: Li, K, Na, Nd, Ce, Zr95, Cs134, Eu154, Rh106, Eu155, and Ta182)

The amounts of U and Zr that are added will be weighed. Driver fuel is a U-10% Zr alloy, whereas blanket fuel is primarily U metal. For driver fuel, some Zr is left behind with the cladding after electrorefining.

Negligible Zr is left with the blanket cladding. Some U is left with both driver fuel and blanket fuel cladding.

Chemical analyses will be performed on a small number of cladding hulls taken from individual batches to determine the amounts of U and Zr left with the cladding hulls. This information will be used to determine the amounts of U and Zr that must be added. It is anticipated that the amounts of driver and blanket fuel cladding mixed for a batch will be adjusted to optimize the U content of the mixture rather than the Zr content. Production records generated during these measurements will be used in conjunction with a statistical sampling plan to verify the consistency of the MWF product. Based on casting experience to date, it is anticipated that the Zr concentration in each ingot of MWF can be controlled to within 1 wt% of the 15 wt% target.

Microstructure

The microstructure of the MWF has been investigated over a range of Zr contents from 0 to 90%. [5] The main phases observed in the alloy are the Fe solid solution phases ferrite (α -Fe) and austenite (γ -Fe), as well as the Laves intermetallic, $Zr(Fe,Cr,Ni)_{2+x}$. For MWF ingots with 5-20 wt% Zr, a eutectic microstructure is observed. This microstructure is observed no matter which cladding (HT9, 304SS, 316SS, or D9) is added to the waste form. Changing the type of cladding only affects the Cr, Ni, and Fe concentrations of the various phases, but not the types of phases that are present. The relative proportion of $Zr(Fe,Cr,Ni)_{2+x}$ increases with increasing zirconium content until ~42 wt% Zr, when the alloy is ~100% intermetallic.

The intermetallic phases are the primary hosts for radionuclides and noble metal fission products. In MWFs with no Zr, a complex mixture of stainless steel phases and phases rich in noble metals is formed. The presence of Zr results in the formation of the phase, $Zr(Fe,Cr,Ni)_{2+x}$, which sequesters noble metals and results in a simple microstructure. Although the chemical and physical durabilities of MWFs made with low Zr contents (or without Zr) may be acceptable for disposal, maintaining the same phase assemblages in all MWFs will simplify meeting the requirement to identify the phase assemblage specified in the WA-SRD. [WA-SRD-1999, Section 4.2.3.1.E.1]. Although this specification is written for HLW glass, it will likely also be a requirement for heterogeneous waste forms such as the MWF. This expectation is based on the fact that the WA-SRD

requires the Producer report the chemical and phase projection for the IPWF. [1]

Testing

Various mechanical properties of the MWF have been measured. Tensile, compression, impact, and microhardness tests have all been performed on alloys with a range of Zr contents. The major conclusions derived from these tests are listed as follows:

5. SS-15Zr alloys fail before yielding during the tensile tests; the failure stress (~270 MPa) is comparable to the yield strength for Type 316 stainless steel (SS316).
6. In compression, the yield strength increases and the failure strains decrease with increasing zirconium content. This occurs because the $Zr(Fe,Cr,Ni)_{2+x}$ content of the alloy increases with zirconium content.
7. The alloys fail in a brittle manner during Charpy V-notched impact tests and show little deformation.
8. The average microhardness of the as-cast SS-15Zr alloy is almost twice that of SS316. The hardness of the $Zr(Fe,Cr,Ni)_{2+x}$ intermetallic is more than three times that of SS316.

The thermophysical properties of MWF alloys with 5, 15, and 20 wt% Zr have been measured, including the density, the specific heat, the coefficient of thermal expansion, the thermal diffusivity, and the thermal conductivity at temperatures up to 900°C. The room temperature density of the SS-Zr alloys tested varied from 7.56 to 7.9 g/cm³. In general, alloy density decreased with increasing zirconium content, since the amount of $Zr(Fe,Cr,Ni)_{2+x}$ was increasing. This is because $Zr(Fe,Cr,Ni)_{2+x}$ has a lower density than stainless steel (7.45 versus 7.9). The addition of noble metal fission products (e.g., Nb, Pd, Ru, etc.) increases the density of alloys. The specific heat for the alloys with the three different Zr contents varied from ~0.45 J/gm-K to 0.7 J/gm-K as the temperature was increased from room temperature to ~1000°C. A peak in the curves was observed at 550°C due to a magnetic transition in the ferrite present in the alloys. Not much difference in thermal expansion was observed for SS-15Zr and SS-20Zr alloys. From 100°C to 900°C, the thermal expansion increased from $\sim 1.0 \times 10^{-5} \text{ K}^{-1}$ to $\sim 1.2 \times 10^{-5} \text{ K}^{-1}$. For the SS-5Zr alloy the values ranged from $\sim 1.4 \times 10^{-5} \text{ K}^{-1}$ to $\sim 1.7 \times 10^{-5} \text{ K}^{-1}$ for the same range in temperatures. The

measured thermal diffusivity for the SS-Zr alloys increased from $\sim 0.035 \text{ cm}^2/\text{s}$ to $\sim 0.055 \text{ cm}^2/\text{s}$ for temperatures increased from room temperature (RT) to $\sim 900^\circ\text{C}$. The thermal conductivity of the alloys increased from $\sim 0.12 \text{ W/cm-K}$ to $\sim 0.22 \text{ W/cm-K}$ as the temperature was increased from room temperature to $\sim 600^\circ\text{C}$.

Based on the physical property tests described above, it is evident that the MWF has density, thermal conductivity, coefficient of thermal expansion, and specific heat values that are comparable with those of SS316. The high thermal conductivity implies that the SS-Zr waste form alloys are capable of containing a significant quantity of radioactive (heat-generating) isotopes while maintaining a relatively even temperature distribution.

The chemical durability of the MWF has been measured using a variety of testing methods. These methods include static immersion, pulsed flow, electrochemical, and vapor hydration tests.

The static immersion test is based on Materials Characterization Center static leach test procedure (MCC-1). This test procedure was originally developed to evaluate the relative chemical durability of various waste forms and has recently been standardized by ASTM as method C1220 [6]. The MCC-1 test was itself based on tests used to study the weathering of rocks and minerals. The test involves immersing a monolithic sample in a static solution for an extended duration, at a fixed temperature. The MCC-1 tests with the MWF were conducted in simulated J-13 well water as well as other solutions. Changes in specimen mass and solution composition are evaluated after completion of a particular test. Sample surfaces are also examined using metallographic analysis to determine what types of corrosion products may have formed. It has been found that MWF alloys are very corrosion resistant both in simulated J-13 well water and deionized water. The corrosion behavior of the MWF is similar over the anticipated range of zirconium (5 to 20 wt%) and noble metal contents (0 to 4 wt%). The normalized losses of sample constituents in simulated J-13 and deionized water solutions are similar. [7] Although testing at 200°C increases alloy corrosion, the normalized losses are only marginally higher than those obtained from the 90°C tests.

The MWF has also been tested in static solutions using drill shavings of MWF, as mentioned earlier.

Test method ASTM C 1285, in which crushed samples are reacted in a static solution (e.g., deionized water) at a fixed test temperature (e.g., 90°C), was employed for testing the MWF. The extent of reaction of the MWF was too low for reliable measurement in these tests.

The pulsed-flow immersion test is similar to the static immersion test in that it involves exposing a monolithic sample to a fixed-temperature static solution for an extended time period. The main difference for the pulsed-flow test is that periodically some of the test solution is removed for analysis and replaced with fresh solution. The test provides a measure of elemental release into solution as a function of time. It was observed that the Tc and U releases from the metal samples were small (the normalized release rates based on Tc and U were both less than $0.005 \text{ g/m}^2\text{d}$). Uranium release rates were greater than those of Tc. Release rates for Tc were unaffected by minor variations in the alloy noble metal content. Uranium release rates were similar for alloys that contain 5, 15, and 20 wt% Zr. The Tc and U releases from the metal alloys occur slower than the U and Tc release from simulated high-level waste glass. [8]

The polarization resistance method [9] was used to measure the corrosion behavior of various alloy samples. These tests were conducted at several temperatures using a corrosion cell filled with distilled water or simulated J-13 well water adjusted to various values of pH. A potential was applied to the immersed MWF sample and the resulting current was measured using a potentiostat. Corrosion rates were calculated from the results of tests with MWF samples in different solutions and at different temperatures. The measured rates are accurate to within an order of magnitude of the true corrosion rates. These rates were consistent with the low corrosion rates observed for the MWF in the immersion tests. The alloys were corrosion-resistant even under highly aggressive test conditions, such as in pH=2 solution. The test results show that the MWF alloy exhibits corrosion resistance similar to that of candidate waste disposal container materials, such as Alloy C-22.

In the vapor hydration test (VHT) monolithic test samples are exposed to water vapor at high temperatures. This test method is used as an accelerated test to measure the chemical durability of glass waste forms. It has also been employed as a corrosion test for the MWF. The test is conducted by

suspending a disk-shaped monolith by a Teflon thread in a sealed stainless steel container that also contains a small pool of deionized water beneath the specimen. The sealed vessel is heated to the test temperature (typically 200°C for test with the MWF), causing the water to vaporize and create a saturated vapor environment. The amount of water added to the vessel is carefully controlled to prevent fluid dripping from the specimen. This keeps the dissolution products on the surface of the sample in a thin film of water, which becomes highly concentrated. Surface layers form as residual layers of leached material or precipitated alteration phases. The thickness of the surface reaction layer is measured at the conclusion of the test, and the amounts and natures of the secondary phases that form are identified. It was observed that the corrosion behavior of the MWF is similar to that of stainless steel in this test environment, and only a thin oxide layer is formed. The typical layer thickness formed during 182-day tests at 100°C was in the range of 0.1 μm to 0.5 μm for various MWF samples.

POSSIBLE ATTRIBUTES OF MWF FOR USE IN MEASURING PRODUCT CONSISTENCY

As described above, many of the physical and chemical properties of the MWF have been measured using small-scale samples. In order to track product consistency during production mode, a selected attribute of the MWF must be measured on large-scale ingots, on samples from large-scale ingots, or on a smaller ingot made in a similar fashion. The attribute should be one that has or reflects an impact on a physical, chemical, or radiological property that affects the performance of the MWF in the disposal system. A range of acceptable values for each of these properties will be identified in the waste form production specifications for the MWF. The product consistency test must be able to determine when a MWF product lies outside the range of acceptability.

In terms of physical properties, no obvious MWF attribute is available for measuring product consistency. The MWF is not required to have load-bearing capacity when inside a storage canister. The handling properties of the waste form will be important only during the manufacturing and packaging at the time of production. It is important that the waste form is never so brittle that it will fall apart during handling. Based on the measurements discussed above, the MWF has more than adequate physical properties. The only way these properties would be affected is if the Zr content of the waste form was too high, since

the physical robustness of the MWF has been shown to decrease once the MWF is comprised entirely of the Zr intermetallic phase. This occurs at Zr contents around 40 wt%. Restricting the Zr content to below 20 mass% will ensure that the MWF is physically robust.

The chemical durability of the MWF depends on the chemical durabilities of the steel and Zr intermetallic phases. The corrosion of these phases occurs mostly independently, and there is negligible feedback effect of constituents dissolved in the solution contacting the MWF. We expect that the least durable phase in the MWF will be used to bound the release of all radionuclides for performance assessment. In the case of the MWF, the radionuclides are more soluble than the primary components of the phases in which they are contained. Therefore, their release can be measured directly. This is in contrast to HLW glass and the CWF, for which the release of a nonradioactive matrix component (e.g., B or Si) is used as an upper bound for the release of radionuclides. Evidence to date suggests that U is the most soluble and readily released radionuclide in the MWF. The U is contained in the Zr intermetallic phase. Therefore, the release rate of U will likely be used as an upper bound for all radionuclides in the MWF for performance assessment purposes.

The requirement in the WA-SRD regarding the radionuclide inventory addresses the inventory for an individual canister. The distribution of radionuclides between phases must be known to meet requirements in section 4.2.3.1, subsections E and F, of the WA-SRD [1], and to identify what phases bound the release of radionuclides for modeling purposes.

USING THE ZR-CONTENT AS A MEASURE OF MWF PRODUCT CONSISTENCY

It may not be necessary to measure the concentrations of all components in the MWF. Determination of the U- and Zr-contents or only the Zr-content may be sufficient to assure processing was adequately controlled. The U-content is not expected to significantly affect the chemical or physical durability of the MWF, but the Zr-content is. This is because the Zr-content is crucial to the formation of the Zr(Fe,Cr,Ni)_{2+x} intermetallic phase. Since the U in the MWF will be low-enrichment (<20% U-235) U, the U-content will not have a strong impact on the radiological properties of the MWF. Although the Zr-

content will not affect the radiological properties directly, it will affect the disposition of most radionuclides in the MWF and the rate at which they may be released. Therefore, the Zr-content is one of the most important aspects of the MWF because it impacts the chemical, physical, and radiological properties. Verification that the Zr-content of the MWF is within the process range provides the best measure of product consistency.

If the Zr concentration for a particular ingot is known to be within the range of 5 to 20 wt%, then the ingot will have a eutectic microstructure with two primary phases, viz. an Fe solid solution phase and a Zr intermetallic phase. This is based on the investigations described above that studied the SS-Zr system with varying Zr concentrations. Once the microstructure of the ingot is known to be eutectic and to consist of these two primary phases, then the chemical and physical properties of the ingot can be inferred, based on the testing described above for SS-Zr samples with varying compositions. As a result, once the microstructure of all of the ingots has been determined to be eutectic with $Zr(Fe,Cr,Ni)_{2+x}$ and Fe solid solution phase as the two primary phases then knowledge of the limited property ranges for that microstructure ensures that the WA-SRD requirement that “the physical and chemical properties of a waste form qualified for disposal are consistent for every waste package” will be met.

METHODS FOR MONITORING THE MWF COMPOSITION OR ZR CONTENT

A variety of approaches have been evaluated for measuring the Zr content of an ingot. These include X-ray fluorescence, hardness measurements, density measurements, X-ray diffraction (XRD), chemical analysis, measurement of the ferrite content, and general microstructural analysis. Each of these approaches is discussed in terms of its possible usefulness for measuring the Zr content of the final MWF product.

To perform some of these measurements, a small sample must be generated from a large ingot. Samples can be generated either when the alloy is still molten or after it has solidified. When the alloy is molten, a process known as injection-casting can be used to generate pin-samples; a specially equipped furnace is required for this process. Injection-cast samples can then be examined in the hot cell or transferred into the laboratory for analysis. For sampling solidified, large-scale ingots, drilling has

been employed to produce small shavings, and core-drilling has been used to generate cylindrical samples. These samples can then be handled like the injection-cast samples.

X-ray Fluorescence

X-ray fluorescence can be used to measure the Zr content of an as-cast MWF. However, it yields only the concentration of Zr near the surface because of the limited penetration depth (and escape depth) of X-rays. Surface slag would need to be removed and it would be necessary to demonstrate that the measured surface concentration is representative of the bulk composition. Although this can be done easily using small laboratory-scale samples, implementation as an in-cell technique would be difficult. For X-ray fluorescence to be a viable technique, the influence of a surface slag and possible contamination of the MWF by the casting crucible would need to be evaluated or minimized by sample preparation. In addition, the uniformity of the Zr concentration across the surface of the MWF and its relationship with the bulk distribution would need to be evaluated.

Hardness

The hardness of the MWF ingot can be measured. A correlation between hardness and Zr content is expected because the Zr intermetallic phases are much harder than the stainless steel phase(s). To prove the viability of this technique, it would need to be demonstrated that hardness is sufficiently sensitive to Zr concentration to be used diagnostically. Hardness could also be sensitive to other variations in the MWF composition, such as variations in the Mo content. Finally, unless a cross section of the MWF product is obtained (which may be impractical), hardness measurements would only determine the hardness of the MWF surface. The relationship of surface hardness to the bulk of the product would need to be evaluated.

Density

Analyses were conducted to determine if the density of an MWF product ingot is related to its Zr content. The densities of laboratory samples of SS-Zr alloys with different Zr contents have been measured. Helium pycnometry has been employed to provide a suitable volume measurement system that overcomes uncertainties introduced by the presence of shrinkage voids or other casting artifacts. Measurement of the densities of laboratory-scale MWF samples indicates the density is not sufficiently sensitive to Zr content for monitoring product consistency.

In situ X-ray Diffraction

X-ray diffraction measurements can be made *in situ* using the MWF itself or using a specimen cut or drilled from the bulk. The response will be sensitive to the near surface structure because of the shallow penetration depth of X-rays. As was the case for X-ray fluorescence, the surface slag would need to be removed prior to analysis and the surface structure may not be representative of the bulk MWF. In order for this technique to be useful, experimental verification using a range of surrogate MWF compositions would be needed to relate the XRD response to the $Zr(Fe,Cr,Ni)_{2+x}$ content of the MWF. Sampling to provide material from the interior of the MWF for X-ray diffraction analysis would require drilling or sectioning.

Microstructural Examination

Examination of the microstructure of an MWF ingot would provide a measure of the amount of intermetallic phases present in the ingot and the chemical composition could be measured using X-ray emission spectroscopy. However, acquisition of a specimen for examination would likely require even greater effort than that for chemical analysis, X-ray diffraction, or X-ray fluorescence. This is because care would be required to avoid altering the microstructure as the specimen is removed from the MWF, and sample preparation for subsequent analysis would be arduous and time consuming.

Chemical Analysis

Chemical analysis of the MWF ingots would provide a direct measurement of the Zr concentration (and other components). This approach requires drilling or cutting into the ingot to obtain an analytical sample, which could be in the form of a small section or a collection of drill shavings. For this technique to be useful, the effects of surface slag would need to be determined or minimized. In general, the slag layers that have been observed on the top surface of MWF ingots are only a few microns thick. An investigation has been performed to compare the compositions of drill shavings and core-drills for samples taken from the top, middle, and bottom of cross-sections of three SS-Zr alloy ingots. Additionally, a drill was used to produce shavings that could be used for chemical analysis. The drill shavings came from the bottom surface of the ingot to avoid the slag layer that is present on the top of the ingot. To avoid any surface contamination that may be present on the bottom of the ingot, a one-half inch hole was drilled into the ingot before shavings were collected for chemical

analysis. No statistically significant differences were observed between the measured elemental composition of the turning samples and the samples obtained from the top, middle, and bottom regions of each ingot. Therefore, chemical analysis of drill shavings will be representative of the bulk MWF.

FINAL RECOMMENDATIONS

The intent of the Product Consistency requirement in the WA-SRD is to ensure that the production of waste forms was adequately controlled so that the chemical, physical, and radiological properties of all waste forms will meet qualification requirements. In the case of HLW glasses, the wide range of glass compositions requires verification that the glass composition matches the target composition and that the glass has an acceptable chemical durability. The compositions of MWF products will not vary significantly and process control can be demonstrated almost entirely using production records. The PCT used to track the consistency of HLW glasses is not considered to be an appropriate test for tracking the consistency of the MWF because of the low solubilities of the major components in the MWF and the difficulty of sample preparation.

It is recommended that the Zr-content be tracked as a measure of product consistency and process control. The Zr-content will be measured intermittently in the cladding hull feed stream to confirm values predicted by computer models. The amount of added Zr can be used to calculate the minimum Zr-content in the MWF. The lower Zr limit (5 mass%) ensures that there is a sufficient volume of the $Zr(Fe,Cr,Ni)_{2+x}$ intermetallic phase to sequester the radionuclides. This is important to meet the requirement of phase identification as well as chemical durability. Drill shavings can be taken for each ingot to provide a check of the Zr content. Chemical analyses can be performed on the shavings to provide a very accurate measurement of the MWF composition, which can be related to the microstructure. This in turn tells us the physical, chemical, and radiological properties of the produced waste forms are as intended. Coupled with the data base for MWF samples evaluated during waste form development, chemical analysis will provide sufficient information to ensure that the physical, chemical, and microstructural properties of the MWF are acceptable and to monitor product consistency.

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