Measurement and Calculation of Radionuclide Activities in Savannah River Site High Level Waste Sludge for Acceptance of Defense Waste Processing Facility Glass in a Federal Repository - 9399

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ABSTRACT

This paper describes the results of the analyses of High Level Waste (HLW) sludge slurry samples and of the calculations necessary to decay the radionuclides to meet the reporting requirement in the Waste Acceptance Product Specifications (WAPS) [1]. The concentrations of 45 radionuclides were measured. The results of these analyses provide input for radioactive decay calculations used to project the radionuclide inventory at the specified index years, 2015 and 3115. This information is necessary to complete the Production Records at Savannah River Site's Defense Waste Processing Facility (DWPF) so that the final glass product resulting from Macrobatch 5 (MB5) can eventually be submitted to a Federal Repository.

Five of the necessary input radionuclides for the decay calculations could not be measured directly due to their low concentrations and/or analytical interferences. These isotopes are Nb-93m, Pd-107, Cd-113m, Cs-135, and Cm-248. Methods for calculating these species from concentrations of appropriate other radionuclides will be discussed. Also the average age of the MB5 HLW had to be calculated from decay of Sr-90 in order to predict the initial concentration of Nb-93m. As a result of the measurements and calculations, thirty-one WAPS reportable radioactive isotopes were identified for MB5. The total activity of MB5 sludge solids will decrease from 1.6E+04 μCi (1 μCi = 3.7E+04 Bq) per gram of total solids in 2008 to 2.3E+01 μCi per gram of total solids in 3115, a decrease of approximately 700 fold.

Finally, evidence will be given for the low observed concentrations of the radionuclides Tc-99, I-129, and Sm-151 in the HLW sludges. These radionuclides were reduced in the MB5 sludge slurry to a fraction of their expected production levels due to SRS processing conditions.

INTRODUCTION

The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) just completed immobilizing the High Level Waste (HLW) sludge from Macrobatch 5 (MB5) into a borosilicate glass for eventual disposal in a Federal Repository. A macrobatch is nominally 1.5 million liters or approximately 400,000 gallons of slurry and takes one to two years to process. A series of Waste Acceptance Product Specifications (WAPS) [1] have been formulated for acceptance of the glass at a future repository. One of these requires that the "Producer shall report the inventory of radionuclides (in Curies [1 Ci = 3.7E+10 Bq]) that have half-lives longer than 10 years and that are, or will be, present in concentrations greater than 0.05 percent of the total inventory for each waste type indexed to the years 2015 and 3115." As part of the strategy to meet this requirement, the DWPF reports for each macrobatch all radionuclides with half-lives greater than 10 years that have concentrations greater than 0.01 percent of the total inventory from the time of production through the 1100 year index period. In order to meet this requirement, sludge slurry samples from MB5 were submitted to the Savannah River National Laboratory (SRNL).

EXPERIMENTAL

Tank Sampling

A three liter sample of a well-mixed SRS Tank 40 was received at the SRNL Shielded Cells Facility. The sample was transferred to a high-density polyethylene bottle, settled overnight, and the resulting supernate employed to rinse the original sampler of any remaining solids. The final 3-L sample was subsampled to obtain a more manageable analytical sample.

General Analytical Methods

Aliquots of the samples were dissolved remotely in the facility and submitted for radioactive analyses. Two digestion methods were employed: hot aqua regia in sealed Teflon vessels and an alkali fusion with $NaOH/Na_2O_2$ in Zr crucibles. Details of these digestion methods have been described elsewhere [2]. The digestions were performed in quadruplicate. A reference glass standard referred to as ARG-1 [3] was dissolved along with the samples to ensure the completeness and reproducibility of each digestion method. Dilute aliquots of each digestion were removed from the cells for analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and various counting techniques.

Direct Measurement Methods

ICP-MS

Inductively coupled plasma – mass spectrometry (ICP-MS) was employed to analyze separate sub-samples of the aqua regia digestions of MB5 dried solids. Measurements were first converted to weight percents on a dried solids basis and then converted to activities using the specific activity of each isotope taken from References 4 and 12. The isotopes obtained from direct ICP-MS measurements included: Zr-93, Tc-99, Sm-151, Th-232, U-233, U-234, U-235, U-236, Np-237, U-238, Pu-239, Pu-240, and Pu-242.

Gamma Counting

Gamma Pulse Height Analysis (PHA) was performed on separate sub-samples of the alkali fusion digestions of MB5 dried solids. Detectors were carefully calibrated with known standards. Since detection efficiencies for gamma-rays vary with energy, they were determined for these specific radionuclide energies during the calibration process. The counting geometry was established during calibration and carefully duplicated for these measurements. Samples were diluted as necessary to achieve accurate counting. The isotopes obtained from Gamma PHA counting included: Co-60, Cs-137, Eu-154, and Eu-155.

Liquid Scintillation Counting

Liquid scintillation counting was performed on separate sub-samples of the alkali fusion digestions of MB5 dried solids. The scintillation cocktail used for the analysis was Ultima Gold AB since it is specifically formulated for alpha-beta discrimination and is the best choice for samples dissolved in mineral acids. Measurements were performed on one of three Packard Instruments which automatically correct for quenching and many other interference problems commonly associated with liquid scintillation counting. This method was used to determine total beta activity. Diluted aliquots of digested slurry were analyzed for 10 minutes. Diluted aliquots of digested slurry were also spiked with an alpha standard and analyzed for 10 minutes to measure and correct for any alpha//beta discrimination cross-talk issues.

Separation Measurement Methods

These analytical methods involved separation techniques that enabled radionuclides that were at low concentrations to be measured more accurately and to determine more reliable and lower detection limits for the radionuclides that had concentrations so low that they could not be detected. These techniques are now SRNL procedures and will only be summarized here. Aliquots of the alkali fusions or the aqua

regia dissolutions were analyzed along with blanks. In all cases, the activity in the blanks did not contribute any significant activity to the radionuclides being analyzed.

Ni-59/-63 Method

This separation is based on isolation of Ni from the dissolved sludge using a column containing dimethylglyoxime as an extractant that is specific for Ni. Each of the solutions resulting from the alkali fusions of the four samples of dried sludge slurry was spiked with a stable Ni carrier to trace the Ni separation and was then passed through a column containing the above extractant. The absorbed Ni was then eluted from each column. The Ni-59 was measured in the eluted solutions by its characteristic X-rays and Ni-63 by its beta particles. Total Ni in each eluted solution was measured by ICP-AES. The radiochemical Ni analyses were corrected for the Ni carrier recoveries as measured by ICP-AES.

Se-79 Method

Four aliquots of wet sludge slurry were spiked with a known amount of stable Se as a carrier. The samples were digested with concentrated nitric acid. The Fe in the dissolutions was reduced to Fe (II) using ascorbic acid to ensure it would not interfere with subsequent decontamination steps designed to extract Y-90, the lanthanides and the actinides from the Se traced dissolutions. The dissolutions were then treated with resins (Bio-Rad AMP-1, Eichrom Sr, RE, and Actinide resins) to reduce levels of Sr-90, Cs-137, Y-90, the lanthanides and the actinides to levels low enough to allow for their removal from the Shielded Cells. The Se traced dissolutions were then further decontaminated with a Bio-Rad AMP-1, Eichrom Sr and RE resin treatment. The total Se was reduced to Se metal using titanium (III) chloride, hydroxylamine hydrochloride, and ascorbic acid. The precipitated Se metal was then washed repeatedly with deionized water and dilute nitric acid. The Se metal was then dissolved with concentrated HBr, and the resulting $SeBr_4$ was extracted by solvent-solvent extraction using a tri-butyl phosphate/n-paraffin solvent extraction system. The Se was back extracted from the solvent. Aliquots of the purified Se fraction were then analyzed. A portion was neutron activated in a Cf-252 neutron source at SRNL to determine the total amount of Se present in order to calculate the recovery of Se from the radiochemical separation. A second portion was counted by liquid scintillation to determine the Se-79 beta activity. The yields of the stable Se carrier were applied to the Se-79 beta activity result to determine Se-79 activities in the sample aliquots initially treated.

Sr-90 Method

Aliquots of each sample from the alkali fusions were spiked with a stable Sr carrier, and a stable Ce carrier. The Sr carrier was used for separation yielding purposes and the Ce carrier was used to enhance the separation rates of undesirable isotopes such as Y-90, the lanthanides or the actinides. The spiked sample aliquots were initially oxidized using nitric acid. The Sr in the samples was extracted using commercially available Sr extraction resin. This resin also extracts some of the Pu under the conditions used to extract the Sr. The Pu was washed from the resin using an oxalic acid/nitric acid mixture. The Sr was eluted from the resin, and the resulting solution concentrated. A portion of the purified Sr solution was neutron activated in a Cf-252 neutron activation facility at SRNL to determine the total Sr and in order to calculate the fraction of Sr isolated by the procedure. A second portion of each of the Sr fractions was stored for five to seven days to allow Y-90 to grow in. Each fraction was then counted by liquid scintillation analysis to determine the Y-90 activity. The Sr-90 beta activity in each case was calculated from the Y-90 activity. The yields of the stable Sr carriers were applied to the Sr-90 beta activity results to determine Sr-90 activities in the original aliquots of the solutions resulting from the dissolution of the dried sludge slurry samples.

Gamma Counting Following Cs-137 Removal

This method was used to determine Ru-106, Sb-125, Ba-133, Ce-144, Sn-121m, Sn-126 and Am-241. These gamma emitters could not be determined directly because of the high Cs-137 activity in the

samples. Consequently the Cs-137 was removed. Aliquots of each of the four alkali fusions were treated with two batch additions of an ammonium phosphomolybdate resin to selectively remove the Cs-137 from the aliquots. This allowed gammas for isotopes at low concentrations to be detected or allowed lower detection limits to be determined for those isotopes that were not detected. The Cs-137 decontaminated aliquots were then gamma counted in two different detectors. The first was a high purity coaxial germanium detector to detect the gamma rays from Ru-106, Sb-125, Ba-133, Ce-144, Sn-126, and Am-241. Only Sb-125 and Am-241 were detected. Because of their low concentrations, the other isotopes were not detected. To obtain reliable and lower detection limits for these radionuclides, each of the solutions was counted for 27.8 hours. The detection limits were used to calculate the maximum activity of each for input to the projection calculations. Of this group of radionuclides, only Sn-126 has a half-life greater than 10 years. Even though the others have half-lives less than 10 years, their activities were included to calculate the total Curies present in SB3 at the selected decay times. The second detector was a Be thin window, semi-planar, high purity germanium detector. This detector has a high counting efficiency for low energy gamma rays (37.2 keV) that are used to measure Sn-121m. The Sn-121m concentration was so low that it was not detected. Again to obtain a reliable low detection limit, each of the four aliquots was counted for 13.9 hours.

I-129 Method

The radionuclide I-129 is a long-lived beta emitting fission product ($t_{1/2}$ = 1.6E+07 years) that is in SRS wastes. Four aliquots of wet sludge slurry were spiked with a known amount of stable KI to act as an iodine tracer/carrier. The samples were digested with 8M nitric acid. The iodate/iodine in the samples was reduced with sodium sulfite to minimize losses of iodine in the Shielded Cells Facility I-129 procedure. The Fe in the dissolutions was reduced to Fe (II) using ascorbic acid to ensure it would not interfere with subsequent decontamination steps designed to extract Y-90, the lanthanides and the actinides from the KI traced dissolutions. The dissolutions were then treated with resins (Bio-Rad AMP-1, Eichrom Sr, RE, and Actinide resins) to reduce levels of Sr-90, Cs-137, Y-90, the lanthanides and the actinides. The traced samples were then rendered caustic, treated a second time with a sodium sulfite reduction, and filtered to ensure Sr-90 and Y-90 levels were reduced low enough to allow for sample removal from the Shielded Cells. The samples were decontaminated a final time with a resin treatment to remove Cs-137 and the actinide elements. The solution was then treated with $AgNO_3$ in order to precipitate the iodide ion as AgI. The precipitate was analyzed by low energy gamma spectroscopy to determine the amount of I-129 present. I-129 is detected by its characteristic gamma and x-ray emissions. The precipitate was then neutron activated in a Cf-252 neutron source at SRNL to determine the total amount of iodine present in order to calculate the recovery of I-129 in the radiochemical separation.

Pu-238/-241 Method

Pu-241 is a beta-emitting Pu isotope that cannot be measured directly in the dissolved dried sludge slurry solutions because of its low concentration. Pu-241 has a relatively short half-life (15 years). Its concentration, along with that for Pu-238, was determined by isolating the Pu from each solution by a thenoyltrifluoroacetone extraction procedure. The extracted Pu was then analyzed by beta and alpha counting to determine the ratio of beta activity from Pu-241 to the alpha activity from the other isotopes of Pu (Pu-238, Pu-239, Pu-240, and Pu-242). In the original dissolution solutions, the total alpha activity from the Pu isotopes was determined by alpha counting and ICP-MS. Knowing the total alpha activity from Pu in the solutions resulting from the extraction allows the concentration of Pu-241 in the original dissolution solutions to be calculated using the beta/alpha ratio determined in the extracted solution. In the extracted solution, the alpha counting technique also gives the alpha counts due specifically to Pu-238 so that the total amount of Pu-238 can be determined. The activities of these two radionuclides were then used in the calculations to determine the reportable radionuclides.

Am/Cm Method

This method was used for Am-241, Am-242m, Cm-242, Am-243, Cm-243, Cm-244, Cm-245, Cm-246, Cm-247, Bk-247, Cf-249, Cf-250, and Cf-251. These radionuclides are neutron activation products produced in the SRS reactors. These isotopes are difficult to measure because of their low concentrations in the sludge slurry and the dilutions necessary to get the dissolved slurry samples out of the Shielded Cells. Of these isotopes, the Am-241 can be easily and accurately analyzed directly by long term gamma counting of the dissolved sludge (see Gamma Counting method). For the other radionuclides listed above, a separation method has been has developed by SRNL for isolating Am, Cm, Bk and Cf from a wet sludge slurry solution. The slurry is digested in the Shielded Cells Facility with concentrated nitric acid. The actinides are then extracted from the dissolution using a commercially available ion exchange resin (Eichrom RE). As Y-90 co-extracts with the trivalent actinides on RE resin, the treated samples were held in the Shielded Cells Facility for two weeks to allow the Y-90 to decay. The solutions were purified further with a second RE resin extraction followed by an Eichrom Ln resin extraction. The Am, Cm, Bk, and Cf extracts were then analyzed by alpha and low energy gamma counting techniques as well as by ICP-MS. The radionuclides Cm-242, Am-242m, and Cm-244 were measured by alpha spectroscopy, Am-241, Am-243, Cm-243, Cm-245, Cm-247, Bk-247, Cf-249, and Cf-251 were measured by low energy gamma spectroscopy, and Cm-246 was measured by ICP-MS. The fraction of each actinide element isolated by this ion exchange technique was determined by comparing the measured concentrations of Am-241 in the eluted solutions with their respective concentration in the original dissolved slurry that was measured by direct gamma counting of Cs-137 removed aliquots of the dissolved slurry.

By using this technique, the radionuclides Cm-242, Am-242m, Am-243, Cm-244, and Cm-246 were detected and measured along with the Am-241. All the other radionuclides had concentrations below the detection limit of the analytical methods. These radionuclides were Cm-243, Cm-245, Cm-247, Bk-247, Cf-249, and Cf-251. For these, the detection limits were then used as the maximum concentrations or activities that could be present. The activity of Cf-250 in the input for the calculations was set identical to that of Cm-242 since the latter bounds the Cf isotope's alpha particle energy at 6.0 MeV.

Sm-151/Pm-147 Method

Aliquots of each sample from the alkali fusions were spiked with a stable Sm carrier. The Sm carrier was used for separation yielding purposes. The spiked sample aliquots were initially oxidized using nitric acid. The Sm and Pm along with other trivalent species in the samples were extracted using Eichrom RE resin. The Sm and Pm where then extracted from the other radionuclides present using Eichrom Ln resin. A portion of the purified Pm/Sm solution was neutron activated in a Cf-252 neutron activation facility at SRNL to determine the total Sm and in order to calculate the fraction of Sm isolated by the procedure. A second portion of each of the Pm/Sm fractions was then counted by liquid scintillation analysis to determine the Pm-147 and Sm-151 activity. The Pm-147 measurement was conducted using a higher energy beta window which was free of any interference from the low energy Sm-151 beta. The Sm-151 beta result is corrected for any Pm-147 events occurring in its beta counting window when necessary. The yields of the stable Sm carriers were applied to the Sm-151 and the Pm-147 beta activity results to determine Sm-151 and Pm-147 activities in the original aliquots of the solutions resulting from the dissolution of the dried sludge slurry samples. A Pm-147 spiked sample was run through the process to monitor and correct for any slight differences in the chemical recoveries of Sm and Pm.

Calculated Activities of the Remaining Radionuclides

Nb-93m

The radionuclide Nb-93m ($t_{1/2}$ = 16.1 years) [6] is in SRS HLW as the decay product of the radioactive fission product Zr-93 ($t_{1/2}$ = 1.53E+06 years). For previous macrobatches both the Zr-93 and Nb-93m became reportable after the waste was ~100 years old [15,16,17]. The concentration of Nb-93m during MB5 vitrification can be calculated if the age of the sludge and the concentration of Zr-93 are known.

The age of the waste can be calculated from the measured concentration at mass 90 that is composed of Sr-90 ($t_{1/2}$ = 28.5 years) and its daughter Y-90 ($t_{1/2}$ = 2.67 days) that decays to stable Zr-90. The radionuclide Sr-90 is the initial long lived radioactive product of the isobaric decay chain at mass 90. In the ICP-MS analysis of the aqua regia dissolutions of the MB5 total solids, the concentration at mass 90 which is composed of Sr-90, Y-90, and Zr-90 was 0.0118 wt%. The concentration of Sr-90 determined by radioactive counting was 0.00530 wt% (see Sr-90 method). Thus the fraction of Sr-90 that remained in this sludge is 0.449. With the half-life of Sr-90 and standard equation for radioactive decay [5], the age of the sludge can be calculated. The result is 33 years.

The concentration of Zr-93 in MB5 measured by ICP-MS is 0.0105 wt%. Because of the large difference in the half-lives of Zr-93 and its radioactive daughter Nb-93m, these radionuclides are in secular equilibrium. Consequently, the initial concentration (wt%) of Nb-93m as input to the decay calculations can be calculated from the age of the waste and radioactive decay equation for two radionuclides that are in secular equilibrium as shown in Equation 5-4 on page 130 in Reference 5.

Pd-107

The noble metal Pd-107 is a pure beta emitter with a very long half-life (6.5E+06 years). This radionuclide could not be detected in the MB5 dissolved dried slurry samples by ICP-MS due to the presence of natural silver. Natural Ag contains the isotope Ag-107, which interferes with the measurement of Pd-107. The concentration of Pd-105 could be measured in the solutions thus the concentration of Pd-107 was calculated from the concentration of Pd-105. This was done by multiplying the ratio of the product of the fission yields and masses for Pd-107 and Pd-105 by the measured wt% for Pd-105 as determined by ICP-MS.

Cd-113m

With a half life of 13.7 years and specific activity of 217 Ci/g [4], Cd-133m may also qualify as a WAPS reportable radionuclide. However, Cd-113m primarily decays by beta emission and thus would require a careful separation technique to measure in sludge slurry. Also, the determination of Cd-113m by ICP-MS of the dissolved dried solids is essentially impossible because of the presence of natural Cd in the sludge. Natural Cd is 12.3 % Cd-113 with its half-life is greater than 1.1E+11 years [6]. This makes its activity negligible at all times [7]. Finally, the fission yield of Cd-113m is very small, 1.66E-04% [8], and thus its concentration is expected to be very small in the HLW sludge.

An upper limit of the mass concentration of Cd-113m can be estimated by using the fission yield scaling factor (FYSF) [9]. The FYSF relates the concentration of a fission product in the total sludge solids to the fission yield and the atomic mass of that fission product. The atomic mass of that isotope has to be included in the equation because fission yields are given in terms of atoms produced per 100 fissions of U-235 and not in terms of mass percent of the isotope produced. The equation for the concentration in weight percent is then:

$$\text{Concentration (wt\%)} = \text{FYSF (fission yield} \times \text{atomic mass)} \quad (1)$$

Thus the FYSF for each measured isotope can be calculated from:

$$FYSF_i = wt\%_i / (fy_i \times am_i) \quad (2)$$

Where $FYSF_i \equiv$ the fission yield scaling factor based on isotope i
$wt\%_i \equiv$ the weight per percent of isotope i in the HLW total dried solids
$fy_i \equiv$ the fission yield of isotope i
$am_i \equiv$ the atomic mass of isotope i.

Several of the U-235 fission products have the six critical chemical and nuclear properties that allow calculation of a constant FYSF for a particular sludge. These properties have been discussed [9]. In MB5, there are 14 isotopes that have these six properties. The FYSF's calculated for these 14 isotopes are presented in the Table I. The measured concentrations in Table I were determined from ICP-MS analysis of the aqua regia digestions. The average of the FYSF's calculated for the 14 fission products is 3.18E-05 with a relative standard deviation of 13%.

Table I. Calculated Values of the Fission Yield Scaling Factor (FYSF) for 14 U-235 Fission Products in MB5

Isotope	Measured Wt% of Total Solids	Fission Yield	FYSF
Ru-101	1.29E-02	5.20	2.45E-05
Ru-102	1.17E-02	4.30	2.67E-05
Rh-103	8.40E-03	3.03	2.69E-05
Ru-104	6.75E-03	1.88	3.45E-05
La-139	3.00E-02	6.41	3.36E-05
Ce-140	3.55E-02	6.22	4.08E-05
Pr-141	2.72E-02	5.80	3.33E-05
Ce-142	2.88E-02	5.85	3.47E-05
Nd-143	2.40E-02	5.96	2.82E-05
Nd-144	2.75E-02	5.50	3.47E-05
Nd-145	1.68E-02	3.93	2.95E-05
Nd-146	1.42E-02	3.00	3.25E-05
Sm-147	9.35E-03	2.25	2.83E-05
Nd-148	9.28E-03	1.67	3.76E-05
Average	-	-	***3.18E-05***[a]

[a] relative standard deviation 13%

With the FYSF for MB5, the maximum possible concentration in terms of weight percent of dried solids can be estimated for the other U-235 fission products. These estimations are a maximum for the other fission products because they do not have the necessary six properties as the fission products given in Table I. For example, the radionuclide Cd-113m has a very large neutron absorption cross section (20,000 barns [6]), and thus it was transmuted in the reactors at SRS to stable Cd-114 while the reactors were in operation. Consequently, the concentration calculated for Cd-113m with Equation (1) and a fission yield of 1.66E-04% can be considered the maximum concentration and is estimated below:

$$\text{Concentration Cd-113m (wt\%)} = 3.18\text{E-}05 \times 1.66\text{E-}04 \times 113 = 5.97\text{E-}07 \text{ wt\%}.$$

Cs-135

The radionuclide Cs-135 cannot be detected by ICP-MS in the sludge slurry due to its low concentration and the large amount of natural Ba-135. Cs-135 cannot be detected by counting techniques either because of its long half-life ($t_{1/2}$ = 2.3E+06 years). The detection by ICP-MS of Cs-135 in the supernate is possible because Ba-135 is insoluble in caustic supernate. The same philosophy applies to Ba-137 and Cs-137. Thus, Ba does not interfere with the analyses of Cs-135 or Cs-137 in the supernate. By using the ratio of Cs-135 to Cs-137 in the supernate, and the amount of Cs-137 in the sludge slurry, the activity for Cs-135 in the sludge slurry can be calculated. The weight percent of Cs-135 was then converted to μCi/g and used in the calculations to determine if Cs-135 was reportable.

Cm-248

The radionuclide Cm-248 is another radionuclide that needs to be considered as possibly reportable but which cannot be measured due to its low concentration. The concentration of this isotope had to be estimated using the ratio of Cm-248 to Cm-247 predicted for the DWPF design basis glass [10]. The predicted ratio of the mass of Cm-248 to the mass of Cm-247 was 0.023. An upper limit of the concentration of Cm-248 was calculated by multiplying the upper limit for the concentration of Cm-247 measured by the Am/Cm method by this ratio. This upper limit was then converted to activity of Cm-248. This result was entered into the reportable isotope projection calculations.

RESULTS

Nonradioactive Composition of Macrobatch 5

The elemental composition of MB5 is given in Table II on a total solids basis. Less than values indicate the instrumental detection limit was reached. This is a typical PUREX sludge composition at the Savannah River Site.

Table II. Elemental Concentrations in DWPF Macrobatch 5 (MB5) Samples in Weight Percent of Total Solids [Number of Samples Included in Average, %RSD]

Element	MB 5	Element	MB5
Al	9.52 [40, 0.4]	Mo	<0.014
B	<0.011	Na	11.0 [4, 0.6]
Ba	0.0479 [8, 1.1]	Ni	0.894 [8, 1.9]
Ca	1.41 [8, 6.6]	P	0.297 [4, 7.5]
Cd	0.194 [4, 3.4] [a]	Pb	0.0417 [3, 11]
Ce	0.0401[4, 2.0] [a]	S	0.332 [4, 4.7]
Cr	0.0767 [4, 0.5]	Sb	<0.069
Cu	0.0331 [4, 1.8]	Si	0.899 [4, 2.0]
Fe	14.3 [8, 1.6]	Sn	<0.20
Gd	0.0147 [4, 5.8] [a]	Sr	0.0235 [8, 4.6]
Hg	0.814 [4, 3.4] [c]	Ti	0.0166 [4, 0.9]
La	0.0300 [4, 2.3] [a]	U	5.29 [4, 3.1] [b]
Li	0.0221 [4, 2.3]	V	<0.0055
Mg	1.17 [8, 4.0]	Zn	<0.045
Mn	3.18 [8, 1.2]	Zr	0.04 [4, 54]

[a] Calculated from MS data for Cd-113, La-139, Ce-140, Gd-157, respectively

[b] Calculated from MS data for U-234, -235, -236 and -238

[c] Calculated from CV-AA data

Radioactive Composition of DWPF Macrobatch 5

The complete list of radionuclides and their activities that were considered in the determination of reportable radionuclides are provided in Table III. For those radionuclides with measured concentrations, the initial activities were calculated by using the weight percent reported for each radioisotope and its specific activity with the following equation: $A_o = M_o * SpA$, where A_o = Initial Activity, M_o = mass in weight percent and SpA = specific activity of the isotope.

Table III. List of Radionuclides and Activities Used as Input to the *RadDecay*® Program and the Determination Method for Each Isotope

Radionuclide	Wt% of Total Solids	Activity (μCi/g)[a]	Determination Method
Ni-59	7.02E-04	5.67E-01	Ni-59/-63
Co-60	7.57E-08	8.56E-01	Direct Gamma Counting
Ni-63	1.07E-04	6.58E+01	Ni-59/-63
Se-79	2.31E-05	1.61E-02	Se-79
Sr-90	5.30E-03	7.23E+03	Sr-90
Y-90[b]	1.33E-06	7.23E+03	Secular equilibrium w/ Sr-90
Zr-93	1.05E-02	2.64E-01	ICP-MS
Nb-93m	7.41E-08	2.09E-01	Calculated from Zr-93 and Waste Age
Tc-99	8.31E-04	1.41E-01	ICP-MS
Pd-107	1.16E-04	5.98E-04	Calculated from Pd-105
Cd-113m	5.97E-07	1.29E+00	Based on Fission Yield
Sn-121m	<5.38E-08	<3.18E-02	Cs-Removed Gamma Counting
Sb-125	<1.81E-08	<1.86E-01	Cs-Removed Gamma Counting
Te-125m[b]	<1.04E-09	<1.86E-01	Secular equilibrium w/ Sb-125
Sn-126	<1.14E-03	<3.24E-01	Cs-Removed Gamma Counting

I-129	2.95E-04	5.20E-04	I-129
Ba-133	<3.66E-08	<9.14E-02	Direct Gamma Counting
Cs-135	1.02E-04	1.18E-03	Calculated from Cs-135/-137 ratio
Cs-137	2.87E-04	2.49E+02	Direct Gamma Counting
Ba-137m [b]	4.45E-11	2.39E+02	Secular equilibrium w/ Cs-137
Pm-147	<1.55E-06	<1.44E+01	Pm-147/Sm-151
Sm-151	4.28E-04	1.13E+02	Pm-147/Sm-151
Eu-154	4.28E-06	1.15E+01	Direct Gamma Counting
Eu-155	2.61E-07	1.22E+00	Direct Gamma Counting
Th-232	4.62E-02	5.07E-05	ICP-MS
U-233	<1.97E-04	<1.91E-02	ICP-MS
U-234	5.44E-04	3.40E-02	ICP-MS
U-235	2.96E-02	6.41E-04	ICP-MS
U-236	1.26E-03	8.12E-04	ICP-MS
Np-237	3.69E-03	2.60E-02	ICP-MS
U-238	5.25E+00	1.77E-02	ICP-MS
Pu-238	7.13E-04	1.22E+02	Pu-238/-241
Pu-239	1.66E-02	1.03E+01	ICP-MS
Pu-240	1.98E-03	4.51E+00	ICP-MS
Pu-241	1.05E-04	1.08E+02	Pu-238/-241
Pu-242	1.53E-04	5.83E-03	ICP-MS
Am-241	5.14E-04	1.76E+01	Direct Gamma Counting
Am-242m	7.20E-07	7.00E-02	Am/Cm
Am-243	8.23E-04	1.64E+00	Am/Cm
Cm-242	1.75E-09	5.78E-02	Am/Cm
Cm-243	<1.15E-06	<5.96E-01	Am/Cm
Cm-244	1.12E-04	9.07E+01	Am/Cm
Cm-245	<2.04E-05	<3.49E-02	Am/Cm
Cm-246	6.19E-06	1.90E-02	Am/Cm – ICP-MS
Cm-247	<6.09E-03	<5.65E-03	Am/Cm
Bk-247	<1.32E-06	<1.36E-02	Am/Cm
Cm-248	<1.39E-04	<5.91E-03	Calculated Ratio Cm-247/-248
Cf-249	<1.69E-07	<7.39E-03	Am/Cm
Cf-250	5.29E-08	5.78E-02	Am/Cm
Cf-251	<1.01E-06	<1.88E-02	Am/Cm
	TOTAL	***1.55E+04***	

[a] Less than values represent the minimum detection limit value and hence are an upper bound for that isotope's activity.

[b] Included because this isotope is in secular equilibrium with a parent for which a measured value was available.

The total measured alpha activity of the digested samples was 2.26E+02 μCi/g. Total beta activity was measured at 1.45E+04 μCi/g.

Based on radionuclides and activities provided in Table III, a commercially available computer program was used to identify which radionuclides were reportable through calendar year 3115. The initial activities for 50 isotopes were entered into *RadDecay*® version 3.0 [11] and the results of two calculations with the index years 2015 and 3115 (1110 years) performed. Additional calculations were performed for every 100 years up to 1100 years. Microsoft Excel spreadsheets were used to calculate the total activity in μCi/g of dried sludge solids at each time and the percent of the activity that each of the radionuclides contributed.

The calculations performed by *RadDecay*® v. 3.0 were verified against a separate program called *Radioactive Decay Calculator* [12]. In addition to this check, a separate independent evaluation utilizing the input radionuclides and an earlier version of *RadDecay*®, v. 1.13, was conducted. The reportable radionuclides determined by this evaluation were the same as those reported here.

The total Curie content of the dried sludge in the year 2015 is 1.31E+04 μCi/g. This value is greater than the 6.80E+03 μCi/g total represented by the reportable radionuclides. The difference is due to the significant contribution to the activity from radionuclides having half-lives shorter than 10 years. These radionuclides include (in decreasing order of activity contribution): Y-90, Ba-137m, Pm-147, Eu-154, Eu-155, Sn-121, and Np-239.

The total Curie content of the dried sludge in 3115 is 2.32E+01 μCi/g. This value is slightly greater than the 2.13E+01 μCi/g total represented by the radionuclides identified as reportable. The difference is due to the minor contribution to the total activity from radionuclides having half-lives shorter than 10 years. These radionuclides include (in decreasing order of activity contribution): Np-239, Sb-126m, Sb-126, Pa-233, Th-234, Pa-234m, and Pu-243. Figure 1 shows the total and reported activity in μCi per gram of total solids in the DWPF MB5 over the index year period from 2015 through 3115.

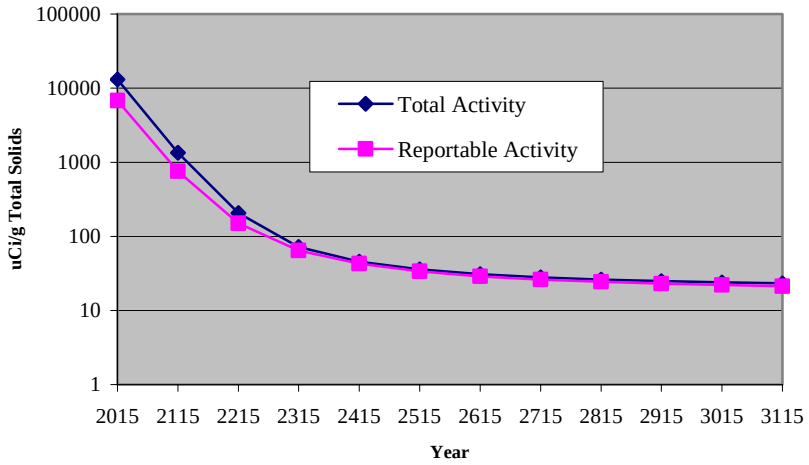

Figure 1. Total and Reportable μCi/g of Total Solids vs. Index Years between 2015 and 3115 for DWPF Macrobatch 5

Twenty-nine radionuclides have been identified as reportable for DWPF MB5 as specified by WAPS 1.2. Consistent with the strategy detailed in the Waste Form Qualification Report (WQR) [13] and Waste Form Compliance Plan (WCP) [14], each of these radionuclides has a half-life greater than 10 years and contributes more than 0.01 % of the radioactivity on a Curie basis at some point from

production through the 1100-year period between 2015 and 3115. The 29 reportable radionuclides are given in Table IV. The calculations at every one hundred years out to 1100 years demonstrated that only one radionuclide became reportable during this time period that was not already reportable at 2015 or 3115, Am-242m (shown in Figure 2), which was reportable for the years between 2215 and 2615, but no longer reportable in 2715.

Table IV. Reportable Radionuclides in DWPF Macrobatch 5

Ni-59	Ni-63	Se-79	Sr-90	Zr-93	Nb-93m
Tc-99	Sn-126 [a]	Cs-137	Sm-151	U-233 [a]	U-234
Np-237	U-238	Pu-238	Pu-239	Pu-240	Am-241
Pu-241	Pu-242	Am-242m	Am-243	Cm-244	Cm-245 [a]
Cm-246	Cm-247 [a]	Bk-247 [a]	Cm-248 [a]	Cf-251 [a]	

[a] Based upon an analytical detection limit.

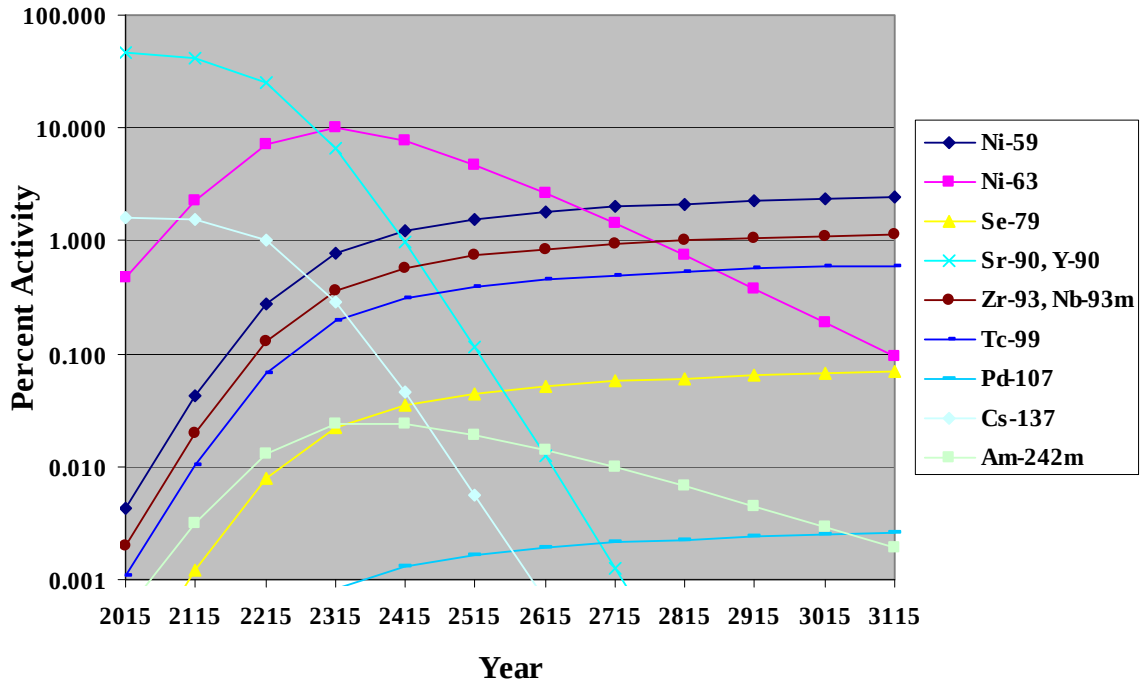

Figure 2. Percent of Total Activity for Select Radionuclides in DWPF Macrobatch 5 over the Index Years 2015 through 3115

The WCP and WQR require that all of the radionuclides present in the Design Basis glass be considered as the initial set of reportable radionuclides. All of the radionuclides in the Design Basis glass are reportable except for three radionuclides: Pd-107, Cs-135, and Th-230. At no time during the 1100-year period between 2015 and 3115 did any of these three radionuclides contribute to more than 0.01% of the radioactivity on a Curie basis.

Seven of the 29 reportable radionuclides for MB5 are not part of either the design-basis list of radionuclides [14] or the list of Pu and U isotopes identified in WAPS 1.6. These include Am-242m, Cm-245, Cm-246, Cm-247, Bk-247, Cm-248, and Cf-251. One of these radionuclides (Cm-246) was

also reported for MB2 [15], three of these radionuclides (Cm-245, Cm-246, and Cf-251) were also reported for MB3 [16], and six of these radionuclides (Am-242m, Cm-245, Cm-246, Cm-247, Cm-248, and Cf-251) were reported for MB4 [17].

The list of reportable radionuclides that were determined for MB2 [15] contained two radionuclides that were not reportable for MB3, MB4 or in the current MB5. These radionuclides were I-129 and Th-229. Sn-121m was reportable for MB2, MB3, and MB4, but due to an improved detection limit is not reportable for MB5. Similarly, Cf-249 was reportable for MB4, but due to an improved detection limit for the input value, it is not reportable for MB5. C-14, reported in the first two batch analyses, has been excluded from consideration for future sludge batches [16] because it does not carry into the glass. For easier comparison, the reportable nuclides for MB2, MB3, and MB4 have been reproduced in Table V through Table VII.

Table V. Reportable Radionuclides in DWPF Macrobatch 2 [15]

C-14	Ni-59	Ni-63	Se-79	Sr-90	Zr-93
Nb-93m	Tc-99	Sn-121m	Sn-126	I-129	Cs-137
Sm-151	Th-229	U-233	U-234	Np-237	U-238
Pu-238	Pu-239	Pu-240	Am-241	Pu-241	Pu-242
Am-243	Cm-244	Cm-246			

Table VI. Reportable Radionuclides in DWPF Macrobatch 3 [16]

C-14	Ni-59	Ni-63	Se-79	Sr-90	Zr-93
Nb-93m	Tc-99	Sn-121m	Sn-126	Cs-137	Sm-151
U-233	U-234	Np-237	U-238	Pu-238	Pu-239
Pu-240	Am-241	Pu-241	Pu-242	Am-243	Cm-244
Cm-245	Cm-246	Cf-251			

Table VII. Reportable Radionuclides in DWPF Macrobatch 4 [17]

Ni-59	Ni-63	Se-79	Sr-90	Zr-93	Nb-93m
Tc-99	Sn-121m	Sn-126	Cs-137	Sm-151	U-233
U-234	Np-237	U-238	Pu-238	Pu-239	Pu-240
Am-241	Pu-241	Pu-242	Am-242m	Am-243	Cm-244
Cm-245	Cm-246	Cm-247	Cm-248 [a]	Cf-249	Cf-251

[a] Based upon an analytical detection limit.

The WQR requires that the relative concentrations of the uranium and plutonium isotopes be provided from the analysis of each macrobatch in order to meet the WAPS IAEA Safeguards Reporting for HLW Specification (WAPS 1.6). The data for uranium isotopes are given in Table VIII.

Table VIII. Uranium Isotope Distribution in DWPF Macrobatch 5

Isotope	Weight Percent	Percent Distribution
U-233	<1.97E-04	0.00373
U-234	5.44E-04	0.0103
U-235	2.96E-02	0.561
U-236	1.26E-03	0.0238
U-238	5.25E+00	99.4
Total	6.76E+00	100

The data for the plutonium isotopes is given in Table IX.

Table IX. Plutonium Isotope Distribution in DWPF Macrobatch 5

Isotope	Weight Percent	Percent Distribution
Pu-238	7.13E-04	3.66
Pu-239	1.66E-02	84.9
Pu-240	1.98E-03	10.1
Pu-241	1.05E-04	0.536
Pu-242	1.53E-04	0.783
Total	2.45E-02	100

All of the Pu isotopes and U-233, -234, and -238 are already reportable since they meet the requirement of having half-lives greater than 10 years and a contribution to the overall activity of greater than 0.01% on a Curie basis through the year 3115. In order to be compliant with WAPS 1.6, U-235 and U-236 also become reportable even though they contribute less than 0.01% to the total activity (U-235 at 0.003% and U-236 at 0.004% in 3115).

Fractional Losses of Tc-99, I-129, and Sm-151 from DWPF Macrobatch 5

During performance of this work it became apparent that the measured concentrations of Tc-99, I-129 and Sm-151 were much less then their expected concentrations based on other U-235 fission products measured. Using the FYSF the maximum amount of Tc-99, I-129, and Sm-151 that should have been present in the sludge solids of MB5 can be calculated using Equation 1. The cumulative fission yields for the isotopes are 6.11, 0.54, and 0.419 %, respectively [8], and their half-lives are 2.13E+05, 1.57E+07, and 90 years, respectively [4]. Results for the calculations are given in Table X along with the measured concentrations. The percentage of each radionuclide that is not in the sludge solids is also presented in the table. Clearly, the concentration of each radionuclide has been lowered considerably from what its concentration could have been in the sludge based on the concentrations of the 14 radionuclides used to calculate the FYSF.

Table X. Comparison of Calculated Maximum Concentration and Measured Concentration for Tc-99, I-129, and Sm-151 in MB5 Sludge Solids

Radionuclide	Calculated Maximum Weight Percent	Measured Weight Percent	Percent Missing From MB5 Sludge Solids
Tc-99	1.92E-02	8.31E-04	95.7
I-129	2.2E-03	2.95E-04	87
Sm-151	2.01E-03	4.28E-04	78.7

One mechanism for reducing the concentrations of Tc-99 and I-129 from the HLW sludges at SRS is their solubility in caustic. The HLW produced from separations processes at SRS is initially acidic. Prior to

being stored in the mild steel tanks at SRS, the HLW is made caustic. Here the isotopes that are insoluble in caustic are separated from those that are soluble and each is then stored in separate tanks (sludge tanks and salt tanks). Another study has shown that most of the Tc-99 is soluble in caustic and does not precipitate with the sludge solids [9]. In that study, it was shown that in MB2, 95% of the Tc-99 had been transferred to the salt tanks with the caustic supernate. Similarly, a portion of the I-129 could be soluble in caustic as iodide. Furthermore, I-129 could be volatilized from the hot acid dissolutions of the irradiated targets and fuel rods during processing at SRS. Solubility in caustic cannot account for the loss for Sm-151 because of its low solubility in caustic. In fact, Sm-147 with its long half-life of 1.06E+11 years [6] is one of the radionuclides used to calculate the FYSF for MB5 (see Table I).

Radioactive decay is an obvious mechanism for lowering the concentration of a radionuclide in the sludge solids. However this is not a factor for Tc-99 and I-129 because of their very long half-lives. Also for the radionuclide Sm-151, with its 90 year half-life, it can be calculated that the sludge solids would have to be out of the reactor for ~200 years to account for all of this decrease. This is clearly impossible since the SRS reactors did not go critical until 1953 – 1954. However, Sm-151 has a U-235 thermal neutron cross section 15,200 barns [6] so transmutation in a reactor could account for a significant portion of the loss.

CONCLUSIONS

Twenty-nine radionuclides have been identified as reportable for DWPF MB5 as specified by WAPS 1.2. Consistent with the strategy detailed in the WCP and WQR, each of these radionuclides has a half-life greater than ten years and contributes more than 0.01% of the radioactivity on a Curie basis at some point from production through the 1100 year period between 2015 and 3115. The 29 reportable nuclides are:

Ni-59	Ni-63	Se-79	Sr-90	Zr-93	Nb-93m
Tc-99	Sn-126	Cs-137	Sm-151	U-233	U-234
Np-237	U-238	Pu-238	Pu-239	Pu-240	Am-241
Pu-241	Pu-242	Am-242m	Am-243	Cm-244	Cm-245
Cm-246	Cm-247	Bk-247	Cm-248	Cf-251	

The WCP and WQR require that all of radionuclides present in the Design Basis glass be considered as the initial set of reportable radionuclides. For MB5, all of the radionuclides in the Design Basis glass that qualify are reportable except for three radionuclides: Pd-107, Cs-135, and Th-230. At no time through the year 3115 did any of these three radionuclides contribute to more than 0.01% of the radioactivity on a Curie basis.

Two additional uranium isotopes (U-235 and -236) must be added to the list of reportable radionuclides in order to meet WAPS 1.6. All of the Pu isotopes and other U isotopes (U-233, -234, and -238) identified in WAPS 1.6 were already determined to be reportable according to WAPS 1.2 This brings the total number of reportable radionuclides for MB5 to 31.

Other conclusions include:

- The average age of the sludge based on Sr-90 in MB5 is 33 years.
- The concentrations of Tc-99, I-129, and Sm-151 are greatly reduced in SRS sludge by the processing history.

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