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Technetium-99 Behavior in Savannah River Site High Level Waste Sludges During Waste Processing

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ABSTRACT

This paper presents results of a study of the behavior of technetium-99 (Tc-99) during high level waste (HLW) processing operations at Savannah River Site (SRS). Its behavior during HLW processing is important to understand because Tc-99 can fractionate in the waste and appear in both the sludge and the salt tanks at SRS. It can also be soluble in groundwaters and thus is an important radionuclide that may dictate how much waste has to be removed from a tank to prepare it for permanent closure.

The HLW processing steps considered in this study are listed below.

- The initial caustic neutralization of the acidic waste streams generated in the SRS canyons to prepare the waste for storage in the mild steel tanks in the SRS Tank Farm. Waste that is insoluble in caustic precipitates while soluble elements remain in the supernates. At SRS insoluble components are segregated into sludge tanks and soluble components into the salt tanks.
- The operations in the SRS Tank Farm that wash the sludge in preparation for immobilization for permanent disposal.
- The sludge immobilization process in the Defense Waste Processing Facility (DWPF) that solidifies the solids into a stable borosilicate glass.

The data in this study are from tests performed at SRNL with both a simulated HLW doped with Tc-99 and tests performed remotely in the Shielded Cells with a sample of actual radioactive HLW that contained Tc-99 and other radionuclides generated in the SRS reactors.

Detailed results are discussed in the paper.

INTRODUCTION

Technetium-99 (Tc-99) is a U-235 fission product that was formed in the Savannah River Site (SRS) reactors during their operation. Tc-99 has a long half life (2.1×10^5 years¹) and thus essentially all of the Tc-99 produced in the SRS reactors is present in the high level waste (HLW) at SRS. The HLW at SRS is stored as caustic sludge slurries or as caustic supernates in million gallon mild steel tanks in the SRS Tank Farm. The sludge slurries are stored in tanks designated as sludge tanks and the caustic supernates in tanks designated as salt tanks. The sludge tanks hold most of the sludge solids and radionuclides that are insoluble in caustic. The salt tanks hold the caustic supernates that contain most of the radionuclides that are soluble in caustic. The fission product Tc-99 is of special interest because it can form two species in the wastes depending on the oxidation state of the Tc-99.² One species contains Tc-99 in the +4 state and is the oxide TcO₂. This oxide is insoluble in caustic and thus would be with the solids in the sludge

tanks. The other species contains Tc-99 in the +7 oxidation state. This is the pertechnetate anion, TcO_4^- , which is soluble in highly alkaline solutions. Thus this form of Tc-99 would follow the alkaline supernates and be in the salt tanks.

This report presents results of a study of the behavior of Tc-99 under conditions pertinent to the storage, retrieval, and processing of the HLW at SRS. Results are presented for both simulated HLW solutions doped with Tc-99 and for an actual HLW radioactive sludge containing Tc-99. This sludge is Sludge Batch 2 (SB2). In the years between 1983 and 1999, SB2 was prepared in the SRS Tank Farm by blending sludges from several sludge tanks. A sludge batch is nominally 1.5 million liters. After blending is complete, the batch is washed to prepare it for vitrification in the Defense Waste Processing Facility (DWPF). During the years 2001 to 2004 the DWPF immobilized the sludge and radionuclides in SB2 into a durable borosilicate glass for permanent disposal in a Federal Repository.

Prior to presenting the results of this study, it is helpful to present a summary of the HLW management processes at SRS. These are neutralization of the acid waste, separation of the sludge solids from the alkaline supernates, washing of the sludge solids, and finally immobilization of the sludge slurries for permanent disposal. These steps are summarized below.

Summary of HLW Management Processes at SRS

The high level waste solutions that resulted from the various separation processes at SRS to produce strategic radionuclides for the United States were primarily nitric acid solutions. On this basis it appears that most of the Tc-99 would be in the +7 oxidation state. These acidic waste solutions were evaporated to remove water and recover as much of the nitric acid as possible. This evaporation produced some solids in the concentrated wastes. These solids and their supernates were then made caustic for long term storage in the mild steel tanks at SRS. During caustic addition more solids precipitated. Those fission products that were insoluble in caustic also precipitated along with other insoluble species in the waste. This formed a hydrous oxide sludge in the waste. The soluble fission products remained in the supernate of the sludge. Most of this supernate of the sludge was decanted to another tank and then evaporated further to reduce the volume of HLW requiring storage. The remaining hydrous sludge solids and the remaining supernate were then pumped as slurries to sludge tanks. The concentrated supernates that were decanted from the sludge slurries were then gravity drained to the salt tanks. Thus the sludge tanks contain the most of the insoluble fission products and the salt tanks contain most of the soluble fission products. As a result the Tc-99 can be fractionated between the sludge and salt tanks. When a sludge batch is prepared for processing in the DWPF, it is washed in the Tank Farm with inhibited water to reduce the concentration of dissolved Na in the waste. Inhibited water (IW) is a solution of 0.010M NaOH and 0.010M NaNO_2 . It is necessary to use this type of solution in order to inhibit corrosion of the mild steel tanks.

The fraction of Tc-99 in the sludge tanks and in the salt tanks has been estimated based on process inventory records. It has been estimated that ~60% is in the salt tanks and ~40 percent is in the sludge tanks.⁴ Using results from the present study, it is now possible to calculate this fraction for Tc-99 based on the analysis of the sludge slurry. As mentioned before, results will be presented for SB2 slurry that was processed in the years 2000 to 2004. The final waste processing step is the immobilization in the DWPF of the radionuclides and other elements in a sludge slurry into a stable borosilicate glass for final geologic disposal. In the DWPF process, the primary mechanism for the loss of Tc-99 is volatilization at 1150°C from the DWPF melter because Tc-99 can form an oxide (Tc_2O_7) that has a boiling point of only 311°C.²

TESTS WITH SIMULATED HLW DOPED WITH Tc-99

The results of the tests described in this section indicate that 70 to 80% of the technetium in an acidic HLW stream is not precipitated with the HLW sludge solids during the caustic precipitation of the solids and their subsequent rinsing and washing in HLW processing operations. This means that 70-80% of the Tc-99 would be in the salt tanks and 20-30% in the sludge tanks. This range is somewhat higher than the fraction of ~60% estimated earlier to be in the salt tanks.³

Preparation of the Acidic Simulated HLW Solution

To determine the fractionation of Tc-99 during the precipitation of the sludge solids from an acidic HLW salt solution, tests were performed starting with a simulated HLW solution doped with Tc-99. One hundred milliliters of solution were prepared using nitric acid and nitrate salts of the major components of the waste. The solution was doped with a known amount of Tc-99. Composition of the solution is given in Table I. Its final acidity was 2.0M.

Table I Composition of Acidic Simulated HLW Solution

Component	Final Concentration (M)
Fe(NO ₃) ₃ ·9H ₂ O	0.35
Al(NO ₃) ₃ ·9H ₂ O	0.11
UO ₂ (NO ₃) ₂ ·6H ₂ O	0.048
CaCl ₂	0.038
Ni(NO ₃) ₂ ·6H ₂ O	0.064
Mn(NO ₃) ₂	0.069
HNO ₃	2.0

To dope the solution with Tc-99, exactly 65 µL of a stock solution containing 7.2E+08 dpm/mL of Tc-99 was added to the acidic waste solution. The Tc-99 solution was obtained commercially and had been prepared by dissolving solid NH₄TcO₄ in 0.5M HNO₃. Thus the initial form of the Tc-99 was the soluble pertechnetate anion as it probably is in the acidic HLW salt solutions. This quantity of Tc-99 provides a Tc-99 concentration of 5.0 mg/L or 5.0E-05M. The molar ratio of this concentration to that for Fe is only ~5 times greater than that in a typical actual SRS HLW solution; thus the behavior of the Tc-99 in this solution should be similar to its behavior in a HLW solution.

Tests with Simulated HLW Solution to Measure Tc-99 Behavior During Precipitation and Washing the HLW in the SRS Tanks

Four tests were performed, each in a 40 mL centrifuge tube equipped with a Teflon[®]-coated magnetic stirring bar. For each test a 10.0 mL aliquot of the acid solution was put into each tube. At SRS the acidic HLW from the various processes is made caustic in a stainless steel (SS) tank. Thus in one of the tests with the simulated waste (Test 3) a SS rod was added to determine if this might reduce the Tc to the 4+ oxidation state and affect the fraction soluble. This rod remained in Test 3 until the completion of the test. Caustic was then added to each acidic solution to make the final hydroxide concentration in each ~1.2M. This is the minimum initial hydroxide concentration for fresh HLW in the SRS processes. With stirring, exactly 1.2 mL of 50 wt% NaOH solution was added to each centrifuge tube. The solutions were

added in 0.10 mL increments over a 30 minute period eventually producing a dark brown-black suspension. The final pH of each solution was >12 as measured by pH paper. The final suspension was mixed at ambient laboratory temperature overnight and then centrifuged for 45 minutes at which point no further separation of the supernate and the solids was observed. Aliquots of each supernate were placed into a clean plastic sample bottles for later analysis.

Initially the acidic solution was a pale green. Upon addition of sodium hydroxide, the solution became golden yellow with the precipitation of white and dark brown-black solids. The white solids are probably a mixture of $\text{Al}(\text{OH})_3$ and $\text{Mn}(\text{OH})_2$. The darker solids are principally $\text{Fe}(\text{OH})_3$. The suspension became darker with continued addition of NaOH resulting in a dark brown-black color. After centrifuging the mixture, the supernate was colorless and the solids were brownish black.

A caustic salt solution (2M NaOH and 2M NaNO_3) was used to rinse the solids to lower the concentration of caustic prior to washing the solids with IW. In Test 1, 3 mL of the rinse solution was used. In Tests 2-4, 1 mL was used. The solids were agitated for approximately five minutes and then centrifuged. Samples of the rinse solutions were taken for later analysis. The solids were rinsed one more time in Test 1 and two more times for the other three tests. These rinse solutions were combined with their respective prior rinse solutions. The rinse solutions were saved for later analysis for Tc-99. We then air dried the rinsed sludge solids in the centrifuge tubes.

To simulate washing the sludge in the SRS Tank Farm, IW (0.010 M NaOH and 0.010 M NaNO_2) was used. For Test 1, 3mL of the IW used. For each of the other three tests, only 1mL of the IW was used. These were pipetted into the centrifuge tubes containing the air-dried sludge solids and each was gently agitated for five minutes until all of the solids had been wetted by the wash solution. The slurries were then centrifuged until a clear supernate liquid was formed. Aliquots of the supernate were taken for analyses. For each test the washing sequence was repeated four more times. All the wash solutions for each respective test were combined for analysis of Tc-99.

Aliquots of the initial supernates, the rinse solutions and the wash solutions were submitted to the Analytical Development (AD) personnel of SRNL for determination of T-99 concentration in each solution by beta counting. Then the total amount of Tc-99 in each solution could be calculated knowing the total volume of the solution. The fraction of Tc-99 removed by each solution was then calculated by knowing the amount of Tc-99 added to each test.

Table II shows the fractions of the added Tc-99 found in the original supernate, the rinse solutions and in the wash solutions. The fraction of Tc-99 remaining in the sludge solids was then calculated and is presented in Table II.

Table II Fraction of Tc-99 in the Supernate, Rinse Solutions, Wash Solutions and Insoluble Solids in Tests with Simulated HLW

Test No.	Supernate	Rinse	Wash	Fract. Not In Solids	Fract. In Solids
1	0.35	0.11	0.25	0.71	0.29
2	0.22	0.14	0.11	0.47	0.53
3	0.11	0.21	0.39	0.71	0.25
4	0.46	0.21	0.12	0.79	0.21

Results indicated that, with the exception of Test 2, 70 to 80% of the original technetium in the acidic waste solution remained soluble or was readily separated from the sludge solids during the rinsing and washing steps. An explanation of the high fraction (0.53) of insoluble technetium in Test 2 is not

immediately apparent. The addition of the stainless steel rod in Test 3 appeared to lower the amount of technetium in the original supernate. However, the Tc-99 was readily removed during subsequent rinses and washes of the sludge solids leaving only 28% of the technetium in the sludge solids. Thus, any change in the redox of the solution as a result of the presence of the stainless steel rod, did not form an irreversible, insoluble phase of Tc-99. On the basis of these tests it appears that 70-80% of the Tc-99 in an acidic HLW solution could be in the salt tanks in the SRS Tank Farm.

EXPERIMENTAL METHODS USED TO MEASURE THE COMPOSITION OF THE RADIOACTIVE SB2 SLUDGE SLURRY

For this study, the composition of radioactive SB2 sludge slurry is given in terms of weight percent of an element in the total dried solids of an aliquot of the slurry. The slurry includes both the insoluble sludge solids and the dissolved solids in the caustic supernate of the sludge slurry. The dissolved solids are primarily sodium salts of hydroxide, nitrate, and nitrite ions. Some sulfate is also present.

Dissolving the Dried Sludge Slurry

Aliquots of the thoroughly mixed SB2 slurry were dried and then dissolved remotely in the Shielded Cells of SRNL. Details have been published³ and will only be summarized here. Four aliquots of the slurry were taken after the slurry was thoroughly mixed. These were dried at nominally 100°C, dissolved by hot aqua regia in sealed Teflon vessels. The resulting solutions were diluted, removed from the Shielded Cells and sent to AD personnel for analyses. The results presented in this paper averages of the results of the four aliquots of the sludge slurry. An appropriate standard was also dissolved in triplicate with the samples and analyzed to determine if the dissolutions were complete and analytical methods accurate. Blank solutions were prepared to check for impurities that might be introduced during the dissolution methods. Results of the standards indicated that dissolutions were indeed complete and the analyses accurate. Results of the blanks indicated that the concentrations of impurities were negligible.

Analytical Methods

For this study, three analytical methods were used. The solutions were analyzed by Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES) for the major nonradioactive elements. For U-235 fission products including Tc-99, the solutions were analyzed by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). Finally, the solutions were analyzed by gamma counting for Cs-137.

CALCULATION OF THE FRACTION OF Tc-99 REMOVED FROM THE SB2 SLURRY BY SRS HLW WASTE OPERATIONS

The sample of SB2 slurry used in this study was a ~2L sample of the SB2 batch. It was sent to SRNL for characterization and to demonstrate the DWPF process on SB2.³ In the Tank Farm, the final washing of SB2 with IW in order to make the Na concentration slurry supernate acceptable for processing in the DWPF (0.5 to 0.6M) had not been completed. At SRNL the sample was washed to a final Na concentration of 0.57M in the supernate. Originally the Na concentration was 2.8M. Calculation of the fraction of Tc-99 that could have been in SB2 but was not in the final SB2 slurry sample was calculated using a factor called the Fission Yield Scaling Factor (FYSF) determined for the SB2 sludge slurry. The predicted weight percent of Tc-99 was calculated using the FYSF and the assumption that Tc-99 is completely insoluble in the caustic waste solution. Based on the measurement of the weight percent of Tc-99 in the dried slurry, the fraction of Tc-99 that had been removed from SB2 was calculated. Discussion of the FYSF will be presented prior to presenting the results.

The Fission Yield Scaling Factor and Its Calculation

The fission yield scaling factor is a factor that relates the concentration of a fission product in a sludge slurry to its fission yield and the atomic mass of that fission product. As stated before, this factor allows the concentration of a fission product to be predicted based on its fission yield and atomic mass if the fission product has a long half life or is stable. Prior to discussing the FYSF, some background information is helpful.

The fission products in SRS high level waste results primarily from the fission of U-235 used in the SRS reactors to make neutrons to irradiated natural U to produce Pu-239 for the United States. There was some fission of the Pu-239 in the reactors but this was negligible because of the small concentration of Pu-239 compared to the concentration of U-235 in the natural U that was being irradiated. The fission yield of an isotope is the fraction of the total number of fissions that lead to that isotope. These fission yields are well known from many studies and their values have been compiled and published.¹ It is usually given as a percent fission yield. Figure 1 shows the fission yields for slow neutron fission of U-235 as a function of isotopic mass number.

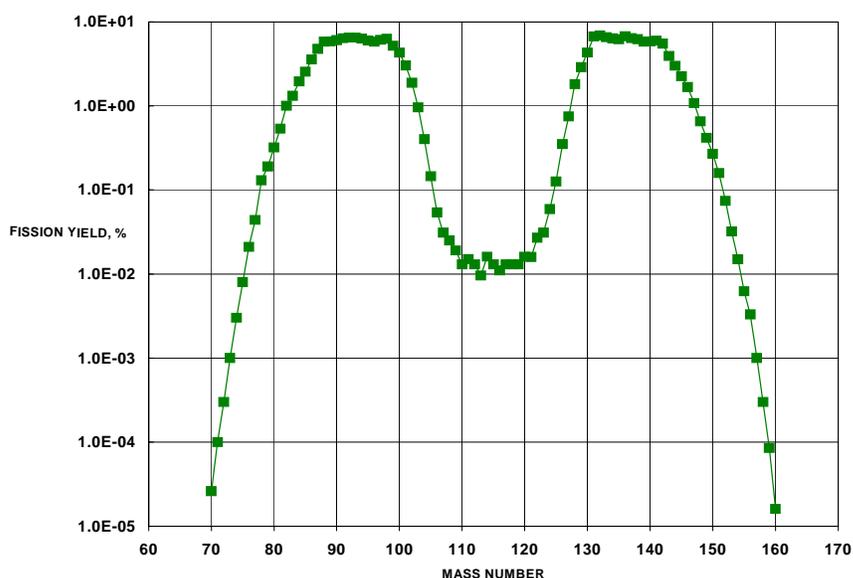


Figure 1. Fission Yields (in percent) as a Function of Atomic Mass Number for Slow Neutron Fission of U-235.

Assignment of specific isotopes to these mass numbers is done by considering the half lives of the various radionuclides in the respective isobaric fission chains from fission of U-235. Immediately after fission, the primary products in each of these chains are neutron rich. Thus they then beta decay increasing in atomic number while the atomic mass remains constant. The radionuclides in each isobaric chain decay until a stable isotope or an isotope with a long half life is reached. This isotope is then the major isotope in the HLW from that isobaric chain. For example for the isobaric chain of mass 99, the major isotope is Tc-99.

Calculation of the fission yield scaling factor will now be discussed. The FYSF is simply a factor that relates the concentration of a fission product in a sludge slurry to its fission yield and the atomic mass of that fission product. Since the concentrations of the fission products are presented in this paper in terms of weight percent of an isotope in the dried slurry, 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. The equation for the concentration is then

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

Thus the FYSF for each measured isotope can be calculated from the Equation 2.

$$\text{FYSF}_i = \text{wt\%}_i / (\text{fy}_i \times \text{am}_i) \quad (\text{Eq. 2})$$

Where

- FYSF_i = the fission yield scaling factor based on isotope i
- wt%_i = the weight per percent of isotope i in the total dried solids of the HLW slurry
- fy_i = the fission yield of isotope I
- am_i = the atomic mass of isotope i.

For those isotopes that meet following six criteria their fission yield scaling factors should be equal in a specific sludge batch.

1. They must be stable or have long half lives and thus have not decayed significantly since the waste was generated.
2. The isotopes must have low solubilities in NaOH and thus occur predominantly in the slurries in the Sludge Tanks rather than the salt supernates in the Salt Tanks.
3. The isotopes must have low neutron cross sections and thus were not transmuted while in a SRS reactor during its operation.
4. A significant amount of the isotope must not have been formed in the reactor by neutron absorption.
5. The isotope must not have been added from any of the processing chemicals used at SRS.
6. Lastly, the isotope must have a mass or decay energy such that interferences do not occur in the analysis of the isotope in the dissolved dried sludge slurry. An example in ICP-MS would be rare earth oxides formed in the Ar plasma that occur at the same mass as the fission product being measured.

Eleven U-235 fission products meet the above six criteria. These isotopes are Ru-101, Ru-102, Rh-103, La-139, Pr-141, Nd-143, 144, 145, 146, Sm-147, and Nd-148. Note that there are three isotopes from the low mass fraction in the fission yield curve and eight from the high mass fraction. The fission yield scaling factor for each of these isotopes was calculated using Equation 2. Results for SB2 are presented in Table III.

Note that the factors for the eleven isotopes are in good agreement. The average FYSF based on the eleven isotopes was 2.4E-05 wt%/(fy × am) with a 7.7% RSD. It is now possible to calculate the predicted concentration of any U-235 fission product in the dried SB2 slurry using this value for the FYSF, and assuming that the isotope meets the six criteria stated above. The applicable equation is Equation 1 using the average FYSF given in Table III.

Table III Calculated Values of the Fission Yield Scaling Factor (FYSF) for Eleven U-235 Fission Products in Sludge Batch Two

Isotope	Meas. Wt% ^a	Fission Yield	FYSF
Ru-101	1.32E-02	5.18	2.5E-05
Ru-102	1.20E-02	4.29	2.7E-05
Rh-103	7.77E-03	3.03	2.5E-05
La-139	2.10E-02	6.60	2.3E-05
Pr-141	1.84E-02	5.90	2.2E-05
Nd-143	1.89E-02	6.00	2.2E-05
Nd-144	1.95E-02	5.45	2.5E-05
Nd-145	1.31E-02	3.95	2.3E-05
Nd-146	1.11E-02	3.00	2.5E-05
Sm-147	7.86E-03	2.26	2.4E-05
Sm-148	6.86E-03	1.69	2.8E-05
Average	-	-	2.4E-05

^aWeight percent of total dried solids in SB2.

Plots comparing measured and predicted concentrations for the measured isotopes in the SB2 slurry can now be generated.

Measured and Predicted Concentrations of High Mass Fission Products in Sludge Batch Two

Figure 2 compares the measured and predicted concentrations of the high mass fission products measured by the ICP-MS in the total solids of the SB2 slurry.

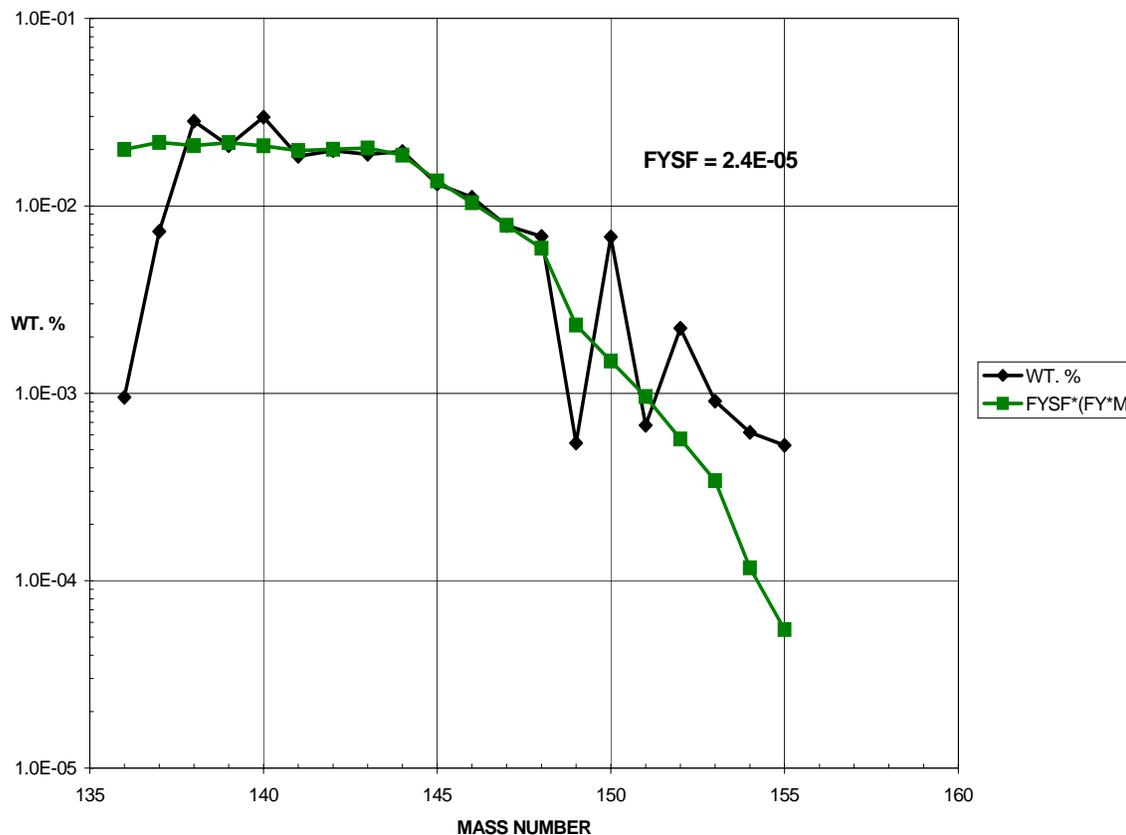


Figure 2. Measured and predicted concentrations for high mass fissions products in SB2

The measured concentrations are the diamonds and the predicted are the squares. Note that the results for the high mass isotopes in Table III fall on the line as expected. Why some of the measured results are above and below is explained as follows. The isotopes at masses 149 and 151 are Sm-149 and Sm-151. Both have high neutron absorption cross sections and are transmuted in the reactors giving higher values than predicted for Sm-150 and Sm-152. The values at masses 138 and 140 are the major isotopes of natural Ba and Ce, respectively. They are above the predicted concentrations because some natural Ba and Ce could have been added to the waste as an impurity in the processing chemicals used at SRS. The U-235 fission product at mass 136 is stable Xe-136. This inert gas xenon is lost in the processing steps at SRS. What was detected at mass 136 was the natural Ba-136 which is ~8% of the natural Ba. The isotope at mass 137 is primarily Ba-137 the decay product of Cs-137. (Most of the Cs is probably in the salt tanks because it has an appreciable solubility in caustic.) At masses 153 to 155 the measured concentrations are due the fission products Eu-153, Gd-154, and Gd-155, along with interferences from the oxides of Ba-137, Ba-138, and La-139 formed in the Ar plasma of the ICPP-MS. Consequently the concentrations at measured at these masses are greater than the predicted concentrations.

Figure 3 shows the results for the measured and predicted concentrations for the low mass fission products in the SB2 sample.

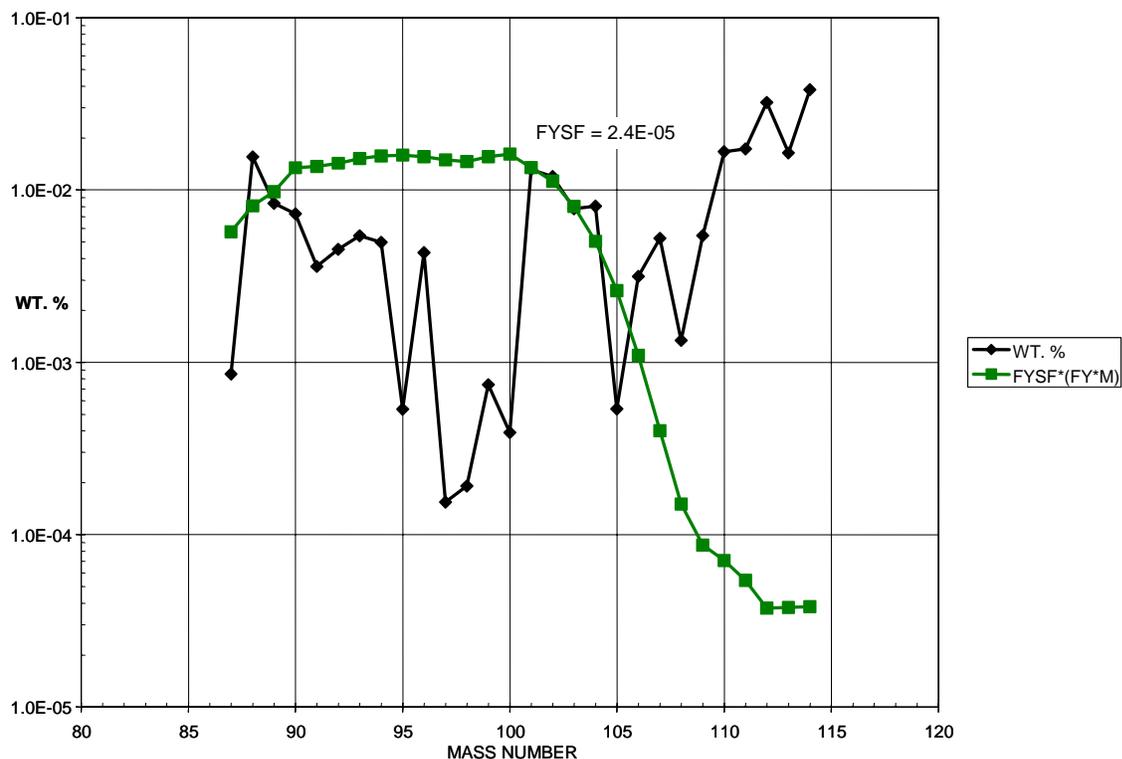


Figure 3. Measured and predicted concentrations for low mass fissions products in SB2

Note that the results for Ru-101, Ru-102, and Rh-103 fall directly on the line as expected. The measured concentration for Tc-99 along with the isotopes at masses 95, 97, 98, and 100 are well below their predicted concentrations. The isotopes these latter four mass the Mo fission products. Their measured concentrations are low because Mo can form the molybdate anion that is soluble in caustic. Note that the concentration at mass 88 in Figure 3 is above the predicted. This isotope is Sr-88 that both a fission product and an isotope of natural Sr-88 with an abundance of 83%. Apparently some natural Sr got into the waste as an impurity in some chemical that was used in the separations process at SRS. The isotope at mass 87 is Rb-87 which is soluble in caustic and thus probably primarily in salt tanks. Fission product zirconium has isotopes at masses 91-94 and 96. However, zirconium is insoluble in caustic; thus the reason of its concentration being lower than predicted is not immediately apparent. The fission product at mass 104 is stable Ru-104. Reason for its concentration being higher than predicted is also not apparent. The isotope at mass 106 is the fission product Pd-106. Its measured concentration is less than predicted suggesting that some of the Pd may be soluble in caustic and thus in the salt tanks. The isotopes at mass 107 to mass 114 are isotopes of natural Ag and Cd that were in the sludge. Silver was used at SRS to scavenge radioactive iodine when dissolving the fuels or targets and Cd was used as to adjust the spectrum of neutron energies in certain charges in the reactors.

It is now possible to calculate the fraction of Tc-99 that was not in the SB2 slurry when it was being processed by the DWPF.

Calculation of the Fraction of Tc-99 not Present in the Sludge Batch Two Slurry

The results of the calculation of this fraction are given in Table IV. If Tc-99 met all six of the criteria listed previously, 100% of it would indeed be in the sludge slurry. However results indicate that based on the predicted concentration only 5% of it is present. The remaining 95% of the Tc-99 that could have been in the slurry must be in the salt tanks.

Table IV Fraction of Tc-99 Removed from Sludge Batch 2 Slurry by SRS Waste Management Processes

Isotope	Fission Yield (Percent)	Meas. Conc. (Wt% in Dried Slurry)	Pred. Conc. ^a (Wt% in Dried Slurry)	Percent Removed ^b
Tc-99	6.10	7.4E-04	1.4E-02	95%

^aCalculated by multiplying the FYSY, 2.4E-05, times the product of the fission yield times the atomic mass.

^bCalculated from the equation $1 - (\text{Meas. Conc.} / \text{Pred. Conc.})$.

Based on the properties of properties of Tc-99, it meets five of the six criteria listed above. The criterion it does not meet is the low solubility in caustic. Apparently because of the solubility of Tc-99 in caustic (probably as a result of being in the form of pertechnetate anion), the fraction of Tc-99 that is in the salt tanks from SB2 is 95%. This fraction is higher than that found in the tests with simulated sludge spiked with Tc-99. Since some Tc-99 still remained in the SB2 slurry, a test was performed to determine how much of that Tc-99 could be removed from an unwashed SB2 slurry by extensive washing with IW. In this test the sludge was washed more than it could be done in the Tank Farm. In the Tank Farm there are lower limits on concentrations of hydroxide and nitrite to keep inhibiting the corrosion of the mild steel of the tanks.

Fraction of Tc-99 and Other Selected Elements that could be Removed from an Unwashed SB2 Slurry by Extensive Washing

This test was performed in the Shielded Cells using the unwashed sample of SB2 where the initial Na in the slurry supernate was 2.8M. As stated before IW is a solution of 0.010M NaOH and 0.010M NaNO₂ that is used in the SRS Tank Farm to wash sludges. For this test we put approximately 30 grams of a slurry from SB2 that had not been washed on a filter and then filtered the slurry. Based on the initial characterization of the unwashed slurry,³ approximately seven grams of sludge solids were left on the filter. These solids were then washed on that same filter, four times with 40 mL of IW and then twice with 100 ml of IW to completely wash the solids. After each addition of wash solution to the filter, the solids and wash solution were mixed for approximately five minutes to wash the solids. After the mixing, each wash solution was completely removed from the solids by filtering, leaving only damp sludge solids on the filter. After the test, aliquots of the individual wash solutions were removed from the shielded cells and sent to AD for analysis. They were analyzed for the major elements in the SB2 sample by ICP-ES, for U-238 and the U-235 fission products Tc-99 and Pd-105 by ICP-MS, and for Cs-137 by gamma counting. The fission product Pd-105 was chosen to follow because its concentration in the washed SB2 slurry was less than that predicted (see Figure 3) indicating that some of the Pd-105 may have been soluble in caustic and would be in the salt tanks. After the washing test was complete, duplicate samples of the final washed solids and the initial unwashed solids were dissolved by hot aqua regia to compare their compositions before and after washing.

The concentrations of Tc-99 in the various wash solutions along with the concentration of other selected elements are shown in Figure 4 in a semi log plot.

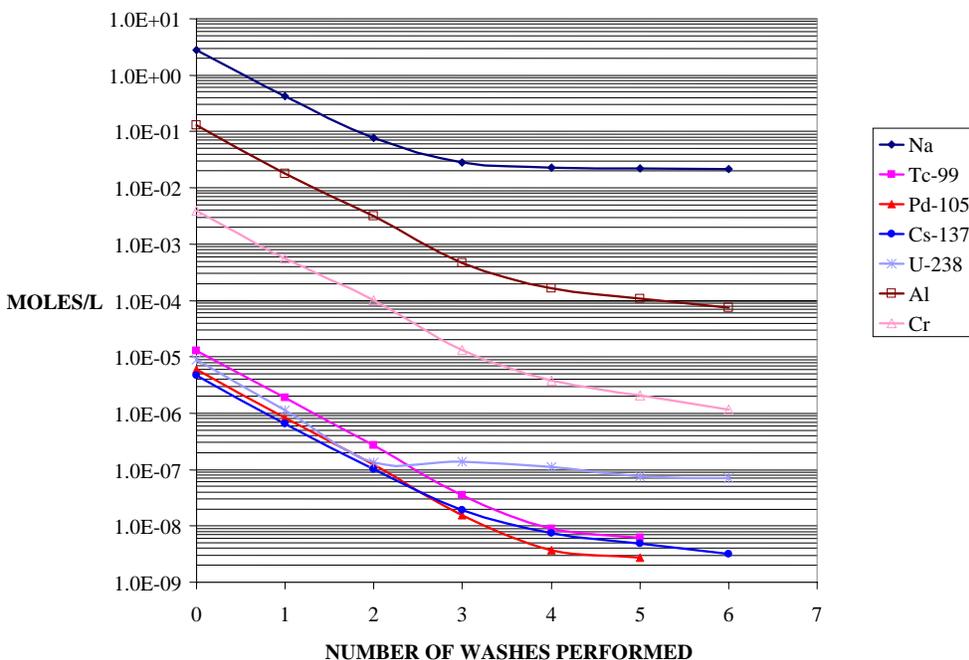


Figure 4. Molar Concentrations in the Supernate and Wash Solutions of the Extended Washing of the Solids in a Sample of SB2 at SRNL.
(Washes 1-4 were with 40 mL IW solution and 5-6 were with 100 mL of IW solution.)

The concentration of Na in the wash solution decreased after only three washes from the initial concentration of 2.8M to a constant value of 0.02M which is its concentration in the IW solution. The concentrations of the other elements including Tc-99, Pd-105, and Cs-137 initially followed the same trend for the first four washes. However it appears that their concentrations continued to decrease slightly rather than reaching a constant value. However in these solutions the concentrations of these isotopes were very low. For example, in the final wash solution, the concentrations of Tc-99 and Pd-105 were too low to be detected by the ICP-MS; however, Cs-137 could still be detected by gamma counting of the wash solutions. Note that the U-238 concentration no longer decreases after wash two indicating that after wash two some of the U-238 is being dissolved from the solids into the wash solution. This behavior has been observed in dilutions of a simulated HLW slurry containing waste solids of Fe, Al, Mn, Ni, and U that were precipitated from an acidic simulated HLW solution.⁴ In that study, the U began to dissolve from the simulated HLW solids at Na concentrations below 0.12M.⁵

For the first three washes, the concentrations of all the elements in the wash solutions except U-238 decrease linearly in Figure 4. Since this is a semi log plot, this linearity indicates that a constant fraction of each element is being removed by each of the first three wash solutions. This indicates that the main mechanism for removing these elements from the sludge solids is dilution of each element in the wash solution adhering to the solids after each successive. One is simply removing the soluble elements in the sludge slurry by dilution rather than the dissolution of a slightly soluble compound of that species. The equation for this type of washing mechanism is given below.⁵

$$C_n = \left(\frac{v}{V+v} \right)^n \cdot C_o \quad \text{Eq. 3}$$

Where

C_n is the concentration in the nth wash

C_o is the initial concentration

V is the volume of the wash solution (in this case 40 mL)

v is volume of supernate or wash solution that remains adhering to the solids after each wash.

Taking the log of both sides results in the following equation.

$$\log C_n = n \log \left(\frac{v}{V+v} \right) + \log C_o \quad \text{Eq. 4}$$

Since 40 mL were used in each four washes and the volumes adhering to the solids after filtering should remain the same after each 40 mL wash, the factor $\log(v/(v+V))$ is a constant. Thus a plot of $\log C_n$ versus n for each 40 mL wash should be linear. As shown in Figure 4 this is indeed true for all the elements except U-238. As stated earlier, at low Na concentrations some U-238 is being dissolved out of the sludge solids.

The total fraction of each element removed by the extended washing was calculated by comparing the composition of the unwashed total dried solids to the composition of dried washed solids. Table V presents these concentrations for several elements along with ratios of their respective concentrations.

Table V. Concentration of Elements Measured in the Unwashed and Totally Washed Solids of the SB2 Slurry

Element	Weight % In Unwashed Solids	Weight % In Washed Solids	Ratio of Wash' to Unwash'
Al	4.2	6.8	1.6
Ca	1.2	2.9	2.4
Cd	0.074	0.17	2.4
Cr	0.15	0.18	1.2
Fe	13.	30.	2.3
Mg	0.98	2.4	2.4
Mn	1.8	4.0	2.2
Na	21.	2.8	0.13
Ts-99	8.0E-04	1.1E-03	1.4
Pd-105	5.1E-04	6.3E-04	1.2
Cs-137	3.4E-04	2.7E-04	0.79
U-238	3.7	7.9	2.1

For all the elements that are insoluble in caustic (Ca, Cd, Fe, Mg, and Mn) this ratio is a constant of 2.3 with a %RSD of only 3%. These concentrations increase in the washed solids due to the removal of the soluble elements such as Na and its associated anions of hydroxide, nitrate, and nitrite from the sludge slurry. For those elements, such as Al, Cr, Tc-99, and Pd-105, that have some solubility in the sludge slurry supernates the ratio is lower. For the Na the ratio is very low because most of the Na was in the unwashed slurry supernate. This is also true with the Cs-137 which has the next lowest ratio.

The fractions of elements removed by the extensive washing were then calculated by comparing their measured concentrations in the washed solids with the concentrations predicted by assuming that they were completely insoluble in the sludge supernate and none had been washed out. Results of this comparison are shown in Table VI. The predicted concentrations were calculated by multiplying the concentration of the element in the unwashed dried slurry by the factor of 2.3 based on the element Ca, Cd, Fe, Mg, and Mn.

Table VI. Fractions of Elements Removed from SB2 Slurry by Supernate Removal Followed by Extended Washing of the Solids

Element	Wt% in Unwash' Dried Solids ^a	Measured Wt% in Washed solids	Pred. Wt% in Washed Solids ^b	Percent Removed by Washing ^c
Tc-99	8.0E-04	1.1E-03	1.9E-03	41
Pd-105	5.1E-04	6.3E-04	1.2E-03	47
Al	4.1	6.8	9.5	29
Cr	0.15	0.18	0.35	48
U-238	3.7	7.9	8.6	8.1
Cs-137	3.4E-04	2.7E-04	7.6E-04	64
Na	21	2.8	49	94

^aWeight percent in total dried solids of the unwashed slurry. This includes the amount of the element in the sludge supernate and the amount of the element in the solids.

^bCalculated by multiplying the weight percent in the total dried solids by 2.3, the ratio of concentrations for elements that are insoluble.

^cCalculated from the equation $1 - (\text{wt\% in washed solids} / \text{predicted wt\%})$.

For both Tc-99 and Pd-105, ~56% of each element in the unwashed sludge slurry was insoluble in IW and not removed by washing. It should be emphasized that this fraction of Tc-99 was not 56% of the total amount of Tc-99 that could have been in the sludge. It is 56% of the Tc-99 that was in the 5% of the Tc-99 that was in the sludge slurry sample being processed by the DWPF (see Table III). On this basis only approximately 2% ($0.56 \times 5\%$) of the original Tc-99 that could have been in this sludge was insoluble in caustic and thus probably in the +4 state.

Possible Losses of Tc-99 in DWPF Processing

As mentioned before the final step in the sludge waste processing at SRS is the immobilization of the sludge into a stable borosilicate glass for geologic disposal. This is performed in the DWPF where the properly prepared sludge slurry is mixed with glass forming frit and pumped to a melter at 1150°C. Here the water is flashed off and the sludge solids and frit melt into a homogenous solution. The primary process where Tc-99 may be lost in the DWPF process is volatilization from the DWPF melter since Tc-99 can form an oxide that has a boiling point of ~311°C.² For example, in laboratory and large scale melter studies it has been shown that substantial amounts (up to 60%) of the Tc-99 can be volatilized from the molten glass.⁶ The fraction of Tc-99 lost in this process has been measured during the processing of SB1A in the years 1996 to 1998. These results have been published previously⁷ and are summarized here in order to complete the discussion of the behavior of Tc-99 in the sludge waste processing. This determination was made by comparing the amount of Tc-99 in the feed to the DWPF melter to the amount measured in three glass samples taken from the pour stream of the melter taken during processing.

Processing of SB1A, which took ~30 months, ~0.9 million kilograms of HLW glass were produced and placed in 495 canisters. During processing of SB1A, glass samples were taken from the pour stream of the melter while three different canisters were being filled. These were canisters 50, 61, and 409 of the campaign. The concentration of Tc-99 was measured in each of these glass samples and compared to the predicted concentration from the composition of the sludge slurry being immobilized. The predicted concentrations were calculated using a waste dilution factor (WDF). The WDF is the factor that the concentrations in the feed are diluted by the addition of the glass forming frit. Values for the WDF were calculated based on the concentrations of the four major element sin the waste (Fe, Al, Ca, and Mn) and their respective concentrations measured in the glass samples from the three canisters. For each of the three canisters, the average WDF calculated for each of the four elements was a constant with a %RSD of 7% or better. The predicted concentration of Tc-99 in a glass sample was then calculated by dividing its concentration in the feed by the appropriate WDF for that glass sample. Results are summarized in Table V.

Table V Measured and Predicted Tc-99 Concentrations in Glass from DWPF Melter Pour Stream Sampled During Filling of Three Canisters During SB1A Processing ^a

	Date Filled	Measured Wt. %	Predicted Wt. %	Percent Difference ^b
Canister 50	9/21/96	4.3E-04	4.5E-04 ^c	4.4
Canister 61	9/23/96	4.1E-04	4.2E-04 ^d	2.4
Canister 409	6/30/98	4.7E-04	4.5E-04 ^e	-4.4

^a See Reference 7 for details.

^b Calculated from ((Pred. Conc.-Meas. Conc.)/Pred. Conc) X 100)

^c Calculated by dividing the Tc-99 concentration in the DWPF feed by the WDF of 2.8 based on measurements of Fe, Al, Ca, and Mn in the feed and Canister 50 glass.

^d Calculated by dividing the Tc-99 concentration in the DWPF feed by the WDF of 3.1 based on measurements of Fe, Al, Ca, and Mn in the feed and Canister 61 glass.

^e Calculated by dividing the Tc-99 concentration in the DWPF feed by the WDF of 2.8 based on measurements of Fe, Al, Ca, and Mn in the feed and Canister 409 glass. The negative value indicates that the measured concentration was larger than the predicted.

The results in the last column of Table V indicate that only a small fraction of the Tc-99 volatilizes from the melter to the DWPF off gas system. For Canister 409 the measured concentration was slightly greater than the predicted but this is due to the analytical uncertainty of the data since one is calculating a small difference two relatively larger numbers.⁸

One reason that Tc-99 does not volatilize from the DWPF melter is that the water and chemicals in the sludge slurry cause a cold cap to be formed on the melter. During feeding and pouring it has been estimated that the melt surface is 95% covered by the cold cap. In the laboratory and other studies where larger losses were encountered, no cold cap was present.⁶ Also in a small scale melter operated remotely at SRNL, Tc-99 losses were determined to be much higher than in the DWPF melter (31% compared to the 4%).⁷ Even though this melter was slurry fed, the feed rate was too slow to allow the formation of a cold cap and thus the Tc-99 losses were higher. Another possibility for the lower volatility of the TC-99 is that the Tc-99 could have been reduced to the +4 state by the formic acid added in one of the DWPF pretreatment steps. The +4 state forms a less volatile oxide than the +7 state.⁶

CONCLUSIONS

The results in this paper support the following conclusions concerning the behavior of Tc-99 during waste processing operations at SRS.

1. Based on three out of the four tests with an acidic simulated HLW solution doped with Tc-99, 70 to 80% of the Tc-99 remains with the supernate of the caustic waste and would be in the salt tanks in the SRS Tank Farm. The fourth test indicated that ~50% could be in the salt tanks.
2. Based on a Fission Yield Scaling Factor for SRS Sludge Batch 2, 95% of the Tc-99 that could have been in SB2 had been removed by the HLW management processes at SRS and was in the salt tanks at SRS rather than the sludge tanks.
3. The mechanism for removing elements from a HLW sludge slurry at SRS by washing with inhibited water in the SRS Tank Farm is simply dilution of the those elements that are already dissolved in the supernate of the slurry and then removal of the dilution water.
4. Based on results of another published study⁷ but summarized here for completeness, the Tc-99 losses while vitrifying the radionuclides in a HLW sludge were only ~4%.

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