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WSRC-TR-2005-00098
Revision 0

MEASURING AND PREDICTING FISSION PRODUCT NOBLE METALS IN SAVANNAH RIVER SITE HIGH LEVEL WASTE SLUDGES

N. E. Bibler

April 2005

Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

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Printed in the United States of America

Prepared For
U.S. Department of Energy

WSRC-TR-2005-00098
Revision 0

Key Words:
Noble Metals
HLW Sludges
Fission Products

Retention:
Permanent

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EXECUTIVE SUMMARY

The noble metals Ru, Rh, Pd, and Ag were produced in the Savannah River Site (SRS) reactors as products of the fission of U-235. Consequently they are in the High Level Waste (HLW) sludges that are currently being immobilized into a borosilicate glass in the Defense Waste Processing Facility (DWPF). The noble metals are a concern in the DWPF because they catalyze the decomposition of formic acid used in the process to produce the flammable gas hydrogen. As the concentration of these noble metals in the sludge increases, more hydrogen will be produced when this sludge is processed.[a] In the SRS Tank Farm it takes approximately two years to prepare a sludge batch for processing in the DWPF. This length of time is necessary to mix the appropriate sludges, blend them to form a sludge batch and then wash it to enable processing in the DWPF. This means that the exact composition of a sludge batch is not known for ~two years. During this time, studies with simulated nonradioactive sludges must be performed to determine the desired DWPF processing parameters for the new sludge batch. Consequently, prediction of the noble metal concentrations is desirable to prepare appropriate simulated sludges for studies of the DWPF process for that sludge batch. These studies give a measure of the amount of hydrogen that will be produced when that sludge batch is processed. This report describes in detail the measurement of these noble metal concentrations in sludges and a way to predict their concentrations from an estimate of the lanthanum concentration in the sludge. Results for two sludges are presented in this report. These are Sludge Batch 3 (SB3) currently being processed by the DWPF and a sample of unwashed sludge from Tank 11 that will be part of Sludge Batch 4.

The concentrations of the noble metals in HLW sludges are measured by using mass spectroscopy to determine concentrations of the isotopes that comprise each noble metal. For example, the noble metal Ru is comprised of isotopes with masses 101, 102, and 104. The element Rh has a single isotope with mass 103. The element Pd is comprised of five isotopes. These are at masses 105-108 and mass 110. As does Rh, Ag has only one isotope. This is at mass 109. However, results in this report show that the Ag concentration in the two samples was due to natural Ag being in the samples. Natural Ag has masses at 107 and 109. The Ag-107 interferes with the measurement of Pd-107. This Ag was used in one of the processes at SRS. The results also show that natural Cd is in the two samples. Cadmium has isotopes at masses 106, 108 and 110, thus it interferes with the analysis of the Pd isotopes at these masses. Cadmium was also used in one of the processes at SRS. However, the concentrations of the Pd isotopes at masses 106, 107, 108 and 110 could be calculated using the fission yields for the Pd isotopes, and the measured concentration of Pd at mass 105 where there is no Ag or Cd interference. Based on the measurements of the concentrations of the isotopes of each noble metal, the total concentration of that noble metal can be determined by summing the concentrations of the individual isotopes. The results in this report show that the relative concentrations of the isotopes of Ru and Rh are in proportion to their yields from the fission of U-235 in the reactors. These results were expected since these elements are very insoluble in caustic and thus are primarily in the sludge tanks rather then the salt tanks of the SRS Tank Farm. The relative concentration of Pd is somewhat lower than that based on the relative fission yields of its five isotopes. This indicates that some of the Pd is in the salt tanks rather than the sludge tanks of the Tank Farm.

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[a] Koopman, D. C., *Review of Catalytic Hydrogen Generation in the Defense Waste Processing Facility (DWPF) Chemical Processing Cell*, WSRC-TR-2002-00034, Savannah River Site, Aiken, SC 29808 (2002).

The concentrations of the noble metals were predicted using the High Level Waste Characterization System (WCS)[b] at SRS. This system keeps record of the inventory of the major compounds and select radionuclides that are in each of the SRS HLW tanks. Using this system, the Closure Business Unit (CBU) can predict the major composition of a sludge batch by knowing the tanks involved in that batch and the estimates of the volume of sludge from each tank that will be blended to make the final sludge batch. The system does not track the inventories of Rh, Pd, and Ag. It does track Ru, but Ru is not included in the projections by CBU. However, another U-235 fission product is tracked by WCS. This fission product is La. The element La was not used in any of the chemical processes at SRS. Results in this study show that it is in the HLW primarily as a U-235 fission product. This fission product is comprised solely of the isotope La-139 which can be measured along with the isotopes of the noble metals that do not have interferences from Ag or Cd. The concentrations of La in SB3[c] and in the Tank 11 sample[d,e] have been estimated by the CBU using WCS projections. . Based on these estimates, the concentrations of the noble metals were predicted based on their fission yields and the fission yield for La-139.

Comparison of the predicted and measured SB3 values show that predicted values for Ru and Rh are 6-7X higher and values for Pd 17X higher. The much higher predicted Pd concentration could be due to some of the Pd in the sludge being in salt tanks which is not accounted for in the prediction. The measured concentration of Ag was much higher than the predicted due to natural Ag being in SB3. For the Tank 11 sample the predicted results for Ru and Rh are only 1.3 and 1.8X higher, respectively, while the predicted result for Pd is 11X higher. Again the measured concentration of Ag was much higher than the predicted due to natural Ag being in the Tank 11 sample. These results indicate that the predictions can be used as guidance in preparing simulated sludges for studies performed before samples from the actual sludge batch are available. With regard to hydrogen production such studies would be conservative since the predicted concentrations may be higher than the actual concentrations.

This report also compares predictions of noble metals based on La-139 measured by mass spectroscopy and by excitation spectroscopy. The results indicate that mass spectrometer measurements are better for La-139. This is also true for noble metals as well as other trace elements in the sludges.

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[b] Hester, J. R., *High Level Waste Characterization System,* WSRC-TR-96-0264, Savannah River Site, Aiken, SC 29808 (1996).

[c] Appendix A of Peeler, D. K., Bibler, N. E., and Edwards, T. B., *An Assessment of the Impacts of Adding Am/Cm and Pu/Gd Waste Streams to Sludge Batch 3 (SB3) on DWPF H2 Generation Rates and Glass Properties (U),* WSRC-TR-2002-00145,Rev 0, Savannah River Site, Aiken, SC 29808 (2002).

[d] Lilliston, G. R., *Washing and Addition Strategies for the Combination of Sludge Batch 4 (Tanks 4,5,6,8 and 11) with Sludge Batch 3 as Feed into DWPF,* CBU-PIT-2004-00031, Savannah River Site, Aiken, SC 29808 (2004).

[e] The results in Reference d have been published in Bannochie, C. J. and Fellinger, T. L., *Tank 11H Analytical Results as Input to DWPF Sludge Batch 4,* WSRC-TR-2004-00473, Rev. 0, Savannah River Site, Aiken, SC 29808 (2004).

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ADS	Analytical Development Section
CBU	Closure Business Unit
DWPF	Defense Waste Processing Facility
HHW	High Heat Waste
HLW	High Level Waste
HM	H Modified PUREX Process
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LHW	Low Heat Waste
PUREX	Plutonium Recovery and Extraction Process
SB3	Sludge Batch 3
SB4	Sludge Batch 4
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SSMS	Spark Source Mass Spectroscopy
WCS	Waste Characterization System

1.0 INTRODUCTION AND BACKGROUND

The noble metal fission products, Ru, Rh, Pd, and Ag were produced in the Savannah River Site (SRS) reactors while they were operating from the late 1954 to the early 1990's. These noble metals are products from the nuclear fission of U-235 to produce neutrons primarily for production of Pu-239 and H-3 for United States defense purposes. Many other fission products are formed most of which are highly radioactive such as Sr-90 and Cs-137. In the separations processes to recover unreacted U-235, no effort was made to recover the fission products and they were sent to the SRS High Level Waste (HLW) tanks for temporary storage. Currently the Defense Waste Processing Facility (DWPF) is immobilizing the HLW sludges into a borosilicate glass for permanent geologic disposal and the noble metals are a concern. In the DWPF, the noble metals catalyze the decomposition of formic acid to produce flammable hydrogen (H_2) during melter feed preparation. Studies have shown that the higher the noble metal concentration, the higher the rate of H_2 production.[1] Limits on the rates of H_2 production have been established in the DWPF and purge systems have been installed to prevent the formation of flammable mixtures in the melter feed process vessels (the Sludge Receipt and Adjustment Tank (SRAT)) and the Slurry Mix Evaporator (SME)). Also at Savannah River National Laboratory (SRNL) each sludge batch is processed on a small scale (1-3 liters) with the DWPF SRAT and SME process conditions to determine if the H_2 production rate is below the DWPF limit for H_2 production. Recently a campaign in the Shielded Cells of SRNL has shown that this is the case in the SRAT and SME for Sludge Batch 3 (SB3).[2] Studies with nonradioactive sludges prepared to simulate the final composition of SB3 were also used to support processing SB3.[3]

Approximately two years are usually required for the SRS Closure Business Unit (CBU) to prepare a sludge batch by blending and washing sludges from selected tanks to form a final sludge batch. Each batch can be as large as 800,000 gallons. During this time, SRNL actively tests nonradioactive sludges prepared to simulate the projected compositions of the sludge batch being prepared by CBU based on different washing scenarios in the Tank Farm. An important purpose of the nonradioactive testing is to determine the maximum rate of H_2 production in the SRAT and SME process with the projected compositions. Unfortunately the projected compositions furnished by CBU do not contain projections of the possible concentrations of the fission product noble metals Ru, Rh, Pd, and Ag in the new sludge batch. Therefore a sludge simulant that accurately assesses the rate of H_2 production in the SRAT or SME processes is difficult to prepare. Usually upper bounds of the concentrations of the fission product noble metals are chosen to be conservative in these tests with simulated sludge.

This report discusses in detail a method developed to predict fission product noble metal concentrations in sludge batches based on the projections furnished by CBU for the major and minor elements in a sludge batch. These projections are based on the WCS at SRS. Two sludges were chosen for this study. These are SB3 that is currently being processed by the DWPF and a recent sample from SRS Tank 11 that will be part of SB4 now being prepared by CBU. After a discussion of the formation of the fission product noble metals and the isotopes that make them up, the report discusses the method for accurately measuring the concentrations of these isotopes. The measured results are then presented and compared to the predicted.

2.0 FISSION PRODUCTS AT SRS

2.1 Formation in SRS Reactors

In the reactors at SRS, the fission of U-235 in reactor fuel rods was used to produce neutrons to irradiate U-238 and Li-6 in reactor target rods to produce Pu-239 and H-3. Initially these neutrons have very large energies and velocities. In the SRS reactors, heavy water (D_2O) was used to remove kinetic energy from the neutrons by atomic collisions. The resulting neutrons are called thermal neutrons because their final energies are in thermal equilibrium with the other atoms in the system. Some of these thermal neutrons are captured by other U-235 atoms and produce more fissions. The fission reaction not only produces neutrons but also produces fission products such as Sr-90, Cs-137 and isotopes of the noble metals Ru, Rh, Pd, and Ag. Most fission products are radioactive with half lives ranging from fractions of seconds to millions of years. However some of them are stable and not radioactive.

A good discussion of the fission process is given in Reference 4 and will only be summarized here. In the fission reaction a U-235 atom absorbs a thermal neutron to form an excited nucleus of U-236. This nucleus then splits to give two or three neutrons and two fission products of lighter masses than the U-236. A considerable amount of energy is also released. The U-236 nucleus may split in a variety of ways to give fission products of many masses. An example of one fission reaction is given below:

U-235 + n • U-236 • 2n + Tc-103 + In-131 + energy

The U-235 nucleus contains 92 protons and 143 neutrons. In the above reaction the numbers of neutrons and protons are conserved. The isotope Tc-103 has 43 protons and 60 neutrons and In-131 has 49 protons and 82 neutrons. Both of these nuclei are neutron rich and undergo beta decay that converts a neutron to a proton in the atomic nucleus but does not change the mass of the nucleus. The beta decay half life for Tc-103 is 54 seconds and the beta decay half life for In-131 is 0.28 seconds.[5] Each of these nuclei continue to decay until an isotope is formed that has a long half life or is stable. Since the mass of the nuclei do not change with beta decay, the nuclei decay along isobaric (equal mass) chains. In this example the isobaric decay chain of mass 103 ends at the noble metal Rh-103 which is stable. The isobaric decay chain for mass 131 ends at Xe-131 which is also stable. The percentage of fissions that form the various isobaric decay chains have been extensively measured over the years since fission was discovered. These percentages are called fission yields and compilations have been published. The fission yields used in this study were taken from Reference 5. The fission yield for mass 103 is 3.03 atoms of mass 103 formed per 100 fissions of U-235. For mass 131 the fission yield is 2.89 atoms of mass 131 formed per 100 fissions of U-235. Fission yields of the various nuclei are not equal due to different nuclear shell closures. As a result, many different isotopes of each mass can be formed from the fissions of U-235. For example, for mass 103 there are 5 isotopes in the isobaric chain leading to stable Rh-103. For mass 131 there are 5 leading to Xe-131. A plot of the isobaric fission yields from the thermal neutron fission of U-235 is shown in Figure 2-1. The fission yields are in terms of atoms formed per 100 fissions. The masses of the fission product noble metals range from 101 to 110.

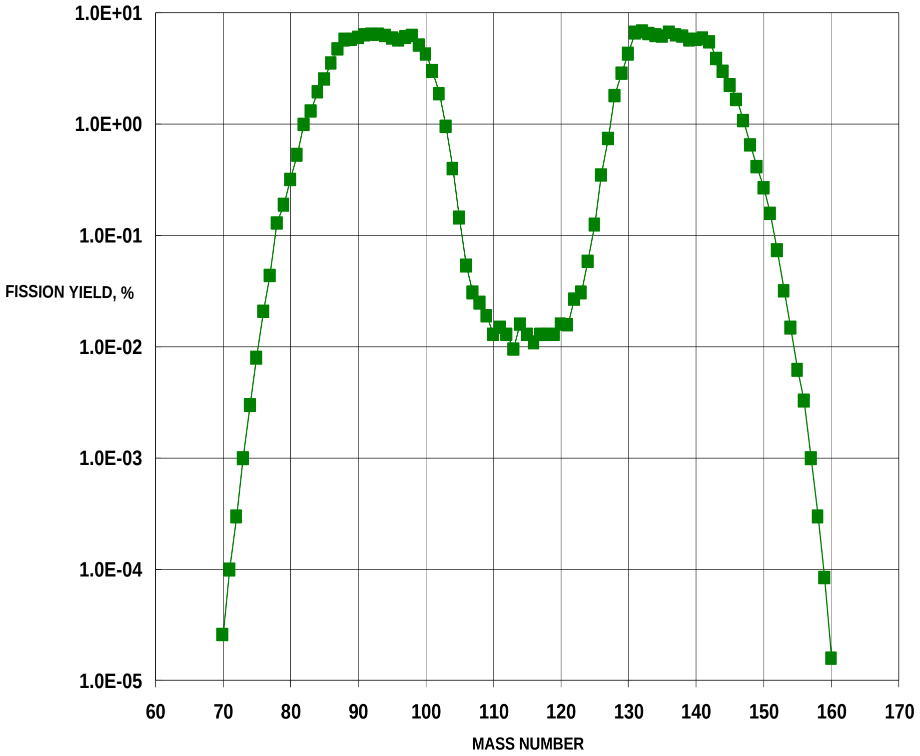

Figure 2-1. Distribution of Mass Chains in the Thermal Neutron Fission of U-235. (Taken from Reference 4, Page 161.)

After irradiation in the reactors, the fuels and targets were processed to recover the unreacted U-235 and the Pu-239 and other special isotopes produced. These processes involved dissolving the fuel and target materials and going through several separation processes to recover the desired isotopes. In these processes essentially all the nonvolatile U-235 fission products were sent to HLW tanks for temporary storage. Volatile fission products such as Xe-131, Kr-84 and Kr-86 were vented to the atmosphere. The volatile fission product isotopes of iodine (stable I-127, I-129 (1.5E07 year half life), and I-131 (8 day half life) were scavenged from the exhaust gases using Ag saddles to form AgI. A portion of these saddles were later discarded into the waste tanks, but most of them were sent to the burial ground for disposal.

The acid waste streams from the separation processes in the SRS canyons were treated with caustic so they could be sent to the mild steel tanks in the SRS Tank Farm. The caustic solutions were initially sent to fresh waste receipt tanks in the Tank Farm. In these tanks the fission products that were insoluble in caustic settled along with other insoluble waste components to form sludges. Soluble fission products such as such as Cs-137 and Tc-99 remained in the clarified salt solutions above the sludges. These solutions were later decanted, fed to a waste evaporator and sent to salt tanks The sludge slurries were then sent to sludge tanks. The fission product noble metals are primarily insoluble in caustic so they are primarily in the sludge tanks along with nonradioactive sludge components such as Fe, Al, Mn, Ni, and La.

2.2 Fission Product Noble Metals in SRS HLW Sludges

As mentioned before, the fission product noble metals in the HLW sludges are Ru, Rh, Pd, and Ag. The Ru contains isotopes of mass 101, 102, and 104 from the isobaric decay chains. The Rh has only one isotope, Rh-103, that results from the 103 isobaric chain. The Pd is formed by five isobaric decay chains. These are at masses 105, 106, 107, 108 and 110. The fission product Ag has only one isotope at mass 109. These isotopes, their fission yields and their nuclear decay half lives are shown in Table 2-1. Note that only one isotope is radioactive.

Table 2-1. Fission Product Noble Metal Isotopes in SRS High Level Waste Sludges

Noble Metal Isotope	Fission Yield,%	Half Life
Ru-101	5.2	Stable
Ru-102	4.30	Stable
Rh-103	3.03	Stable
Ru-104	1.88	Stable
Pd-105	0.96	Stable
Pd-106	0.402	Stable
Pd-107	0.146	6.5E+06y
Pd-108	0.054	Stable
Ag-109	0.031	Stable
Pd-110	0.025	Stable

2.3 Calculation of the Theoretical Mass Distribution of the Fission Product Noble Metals

Knowledge of the theoretical mass distribution based on fission yields of the fission product noble metals is helpful in preparing nonradioactive HLW simulants for SRAT and SME testing. This distribution can be calculated from the information in Table 2-1. For each fission product noble metal isotope that is insoluble in caustic, its concentration in weight percent in total dried solids of a sludge slurry is directly proportional the product of it fission yield times its atomic mass. The atomic mass is included in the equation because fission yields are given in terms of atoms per 100 U-235 fissions rather than the masses of each atom per 100 fissions. On this basis, the weight fraction of Rh in the total weight of fission product noble metals in a dried sludge slurry is given by the following equation

$$F_{Rh} = FY_{Rh}M_{Rh}/(FY_{Rh}M_{Rh}+\bullet\ FY_{Ru}M_{Ru}+\bullet\ FY_{Pd}M_{Pd} + FY_{Ag}M_{Ag})$$

Where F_{Rh} is the relative concentration of Rh-103 in the total fission product noble metals

FY_{Rh} is the fission yield of Rh-103

M_{Rh} is the atomic mass of Rh-103

- $FY_{Ru}M_{Ru}$ is the summation of the products of the fission yield for each isotope that is part of the total Ru times its respective mass.

- $FY_{Pd}M_{Pd}$ is the summation of the products of the fission yield for each isotope that is part of the total Pd times its respective mass.

$FY_{Ag}M_{Ag}$ is the product of the fission yield for Ag-109 times its mass.

For mass fraction of Ru the equation is

$$F_{Ru} = \bullet\ FY_{Ru}M_{Ru} /(FY_{Rh}M_{Rh}+\bullet\ FY_{Ru}M_{Ru}+\bullet\ FY_{Pd}M_{Pd} + FY_{Ag}M_{Ag})$$

For mass fraction of Pd the equation is

$$F_{Pd} = \bullet\ FY_{Pd}M_{Pd} /(FY_{Rh}M_{Rh}+\bullet\ FY_{Ru}M_{Ru}+\bullet\ FY_{Pd}M_{Pd} + FY_{Ag}M_{Ag})$$

If natural Ag is absent, the equation for predicting the mass fraction of fission product Ag is

$$F_{Ag} = FY_{Ag}M_{Ag} /(FY_{Rh}M_{Rh}+\bullet\ FY_{Ru}M_{Ru}+\bullet\ FY_{Pd}M_{Pd} + FY_{Ag}M_{Ag})$$

When this is done, the relative concentrations of Ru/Rh/Pd/Ag on a mass basis such as weight percent should be 0.71/0.19/0.10/0.0021. These calculations of mass ratios assume that all these species are completely insoluble and that no natural isotopes of these fission product noble metals are present in the waste. Consequently, the concentrations of the noble metals should be in this ratio when preparing HLW simulants in order to simulate the fission product noble metals correctly.

3.0 MEASUREMENT OF FISSION PRODUCT NOBLE METALS IN SRS HLW SLUDGES

3.1 Analytical Technique

In 1990 a study was performed on the measurement of fission product noble metals in SRS HLW sludges.[6] In that study two techniques were evaluated to analyze the solutions that resulted from dissolution of dried HLW sludge samples. These techniques were Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The dissolutions were performed at 115°C using Aqua Regia to dissolve samples of the dried slurry in Teflon vessels that could be tightly sealed during the dissolution.[7] In that study it was determined that the better technique for measuring noble metals was ICP-MS primarily because of it greater sensitivity and because ICP-AES had too many spectral interferences for the noble metals. In the ICP-MS technique a solution is passed through a high-temperature plasma where it is vaporized and the elements volatized into a mass spectrometer where the isotopic concentrations are measured as a function of the mass of the element. With this technique, concentrations down to ~10 parts per trillion can be measured. The disadvantage of this technique is that isotopes of different elements that have the same mass are measured together. For example, in a sample, the isotopes of Pd-108 and Cd-108 would both be measured at mass 108 if both were present in the solution. Table 3-1 lists the noble metal fission products that appear at each mass and the possible interfering isotopes that also appear at that mass.

Table 3-1. Fission Product Noble Metal Isotopes and Interfering Natural Isotopes in SRS HLW Sludges

Mass	Fission Noble Metal	Possible Interfering Natural Isotopes
101	Ru	Ru-101
102	Ru	Ru-102
103	Rh	Rh-103
104	Ru	Ru-104
105	Pd	Pd-105
106	Pd	Pd-106, Cd-106
107	Pd	Ag-107
108	Pd	Pd-108, Cd-108
109	Ag	Ag-109
110	Pd	Pd-110,Cd-110

Note that the fission product noble metals of Ru, Rh, and Pd at masses of 101 through 105 also have natural isotopes at those masses. Consequently if any these elements had been used in the separations processes at SRS they would affect the results for the fission product noble metals. However Ru, Rh, and Pd were never used in any of the separation processes at SRS. Further, a study in 1999 showed the isotopic distribution of Ru in a HLW waste sample was definitely that of fission product Ru and not natural Ru.[8] Natural Ag and Cd, if present, interfere with the analysis of the fission products Pd and Ag at masses 106-110. Natural Ag and Cd were used in some of the processes at SRS. As mentioned earlier, Ag was used to scavenge I-131 that was volatilized from the dissolvers in the SRS canyons. Natural Cd was used in some reactor charges to adjust the energy spectrum of the neutrons in some reactor campaigns. As will be shown in the next section, natural Ag and Cd were detected in the samples analyzed for this study. This required the calculation of the concentrations of the fission product Pd isotopes at masses 106, 107, 108, and 110. The presence of natural Ag negated any attempt of measuring the fission product of Ag-109.

3.2 Measured and Calculated Concentrations of Fission Product Noble Metal Isotopes and Interfering Natural Isotopes in Sludge Batch Three

Sludge Batch 3 is currently being characterized for radionuclide content to provide data for acceptance of the glass waste form into the geologic repository. Concentrations of major elements in the sludge and the noble metals were measured as part of the qualification of SB3. Results of these measurements have previously been published.[9] However, the details of how the noble metal concentrations were determined were not presented in that report. Those details are presented here. Table 3-2 presents the data used to calculate concentrations of the noble metals. Results of total concentrations measured by ICP-MS in the mass region 101 to 116 except for mass 115 are presented in Column 2 of Table 3-2. Natural Indium, which is 95.7% In-115, was added to the solutions being analyzed as an internal standard to assess matrix effects on the analyses by ICP-MS. (Indium is also 4.3% In-113, however the software of the ICP-MS automatically subtracts the contribution of In-113 to the mass spectrometric signal at mass 113.) Note that the total concentrations measured at masses 106 and 107 are both higher than the concentration measured at mass 105. If only fission product Pd were present, the concentrations at masses 106 and 107 would be lower since the fission yields at 106 and 107 are lower than the fission yield for Pd-105 (see column 4 of Table 3-2). This result indicates that both natural Ag and Cd are in SB3. These elements have isotopes that interfere with the measurement of the concentrations for four of the five isotopes of the fission product Pd. There are no stable isotopes of Cd or Pd at mass 115 so the addition of In does not affect the analysis of these elements. Table 3-2 presents the isotopic distribution for the natural Ag and Cd in Column 6. The natural distributions for Ru, Rh, and Pd are not included in Table 3-2 because these natural elements are presumed to have negligible concentrations in the waste since they were not used in any of the chemical processes at SRS.

Table 3-2. Measured and Calculated Concentrations for Fission Product Noble Metals and Interfering Natural Isotopes in Sludge Batch 3.

Mass	Total Meas. Wt.%	Fission Product		Natural Isotope		Calc. Pd Isotopic Wt. %	Calc. Cd or Ag Isotopic Wt. %	Calc. Cd or Ag Total Wt %
		Isotope	Yield, %	Isotope	Percent Abundance			
101	1.2E-02	Ru	5.2	NA	NA	NA	NA	NA
102	1.1E-02	Ru	4.3	NA	NA	NA	NA	NA
103	7.3E-03	Rh	3.0	NA	NA	NA	NA	NA
104	6.9E-03	Ru	1.9	NA	NA	NA	NA	NA
105	8.8E-04	Pd	0.96	NA	NA	NA	NA	NA
106	3.1E-03	Pd	0.40	Cd	1.25	3.7E-04	2.7E-03	2.2E-01
107	8.1E-03	Pd	0.15	Ag	51.8	1.4E-04	7.9E-03	1.5E-02
108	1.5E-03	Pd	0.054	Cd	0.89	5.1E-05	1.5E-03	1.7E-01
109	8.0E-03	Ag	0.031	Ag	48.2	NA	8.0E-03	1.7E-02
110	1.9E-02	Pd	0.025	Cd	12.5	2.4E-05	1.9E-02	1.5E-01
111	2.4E-02	Cd	0.017	Cd	12.8	NA	NA	1.9E-01
112	4.2E-02	Cd	0.013	Cd	24.1	NA	NA	1.7E-01
113	2.7E-02	Cd	0.014	Cd	12.2	NA	NA	2.2E-01
114	5.2E-02	Cd	0.012	Cd	28.7	NA	NA	1.8E-01
116	1.1E-02	Cd	0.013	Cd	7.49	NA	NA	1.5E-01

NA = Not Applicable

Since Cd and Ag interfere with the measurement of Pd-106, Pd-107, Pd-108 and Pd-110, their concentrations had to be calculated. Since the concentrations of the fission product Pd isotopes are directly proportional to the product of their fission yields times their mass and the proportionality constants are equal, the concentrations of these isotopes were calculated using the following equation

$$C_i = C_{Pd\text{-}105}(FY_i \times M_i)/(FY_{Pd\text{-}105} \times M_{Pd\text{-}105})$$

where C_i is the concentration of isotope i, of Pd, FY_i is its fission yield, and M_i its mass. $C_{Pd\text{-}105}$ is the concentration of Pd-105, $FY_{Pd\text{-}105}$ is its fission yield, and $M_{Pd\text{-}105}$ its mass. Results of these calculations are presented in Column 7 of Table 3-2. The concentrations of the interfering isotopes were then calculated by subtracting the calculated concentrations for the respective Pd isotopes from the measured concentrations. These results are presented in Column 8 of the Table. As a check, the elemental concentrations of the interfering Ag and Cd were calculated by dividing the calculated concentration of each isotope by its respective natural abundance. These results are presented in the last column of Table 3-2. The elemental concentrations of Ag calculated from its two isotopes are in excellent agreement proving that this is natural Ag. For Cd, the elemental results for the eight isotopes of Cd are in good agreement proving that natural Cd was in the sample. The average concentration is 0.18 wt % with a RSD of 14% based on the eight isotopes. Cadmium was also measured by ICP-AES in these samples. With ICP-AES the result was 0.18 wt % with a RSD of 4% based on analysis of quadruplicate dissolved samples of the dried slurry.[9]

The total elemental concentration of each of the fission product noble metals is the sum of the respective isotopes in Table 3-2. For Ru, the concentration is 3.0E-02 wt % in the total dried solids, for Rh, 7.3E-03 wt %, for Pd, 1.5E-03 wt %, and for Ag,, 1.6E-02 wt %. For Pd, the measured concentration at mass 105 was summed with the calculated concentrations of the other Pd isotopes shown in Column 7 of Table 3-2.

The mass distribution of the noble metals Ru, Rh, and Pd in this sample will now be compared to the mass distribution determined from the fission yields and mass of the noble metal isotopes. In this calculation for SB3, Ag was ignored since there was natural Ag in the sample. The mass distribution of the noble metals (Ru/Rh/Pd) is 0.77/0.19/0.038. Comparison of this to the theoretical mass distribution calculated from the fission yields and masses of the noble metals (0.71/0.19/0.10) clearly indicates that these elements in SB3 are fission products and not naturally occurring elements. The concentration of Pd is low possibly due to some Pd being in the salt tanks.

3.3 Measured and Calculated Concentrations of Fission Product Noble Metal Isotopes and Interfering Natural Isotopes in the 7/29/04 Sample of Tank 11 Sludge

The concentrations of noble metals have been determined by ICP-MS measurement on dissolved samples from a sludge slurry sample taken from Tank 11 on July 29, 2004. This was the second sample taken from Tank 11 after it had been mixed for transfer to Tank 51 in preparation of Sludge Batch 4. A description of the tank sampling procedure and results of the characterization of the sample have been published previously.[10] However in that report details of the method of measuring the noble metals were not included. The same method as described above for the SB3 sample was followed for this Tank 11 sample. Table 3-3 gives the results for the Tank 11 sample in the same format as those in Table 3-2.

Table 3-3. Measured and Calculated Concentrations for Fission Product Noble Metal Isotopes and Interfering Natural Isotopes in the 7/29/04 Tank 11 Sample

	Total	Fission Product		Natural Isotope		Calc. Pd	Calc. Cd or Ag	Calc. Cd or Ag
Mass	Meas. Wt.% (a)	Isotope	Yield, %	Isotope	Percent Abundance	Isotopic Wt. %	Isotopic Wt. %	Total Wt %
101	8.9E-03	Ru	5.2	Ru	NA	NA	NA	NA
102	8.2E-03	Ru	4.3	Ru	NA	NA	NA	NA
103	3.9E-03	Rh	3.0	Rh	NA	NA	NA	NA
104	3.6E-03	Ru	1.9	Ru	NA	NA	NA	NA
105	1.9E-04	Pd	0.96	Pd	NA	NA	NA	NA
106	2.4E-04	Pd	0.40	Cd	1.25	8.0E-05	1.6E-04	1.3E-02
107	5.6E-04	Pd	0.15	Ag	51.8	2.9E-05	5.3E-04	1.0E-03
108	1.4E-04	Pd	0.054	Cd	0.89	1.1E-05	1.3E-04	1.4E-02
109	5.0E-04	Ag	0.031	Ag	48.2	NA	5.0E-04	1.0E-03
110	1.8E-04	Pd	0.025	Cd	12.5	5.0E-06	1.7E-04	1.4E-03
112	2.2E-04	Cd	0.013	Cd	24	NA	NA	9.1E-04
114	9.6E-05	Cd	0.012	Cd	28.7	NA	NA	3.3E-04
116	3.1E-04	Cd	0.013	Cd	7.49	NA	NA	4.0E-03

(a) Concentrations are given in weight percent in total dried solids of the Tank 11 slurry. Results are averages of triplicate samples with relative standard deviations of 2 to 9% for Ru and Rh isotopes and 17% for Pd.

Clearly there is natural Ag in this sample, as shown by the results at masses 107 and 109. In fact the concentrations of elemental Ag calculated from each isotope and its natural abundance are equal. The concentration of Cd is much lower in this sample than in the SB3 sample. In this sample, a reliable measurement of Cd-113 could not be measured at mass 113 because of interference from In-113 that was in the internal standard placed in the sample. However, since Pd does not account for all the concentrations measured by the ICP-MS at masses 106, 107, 108 and 110, there is definitely natural Cd in this sample. Because of the low concentrations measured by ICP-MS for the Cd isotopes, the results calculated for the concentration of elemental Cd from each isotope of Cd are in poor agreement. However the results clearly indicate that natural Cd is present.

The total elemental concentration of each of the fission product noble metal was calculated from their respective isotopes in Table 3-3. For Ru, the concentration is 2.1E-02 wt % in the total dried solids, for Rh, 3.9E-03 wt %, for Pd, 3.2E-04 wt %, and for Ag, 1.0E-03 wt %. It is again interesting to compare the mass distribution of the noble metals Ru, Rh, and Pd in this sample. The element Ag was again ignored since there was natural Ag in the sample. The mass distribution of the noble metals (Ru/Rh/Pd) is 0.83/0.16/0.013. In this sample, again a comparison of this to the theoretical mass distribution calculated from the fission yields of the noble metals (0.71/0.19/0.10) indicates that the elements are fission products and not naturally occurring elements. The concentration of Pd is again low possibly due to some Pd being in the salt tanks.

4.0 PREDICTION OF FISSION PRODUCT NOBLE METAL CONCENTRATIONS IN SRS HLW SLUDGES

4.1 Method of Prediction

The concentrations of fission product noble metals that are produced in a specific reactor charge at SRS can be predicted with some reliability if one concentrates on that reactor charge. Computer codes have been written to predict the production of fission products in U-235 reactor fuels. These codes contain the fission yields for the noble metal isotopes as well as the other fission product isotopes along with their radioactive decay constants. The codes also contain the cross sections for neutron adsorption by U-235 and other components in the reactor fuel including the fission products. If the flux and energy spectra for the neutrons are known then the production of the fission products and their decay in a reactor charge can be estimated. Prediction of noble metal concentrations in specific HLW tank sludges by such *a priori* techniques is completely impossible because the sludges in the HLW tanks are mixtures of fission products from several different reactor irradiations and reactor campaigns. Also the sludges are mixtures of high heat and low heat wastes from the solvent extraction processes in the SRS Canyons. At SRS there is a High Level Waste Characterization System (WCS) that tracks each major waste component in the HLW such as sludge and salt that is added to the Tank Farm.[11] The system WCS tracks the major chemical compounds from the two major processes that were performed at SRS. These were the Plutonium Recovery and Extraction (PUREX) process performed in F-Area canyon and initially in H-Area canyon and the H Modified (HM) PUREX process performed only in H Area canyon. The weight of each major compound ($Fe(OH)_3$, $Al(OH)_3$, $Ni(OH)_3$ and MnO_2) added to the Tank Farm is predicted from H and F canyon receipts. Except for $Al(OH)_3$, these compounds are primarily insoluble in caustic. Thus, they and much of the $Al(OH)_3$ are distributed primarily throughout the sludge tanks in the Tank Farm. Tank to tank transfers of sludge are recorded so the amount of these insoluble compounds in a specific sludge tank can be estimated. The amounts of minor compounds such as $La(OH)_3$ that have been added to a tank are calculated based on the amount of $Fe(OH)_3$ predicted to be in that tank times the ratio of that compound to the concentration of $Fe(OH)_3$.in the four major waste types. These ratios were measured for various waste types in the 1980's in appropriate samples sent to SRTC.[12] The waste types are PUREX High Heat Waste (HHW), PUREX Low Heat Waste (LHW), HM HHW and HM LHW. For example the ratio of $La(OH)_3$ to $Fe(OH)_3$ in HM HHW is 0.0044 while for PUREX HHW it is

0.0024. (See Table 2 of Reference 12.) On this basis, the concentrations of forty different chemical compounds have been estimated in the SRS sludge tanks. The inventory of fission products in HLW is based on fission yields distribution in SRS reactor assemblies, solubility data [13] along with the canyon receipts and the tank to tank transfer records referred to above. The only fission product noble metals that are tracked are Ru, Ru-106 and its daughter Rh-106. Both of these isotopes are radioactive and have short half lives. For example, the half life of Ru-106 is 1.02 years and the half life of its daughter is even shorter.[5] Thus they have decayed to very low levels in the SRS sludges since the SRS reactors have been shut down for more than ten years. Consequently these isotopes cannot be easily measured in the SRS sludges and thus are not suitable for predicting the concentrations of the other noble metal fission products in the sludges. Even though elemental Ru is tracked, unfortunately it is not included in the sludge batch compositions projected by CBU. However, there is one fission product, lanthanum (La), that is tracked by WCS and has been included in the CBU projections.

The natural element La is 99.91% La-139. The isotope La-139 is also a fission product with a fission yield of 6.6%. The compound $La(OH)_3$ is very insoluble in caustic and La is easily detected in HLW sludges by ICP-MS. Furthermore, natural La was not used for any of the chemical processes performed in the F or H-area canyons. Thus, its main source in the HLW sludges was probably La-139 from the fission of U-235. The element La is tracked by WCS and its concentrations in SB3 and in the 7/29/04 sample from Tank 11 were projected by CBU.[14,15] Consequently, if the concentration of La-139 in these samples is known, the concentrations of the fission product noble metal isotopes can be calculated from the following equation

$$C_i = C_{La\text{-}139}(FY_i \text{ x } M_i)/(FY_{La\text{-}139} \text{ x } M_{La\text{-}139})$$

where C_i is the concentration of fission product isotope i, FY_i is its fission yield, and M_i its mass. $C_{La\text{-}139}$ is the concentration of La-139, $FY_{La\text{-}139}$ is its fission yield, and $M_{La\text{-}139}$ its mass. This method was recently used to predict the bounding noble metal concentrations in Sludge Batch 4; However details were not presented in that memorandum.[16]. Those concentrations were based on the bounding La concentrations estimated to be in SB4 by Closure Business Unit (CBU) using the WCS inventories for the sludges expected to be in SB4. [17]

4.2 Predicted and Measured Concentrations of Noble Metal Fission Products in Sludge Batch 3.

In this section the measured and predicted concentrations for the fission product noble metals in SB3 are compared. Results are presented in Table 4-1. The measured concentrations of the individual isotopes of the fission product noble metals were presented in Table 3-2. The total concentrations of the fission product noble metals were published earlier in Reference 15 and are also presented in Section 4.2. Measured results are presented in Column 2 of Table 4-1. The concentrations of fission product noble metals were then predicted based on two values for the La concentration in SB3. The first prediction uses the La concentration predicted to be in SB3 based on WCS. [15]. The second prediction is based on a measured concentration of La in SB3 using ICP-MS.[9] The predictions are in Columns 3 and 5 of Table 4-1. For each method of prediction, the ratio of the predicted concentration to the measured concentration is presented in Columns 4 and 6 of the table.

Table 4-1. Comparison of Measured and Predicted Noble Metal Concentrations in Sludge Batch 3 Based on La. (a)

Noble Metal	Measured Wt. %	Based on WCS Pred. La Conc. (b)		Based on ICP-MS Meas. of La Conc. (c)	
		Predicted Wt. %	Pred./Meas.	Predicted Wt. %	Pred./Meas.
Ru	3.0E-02	1.8E-01	6.0	3.4E-02	1.1
Rh	7.3E-03	4.8E-02	6.6	9.1E-03	1.2
Pd	1.5E-03	2.6E-02	17.3	4.9E-03	3.3
Ag	1.6E-02	5.2E-04	0.033	9.9E-05	0.0062

(a) Concentrations are given in weight percent in total dried solids of the SB3 slurry.

(b) Based on a predicted La concentration of 0.18% in calcined solids (Ref. 15) and a calcine factor of 0.77 weight percent total solids per weight percent calcine calculated from data for SB3 [9].

(c) Based on a measured La concentration of 0.026 weight percent in total solids published in Ref. 9. This is the average of three determinations with a %RSD of 3.2.

In Table 4-1, the predicted concentrations for Ru, Rh and Pd are higher than the measured. The predicted values for the Ag concentrations in the sample are significantly lower than the measured because of the presence of natural Ag in the sample. Obviously this method of prediction cannot be used is natural Ag is present.

For Ru and Rh, the predictions based on the La measured by ICP-MS are in good agreement with the measured values considering the low concentrations being measured by the ICP-MS. This agreement supports the supposition that most if not all the La in SB3 is fission product La and not natural La added with some process chemical used at SRS. The significantly higher predicted values for Pd than the measured values could be a result of a portion of the fission product Pd being soluble in caustic and thus in a salt tank giving a significantly lower measured concentration than the predicted concentration in a sludge tank. This has been shown to be the case for Tc-99 in sludges where the concentration of Tc-99 was considerably less than the predicted concentration if all the Tc-99 had been insoluble in caustic.[18] That study also showed the same effect for Pd-105.[18] In Table 4-1, the results for the prediction by WCS for Ru, Rh, and Pd are significantly higher than the measured. However considering all the tank transfers and canyon receipt records along with the calculations that predict the washing of SB3, the agreement is not bad.

Information concerning the discrepancy between the WCS predictions for the noble metal concentrations and the measured values can be obtained by comparing the measured and predicted concentrations for Fe and La in SB3. As stated in Section 4.0, WCS tracks the Fe going to the Tank Farm based on H and F Canyon receipts and tank-to-tank sludge transfers throughout the sludge tanks. The La concentration is tracked based on the ratio of its concentration relative to that for Fe in various types of HLW sludges (such as HHW and LHW) transferred to the Tank Farm. If there is an error in the prediction of Fe or of La, this error would manifest itself in the predicted concentrations of the noble metals since these are based on the La concentration. Table 4-2 compares the measured and predicted concentrations for Fe and La in SB3.

Table 4-2. Comparison of Measured and WCS Predicted Concentrations of Fe and La in Sludge Batch 3 (a)

Element	Measured Wt. %	Predicted Wt. % (b)	Pred./Meas.
Fe	1.6E+01 (c)	2.2E+01	1.4
La	2.6E-02 (d)	1.4E-01	5.4

(a) Concentrations are given in weight percent in total dried solids of the SB3 slurry.
(b) Based on predicted Fe and La concentrations of 28.5 and 0.182%, respectively, in the calcined solids of SB3 (See Case 6 in Table 2 of Ref. 15) and a calcine factor of 0.77 weight percent total solids per weight percent calcined solids calculated from data for SB3[9].
(c) The average concentration of Fe measured by ICP-ES in eight dissolved of dried SB3 slurry. [9] The %RSD was 4.2.
(d) The average concentration of La measured by ICP-MS in three dissolved samples of dried SB3 slurry. [9] The %RSD was 3.2.

In Table 4-2 the measured concentration for Fe is within 40% of the predicted. This can be considered good agreement for reasons stated above. Because Fe is a major element in the sludge, its concentration in the samples analyzed in the 1980's was by ICP-ES and is probably a reliable result. The predicted value for La is 540% greater than the measured. This large difference can be attributed to the method of measuring La in the samples in the 1980's. The prediction is based on measurements in 1976-1983 of La in the various HLW types by Spark Source Mass Spectroscopy (SSMS).[19] The SSMS method is much less sensitive for La than the ICP-MS that was not available at that time. The SSMS method has been described as a semiquantitative technique for trace metal ions in a mixture of metal oxides.[19] It is highly likely that the result of the SSMS measurement for La was biased high leading to an erroneously high ratio of La to Fe used in the WCS predictions. In 2005 the La was measured much more accurately by ICP-MS which is much more sensitive than SSMS. As will be seen in the next section concerning the Tank 11 sample, the ICP-ES method gave results for La that were also higher than the values measured by ICP-MS for La.

4.3 Predicted and Measured Concentrations of Noble Metal Fission Products in the July 29, 2004 Sample of Unwashed Tank 11 Sludge.

Comparisons of the measured and predicted noble metal concentrations in the July 29, 2004 sample of unwashed Tank 11 sludge are given in Table 4-3. Results of the overall composition of the sample have been published.[10] The measured concentrations in Column 2 of Table 4-3 are averages of the ICP-MS analysis of triplicate samples of dissolved dried Tank 11 unwashed sludge. The predicted concentrations in Column 3 are based on CBU projections using WCS for the La concentration in the Tank 11 sludge that was washed to 1.0M Na.[17] The La concentration in this projection was 0.15% in the dried solids. (See Table 3-1 of Reference 10.) The La concentration in the unwashed sludge was calculated using a washing factor of 7.7 based on Fe, a major insoluble element in the sludge. The projected Fe concentration in the washed sample was 17.4 wt %. The measured concentration in the unwashed sample was 2.26 wt % or 7.7X lower. Consequently, the predicted La concentration in the unwashed sludge would be 0.15/7.7 or 0.019 wt %. The predicted concentrations of fission product noble metals using this calculated La concentration in the unwashed sludge are shown in Column 3 of Table 4-3. The concentration of insoluble elements in a sludge are lower in the unwashed sludge due to the higher concentrations of soluble salts, primarily Na salts, being present. As these salts are washed out, the concentrations of the insoluble salts increases. In Table 4-3, the concentrations of fission product noble metals are also predicted in the unwashed sample from two different measurements of the La concentration in the Tank 11 sample. The first was by ICP-ES using the La concentration reported in

Reference 9. The predicted values of the fission product noble metal concentrations based on this La measurement are presented in Column 5 of Table 4-3. Recently the La concentration in this Tank 11 sample was also measured by ICP-MS for C. J. Bannochie. The predicted values of the fission product The noble metal concentrations predicted by the two measured concentrations of La are compared with the measured noble metal concentrations in Columns 6 and 8, respectively.

Table 4-3 Comparison of Measured and Predicted Noble Metal Concentrations in July 29, 2004 Sample of Unwashed Tank 11 Sample Based on La. (a)

		Based on WCS Predicted La Conc. (c)		**Based on ICP-ES Measurement of La Concentration (e)**		**Based on ICP-MS Measurement of La Concentration (f)**	
Noble Metal	**Measured Wt. %(b)**	**Predicted Wt. %**	**Pred./Meas**	**Predicted Wt. %**	**Pred./Meas.**	**Predicted Wt. %**	**Pred./Meas.**
Ru	2.1E-02	2.6E-02	1.3	3.6E-02	1.6	1.8E-02	0.9
Rh	3.9E-03	6.9E-03	1.8	9.8E-03	2.3	4.9E-03	1.3
Pd	3.2E-04	3.6E-03	11.4	5.3E-03	15.3	2.6E-03	8.2
Ag	1.0E-03	(d)	-	1.1E-04	0.10	5.3E-05	0.053

(a) Concentrations are given in weight percent in total dried solids of the Tank 11 slurry.
(b) Results are averages of triplicate samples of dissolved unwashed Tank 11 sludge.Relative standard deviations of 2 and 9% for Ru and Rh and 17% for Pd.
(c) Based on a La concentration of 0.15% in total solids predicted by WCS for washed Tank 11 sludge and a wash factor of 7.7 as explained in the text.
(d) Ag was not predicted by WCS.
(e) Based on a La concentration of 0.028 wt % in total solids measured by ICP-ES on a single sample of dissolved unwashed Tank 11 sludge.
(f) Based on a La concentration of 0.014 wt % in total solids measured by ICP-MS on duplicate samples of dissolved unwashed Tank 11 sludge. Relative standard deviation was 16%. Measurement furnished by C. J. Bannochie.

The results in Table 4-3 support the same four conclusions that were drawn from the data in Table 4-1 for SB3. These conclusions are:

1. For Ru and Rh the predictions using La measured by ICP-MS in the unwashed sludge sample are in excellent agreement with the measured values indicating that La, Ru, and Rh are U-235 fission products in the Tank 11 sample.

2. The measured values for Pd are significantly lower than the predicted probably due to some transfer of Pd to the salt tanks.

3. The predicted results for Ru and Rh based on WCS are only 25 and 76% higher than the measured concentrations. This agreement is much better than that in the SB3 samples where the WCS projections were 600 to 660% higher than the measured.

4. The concentration of Ag is higher than any of the predictions due to natural Ag being in the Tank 11 sample.

One other conclusion can be drawn from the results in Table 4-3. The La concentration measured by ICP-ES was ~2X higher than that measured by ICP-MS. When the triplicate samples of dissolved Tank 11 sludge were analyzed by ICP-ES, La was detected in only one of the samples at a concentration slightly above the detection limit for the instrument. In the other two, the La was below the detection limit for the instrument. When the same samples were analyzed by ICP-MS, La was detected in all three with results that were well above the detection limit for the ICP-MS. This means that the result for La from the ICP-MS analysis is more reliable than the result obtained using ICP-ES. Using the ICP-MS result for La to predict the Ru and Rh concentrations is thus a more reliable prediction than that using the ICP-ES results.

5.0 CONCLUSIONS

The bases for calculating and predicting the concentrations of noble metal fission products in SRS HLW sludges are presented in this report. The concentrations are calculated from ICP-MS measurements of the isotopes of the noble metals from samples of the dried sludge slurry that were dissolved by Aqua Regia digestion. Predictions based on WCS and on measured values of La in the samples are presented and compared to results of the ICP-MS measurements of the noble metal concentrations. The results presented in this report support the following conclusions.

1. The noble elements Ru, Rh, and Pd and the rare earth element La are present in Sludge Batch 3 and in the 7/29/04 sample of Tank 11 sludge as fission products from the thermal neutron induced fission of U-235 in the SRS reactors.

2. The isotopes of fission product Ru are Ru-101, 102, and 104. The isotope of fission product Rh is Rh-103. The isotopes of fission product Pd are Pd-105, Pd-106, Pd-107, Pd-108 and Pd-110.

3. The calculated mass distribution of the fission product noble metals (Ru/Rh/Pd) based on their fission yields and masses is 0.71/0.19/0.10.

4. Sludge Batch 3 and the 7/29/04 sample of Tank 11 sludge each contain natural Ag and Cd. These interfere with the analysis of five of the six Pd isotopes in the sludges. The concentrations of the five can be calculated from the measured concentration of Pd-105 and the fission yields and masses for the Pd isotopes.

5. The concentration of the Pd is lower than that expected from the fission yields of the Pd isotopes. It is hypothesized that this may be due to some of the Pd being in the salt tanks.

6. Sludge Batch 3 and the 7/29/04 sample of Tank 11 sludge each contain the U-235 fission product La-139. Knowledge of its concentration allows the concentrations of the fission product noble metals to be predicted.

7. The predictions of the concentrations of Ru and Rh calculated from the concentrations of La projected by CBU for SB3 and the Tank 11 sample based on WCS are higher than the predictions based on the measured values of the La concentrations in the two samples. The concentrations predicted by WCS may be high due to erroneously high values for the La concentrations reported in WCS. The values in WCS are based on analyses of sludges in 1976-1983 time frames using the SSMS technique that is not as reliable as current analytical techniques for La. Based on the results for SB3, the predictions for the noble metals are factors of 6 to 7 too high.

6.0 RECOMMENDATIONS

The results and conclusions presented in this report lead to the following recommendations concerning the measurement and prediction of noble metals in SRS HLW sludges.

1. At SRNL, the isotopes of the noble metals such as Ru, Rh, Pd, and Ag should be measured in SRS HLW sludges using ICP-MS analysis of samples of dried sludge slurry dissolved by the Aqua Regia technique. The concentrations of other trace elements in the sludges such as La should also be measured by ICP-MS.

2. When measuring the concentrations of noble metal isotopes in HLW sludges, the concentrations of the Ag and Cd isotopes should be measured to determine if these isotopes are in the sludges as only fission products or as a combination of fission product and natural isotopes. If the natural isotopes are present then the concentrations of several of the Pd isotopes must be calculated as described in this report.

3. When preparing simulants of HLW sludges for various nonradioactive tests, the relative concentrations of the noble metals should have the following distribution if natural Ag is not present.

   Ru/Rh/Pd/Ag = 0.71/0.19/0.10/0.0021

   Based on the results in this report this will give a relative concentration of Pd that is higher than that in the actual sludge. Also, if natural Ag is present, its relative concentration will be much higher.

4. When using WCS to predict noble metal concentrations in sludges, use the La concentrations predicted by WCS to be in those sludges and the fission yields and masses of the noble metal isotopes relative to fission yield and mass of La-139. If natural Ag is present, the predicted value for the Ag concentration will be low and if possible other measurements of the Ag concentration should be used.

5. Based on the results in this report for SB3, the estimates for La in WCS are higher than the actual values in the sludge. This leads to erroneously high predictions for fission product noble metals. (This appears to be due to the method of analyzing La in the four major waste types of HLW sludge that form the bases of the WCS tracking method.)

6. For future data entries into WCS, the results for ICP-MS measurements should be used for La, Ag, and other trace elements tracked by WCS.

7.0 ACKNOWLEDGEMENTS

The author thanks Dr. Ray A Sigg and Dr. Frank S. Moore of the ADS Section for helpful and stimulating discussions concerning fission products from the thermal neutron fission of U-235 in the SRS reactors. The author also thanks Dr. Christopher J. Bannochie of the ITS Section for obtaining the ICP-MS analysis of La in the 7/29/04 sample of Tank 11 sludge. Lastly the author thanks Dr. John R. Fowler of JKLW Enterprises, Aiken, SC, for his comments on drafts of this report and his excellent discussions concerning WCS and the analyses performed in the 1976 to 1983 time frame that support WCS.

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