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Gaseous Diffusion Membrane Leaching with Select Lixiviants: Ammonium Carbonate, Sodium Phosphate and Ammonium thiosulfate

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EXECUTIVE SUMMARY

As part of ongoing efforts by the Department of Energy's Portsmouth/Paducah Project Office to decommission the uranium enrichment gaseous diffusion plant at Paducah, KY, research efforts have been focused on removing the remaining kilogram quantities of technetium-99 (Tc-99) from the facility diffusion cascades to meet Tc-99 Waste Acceptance Criteria (WAC) disposal requirements for decommissioning waste. With the goal being to develop and deploy an in-situ Tc-99 decontamination process for the cascades, we have evaluated the use of lixiviants solutions to leach Tc-99, uranium isotopes and neptunium from a gaseous diffusion membrane (barrier material) collected from the facility. In these bench-top tests, aqueous solutions of ammonium carbonate, sodium tri-phosphate and ammonium thiosulfate were contacted with barrier material sub-samples, with and without ultrasonic treatment (sonication), resulting in significant removal of Tc-99, uranium isotopes and neptunium in some cases.
These results show that leaching with ammonium carbonate or ammonium thiosulfate, with or without sonication, removed technetium to levels below the target Oak Ride Tc-99 WAC of 172 pCi/g of waste material.

Double strike leaching of the barrier material with ammonium carbonate solution gave the lowest residual Tc-99 result of 15 pCi/g waste (all radionuclide concentrations are converted to a WAC equivalent mass basis), which corresponds to about 96% technetium removal. Ammonium carbonate leaching of barrier material under room temperature conditions, without sonication or thermal treatment, also resulted in effective removal of Tc-99 and other radionuclides. Under these conditions, an average of 78.7 ± 0.7 % of the Tc-99 in the barrier material was removed giving a final technetium concentration in the barrier material after leaching of 75.4 ± 2.4 pCi/g waste. Therefore, with or without sonication, ammonium carbonate leaching of the barrier material meets the Oak Ride Tc-99 waste disposal target WAC.

Ammonium thiosulfate single strike leaching with sonication resulted in an average Tc-99 adjusted disposal WAC of 124.3 ± 6.7 pCi /g of waste which corresponds to an average of 65.0 ± 1.9% Tc-99 removal from the barrier material. Ammonium thiosulfate leaching with double lixiviant strike produced a post leached barrier material with a Tc-99 adjusted disposal WAC of 114.7 pCi /g of waste.

Although Tc-99 was largely removed from the membrane sub-samples with ammonium carbonate and ammonium thiosulfate lixiviants, simultaneous uranium leaching resulted in the accumulation of significant quantities of uranium isotopes in the leachates. In practice, uranium leaching, and accumulations may lead to criticality problems during processing if neutron absorbers/poison agents are not utilized.

Raising the lixiviant temperature above room temperature during leaching with ammonium carbonate solution did not enhance the removal of radionuclides (Tc-99, uranium isotopes and Np-237) from the barrier material. This result indicates that the combination of lixiviant sonication and temperature rise rather than elevated temperature alone produced the enhanced leaching effectiveness resulting from sonication.
Tri-sodium phosphate leaching of sub sample barrier material pieces, even with sonication, did not result in significant removal of Tc-99 from the test barrier materials. Only30-40% of the radionuclides were

removed from the barrier material. The adjusted Tc-99 WAC, based on the post tri-sodium phosphate leaching of barrier material, averaged 240.3 ± 3.2 pCi/g of converter; hence the Oak Ridge Tc-99 waste disposal reference WAC of 172 pCi/ converter waste was not met. The original intent to leach the barrier material with trisodium phosphate solution was to determine if this lixiviant could possibly remove sufficient quantities of Tc-99 from the barrier material, enough to meet the Tc-99 WAC for disposal, without significant removal or accumulation of the uranium isotopes in the leachate. However, the leaching results with tri-sodium phosphate did not produce these desired goals.

Based on these results, we recommend the following additional work:

- Evaluations of ammonium carbonate-based lixiviants doped with neutron poison agents to address uranium criticality concerns.

- Evaluations of the effects of leaching time duration, lixiviant concentration, pH, solid/liquid ratio (phase ratio), higher wattage ultrasonic devices (200-360 Watts/40KHz ultrasonic frequency), and higher temperature on radionuclide removal efficiencies with and without sonication.

- Double strike leaching with ammonium carbonate solution and follow up leaching with an oxidizing agent such as a solution of dilute nitric acid (0.5-2 molar) to determine whether higher percentages of radionuclides can be removed by this method.

- Evaluations of other lixiviants to selectively target Tc-99 removal without removing uranium isotopes from the membrane material. This approach will minimize the potential for accumulation of uranium isotopes and reduce criticality concerns.

- Evaluations of electromagnetic induction melting or microwave heating of the barrier material to remove the target radionuclides
  .

- The use of fluorinating agents, such as environmentally compatible nitrogen trifluoride, which under thermal conditions will convert the technetium compounds in the barrier material into more volatile technetium compounds.

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LIST OF ABBREVIATIONS

AD	Analytical Development
AMC	Ammonium Carbonate
ATS	Ammonium Thiosulfate
DL	Detection Limit
LIMS	Laboratory Information Management System
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
MDA	Minimum Detectable Activity
MDL	Minimum Detection Limit
NA	Not Applicable
Na_3PO_4	Tri-sodium Phosphate (TSP)
P2S	Professional Project Services
PPPO	Portsmouth/Paducah Project Office
PUREX	Plutonium and Uranium Extraction Process
SRNL	Savannah River National Laboratory
TTQAP	Task Technical and Quality Assurance Plan
WAC	Waste Acceptance Criteria

1.0 INTRODUCTION

The Department of Energy's Portsmouth/Paducah Project Office (PPPO) is responsible for the large uranium gaseous diffusion plants that are now shutdown. As the plants operated to enrich uranium, some of the source of uranium included material that had been irradiated in the production reactors at the Hanford and Savannah River plants. The spent fuels were processed using the Plutonium and Uranium Extraction Process (PUREX) to recover the uranium and remove the bulk of the fission product impurities. The first cycle PUREX product stream contained the purified uranium but also contained a small amount of impurities. The most notable impurity was technetium, in the form of pertechnetate anion. Following the Paducah flowsheet, the uranium oxide was reacted with anhydrous hydrogen fluoride to produce uranium tetrafluoride. Subsequently, the tetrafluoride reacted with fluorine to produce uranium hexafluoride. Golliher, et al,[1] determined that the technetium was entrained within the uranium in each of these processing steps. Upon entering the gaseous diffusion cascade, some of the technetium impurity was deposited within the barrier material.

It is estimated that more than 500 kilograms[2] of Tc-99 were originally fed to the cascades, with the current Tc-99 inventory in the Paducah cascades at less than 5 kilograms[3]. In addition to the cessation of feeding of Tc-99 contaminated UF_6 to the cascades, most of the Tc-99 had been removed during cascade maintenance operation activities over the last 30 years of operations. At the Oak Ridge Gaseous Diffusion Plant, the converter housing the barrier materials was manually removed and disposed directly; and if this method is implemented at Paducah, it will be labor intensive and very costly. Therefore, developing and deploying an in-situ decontamination process, one which can reduce the manual labor and risk of personnel radiological exposure, offers advantages in terms of schedule duration, costs and safety. An on-site disposal cell at Paducah is also being considered, and the waste acceptance criteria (WAC) are under development. The on-site disposal cell at Oak Ridge Tennessee has a Tc-99 WAC[4] limit of 172 pCi/g of converter waste and is a reference point for this testing. To compare Tc-99 results from this testing in pCi/g of barrier material waste to the Oak Ridge disposal WAC limit of 172 pCi/g of converter waste, a correction factor was needed to convert from a barrier mass basis to a converter mass basis. This factor can be obtained from the Paducah Technetium-99 Sampling Results Graph.[5]

Early preliminary ammonium carbonate lixiviant studies[6] showed significant removal of both technetium and uranium isotopes from cascade components in the form of barrier material (gaseous diffusion membrane) at room temperature with and without sonication. Also, earlier results from two previous scoping tests dealing with the thermal decontamination of Tc-99 from gaseous diffusion membrane materials with just air or vacuum was not effective although superheated steam did show some promise by obtaining a measurable decontamination of Tc-99, as well as uranium isotopes[6].

2.0 SCOPE OF PROJECT

The objective of these follow-up scoping leaching experiments was to demonstrate the following,

- Whether ambient temperature leaching of the barrier material in aqueous solution of 1.0 M ammonium carbonate (AMC) solution, with and without sonication, will consistently result in a significant removal of Tc-99, uranium isotopes and neptunium from the barrier material.
- In this leaching study, a solution of 0.25 M solution of tri-sodium phosphate (TSP) was also evaluated to determine if this lixiviant could possibly remove sufficient quantities of Tc-99 from the barrier material, enough to meet the Tc-99 WAC for disposal, without significant removal of the uranium isotopes.

- Ammonium thiosulfate (ATS) solution, as a lixiviant, was also evaluated on a limited basis in the leaching of these radionuclides out of the barrier material.
- To ascertain the effects of thermally induced temperature changes on the leaching process using mainly AMC lixiviant.

These preliminary laboratory data could eventually be used for the scale up of a viable technology for Tc-99 decontamination from the barrier material. This report documents the scoping investigations performed at SRNL and the planned test matrix is summarized in Table 3-1.

3.0 Experimental Setups, Sample Preparations and Methodology

Samples of contaminated barrier material were obtained from the Paducah Gaseous Diffusion Plant. The Paducah barrier material, with sample identification number 23008-Top, was used for these ammonium carbonate, tri-sodium phosphate and ammonium thiosulfate leaching tests. All chemicals (ammonium carbonate [$(NH_4)_2CO_3$], tri-sodium phosphate [$Na_3PO_4.12H_2O$]) and ammonium thiosulfate [$(NH_4)_2S_2O_3$] used in these leaching tests were analytically pure grade reagents purchased from Sigma Aldrich and were used without further purifications. The lixiviants solutions were prepared from the reagents in deionized water with electrical conductivity less than 5 $\mu S\ cm^{-1}$ at 25 °C. The measured densities of these $(NH_4)_2CO_3$, $Na_3PO_4.12H_2O$, and $(NH_4)_2S_2O_3$ solutions were, 1.039 ± 0.002 g/mL, 1.042 ± 0.005 g/mL and 1.074 ± 0.001 g/mL at 20.5 °C, respectively.

In the acoustic treatment of the barrier material in the presence of ammonium carbonate, tri-sodium sodium phosphate or ammonium thiosulfate leaching solutions (lixiviants), a small tabletop continuous wave ultrasonic cleaning device (without timer) with an average input wattage of 22 Watts was used in the batch leaching process of small pieces of the barrier material inside the lixiviant.

The tests performed are summarized in Table 3-1. Tests with and without sonication of the sample in the lixiviants (tests AMC-2-SON-1, AMC-2-SON-2, AMC-1-NOSON, AMC-2-NOSON, Na_3PO_4-SON-1, Na_3PO_4-SON-2 ATS-SON-1 and ATS-SON-2), as shown in Table 3-1, were performed in duplicate. Single tests involving the use of the same barrier material piece which was leached twice with equal volume of the lixiviant (double strike tests) with sonication (tests AMC-3-SON-DS, Na_3PO_4-SON-DS and ATS-SON-DS) were also performed along with double strike tests in ammonium carbonate and tri-sodium phosphate without sonication (tests AMC-4-NOSON-DS, and Na_3PO_4-NOSON-DS). Effects of temperature on leaching without sonication using ammonium carbonate lixiviant and heating the lixiviant solution up to 53 ± 3 °C using a heating mantle brace around the container were also evaluated (tests AMC-therm-1 and. AMC-therm-2).

During the leaching tests requiring sonication, the piece of the barrier material was fully immersed in the lixiviant solution inside the sonicator. The orifice of the sonicator was tightly covered with aluminum foil and a thermocouple was inserted into the sonicated chamber through the aluminum foil wrap. The duration of the leaching of the barrier material was two hours in all cases. The temperature changes, due to energy dissipation inside the sonicated solution, were recorded at 5-15 minutes intervals. The maximum average recorded temperature during leaching tests involving sonication was 53 ± 3 °C.

In leaching tests without sonication, a piece of the barrier material was introduced into a Teflon® bottle already containing the required volume of the lixiviant solution, and when necessary, a thermocouple was

inserted in a hole through the cap of the Teflon® bottle. These leaching tests without sonication or even stirring of the solution were performed for the same test duration time of 2 hours. These leaching tests were performed at a lixiviant solution temperature of 20.5 ± 1 °C inside a radioactive hood.

3.1 Sample Preparations and Analysis

The sample pieces of the barrier material used for the baseline Tc-99, uranium isotopes and neptunium concentration determinations in the "as-received" Paducah barrier material (sample 23008-TOP) in these leaching tests were obtained from just about the middle portion of the length of sample 23008-Top. The individual sample pieces of the barrier materials used for these leaching tests were usually less than one gram.

Both the baseline "as-received" Paducah barrier material and resulting leached barrier material solids, after complete digestions, were analyzed for Tc-99, uranium isotopes and Np-237 by inductively-coupled plasma-mass spectroscopy (ICP-MS). In the digestion and analytical processes, samples of the barrier material were digested in a combination of concentrated nitric and hydrochloric acids (aqua regia) and a few drops of 50% hydrogen peroxide.

3.2 Leaching Test Categories

Leaching tests performed with these lixiviants (i.e., ammonium carbonate, tri-sodium phosphate and ammonium thiosulfate) using pieces of the gaseous diffusion barrier material involved the following leaching test categories:

- Single strike leaching tests without sonication
- Single strike leaching tests with sonication
- Double strike leaching tests without sonication
- Double strike leaching tests with sonication, and
- Single strike lixiviant leaching tests with heating of the solution (thermally induced leaching).

Only two single strike sonication tests were performed with ammonium thiosulfate lixiviant. In addition to other leaching tests with ammonium carbonate lixiviant, tests were also performed with only ammonium carbonate solution to determine the effect of temperature rise in the test media during sonication. A thermally induced heat leaching test was performed in ammonium carbonate at the maximum observed sonication temperature of 53 ± 3 °C to isolate and distinguish the effect of temperature on the leaching process.

After each leaching test, the samples were retrieved from the lixiviant solution and placed on a sheet of paper towel inside the hood and allowed to air-dry for about 30 minutes before repackaging the samples for storage and later submission for digestion, masking and analysis for Tc-99, uranium isotopes and Np-237. The resulting post leaching solutions (leachates) were normally clear, without any visible solid particles, and were submitted for ICP-MS analysis.

Table 3-1 Overall Test Matrix

Test ID	AD tracking Number: solids	Test with sonication	AD tracking Number: leachates	Comments
AMC-00	LW8652	NA	NA	Baseline Tc-99 and uranium isotope concentrations for the "as received" sample 23008-Top
AMC-1-NOSON	LW8647	No	LW8653	Test performed in duplicate; single strike
AMC-2-NOSON	LW8648	No	LW8654	
AMC-2-SON-1	LW8649	Yes	LW8655	Test performed in duplicate; single strike
AMC-2-SON-2	LW8650	Yes	LW8656	
AMC-3-SON-DS	LW8651	Yes	LW8657 LW8658	A sample piece of barrier material was leached with ammonium carbonate with sonication and after the 2-hour test duration, the lixiviant was decanted and an equal volume of fresh lixiviant used to leach the same sample piece with sonication a second time. (Double lixiviant strike producing two leachate samples).
AMC-4- NOSON-DS	LW9795	No	LW9800 LW9801	A sample piece of barrier material was leached with ammonium carbonate without sonication and after the 2-hour test duration, the lixiviant was decanted and an equal volume of fresh lixiviant used to leach the same sample piece without sonication a second time. (Double lixiviant strike producing two leachate samples).
Na_3PO_4-SON-1	LW9796	Yes	LW9802	I.0 M sodium phosphate used as the lixiviant
Na_3PO_4-SON-2	LW9797	Yes	LW9803	I.0 M sodium phosphate used as the lixiviant
Na_3PO_4-SON-DS	LW9798	Yes	LW9804 LW9805	A sample piece of barrier material was leached with sodium phosphate with sonication and after the 2-hour test duration, the lixiviant was decanted and an equal volume of fresh lixiviant used to leach the same sample piece with sonication the second time. (Double lixiviant strike producing two leachate samples).
Na_3PO_4-NOSON-DS	LW9799	No	LW9806 LW9807	A sample piece of barrier material was leached with sodium phosphate without sonication and after the 2-hour test duration, the lixiviant was decanted and an equal volume of fresh lixiviant used to leach the same sample piece without sonication a second time. (Double lixiviant strike producing two leachate solutions).
AMC-therm-1	LW11046	No	LW11051	Performed in duplicate with thermal heating to reproduce sonication temperature profile.
AMC-therm-2	LW11047	No	LW11052	
ATS-SON-1	LW11048	Yes	*LW11053*	Test in duplicate; single strike with sonication
ATS-SON-2	LW11049	Yes	*LW11054*	
ATS-SON-DS	LW11050	Yes	*LW11055* *LW11056*	A sample piece of barrier material was leached with ammonium thiosulfate (ATS) with sonication and after the 2-hour test duration, the lixiviant was decanted and an equal volume of fresh lixiviant used to leach the same sample piece with sonication a second time. (Double lixiviant strike producing two leachate solutions).

3.2.1 Single strike leaching tests without sonication

In Single strike leaching tests without sonication (duplicate test), two separate pieces of the barrier material, samples were each leached with the lixiviant for 2 hours but without sonication or even stirring of the solution; this test involved just soaking the barrier material in the lixiviant. These leaching tests were also conducted at the same time as the sonicated tests. During these leaching tests, a piece of the barrier material was put into a capped Teflon® bottle already containing the lixiviant. This Teflon® bottle was separated from the sonicated/vibrational region of the laboratory hood floor by about 5 feet. The sample pieces identified as AMC-1-NOSON and AMC-2-NOSON, as shown in Table 3-1, were used for these ammonium carbonate leaching tests. No single strike leaching tests without ultrasonic treatment were performed with tri-sodium phosphate or ammonium thiosulfate lixiviants.

3.2.2 Single strike leaching tests with sonication

In these leaching tests using the three lixiviants, acoustic cavitation of the solutions was used to enhance the leaching of Tc-99 and uranium compounds present in the Paducah barrier material. These single strike sonication tests were performed in duplicate using sample pieces identified as AMC-2-SON-1, AMC-2-SON-2, Na3PO4-SON-1, Na3PO4-SON-2, ATS-SON-1 and ATS-SON-2 as shown in Table 3-1. The temperature of all sonicated solutions was monitored and recorded every 15 minutes during the 2 hours test duration.

3.2.3 Double strike leaching tests without sonication

These leaching tests were performed with ammonium carbonate and tri-sodium phosphate lixiviants and samples used for these leaching tests, as shown in Table 3-1, are identified as AMC-4-NOSON-DS and Na_3PO_4-NOSON-DS. During double lixiviant strike leaching tests without sonication, one new sample piece of the "as-received" barrier material was put into a capped Teflon® bottle already containing the required volume of the lixiviant. Each Teflon® bottle was separated from the sonicated/vibrational region of the laboratory hood floor by about 5 feet if other tests were also performed at the same time in the same hood. After the 2-hour leaching test duration, each sample was retrieved from the capped Teflon® bottle and the resulting leachate solution stored and saved for later analysis. The Teflon® bottles were cleaned with the lixiviant in use and deionized water and an equal volume of fresh lixiviant of the same type was placed into each bottle. The sample pieces which had undergone the first leaching test were again put inside the Teflon® bottles with fresh lixiviant of equal volume to the first contact solution. At the end of the second leaching of the barrier materials, the leached barrier materials were retrieved from each Teflon® bottles, put on a piece of paper towel and airdried for about 30 minutes inside the hood before submission for digestion and analysis. Each resulting second leachate was submitted for analysis for Tc-99, uranium isotopes and neptunium.

3.2.4 Double strike leaching tests with sonication

For a double lixiviant strike leaching test, one (no replicate) sub-sample piece of the barrier material was leached in two successive contacts with sonication. After completion of the first leaching contact, the lixiviant was decanted and the leached solid removed from the sonicator reservoir and the sonicator reservoir was cleaned three times; first two times with fresh lixiviant solution in use and with deionized water the third time. The decanted lixiviant (first-strike leachate) was stored for later analysis for Tc-99 and uranium isotopes and neptunium by ICP-MS. After the reservoir cleaning process, an equal volume of fresh lixiviant was put into the sonicator reservoir before putting the same leached barrier material back

into the sonicator reservoir now containing a fresh lixiviant. Samples used for these leaching tests, as shown in Table 3-1, are identified as AMC-3-SON-DS, Na_3PO_4-SON-DS and ATS-SON-DS.

This same barrier material, which had gone through the first leaching strike process, was subsequently leached with sonication a second time for the same contact duration of two hours. Again, at the end of the second sonication and leaching treatment of the same solid barrier material, the solid was separated from the lixiviant (second-strike leachate) and the solid submitted for digestion/masking and analysis along with the second- strike leachate solution. During each of the double strike leaching test cycles, the temperature of the lixiviant solution containing the barrier sample piece being leached was monitored and recorded every 15 minutes for the duration of the tests.

3.2.5 Temperature Effects on Leaching with Ammonium Carbonate Lixiviant

Previous ammonium carbonate leaching of the barrier material with sonication[6] and current ammonium carbonate leaching tests with sonication showed that there is a significant removal of radionuclides from the barrier material when compared with leaching tests without sonication. In this and previous sonicated leaching tests, the maximum temperature of the lixiviant averaged 53 ± 3 ° C within the tests duration of two hours. The question that had been posed in previous tests, which needed to be addressed in the current tests, dealt with the effect of temperature in the ammonium carbonate lixiviant tests with sonication. These tests were designed to determine whether the enhanced radionuclide decontamination observed during tests with sonication was actually due to the elevated temperature associated with the sonication process.

Experimental set up options available for reproducing sonication tests to identify the effect of temperature rise on the leaching process during sonication included the following (1) chilling the temperature of the sonication treatment to near ambient temperature (about 20 ° C) during the test or (2) heating the test solution matrix to a maximum of 53 ± 3 ° C at the same temperature rise rate and duration observed during tests with sonication. The latter testing approach for reproducing the test was selected.

To address this temperature effect question in these tests, an attempt was made to reproduce the ammonium carbonate leaching test with simply heating of the test matrix (barrier material piece in ammonium carbonate lixiviant) without sonication up to 53 ± 3 ° C following the same temperature generating rate observed during sonication.

To reproduce the temperature profile observed during previous ammonium carbonate sonicated leaching test conditions, an Omega auto-tunable temperature controller (Omega mini benchtop temperature controller model CSC32) with set point ramp rates and soak programming functions was used. The heating of the ammonium carbonate lixiviant and the barrier material sub-samples was achieved with the use of a cylindrical Griffin beaker heating mantle (Glas-Cole) with concentric heating around the lixiviant solution container (glass beaker). The orifice of the glass beaker was tightly covered with aluminum foil wrap and a thermocouple was inserted into the beaker through the aluminum foil.

The Omega temperature controller was programmed to produce an initial temperature rise or ramp rate of 0.7 ± 0.05 ° C/minute (42 ° C /hr.), followed by soak time of 71 minutes at a set point temperature of 54 ° C, which was a typical maximum temperature observed during testing with ammonium carbonate solution with sonication as shown in Appendix A, Figure A1 (inserts $A_1$1 through $A_1$4). The initial ammonium carbonate lixiviant solution ambient temperature at the beginning of the tests averaged 20 ± 0.5 ° C. Therefore, heating of the test vessels required about 49 minutes to reach the soak temperature of 54 ° C (1.0

min./0.7 º C * (54-20 º C). and about 71 minutes at the soak temperature (giving a total test duration of 120 minutes or 2 hours).

4.0 RESULTS and DISCUSSION

4.1 Data Quality/Presentations for Radionuclides and Mass Balance Calculations

In the analysis results presented in all tables in this report, values preceded by "<" (less than sign) indicate that the results were below the minimum detection limits (MDLs), and values proceeded by "≤" (less than or equal to sign) indicate that for replicates, at least one of the analysis results was at or above MDL and at least one of the analysis results was below the MDL. Thus, where replicate analyses were both above and below the detection limit, the average of all replicates above and below the detection limit a "≤ "sign precedes the average value. The standard deviations reported in the analyte tables were calculated only for values that were all above the detection limits. The minimum detectable activity (MDA) is defined as the value above which instrument signal can be considered quantitative relative to the signal-to-noise ratio. The MDL as used in ICP-MS analyses is equivalent to three times the standard deviation of the blank measurements. In the ICP-MS analytical results, one sigma measurement uncertainty for Tc-99 and uranium isotopes reported in all tables is ± 10% and this uncertainty is used in all presentations.

Each radionuclide mass balance is presented as the total amount of the element left on the barrier material after leaching plus the total amount of the element in the leachate phase; this sum should equal the total amount of element in the original "as-received" barrier material piece used for the leaching tests. In other words, the amount of each analyte in the leachate plus the corresponding analyte concentration on the barrier material after leaching should equal the analyte concentration in the original "as-received" barrier material used in the leaching test. The percent difference, which is the difference between the concentration of each analyte in the original "as-received" barrier material and the sum of the concentrations of the same analyte in the leachate and post leached barrier material, is defined as the absolute concentration difference divided by the average concentration*100.

As earlier mentioned, these leaching tests were performed with the second portion of the "as-received" barrier material from the sample identified as sample 23008-Top. A section of the same barrier material, identified as 23008-Mid, had been used in previous tests[6] and it was expected that the top and middle sub-samples contained essentially the same radionuclides in the same concentrations and proportions. To confirm the assumption, one sub-sample of the "as-received" sample 23008-Top, used in this leaching test, was digested and analyzed for Tc-99, uranium-isotopes and neptunium for comparison with previous analysis for sample 23008-Mid. The analysis results for both sub-sample types are compared in Table 4-1, and Figure 4-1.

Table 4-1 "As-received" radionuclide concentrations in barrier materials 23008-Mid and 23008-Top.

Component	23008-Mid, pCi/g	23008**-Top, pCi/g
Tc-99	1530 (*153*)	1.95E+03
U-233	**Below detection limit**	**Below detection limit**
U-234	15.5 (*0.11*)	14.1
U-235	1.3 (*0.08*)	1.35
U-236	**Below detection limit**	**Below detection limit**
Np-237	3.75 (*1.18*)	2.54
U-238	78.7 (*6.2*)	81.7

** Single ICP-MS analytical data. Italicized data are standard deviations.

The pictographic comparison of the radionuclide concentrations on these two barrier material pieces are presented in an overlay plot in Figure 4-1, which shows that although these analyses were performed at different times and during different test periods, the slight differences in concentrations are within the ICP-MS analytical uncertainties for these radionuclides (Tc-99, uranium isotopes and neptunium-237), although the variance for Tc-99 is notably larger than the other radionuclides.

It is worth noting that the overlay plot in Figure 4-1 (Y-axis scale) is on a log scale base 10 to ensure that the relatively small concentrations for U-235 on the "as-received" barrier material can be seen and be compared with the larger Tc-99 concentrations. The actual concentrations for these radionuclides, in pCi/g, are inserted above each bar in the plot.

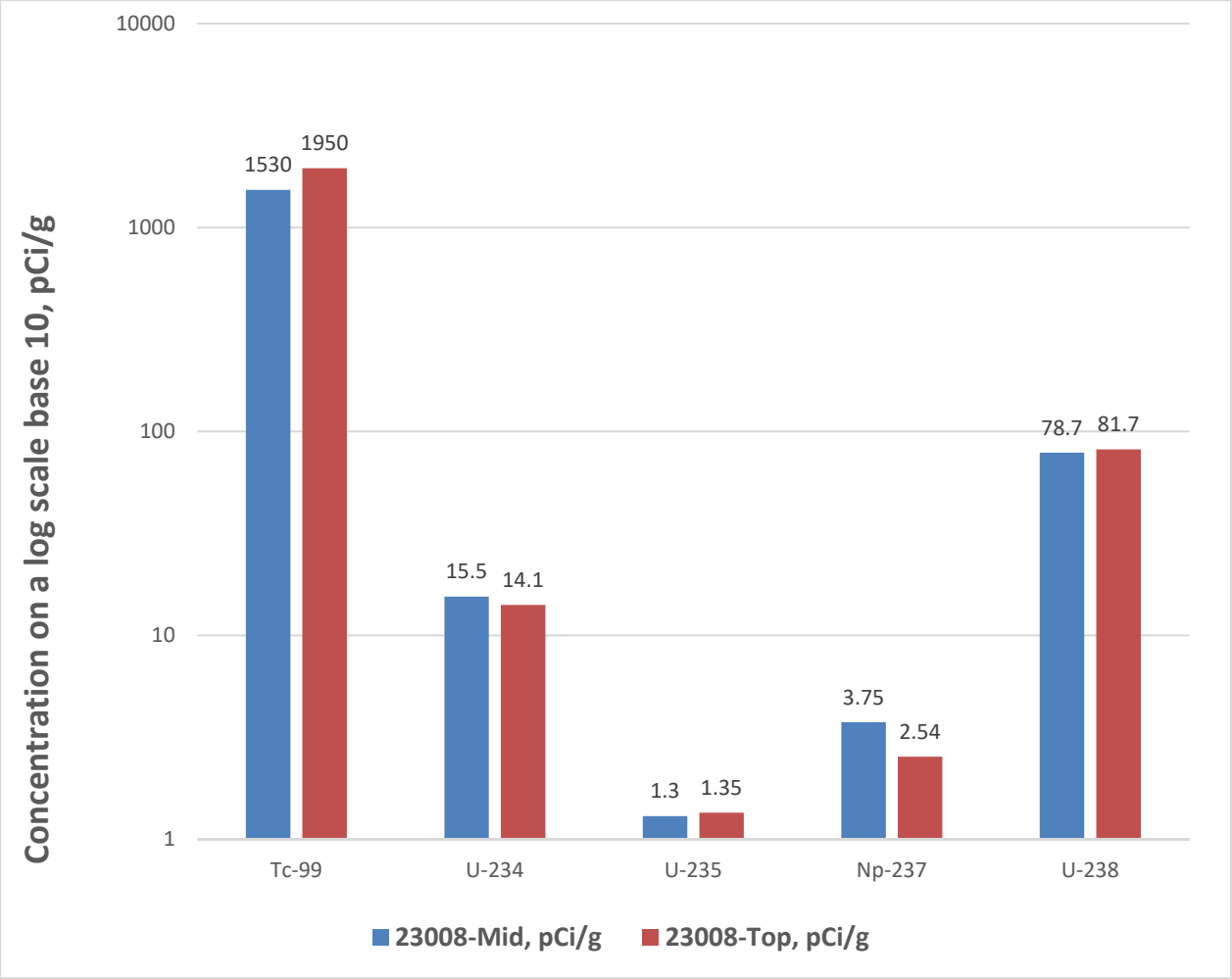


Figure 4-1 Concentration comparisons for radionuclides on "as-received" samples 23008-Mid and 23008-Top.

4.2 Ammonium carbonate leaching test results

4.2.1 Single strike leaching tests in ammonium carbonate without sonication

The two pieces of barrier materials used for these tests were identified as AMC-1-NOSON and AMC-2-NOSON, as shown in Table 3-1. These duplicate leaching tests were performed at an ammonium carbonate solution temperature of 20 °C. The resulting, post leaching solutions (leachates) were clear and without any visible solid particles and were submitted for ICP-MS analysis.

The post leaching analytical results of the digested barrier material samples contacted with ammonium carbonate without sonication are presented in Table 4-2. The calculated Tc-99 concentration of 75.4 ± 2.5 pCi/g waste (mass basis) and corresponds to an average of 78.8 ± 0.6 % Tc-99 removal from the barrier material. The percent removal for the other radionuclides are also provided in the table. Average percentage removal values were 91.7 ± 0.4% for U-235, 93.4 ± 0.4% for U-238 and 31.3 ± 30.4% for Np-237. Post leaching U-234 concentrations were less than the instrument detection limit. The total amounts of these radionuclides in the leachate and the relative amounts left on the barrier material pieces are also provided in Table 4-3 and Figures 4-2 through 4-4, respectively.

Table 4-2 Tc-99, uranium and Np-237 concentrations and decontamination results for the barrier material following Ammonium carbonate leaching without sonication

Component	$(NH_4)_2CO_3$ Leaching without sonication, pCi/g Test AMC-1-NOSON	% Removed & WAC limit Test AMC-1-NOSON		$(NH_4)_2CO_3$ Leaching without sonication, pCi/g Test AMC-2-NOSON	% Removed & WAC limit Test AMC-2-NOSON	
NA	NA	% Removed	Adjusted WAC limit, pCi/g waste	NA	% Removed	Adjusted WAC limit, pCi/g waste
Tc-99	424	78.3	77.1	405	79.2	73.6
U-234	<8.92	**NA**	NA	<8.45	**NA**	NA
U-235	0.108	92	NA	0.116	91.4	NA
Np-237	1.20	52.8	Na	2.29	9.8	NA
U-238	5.18	93.7	NA	5.65	93.1	NA

Table 4-3 Ammonium carbonate leaching <u>without</u> sonication: Total Tc-99, Uranium and Np-237 leachate

	Total concentration in leachate, pCi	
Component	**(AMC-1-NoSON-leachate)**	**(AMC-2-NoSON-leachate)**
Tc-99	1.04E+03	9.23E+02
U-233	<4.72E+00	<4.95E+00
U-234	9.28E+00	8.78E+00
U-235	8.18E-01	7.95E-01
U-236	<3.15E-02	<3.31E-02
Np-237	<3.44E+00	<3.61E+00
U-238	5.24E+01	5.11E+01

4.2.2 Single strike leaching tests in ammonium carbonate without sonication: mass balance

Mass balance calculations were based on: 1) the concentrations of the radionuclides in the leachates, 2) residual amounts in the post leached barrier material pieces coming from sample digestion and analysis, and 3) the concentrations of radionuclides in the "as-received" barrier material. Mass balance results for the duplicate tests without sonication are provided in Tables 4-4 and 4-5.

Table 4-4Ammonium Carbonate Leaching <u>without</u> Sonication (Test AMC-1-NOSON): Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amount on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	1150	292.14	1442.14	1340	6.9
U-234	9.10	<8.92	≤9.1	9.72	undefined
U-235	0.807	0.074	0.93	0.930	5.4
Np-237	0.417	0.83	1.24	1.75	33.8
U-238	51.3	3.57	54.87	56.29	2.6

*Percent difference (% difference) is defined as absolute difference/average*100.

Table 4-5Ammonium Carbonate Leaching without Sonication (Test AMC-2-NOSON): Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amount on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	925	292.8	1217.8	1410	14.6
U-234	8.98	<9.06	≤8.98	10.2	undefined
U-235	0.803	0.084	0.887	0.976	9.6
Np-237	0.703	1.66	2.363	1.84	24.9
U-238	50.30	4.08	54.40	59.1	8.3

*Percent difference (% difference) is defined as absolute difference/average*100.

The Tc-99 mass balance percent difference, as defined above, for the duplicate tests without sonication are 6.9 % and 14.6% giving an average of 10.75% (Tables 4-4 and 4-5). The mass balance percent difference for the U-235 in these un-sonicated duplicate tests were 5.4 % and 9.6%. The percent difference for the U-238 in these same duplicate tests were 2.6% and 8.3%. Uranium-234 concentrations were lower than the instrument detection limits and thus the mass balance values are undefined. Only Np-237 mass balance difference, which were 33% and 24.9% were greater than 20 % (two sigma analytical uncertainties for ICP-MS). These mass balance percent differences for Tc-99 and the uranium isotopes are within the expected analytical uncertainty for ICP-MS analysis of the barrier material for these elements.

4.2.3 Single strike leaching tests in ammonium carbonate with sonication and mass balance

This single strike leaching sonication test was performed in duplicate for samples AMC-2-SON-1, AMC-2-SON-2 as shown in Table 3-1. The temperature profile plots for these sonicated tests are presented in APPENDIX A1, inserts $A_1$1 and $A_1$2. The average maximum temperature attained due to the process of energy dissipation inside the solutions during the sonicated tests was 54.6 ± 2.1 °C, while the initial room temperature was 20 °C. The maximum temperature was attained after about 75 minutes of leaching with sonication. The temperature profiles for these sonicated tests were very similar.

The two post-leaching analytical results for the digested barrier sub-samples following ammonium carbonate contact with sonication are presented in Table 4-6. The calculated Tc-99 concentrations for the two tests were 51.9 and 62.2 piCi/g waste giving an average of 57.1 ± 7.3 piCi/g waste. An average of 84.0 ± 2.1 % of the Tc-99 was leached out of the barrier materials. The percentages of U-235 and U-238 leached out of the barrier samples with a single ammonium carbonate strike with sonication averaged 99.2 ± 0.1 % and 99.3 ± 0.1%, respectively. Post leaching U-234 concentrations in the barrier material were less than the instrument detection limit and it can thus be assumed that most of the U-234 in the barrier materials were leached out of the barrier materials with sonication treatment. Neptunium-237 analysis results were less than the instrument detection limit. The total amounts of these radionuclides in the leachate and the relative radionuclide amounts left on the barrier material pieces after leaching are also shown in Table 4-7 and Figures 4-2 through Figures 4-4, respectively. The amounts of both U-234 and Np-237 in the leachates ranged from 60-81% of the amounts of these radionuclides in the "as-received" barrier material.

As presented in Table 4-8 and Table 4-9, the Tc-99 mass balance percent difference, for the leaching tests with sonication were of 3.3% and 8.1% for the duplicate tests, while the percent difference for the U-235 in these same tests were 0.5% and 8.1 %. The mass percent difference for the U-238 in these duplicate tests were 0.5% and 8.9%. Uranium-234 concentrations were lower than the instrument detection limits and thus the mass balance values are undefined. Neptunium-237 mass balance difference averaged less than

9%. These mass balance percent differences for Tc-99, the uranium isotopes and Np-237 are within the expected analytical uncertainty for ICP-MS analysis of the barrier material for these elements.

Table 4-6 Tc-99, uranium isotopes and Np-237 decontamination results: Ammonium carbonate leaching with sonication: Test AMC-2-SON-1 and Test AMC-2-SON-2

Component	**$(NH_4)_2CO_3$ Leaching with sonication, pCi/g Test** AMC-2-SON-1	**% Removed & WAC limit Test** AMC-2-SON-1		**$(NH_4)_2CO_3$ Leaching with sonication, pCi/g Test** AMC-2-SON-2	**% Removed & WAC limit Test** AMC-2-SON-2	
		% Removed	Adjusted WAC limit, pCi/g waste		% Removed	Adjusted WAC limit, pCi/g waste
Tc-99	285	85.4	51.9	342	82.5	62.2
U-234	<9.06	**NA**	NA	<8.63	**NA**	NA
U-235	0.0111	99.2	NA	0.0117	99.1	NA
Np-237	<1.02	NA	Na	<0.974	NA	NA
U-238	0.538	99.3	NA	0.615	99.2	NA

Table 4-7 Ammonium carbonate leaching <u>with</u> sonication: Total Tc-99, Uranium and Np-237 in leachate

	Total concentration in leachate, pCi	
Component	**(AMC-2-SON-1-leachate)**	**(AMC2-SON-2-leachate)**
Tc-99	1.10E+03	1.03E+03
U-233	<4.70E+00	<4.85E+00
U-234	1.16E+01	1.16E+01
U-235	9.15E-01	1.02E+00
U-236	<3.14E-02	<3.24E-02
Np-237	1.20E+00	1.83E+00
U-238	5.60E+01	6.28E+01

Table 4-8 Ammonium Carbonate Leaching with Sonication (Test AMC-2-SON-1): Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	1100	195.8	1295.8	1340	3.3
U-234	11.6	<8.63	≤11.6	9.69	undefined
U-235	0.915	0.008	0.923	0.927	0.5
Np-237	1.20	0.70	1.9	1.75	8.8
U-238	56.0	0.371	56.4	56.1	0.5

*Percent difference (% difference) is defined as absolute difference/average*100.

Table 4-9 Ammonium Carbonate Leaching with Sonication (Test AMC-2-SON-2): Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	1030	242.14	1270	1380	8.1
U-234	11.6	<8.63	≤11.6	9.98	undefined
U-235	1.02	0.012	1.03	0.956	8.1
Np-237	1.83	<0.974	≤1.83	1.80	undefined
U-238	62.8	0.439	63.24	57.8	8.9

*Percent difference (% difference) is defined as absolute difference/average*100.

4.2.4 Double strike leaching tests in ammonium carbonate without sonication:mass balance

The piece of barrier material sample used for double strike ammonium carbonate leaching without sonication is identified as sample AMC-4-NOSON-DS, as shown in Table 3-1. The leaching tests were also performed at an ammonium carbonate solution temperature of 20 °C.

The post leaching analyses results of the barrier material for Tc-99, uranium isotopic concentrations and Np-237 are presented in Table 4-10, along with the percentages of each element removed from the barrier material for this double ammonium carbonate strike without sonication. The adjusted Tc-99 waste disposal WAC (89.6 piCi/converter) and the percentages of the radionuclides removed are also calculated and presented in the Table 4-10. About 75% of the Tc-99 was leached out of the barrier material without sonication and an average of ~95% of both U-235 and U-238 were also removed in this leaching without sonication. More than 70% of Np-237 was leached from the sample. The quantity of U-234 left on the barrier material after leaching was less than the instrument detection limit and thus it is assumed that most of the U-234 was leached from the sample.

The leachates from the double strike ammonium carbonate leaching of the barrier material piece without sonication were also analyzed for Tc-99, uranium isotopes (U-234, U-235 and U-238) and Np-237. Uranium-233 and U-236 concentrations were below instrument detection limit. The total amounts of these radionuclides in the leachate and the relative amounts left on the barrier material pieces after leaching are also shown in Table 4-11 and Figures 4-2 through 4-4, respectively.

The mass balance calculations are summarized in Table 4-12. All the mass balance differences for these elements (Tc-99, U-234, U-235, U238 and Np-237) are less than 20%.

Table 4-10 Technetium and uranium concentrations and decontamination results for the barrier material following ammonium carbonate leaching: Double strike without sonication

Component	Leaching without sonication, pCi/g Test AMC-4-NOSON-DS	% Removed and WAC Test AMC-4- NOSON-DS	
-	-	% Removed	Adjusted WAC, pCi/g waste
Tc-99	492.96	74.7	89.6
U-234	<4.84E+00	NA	NA
U-235	0.08	94.1	NA
Np-237	0.69	72.8	Na
U-238	3.96	95.2	NA

Table 4-11 Double ammonium carbonate lixiviant strike without sonication: Total Tc-99, Uranium and Np-237 in leachate

	Total concentration in leachate, pCi	
Component	**AMC-4-NOSON-DS-leachate-1**	**AMC-4-NOSON-DS-leachate-2**
Tc-99	8.21E+03	1.92E+02
U-233	<4.46E+00	<4.46E+00
U-234	8.16E+00	2.88E+00
U-235	7.39E-01	2.67E-02
U-236	<2.98E-02	<2.98E-02
Np-237	7.65E-01	3.95E-01
U-238	4.75E+01	1.37E+00

Table 4-12 Ammonium Carbonate Leaching without Sonication Double lixiviant strike (test AMC-4-NOSON-DS) mass balance

Component	Amounts in combined leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in pieces of barrier sample tested, pCi	% difference*
Tc-99	1013	320.9	1.33E+03	1.27E+03	5.0
U-234	11.0	<4.84E+00	1.10E+01	9.18E+00	≤ 18.4
U-235	0.77	0.05	8.18E-01	8.79E-01	7.2
Np-237	1.16	0.45	1.61E+00	1.65E+00	2.7
U-238	48.87	2.58	5.15E+01	5.32E+01	3.3

*Percent difference (% difference) is defined as absolute difference/average*100.

4.2.5 Double strike leaching tests in ammonium carbonate with sonication: mass balance

The piece of barrier material sample used for this ammonium carbonate leaching with sonication is identified as sample AMC-3-SON-DS, as shown in Table 3-1. The temperature profile plots for double strike leaching test are presented in Appendix A (Inserts A_I3 and A_I4). The average maximum temperature attained inside the sonicated solutions during the double strike sonicated tests was 53.7 ± 0.6 °C, which is not significantly different from the average maximum temperatures measured for the two-single strike tests with sonication in section 4.2.2.

The post leaching analyses results of the barrier material for Tc-99, uranium isotopes and Np-237 are presented in Table 4-13, along with the percentages of each element removed from the barrier material. The calculated Tc-99 adjusted waste disposal WAC (14.7 piCi/g waste) and the percentages of the radionuclides removed are also calculated and presented in the Table 4-13. About 95% of the Tc-99 was leached out of the barrier material with double ammonium carbonate strike with sonication and more than 99% of both U-235 and U-238 were also removed in this double strike leaching with sonication. More than 63% of Np-237 was leached out. The quantity of U-234 left on the barrier material after leaching was less than the instrument detection limit and thus it is assumed that most of the U-234 was leached.

The leachates from the double strike ammonium carbonate leaching with sonication were also analyzed for Tc-99, uranium isotopes (U-234, U-235 and U-238) and Np-237. Uranium-233 and U-236 concentrations were below instrument detection limit. The amounts of these radionuclides in the leachate and the relative amounts left on the barrier material piece after leaching are also shown in Table 4-14 and Figures 4-2 through 4-4, respectively.

The mass balance calculations are presented in Table 4-15. All the percent mass balances differences for these elements (Tc-99, U-235 and U238) are less than 20%. The mass balance difference for U-234 and Np-237 are classified as undefined because their measured concentrations were below instrument detection limit; it is assumed that both radionuclides had been completely leached out of the barrier material after double strike leaching with sonication in ammonium carbonate solutions.

Table 4-13 Technetium and uranium concentrations and decontamination results for the barrier material following ammonium carbonate leaching: Double strike with sonication

Component	**Leaching with sonication, Test AMC-3-**SON-DS **Strikes*, pCi/g**	**% Removed and WAC, Test AMC-3**-SON-DS	
-	-	% Removed	Adjusted WAC, pCi/ g waste
Tc-99	80.8	95.9	14.7
U-234	<8.33	NA	NA
U-235	0.007	99.5	NA
Np-237	<0.94	NA	Na
U-238	0.333	99.6	NA

* After first ammonium carbonate strike the solid sample was **not** digested and analyzed for these components of the barrier material.

Table 4-14 Double ammonium carbonate strike <u>with</u> sonication: Total Tc-99, Uranium and Np-237 in leachate

	Total concentration in leachate, pCi	
Component	**(AMC3-SON-DS-1LE)**	**(AMC3-SON-DS-2LE)**
Tc-99	1.06E+03	1.22E+02
U-233	<5.15E+00	<5.15E+00
U-234	1.04E+01	<3.32E+00
U-235	9.29E-01	2.44E-03
U-236	<3.44E-02	<3.44E-02
Np-237	1.49E+00	<3.75E-01
U-238	5.77E+01	1.19E-01

Table 4-15 Ammonium Carbonate Leaching with Sonication: Double Lixiviant Strike (Test AMC-3-SON-DS)): mass balance

Component	Amounts in combined leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in sample piece tested pCi	% difference*
Tc-99	1182	60.76	1241	1470	16.6
U-234	≤13.7	<8.33	≤13.7	10.6	undefined
U-235	0.931	0.005	0.936	1.02	8.1
Np-237	≤1.87	0.70	≤1.86	1.91	undefined
U-238	57.8	0.25	58.08	61.4	5.6

*Percent difference (% difference) is defined as absolute difference/average*100.

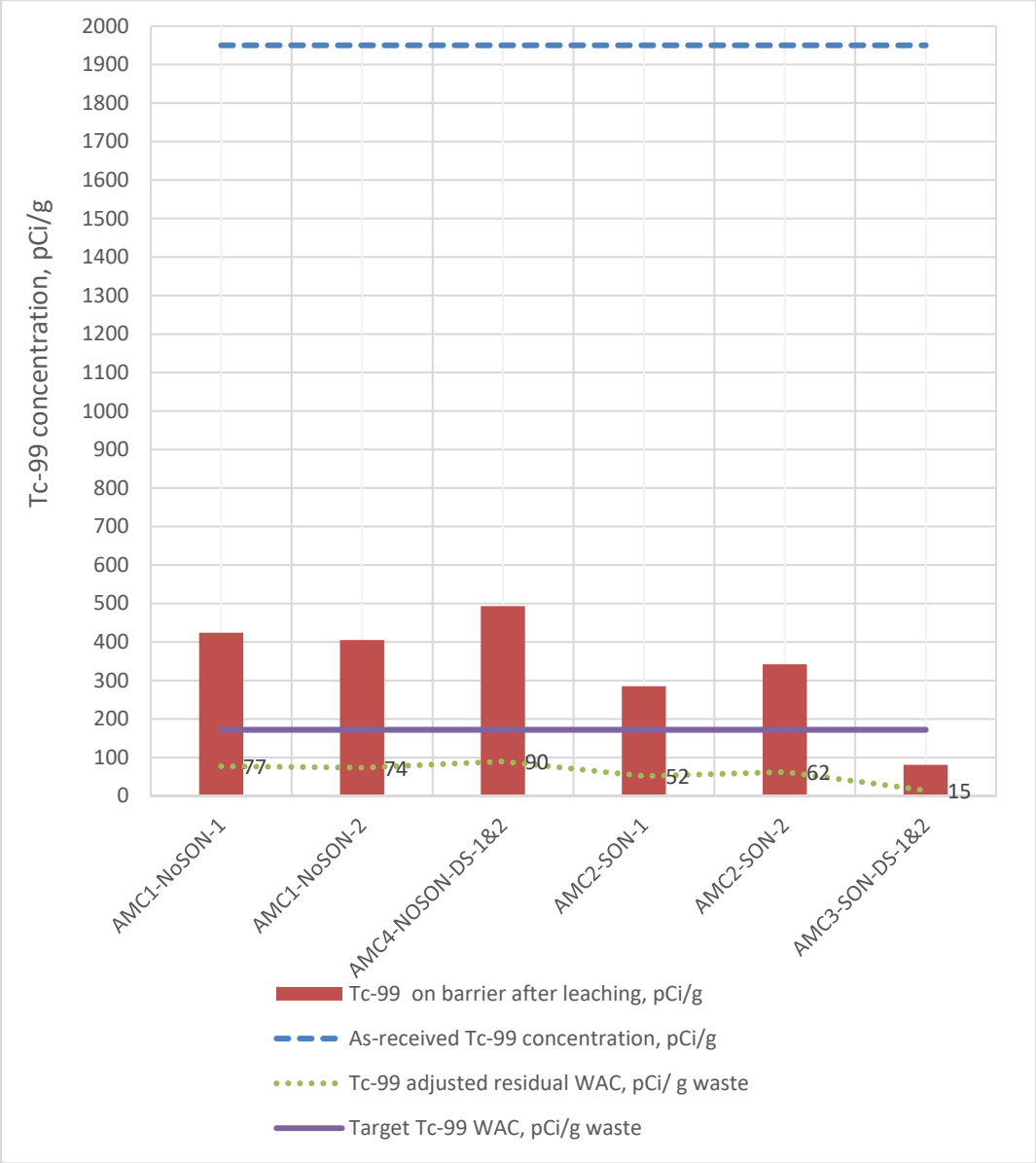
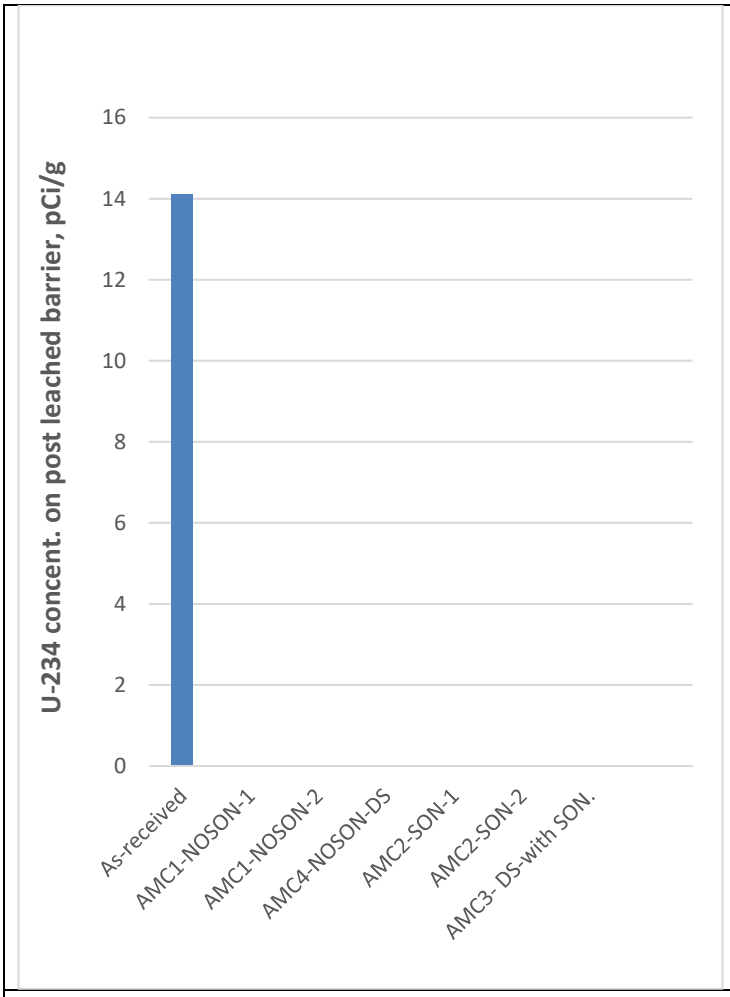
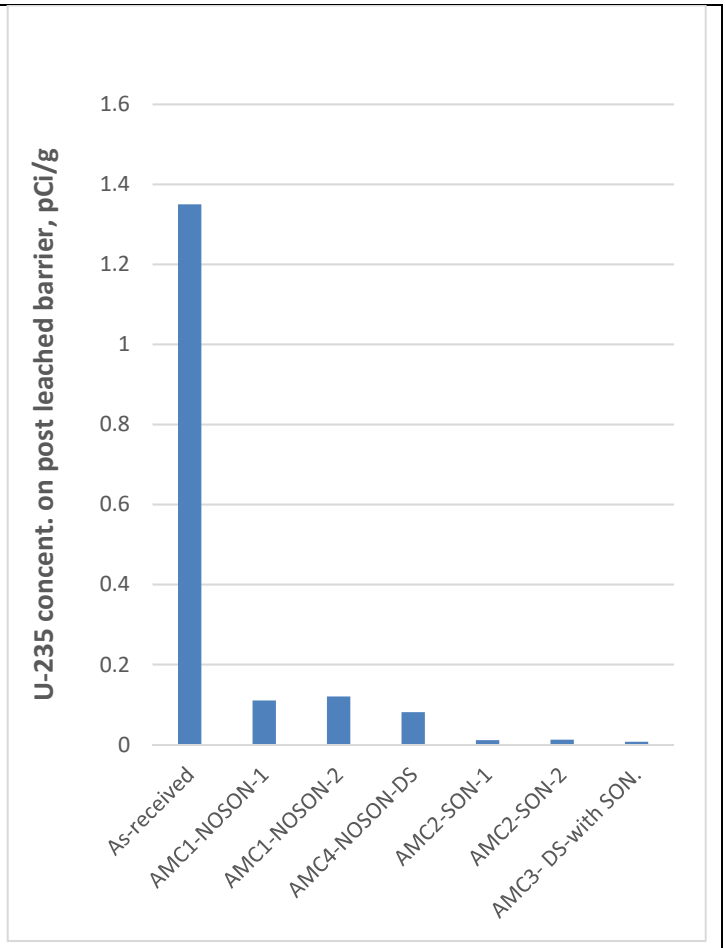


Figure 4-2Tc-99 concentration on post- ammonium carbonate leached barrier material relative to initial "as-received" concentration.



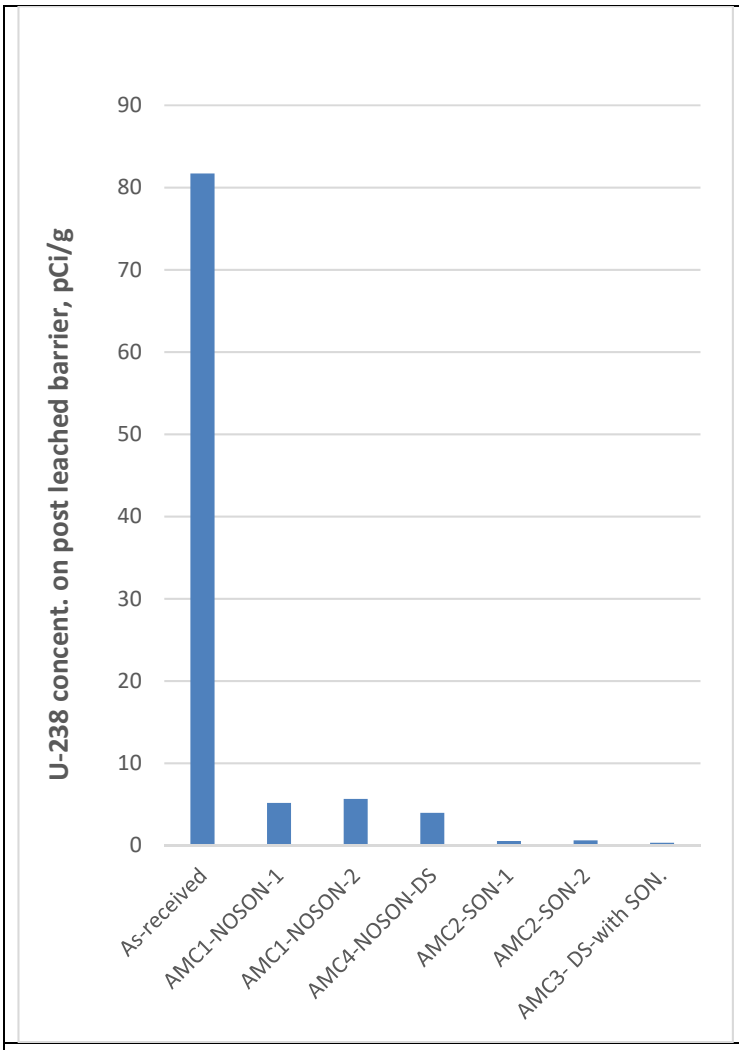
U-234 concentration on post-leached 23008-Top material



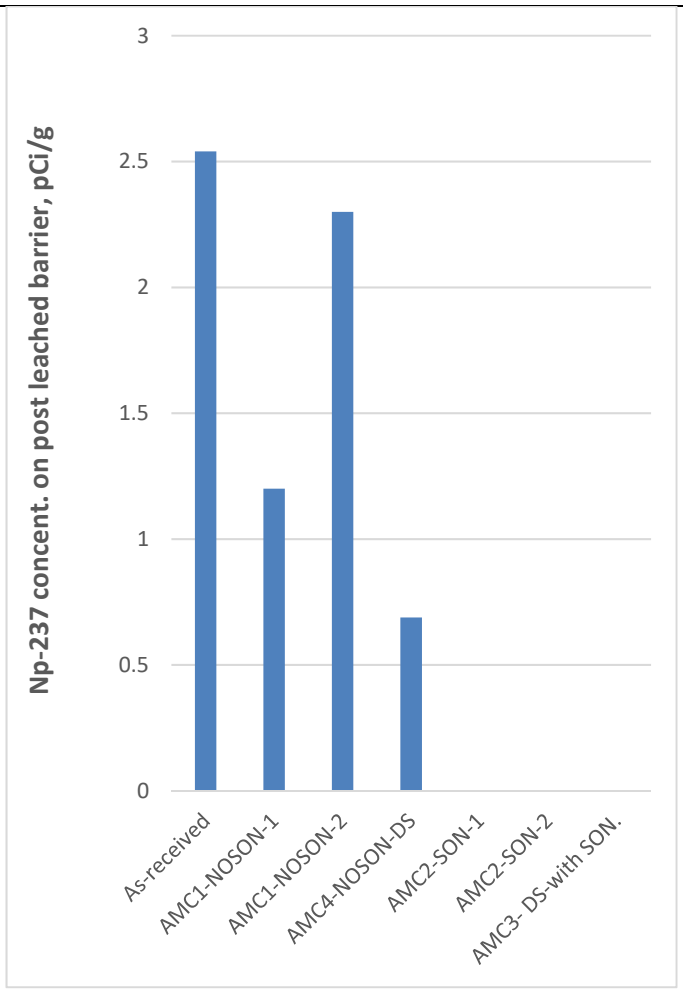
U-235 concentration on post-leached 23008-Top material

A value of zero pCi/g for U-234 implies the value was less than instrument detection limit.

Figure 4-3post-leaching U-234 and U-235 concentrations on barrier material 23008-Top relative to initial "as-received" concentrations.



U-238 concentration on post-leached 23008-Top material



Np-237 concentration on post-leached 23008-Top material*

- A value of zero pCi/g for Np-237 implies the value was less than instrument detection limit.

Figure 4-4 Post-leaching U-238 and Np237 concentrations on barrier material 23008-Top relative to initial "as-received" concentrations.

The post-leaching concentrations or amount of Tc-99, U-34, U-235, U-238 and Np-237 remaining on the barrier material samples after leaching are shown in Figures 4-2, 4-3 and 4-4, respectively. Figure 4-2 also shows overlay plots of the target Tc-99 disposal WAC and the adjusted Tc-99 WAC obtained for each ammonium carbonate leaching category results. All these ammonium carbonate leaching approaches, with or without sonication including double strike tests, showed Tc-99 removal results which meet and exceed the Oak Ridge waste disposal WAC goal (172 pCi/g of converter). However, there is a considerable leaching of the uranium isotopes in all these ammonium carbonate leaching tests as well. As shown in Figure 4-4 (Np-237 insert) most of the Np-237 is removed only when there is leaching with sonication; in all leaching without sonication tests only an average of 50% or the Np-237 is removed from the barrier material.

4.3 Tri-sodium Phosphate Leaching Tests

Taking advantage of the fact the most uranium phosphate compounds are sparingly soluble in near basic conditions and as part of the criticality strategy to minimize uranium leaching out of the barrier material, tri-sodium phosphate was used as a lixiviant in this part of the leaching tests. The expected goal being that with TSP as the lixiviant, sufficient quantities of Tc-99 will be leached out of the barrier material to meet the Tc-99 disposal WAC, while minimal amounts of uranium isotopes will be removed from the barrier material.

Four barrier material leaching tests were performed in the same manner as described above for ammonium carbonate tests. Tri-sodium phosphate leaching tests performed, as summarized in Table 3-1, included the following: duplicate single strike tri-sodium phosphate leaching with sonication treatment (tests Na_3PO_4-SON-1and Na_3PO_4-SON-2), double strike tri-sodium phosphate leaching with sonication (test Na_3PO_4-SON-DS) and double strike tri-sodium phosphate leaching *without* sonication (test Na_3PO_4-NOSON-DS).

4.3.1 Single strike leaching tests in tri-sodium phosphate with sonication (tests Na3PO4-SON-1 and Na3PO4-SON-2)-duplicate test

The two pieces of the barrier materials used for these tests were identified as Na_3PO_4-SON-1 and Na_3PO_4-SON-2. Before the tests, the initial temperature of the tri-sodium phosphate lixiviant solutions was of 20 °C. The average maximum temperature attained due to the process of energy dissipation inside the sonicated tri-sodium phosphate solutions during these duplicate tests was 54.7 ± 0.5 °C. The temperature profile plots for these leaching tests with sonication are presented in Appendix C (inserts C_1 and C_2).

The resulting, post leaching solutions (leachates) were clear and without any visible solid particles and were submitted for ICP-MS analysis for Tc-99, uranium isotopes and Np-237.

The post leaching analytical results for the barrier material pieces are presented in Table 4-16 for Tc-99, uranium isotopes and Np-237 left in the barrier material. The calculated adjusted Tc-99 waste disposal WAC for these duplicate leaching tests were 236.4 and 243.6 pCi/gram of waste and the percent Tc-99 removed were 33.3% and 31.3%. The percentages of the uranium isotopes (U-235, U-234 and U-238) removed ranged from 42 to 49% with an average of 45.4 ± 2.2%. An average of 57 ± 12.7% of the Np-237 in the barrier material was removed from both tests.

The total amounts of these radionuclides in the leachate solutions are also presented in Table 4-17. The concentrations for U-233 and U-236 in the leachates from both tests were below instrument detection limit.

The mass balance calculations are presented in Tables 4-18 and 4-19 for both tests. The last columns in Tables 4-18 and 4-19 contains the percent differences between the concentrations of Tc-99, uranium isotopes and Np-237 in the original barrier materials before leaching and sum of their concentrations from the leachates and residues left on the barrier material after leaching.

The Tc-99 mass balance percent difference, as previously defined, for these single strike tests with sonication averaged 6.8 ± 3.0%, while the percent difference for U-235 and U-238 isotopes in these sonicated tests ranged from 0.5-4.9% with an average of 2.5 ± 1.9%. The mass balance difference for U-234 analyses were slightly higher than what is expected for U-234 analysis by ICP-MS.

The mass balance for U-234 averaged 14.9 ± 4.8% for both tests. The Np-237 mass balance difference average 17.4 ± 7.6%. These mass percent balance differences are within the expected analytical uncertainty for ICP-MS analysis of the barrier material for Tc-99, U-235 and U-238 isotopes.

Table 4-16 Technetium and uranium concentrations and decontamination results for the barrier material following Tri-sodium phosphate leaching

Component	$Na_3PO_4.12H_20$ Leaching with sonication, Test Na_3PO_4-SON-1, pCi/g	% Removed & WAC per converter Na_3PO_4-SON-1		$Na_3PO_4.12H_20$ Leaching with sonication, Test Na_3PO_4-SON-2, pCi/g	% Removed and WAC Na_3PO_4-SON-2	
		% Removed	Adjusted WAC limit, pCi/Converter		% Removed	Adjusted WAC limit, pCi/ g waste
Tc-99	1.30E+03	33.3	236.4	1.34E+03	31.3	243.6
U-234	8.06E+00	42.8	NA	8.00E+00	43.3	NA
U-235	7.18E-01	46.8	NA	6.93E-01	48.7	NA
Np-237	1.32E+00	48.0	NA	8.65E-01	66.0	NA
U-238	4.50E+01	44.9	NA	4.40E+01	46.1	NA

Table 4-17 Tri-sodium phosphate leaching with sonication: Total Tc-99, Uranium and Np-237 in leachate

	Total concentration in leachate, pCi	
Component	**(Na_3PO_4-SON-1-leachate)**	**(Na_3PO_4-SON-2-leachate)**
Tc-99	3.79E+02	3.11E+02
U-233	< 4.63E+00	< 4.81E+00
U-234	6.00E+00	5.49E+00
U-235	4.23E-01	4.78E-01
U-236	< 3.09E-02	< 3.21E-02
Np-237	1.04E+00	8.10E-01
U-238	2.62E+01	2.93E+01

Table 4-18 Tri-sodium phosphate leaching with Sonication (Test Na_3PO_4-1-SON-1): Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	3.79E+02	878.8	1.26E+03	1.32E+03	4.7
U-234	6.00E+00	5.45	1.14E+01	9.53E+00	18.3
U-235	4.23E-01	0.49	9.08E-01	9.13E-01	0.5
Np-237	1.04E+00	0.89	1.94E+00	1.72E+00	12.0
U-238	2.62E+01	30.42	5.67E+01	5.52E+01	2.6

*Percent difference (% difference) is defined as absolute difference/average*100.

Table 4-19 Tri-sodium phosphate leaching with Sonication (Test Na_3PO_4-2-SON-2): Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	3.11E+02	940.7	1.25E+03	1.37E+03	8.9
U-234	5.49E+00	5.6	1.11E+01	9.90E+00	11.5
U-235	4.78E-01	0.49	9.65E-01	9.48E-01	1.8
Np-237	8.10E-01	0.61	1.42E+00	1.78E+00	22.8
U-238	2.93E+01	30.9	6.02E+01	5.74E+01	4.9

*Percent difference (% difference) is defined as absolute difference/average*100

4.3.2 Double strike leaching tests in tri-sodium phosphate with sonication (Test Na_3PO4-SON-DS)

For this double lixiviant strike leaching test with tri-sodium phosphate solution, a new sample piece of the barrier material was leached with sonication and after the 2-hour test duration, the lixiviant was decanted and the leached solid removed from the sonicator reservoir and the sonicator reservoir was cleaned three times; twice with fresh tri-sodium phosphate solution and then with deionized water. The decanted lixiviant (first-strike leachate) was stored for analysis for Tc-99, uranium isotopes and neptunium by ICP-MS. After the reservoir cleaning process, an equal volume of fresh lixiviant was put into the sonicator reservoir before putting the same leached barrier material into the sonicator reservoir.

This same barrier material, which had gone through the first leaching strike with tri-sodium phosphate, was now leached with sonication a second time for the same leaching duration of 2 hours. Again, at the end of the second sonication and leaching treatment, the solid was separated from the lixiviant (second-strike leachate) and the solid submitted for digestion/masking and analysis. The second- strike leachate solution was also analyzed.

During each double strike leaching test cycle with tri-sodium phosphate solution, the temperature of the lixiviant solution containing the samples piece being leached was monitored and recorded every 15 minutes. The temperature profile plots for this double strike leaching tests are presented in Appendix C, inserts C_3, and C_4. The initial lixiviant room temperature was 20 °C. The average maximum temperature attained inside the sonicated solutions during the double strike sonicated tests averaged 53.5 ± 0.7 °C. This average maximum temperature value is not significantly different from the average maximum temperature measured for the two-single strike tests with sonication in section 4.3.1.

The post leaching analyses results of the barrier material for Tc-99, uranium isotopic concentrations and Np-237 are presented in Table 4-20, along with the percentages of each element removed from the barrier material. The calculated adjusted Tc-99 waste disposal WAC (243.6 pCi/g of barrier material waste) and the percentages of the radionuclides removed are also presented in the Table 4-20. About 31% of the Tc-99 was leached out of the barrier material with double strike/sonication and about 48% of both U-235 and U-238 were also removed. Only about 43% of U-234 and about 66% of Np-237 was removed. The overlay plots in Figure 4-5 through Figure 4-7 also shows graphically the amounts (relative to their initial concentrations in the "as-received barrier material) of these radionuclides left on the barrier material after double strike leaching with sonication.

The leachates from the tri-sodium phosphate double strike with sonication leaching of the barrier material piece were also analyzed for Tc-99, uranium isotopes and Np-237. Uranium-233 and U-236 concentrations were below MDL. The concentration of these radionuclides in the leachate are also presented in Table 4-21 and in Appendix D where the amounts of these radionuclides in solution, for all tests involving both ammonium carbonate and tri-sodium phosphate lixiviants under various test condition are compared. As earlier cited, the overlay plots in Appendix D shows that relatively smaller amounts of these radionuclides are present in solution because lesser amounts were leached out of the barrier materials in all tests involving the use of tri-sodium phosphate lixiviant solutions in comparison with leaching results with ammonium carbonate lixiviant.

The mass balance calculations for these tests are summarized in Table 4-22. The mass balance differences for Tc-99, U-235 and U-238 are less than 10%. The mass balance difference for U-234 and Np-237 were above 30% (respectively, 33.8 and 31.1%); possibly because of dilution effects on the smaller concentrations of these two radionuclides in the sample.

Table 4-20 Technetium, uranium and Np-237 concentrations and decontamination results for the barrier material following double strike leaching with sonication in tri-sodium phosphate

Component	Leaching with sonication, Test Na_3PO_4-SON-DS,* pCi/g	% Removed & WAC	
		% Removed	Adjusted WAC, pCi/ g of waste
Tc-99	1.46+03	25.13	243.6
U-234	8.57E+00	39.22	NA
U-235	6.88E-01	49.04	NA
Np-237	6.57E-01	74.13	NA
U-238	4.33E+01	47.00	NA

* After first Tri-sodium phosphate strike the solid sample was **not** digested and analyzed for these components of the barrier material.

Table 4-21 Tri-sodium phosphate double strike leaching with sonication: Total Tc-99, Uranium and Np-237 in leachate strikes 1 & 2

	Total concentration in leachate, pCi	
Component	**Na_3PO_4-SON-DS -1 leachate**	**Na_3PO_4-SON-DS -2 leachate**
Tc-99	3.20E+02	4.20E+01
U-233	< 4.44E+00	< 4.88E+00
U-234	5.29E+00	3.15E+00
U-235	4.57E-01	8.13E-02
U-236	< 2.97E-02	< 3.26E-02
Np-237	1.27E+00	5.88E-01
U-238	2.82E+01	3.94E+00

Table 4-22 Tri-sodium phosphate leaching Double strike with sonication (Tests Na_3PO_4-SON-DS-1 strikes: Material mass balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	3.620E+02	1,041	1.403E+03	1.39E+03	9
U-234	8.44E+00	6.11	1.45E+01	1.01E+01	36.5
U-235	5.38E-01	0.49	1.03E+00	9.63E-01	7.0
Np-237	1.86E+00	0.47	2.33E+00	1.81E+00	25.0
U-238	3.22E+01	30.87	6.31E+01	5.83E+01	7.9

*Percent difference (% difference) is defined as absolute difference/average*100.

4.3.3 Double strike leaching tests in tri-sodium phosphate without sonication (test Na3PO4-NOSON-DS)

The test above (section 4.3.2) was repeated at room temperature with a different piece of barrier material, again, using tri-sodium phosphate lixiviant without sonication treatment.

The post leaching analyses results of the barrier material for Tc-99, uranium isotopes and Np-237 concentrations left on the barrier material are presented in Table 4-23, along with the percentages of each element removed from the barrier material. The calculated adjusted Tc-99 waste disposal WAC (238.2 pCi/g of waste) and the percentages of the radionuclides removed are also presented in Table 4-23. About 33% of the Tc-99 was leached out of the barrier material with double strike and no sonication treatment and ~28% of both U-235 and U-238 were also removed. Only about 18% of U-234 and 16% of Np-237 were leached out of the barrier material with tri-sodium phosphate leaching.

The leachates from the double strike tri-sodium phosphate leaching of barrier material without sonication were also analyzed for Tc-99, uranium isotopes and Np-237. Uranium-233 and U-236 concentrations were below instrument detection limit. The total amounts of these radionuclides in the leachate are presented in Table 4-24 and in Appendix D. The post tri-sodium phosphate treatment membrane concentrations for Tc-99, uranium isotopes and Np-237, following double strike leaching without sonication are presented graphically in Figures 4-5, 4-6 and 4-7 relative to the initial "as-received" concentrations in the barrier material. These results are also compared to the concentrations of these radionuclides in ammonium carbonate leached membranes.

The mass balance calculations are summarized in Table 4-25. With U-234 mass balance difference being the exception, all the mass balances differences for these elements (Tc-99, U-235, U-238 and Np-237) are less than 10%. The mass balance difference for U-234 was the largest at 38.7%. Again, this significant mass difference may due to the relatively small pico-quantity of U-234 in the original sample and analytical dilution effects.

Table 4-23 Technetium, uranium and Np-237 concentrations and decontamination results for the barrier material following double strike leaching without sonication in tri-sodium phosphate

Component	Leaching without sonication, Test Na_3PO_4-NOSON-DS Strikes 1 & 2, pCi/g	% Removed & WAC limit per converter	
-	-	% Removed	Adjusted WAC limit, pCi/Converter
Tc-99	1.31E+03	32.8	238.2
U-234	1.16E+01	17.7	NA
U-235	9.56E-01	29.2	NA
Np-237	2.14E+00	15.7	NA
U-238	5.92E+01	27.5	NA

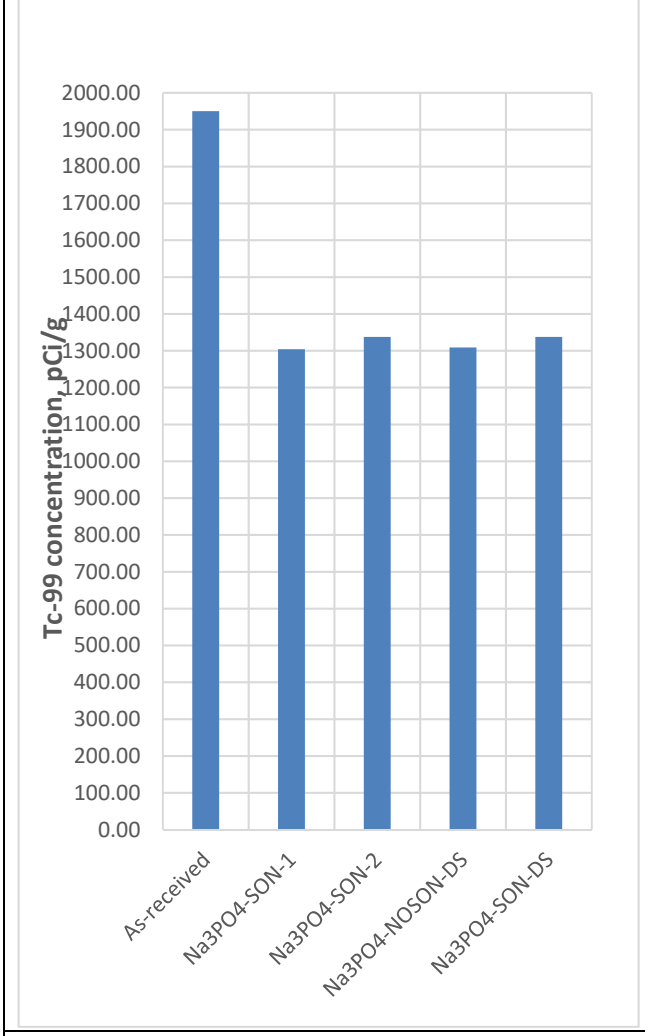
Table 4-24 Tri-sodium phosphate double strike leaching without sonication: Total Tc-99, Uranium and Np-237 in leachates: Tests Na3PO4-NOSON-DS strikes 1&2

	Total concentration in leachate, pCi	
Component	**Na_3PO_4-NOSON-DS -1 leachate**	**Na_3PO_4-NOSON-DS -2 leachate**
Tc-99	2.95E+02	4.58E+01
U-233	< 4.88E+00	< 4.44E+00
U-234	3.15E+00	2.87E+00
U-235	2.72E-01	5.98E-02
U-236	< 3.26E-02	< 2.97E-02
Np-237	7.22E-01	3.55E-01
U-238	1.56E+01	2.71E+00

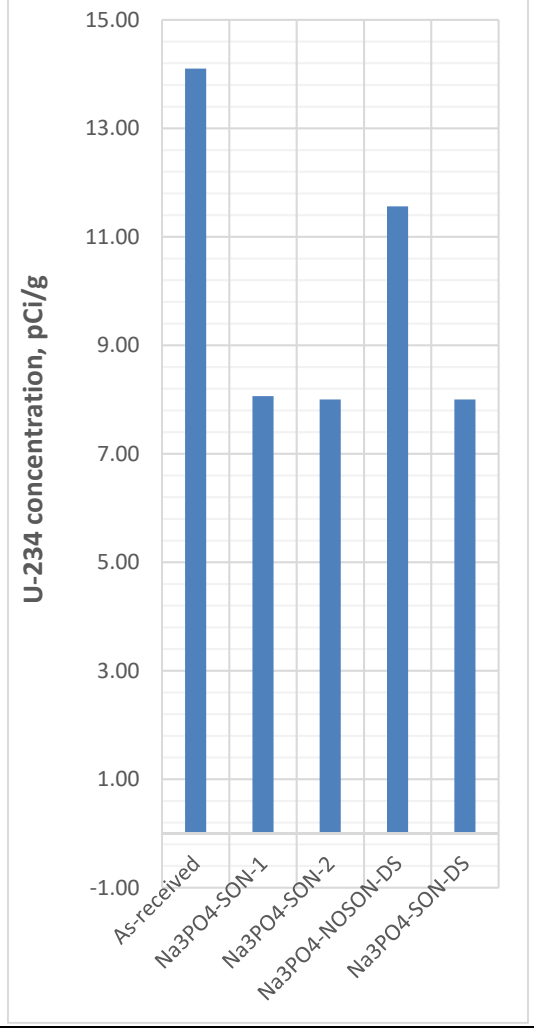
Table 4-25 Tri-sodium phosphate leaching Double strike without sonication
Tests Na3PO4-NOSON-DS strikes): Material mass balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	3.41E+02	850.19	1.19E+03	1.27E+03	6.1
U-234	6.02E+00	7.53	1.35E+01	9.15E+00	38.7
U-235	3.32E-01	0.620	9.52E-01	8.76E-01	8.3
Np-237	1.08E00	2.14	2.47E+00	1.65E+00	39.7
U-238	1.83E+01	38.42	5.67E+01	5.30E+01	6.7

*Percent difference (% difference) is defined as absolute difference/average*100.

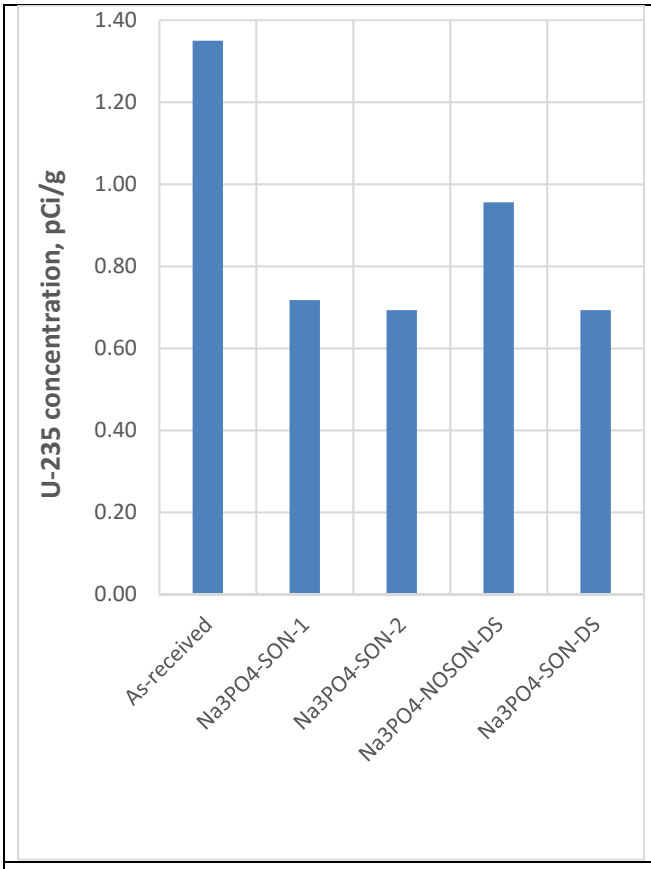


Insert A: Tc-99 concentration in post leached 23008-Top material: Tri-sodium phosphate leaching

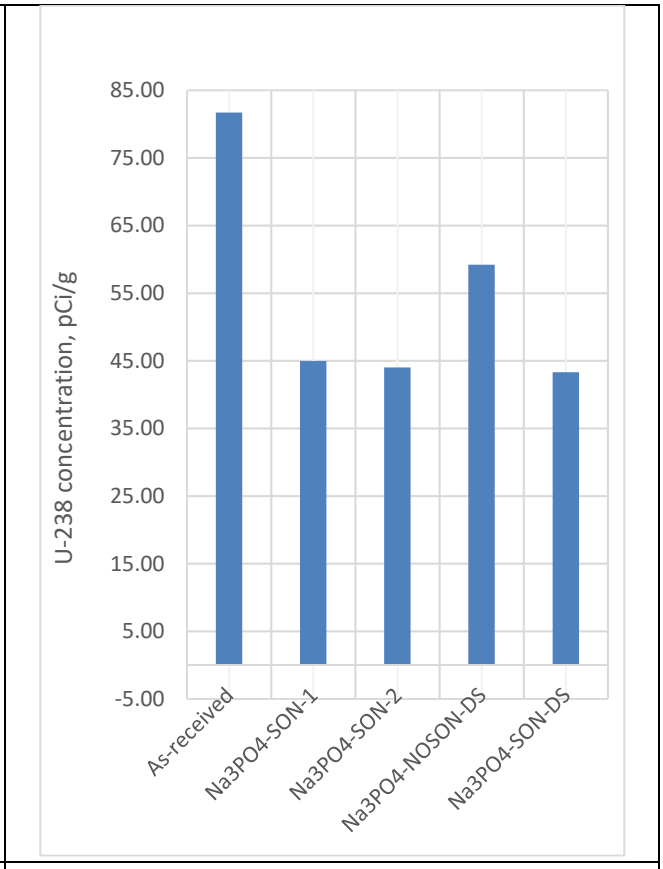


Insert B: U-234 concentration in post leached 23008-Top material: Tri-sodium phosphate leaching

Figure 4-5 Post tri-sodium phosphate leaching Tc-99 and U-234 concentrations on barrier material 23008-Top relative to concentrations in the "as-received" barrier material.

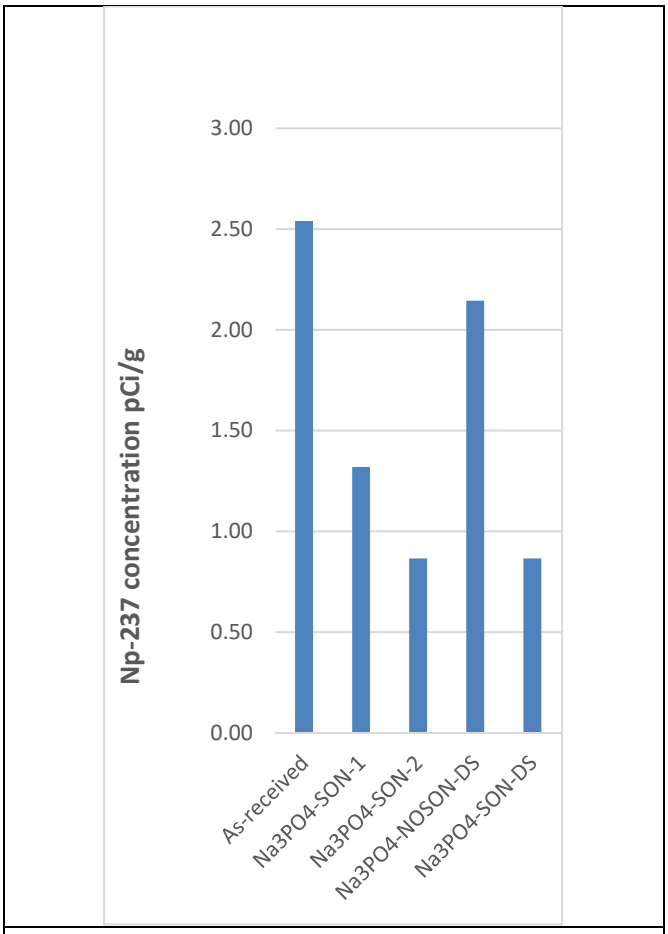


Insert B: U-235 concentration in post leached 23008-Top material: Tri-sodium phosphate leaching



Insert B: U-238 concentration in post leached 23008-Top material: Tri-sodium phosphate leaching

Figure 4-6 Post tri-sodium phosphate leaching U-235 and U-238 concentrations on barrier material 23008-Top relative to concentrations in the "as-received" barrier material



Insert B: Np-237 concentration in post leached 23008-Top material: Tri-sodium phosphate leaching

Figure 4-7 Post tri-sodium phosphate leaching Np-237 concentration on barrier material 23008-Top relative to concentrations in the "as-received" barrier material.

4.4 Ammonium Thiosulfate Leaching Tests

Analyses of leachates from tests where ammonium thiosulfate (ATS) was used as the lixiviant were complicated by the fact that precipitates were observed during sample dilution with 0.3 M nitric acid prior to ICP-MS analysis. The ATS leachate samples, LIMS numbers LW11053-11056, formed white precipitates when they were diluted with nitric acid. To prevent the clogging of the ICP-MS nebulizer with the precipitates, these samples had to be filtered before analysis. Even after filtrating through a 0.45-micron Nalgene filtration unit, the filtrate still turned cloudy after a few minutes prompting an additional filtration step for these samples immediately before analysis. Subsequently, analysis results indicated that most of the radionuclides, especially Tc-99 and Np-237, had co-precipitated with the solids during filtration and were not in the filtrate. Diluting the leachate samples with plain deionized water also did not lead to acceptable analytical results for these radionuclides. Therefore, the overlay plots in Appendix D, which

show the relative amounts of the radionuclides in the leachates for all tests conditions with the three lixiviants used in this study, do not contain plots of radionuclide levels for tests involving the use of ammonium thiosulfate lixiviant.

Leachate analytical results for the radionuclides are used only for material mass balance. However, since initial concentrations for these radionuclides in the "as-received" barrier pieces (Table 4-1; sample 23008-Top) and the post-leached solid sample pieces are known (Tables 4-26 and 4-27), the concentrations of these radionuclides in the leachate can be obtained by difference, if required.

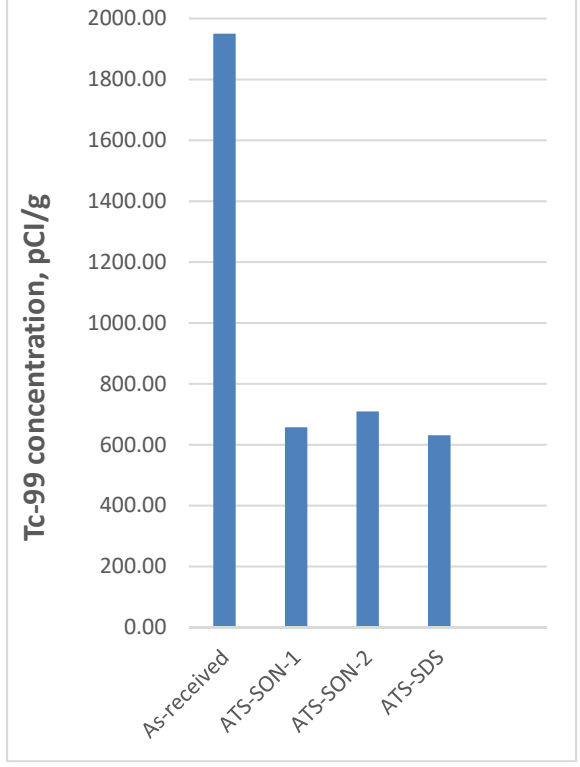
4.4.1 Single strike leaching tests in ammonium thiosulfate with sonication (Tests ATS-SON-1 &Test ATS-SON-2)

The two pieces of barrier materials used for these tests are identified as ATS-SON-1 and Test ATS-SON-2, as shown in Table 3-1. The average maximum temperature attained due to the process of energy dissipation inside the sonicated solutions during these duplicate tests averaged 51.3 ± 3.6 °C The temperature profiles are shown in Appendix B, inserts B_3 and B_4.

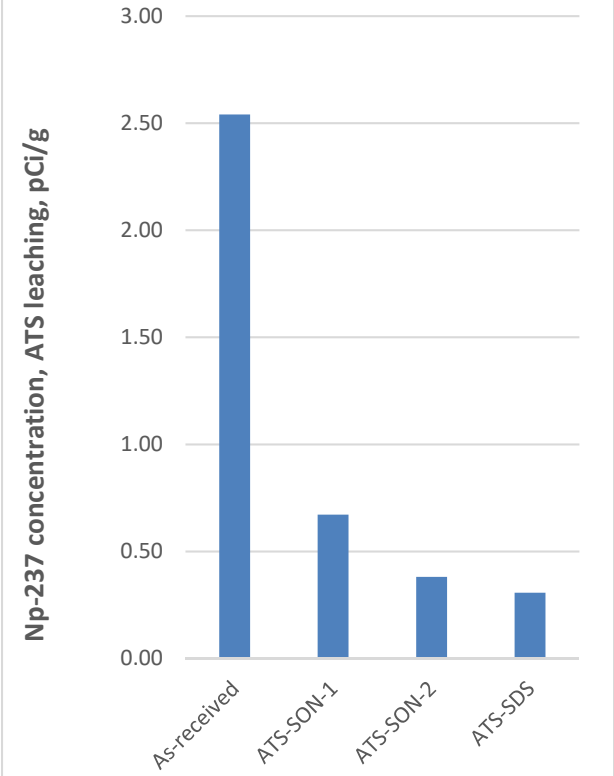
The post ammonium thiosulfate leaching analytical results for the barrier material pieces with sonication are presented in Table 4-26 and in overlay plots in Figures 4-28 through 4-29. For these duplicate tests, the calculated adjusted Tc-99 waste disposal WAC averaged 124.2 ± 6.6 pCi/g of barrier material waste and corresponds to an average of 65.0 ± 1.9 % Tc-99 removal from the barrier material. The percentages of the other radionuclides removed are also presented in Table 4-26 and they averaged 92.0 ± 1.6 % for U-235, 92.0 ± 1.5% for U-238 and 79.3 ± 8.1% for Np-237. Post leaching U-234 concentrations in the barrier material were less than the instrument detection limit.

Table 4-26 Technetium, uranium and Np-237 concentrations and decontamination results for the barrier material following ammonium thiosulfate leaching with sonication

Component	$(NH_4)_2SO_3$ Leaching with sonication, pCi/g Test ATS-SON-1	% Removed & WAC limit Test ATS-SON-1		$(NH_4)_2SO_3$ Leaching with sonication, pCi/g Test ATS-SON-2	% Removed and WAC Test ATS-SON2	
		% Removed	Adjusted WAC limit, pCi/g waste		% Removed	Adjusted WAC, pCi/g of waste
Tc-99	657	66.3	119.5	709	63.6	128.9
U-234	< 4.34E+00	**NA**	NA	< 4.27E+00	**NA**	NA
U-235	1.23E-01	90.9	NA	9.37E-02	93.1	NA
Np-237	6.72E-01	73.5	Na	3.81E-01	85.0	Na
U-238	7.45	90.9	NA	5.74	93.0	NA

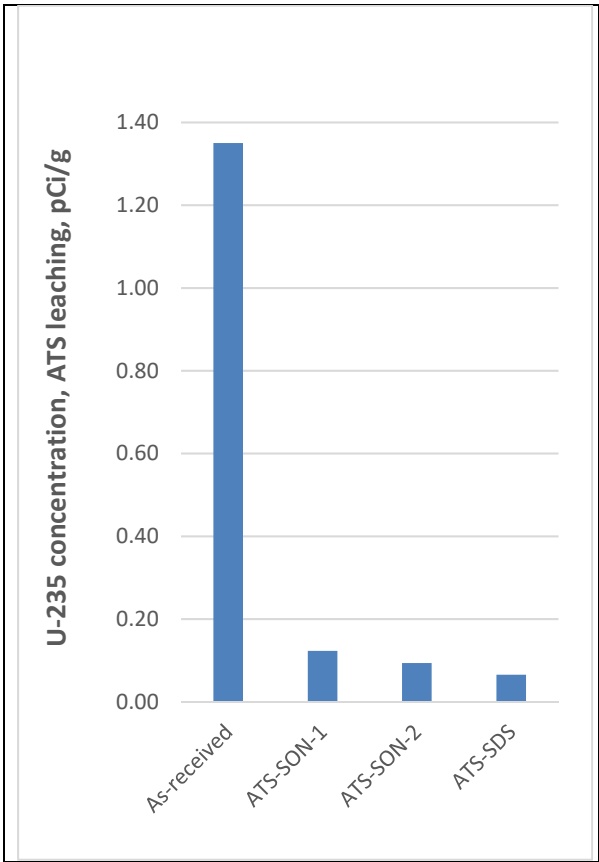


Insert A: Tc-99 concentration in post leached 23008-Top material: ammonium thiosulfate leaching

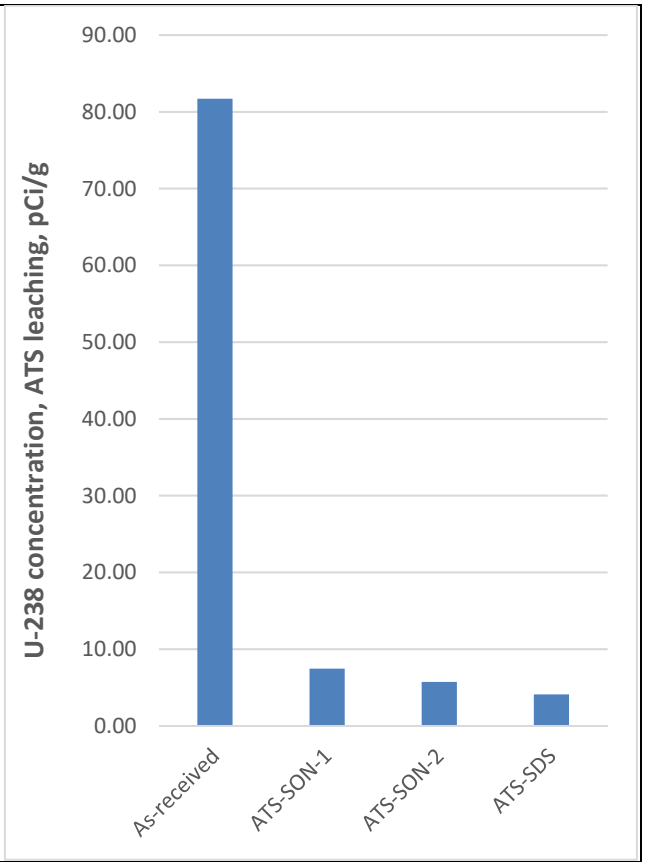


Insert B: Np-237 concentration in post leached 23008-Top material: ammonium thiosulfate leaching

Figure 4-8 Post ammonium thiosulfate leaching Tc-99 and Np-237 concentration on barrier material 23008-Top relative to concentrations in the "as-received" barrier material.



Insert C: U-235 concentration in post leached 23008-Top material: ammonium thiosulfate leaching



Insert D: U-238 concentration in post leached 23008-Top material: ammonium thiosulfate leaching

Figure 4-9 Post ammonium thiosulfate leaching U-235 and U-238 concentration on barrier material 23008-Top relative to concentrations in the "as-received" barrier material.

4.4.2 Double strike leaching in ammonium thiosulfate with sonication (Test ATS-SON-DS)

A piece of the barrier material sample used for ammonium thiosulfate leaching with sonication and double strike is identified as sample ATS-SON-DS, as shown in Table 3-1. The temperature profile plots for these double strike leaching tests are presented in Appendix B (Inserts B_5 and B_6). The average maximum temperature attained inside the sonicated solutions during the double strike sonicated tests was 49.6 ± 3.4 °C, which is not significantly different from the average maximum temperatures measured for the two-single strike tests with sonication in section 4.4.1.

The post leaching analyses results of the barrier material for Tc-99, uranium isotopes and Np-237 are presented in Table 4-27, along with the percentages of each element removed from the barrier material.

The calculated adjusted Tc-99 waste disposal WAC limit (114.7 pCi/g waste) and the percentages of the radionuclides removed are also presented in Table 4-27. About 68% of the Tc-99 was leached out of the barrier material with double strike/sonication and about 95% of both U-235 and U-238 were also removed in this double strike leaching with sonication. About 88% of Np-237 was leached from the sample. The quantity of U-234 left on the barrier material after leaching was less than the instrument detection limit and thus it is assumed that all the U-234 was leached.

Table 4-27 Technetium, uranium and Np-237 decontamination results for ammonium thiosulfate leaching: Double strike with sonication (Test ATS-SON-DS)

Component	**Leaching with sonication, pCi/g Test ATS-SON-DS Strikes 1 &2***	**% Removed & WAC Test ATS-SON-DS Strikes 1 & 2**	
-	-	% Removed	Adjusted WAC, pCi/ g of waste
Tc-99	631	67.6	114.7
U-234	< 4.17E+00	**NA**	NA
U-235	0.066	95.2	NA
Np-237	0.307	87.9	NA
U-238	4.1	95.0	NA

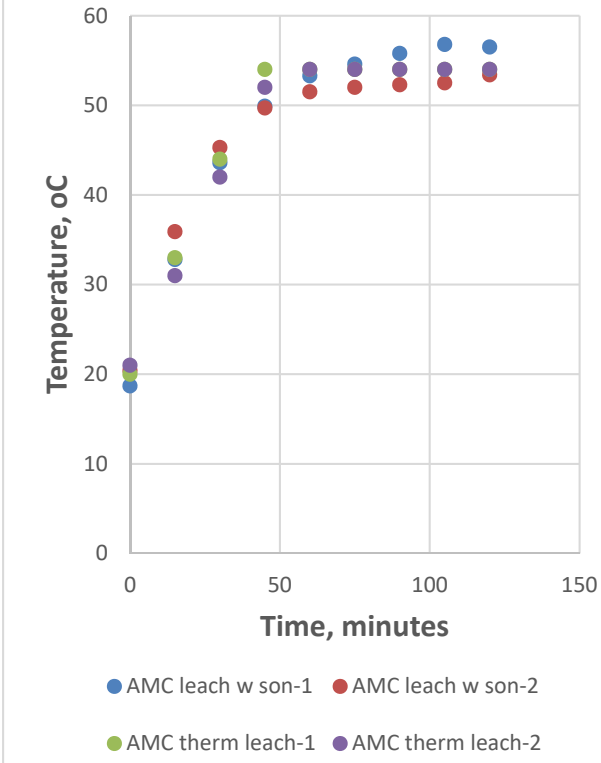
* After first ammonium thiosulfate strike the solid sample was **not** digested and analyzed for these components of the barrier material.

4.5 Effect of temperature on barrier material leaching process

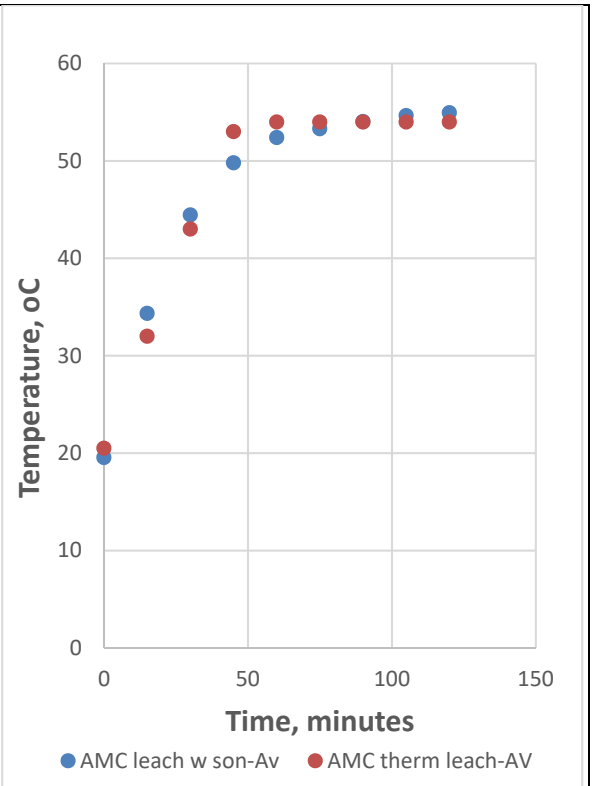
To compare the AMC sonication induced leaching of the barrier material with the AMC thermally induced leaching of the barrier material, the temperature profiles must be comparable. As earlier described, to attain comparable temperature leaching tests conditions (AMC leaching with sonication and AMC leaching with thermal heating) the initial slope parameter (from temperature vs. time profiles curves) for the well-established AMC leaching with sonication (0.7 ° C/minute) was programed into the temperature controller used in the heat induced leaching of the barrier material with AMC lixiviant.

Temperature profiles observed with the Omega controller set up for reproducing this ammonium carbonate leaching experiments without sonication but with heating via a heating mantle housing the container are presented in Figure 4-10 (inserts A and B) and Appendix B, inserts B_1 and B_2. These temperature profile are similar to the temperature profiles generated from the leaching of barrier material pieces in AMC with sonication as shown in Appendix A, Figure A1 (inserts A_11 and A_12); the average maximum temperatures (54.1 ± 0.2 vs. 53.4 ± 1.5 ° C), slopes of the initial temperature rise (0.73 ± 0.04 vs.0.74 ± 0.03 ° C /min.), and the soak times are comparable.

Figure 4-10, insert A, is an overlay plot for the four temperature profiles (two from AMC leaching with sonication and two from AMC leaching with thermal heating of the lixiviant) obtained during these leaching tests with AMC lixiviant solutions. There is little scatter in the data and the trends are similar and have the same orientations. Figure 4-10, insert B, overlay plots are simply an average from each of the two plots from Figure 4-10, insert A. Based on these overlay plots (Figure 4-10, inserts A and B), it can be concluded that the temperature/time profiles for these two leaching conditions with AMC lixiviant solutions are almost identical.



Insert A: Overlay plots for four temperature profiles: two tests with sonication and two tests with thermal heating of AMC lixiviant during leaching of barrier material.



Insert B: Overlay plots of average temperature profiles due to sonication and thermal treatments.

Figure 4-10 Comparative overlay temperature profiles from leaching with sonication and leaching with thermal heating of the ammonium carbonate lixiviant without sonication.

Therefore, the magnitude of the concentrations of the leached radionuclides from the barrier materials pieces, resulting from leaching under these two conditions, can be used to compare, determine and distinguish the effect of temperature versus sonication plus temperature on the leaching process with AMC lixiviant.

The AMC leaching with heating of the solution analysis results for the barrier material from thermal leaching tests (Test AMC-Therm-1 and Test AMC-Therm-2) are presented in Figures 4-11 through 4-12, respectively for Tc-99/Np-237 and U-235/U-238. The post leaching Tc-99 concentration on the barrier materials averaged 480 ± 2.8 pCi/g with an average adjusted WAC limit of 87.3 ± 0.5 pCi/gram of wasted and an average of 75.4 ± 0.2% of Tc-99 was removed from the barrier material pieces. All the U-234 in the "as-received" barrier material was removed and about 98% of both U-235 and U-238 had were removed. Slightly above an average of 60% of the Np-237 in the barrier materials was removed. Significant amount of the radionuclides which were removed from the barrier material pieces were in the leachate as shown in Table 4-29.

The mass balance data are presented in Tables 4-30 and 4-31 for these duplicate leaching tests with heating of the AMC lixiviant. The average mass balance differences for U-235, U238 and Tc-99, respectively, 3.2 ± 0.8, 0.7 ± 0.2 and 19.6 ± 5.1%, are less than the ICP-MS analytical uncertainty of 2 sigma (20%). Only the average mass balance difference for Np-237 was above 20% at 23.3 ±1.8%.

The overlay plots in Figures 4-11 and 4-12 show the relative amounts of these radionuclides leached into solution due to leaching with sonication and leaching with thermal treatment of the lixiviant solutions (leaching with sonication data are from Table 4-6). These overlay plots again show that leaching with sonication removes slightly more Tc-99 from the barrier material when compared with leaching with thermal heating. As summarized in Tables 4-32 and 4-33, AMC leaching with sonication removed all the Np-237 from the barrier materials while AMC leaching with thermal treatment removed only about an average of 62.3 ± 5.1% of the Np-237. Both AMC leaching approaches (with sonication and with thermal treatment), effectively removed more than 98% of both U-235 and U-238, with AMC leaching with sonication removing slightly more of these uranium isotopes from the barrier material (Tables 4-32 and 4-33).

Table 4-28 Technetium, uranium and Np-237 concentrations and decontamination results for the barrier material following ammonium Carbonate leaching with heating

Component	$(NH_4)_2CO_3$ Leaching with sonication, pCi/g Test AMC-Therm-1	% Removed & WAC limit Test AMC-Therm-1		$(NH_4)_2SO_3$ Leaching with sonication, pCi/g Test AMC-Therm-2	% Removed & WAC limit Test AMC-Therm-2	
NA	NA	% Removed	Adjusted WAC limit, pCi/g waste	NA	% Removed	Adjusted WAC limit, pCi/g waste
Tc-99	482	75.3	87.6	478	75.5	86.9
U-234	< 4.05E+00	-	NA	< 4.40E+00	-	NA
U-235	0.0249	98.2	NA	0.0241	98.2	NA
Np-237	1.05	58.7	Na	0.867	65.9	Na
U-238	1.12	98.6	NA	1.08	98.7	NA

Table 4-29 Ammonium Carbonate leaching with heating: Total Tc-99, Uranium and Np-237 Amounts in leachate

	Total concentration in leachate, pCi	
Component	(Test AMC-Therm-1 **leachate)**	(Test AMC-Therm-2 leachate
Tc-99	4.82E+02	4.78E+02
U-234	1.16E+01	1.01E+01
U-235	2.49E-02	2.41E-02
Np-237	1.05E+00	8.67E-01
U-238	1.12E+00	1.08E+00

Table 4-30 Ammonium Carbonate leaching with heating (Test AMC-Therm-1): Material mass balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	8.70E+02	3.56E+02	1.226E+03	1.44E+03	16.0
U-234	1.16E+01	< 3.00E+00	<1.46E+01	1.04E+01	NA
U-235	9.42E-01	1.8E-02	9.60E-01	9.96E-01	3.7
Np-237	1.62E+00	7.75E-01	2.40E+00	1.87E+00	24.6
U-238	5.90E+01	8.30E-1	5.98E+01	6.03E+01	0.8

*Percent difference (% difference) is defined as absolute difference/average*100.

Table 4-31 Ammonium Carbonate leaching with heating (Test AMC-Therm-2): Material mass balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in piece barrier sample tested, pCi	% difference*
Tc-99	7.28E+02	3.26E+02	1.054E+03	1.33E+03	23.2
U-234	1.01E+01	< 3.00E+00	<1.31E+01	9.63E+00	NA
U-235	8.82E-01	1.65E-02	8.98E-01	9.22E-01	2.6
Np-237	1.57E+00	5.60E-01	2.16E+00	1.73E+00	22.0
U-238	5.48E+01	7.34E-01	5.55E+01	5.58E+01	0.5

*Percent difference (% difference) is defined as absolute difference/average*100.

Table 4-32 Average Decontamination Analytical Result Summary: Ammonium Carbonate leaching with Thermal Heating (Test AMC-Therm-1 and Test AMC-Therm-2)[@]

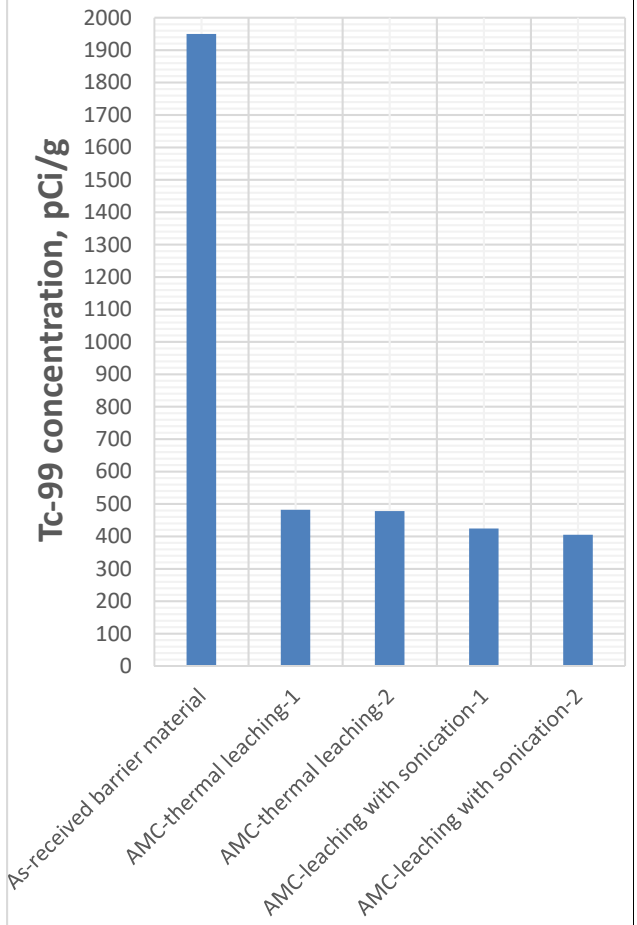
Radionuclide	Ave. residual on post leached barrier, pCi/g	Average WAC pCi/ g of waste	Average % removed
Tc-99	480 ± 2.83	87.27 ± 0.51	75.40 ± 0.14
U-235	0.03 ± 0.00	NA	98.20 ± 0.0
U-238	1.10 ± 0.03	NA	98.65 ± 0.07
Np-237	0.96 ± 0.13	NA	62.30 ± 5.09

[@] Data from Table 4-28

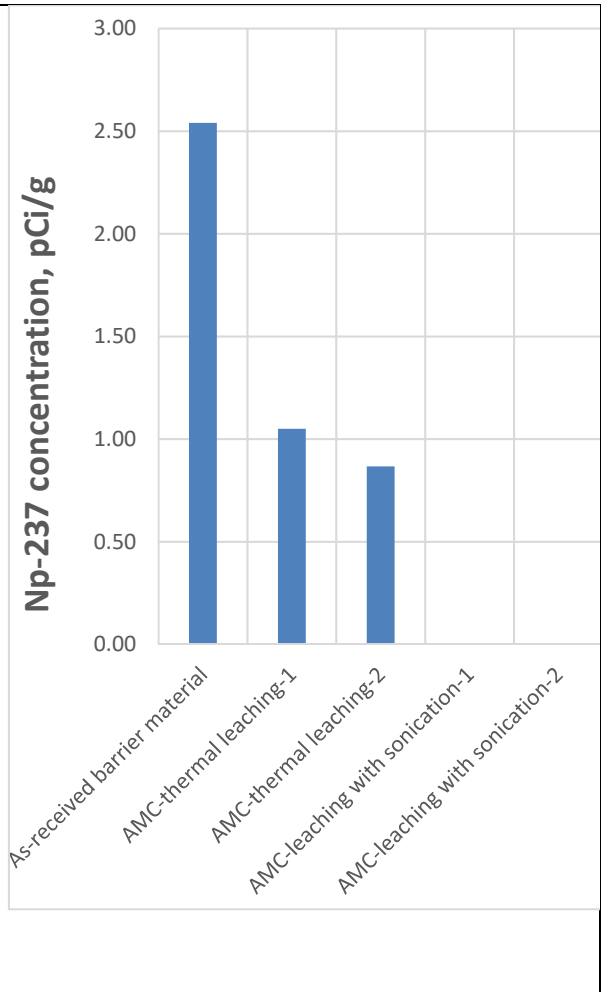
Table 4-33 Average Decontamination Analytical Result Summary: Ammonium Carbonate Leaching with Sonication (Test AMC-2-SON-1 and Test AMC-2-SON-2)[#]

Radionuclide	Ave. residual on post leached barrier, pCi/g	Average WAC pCi/ g of waste	Average % removed
Tc-99	313.5 ± 40.31	57.05 ± 7.28	83.95 ± 2.05
U-235	0.01 ± 0.00	NA	99.15± 0.07
U-238	0.58 ± 0.05	NA	99.25 ± 0.07
Np-237*	< 1.0	NA	100

Data from Table 4-6
* Np-237 concentration was less than instrument detection limit.

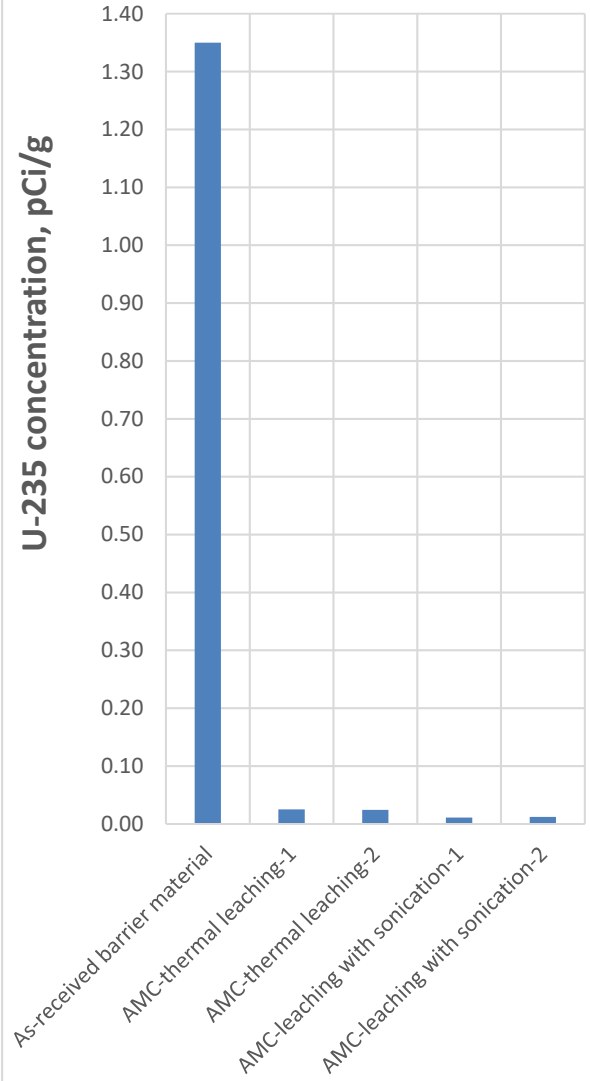


Insert A: Tc-99 concentrations in post leached barrier materials: AMC leaching with sonication and with heating.

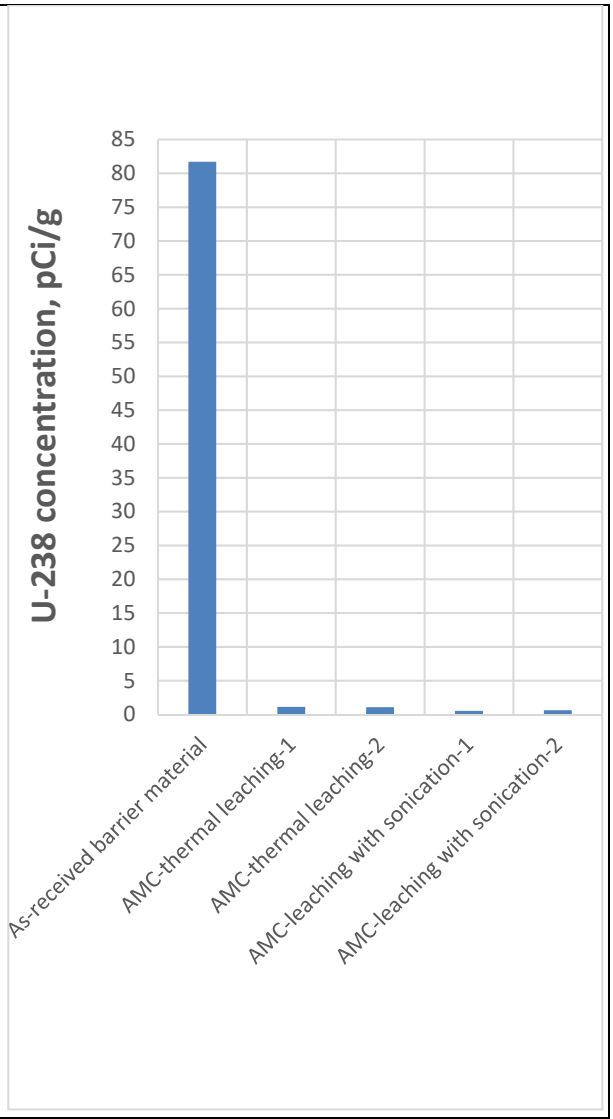


Insert B: Np-237 concentrations in post leached barrier materials: AMC leaching with sonication and with heating.

Figure 4-11 Tc-99 and Np-237 Comparative Overlay Plots: Barrier Material Leaching with Ammonium Carbonate with sonication and thermal heat treatment.



Insert C: U-235 concentrations in post leached barrier materials: AMC leaching with sonication and with heating.



Insert D: U-238 concentrations in post leached barrier materials: AMC leaching with sonication and with heating.

Figure 4-12 U-235 and U-238 Comparative Overlay Plots: Barrier Material Leaching with Ammonium Carbonate with Sonication and Thermal Heat Treatment.

4.6 Summary results for technetium, uranium and neptunium leaching from barrier material with ammonium carbonate, tri-sodium phosphate and ammonium thiosulfate lixiviants

The post leaching concentrations of these radionuclides in each barrier material piece for any test method, relative to other leaching tests methods and lixiviant in use, are presented for Tc-99, U-234, U-235, U-238 and Np-237 in the summary overlay plots in Figures 4-13, 4-14, 4-15, 4-16, and 4-17, respectively. The summary overlay plot shown in Figure 4-13, which shows the concentrations of Tc-99 on the barrier materials after various leaching conditions with different lixiviants also show two horizontal lines; the first horizontal line at 1950 pCi/g mark is the baseline Tc-99 concentration ("as-received" Tc-99 concentration for the barrier material), while the second horizontal line at 172 pCi/g is the target Oak Ridge WAC for Tc-99 disposal (172 pCi/g of converter waste). The goal of this leaching study on the Paducah barrier material, as earlier mentioned, is to obtain a post leaching Tc-99 WAC for disposal for the barrier material comparable to or better than this target Oak Ridge WAC for Tc-99 disposal. The Tc-99 WAC for disposal obtained in this study, using various lixiviants under different conditions, is the non-linear horizontal line which tests across the bottom of the overlay plots in Figure 4-13.

Figures 4-13, 4-14, 4-15, 4-16 and 4-17 overlay plots show, respectively, a summary of the relative amounts of Tc-99, uranium isotopes and neptunium-237 left on the barrier material pieces after leaching with solutions of ammonium carbonate, tri-sodium phosphate and ammonium thiosulfate under all tests conditions as presented earlier in the test matrix in Table 3-1. Similarly, in the overly plots shown in Appendix D (Figures D 1 through D 5) the relative amounts of Tc-99, uranium isotopes and Np-237 in the corresponding leachates for ammonium carbonate and tri-sodium phosphate after each test have been presented for comparison.

Leaching of the barrier material with ammonium carbonate solution dislodged/removed most of the radioactive elements from the barrier material with and without sonication treatment, while tri-sodium phosphate leaching, at all test conditions, failed to leach out satisfactory quantities of Tc-99 to guarantee meeting the Tc-99 WAC for disposal and only about 30% of the uranium isotopes and neptunium were removed from the from the barrier material. Ammonium thiosulfate leaching of the barrier material, although not as good as leaching with ammonium carbonate, produced acceptable Tc-99 decontamination of the barrier material.

Single strike leaching with ammonium carbonate with sonication produced sufficient removal of Tc- 99; more than 83% Tc-99 removed along with more than 99% uranium isotopes removed (Tables 4-6). Double strike leaching of the barrier material with ammonium carbonate solution, with sonication, resulted in the removal of more than 95% of the Tc-99 and almost all the uranium isotopes, including Np-237 (Table 4-13).

Leaching with ammonium carbonate, be it single or double strikes without sonication, resulted in the removal of about 85% of the Tc-99 and reasonable amounts of the uranium isotopes from the barrier material. Insufficient quantities of neptunium were removed when ammonium carbonate leaching was performed without sonication and leaching with ammonium carbonate without sonication seems to remove only surface bound radionuclides.

Overall, leaching with ammonium carbonate solution with or without sonication, with single or double strike leaching resulted in the removal of sufficient quantities of Tc-99 from the barrier material pieces, and resulted in acceptable adjusted WAC for Tc-99 disposal. The adjusted Tc-99 WAC for disposal was 89.6 pCi/ g of barrier waste for double ammonium carbonate strike leaching *without* sonication, while the adjusted Tc-99 disposal WAC averaged 75.4 ± 2.4 pCi/g of barrier waste for ammonium carbonate leaching *without* sonication (single strike). The adjusted Tc-99 disposal WAC averaged 57.0 ± 7.3 pCi/g of barrier waste for sonicated leaching tests (single strike) and 14.7 pCi/ g of barrier waste for double strike tests with sonication.

Sodium tri-phosphate leaching of the barrier material pieces did not perform as well as leaching with ammonium carbonate in terms of transfering most of the bound radionuclides, especially Tc-99, in the barrier membrane into the solution phase (leachate) as shown in the comparative overlay plots for leaching in ammonium carbonate and tri-sodium phosphate (Figures 4-13, 4-14, 4-15, 4-16 and 4-17 and Appendix D). Figure 4-13 to 4-17 show the comparative amounts of radionuclides left on the barrier material pieces after leaching with ammonium carbonate, tri-sodium phosphate and ammonium thiosulfate. In all cases involving these three lixiviants, more radionuclides were left on the barrier material after leaching with tri-sodium phosphate than after leaching with ammonium carbonate or ammonium thiosulfate.

The adjusted Tc-99 disposal WAC for tri-sodium phosphate leaching of the barrier material averaged 240.3 ± 3.2 pCi/g of barrier waste as shown in the overlay plots in Figure 4-13 and Table 4-16. For leaching tests involving the use of tri-sodium phosphate as the lixiviant, the extent of Tc-99 leached out of the barrier material was independent of the nature of the test; that is, the extent of Tc-99 removal was the same for all tests whether it involved double trikes with sonication or single strikes with or without sonication. Almost the same quantity of Tc-99 was removed from the sample barrier material pieces. This finding seems to suggest that the tri-sodium phosphate lixiviant could not penetrate the membrane and as a result only the surface bound Tc-99 was available for removal by leaching with tri-sodium phosphate solutions. As anticipated, the other radionuclides, especially uranium isotopes in the barrier membrane did not fare any better when the leaching was performed with tri-sodium phosphate; limited amounts were also leached out of the barrier material pieces (Figure 4-14 to Figure 4-15). The use of tri-sodium phosphate as a barrier material lixiviant did not result in appreciable removal of Tc-99; the Oak Ridge reference WAC for disposal of Tc-99, 172 pCi/g converter waste, was not attained. Hence, the leaching results with tri-sodium phosphate did not produce the desired goals of minimizing the amount of uranium isotopes leached out of the barrier material while at the same time enhancing Tc-99 removal from the barrier material to meet the disposal WAC.

Because leaching with tri-sodium phosphate solutions failed to remove sufficient amounts of the radionuclides from the barrier membrane material, there is more of each of the radionuclides in the ammonium carbonate leachate for each leaching test than in the corresponding tri-sodium phosphate leachates as presented in Appendix D.

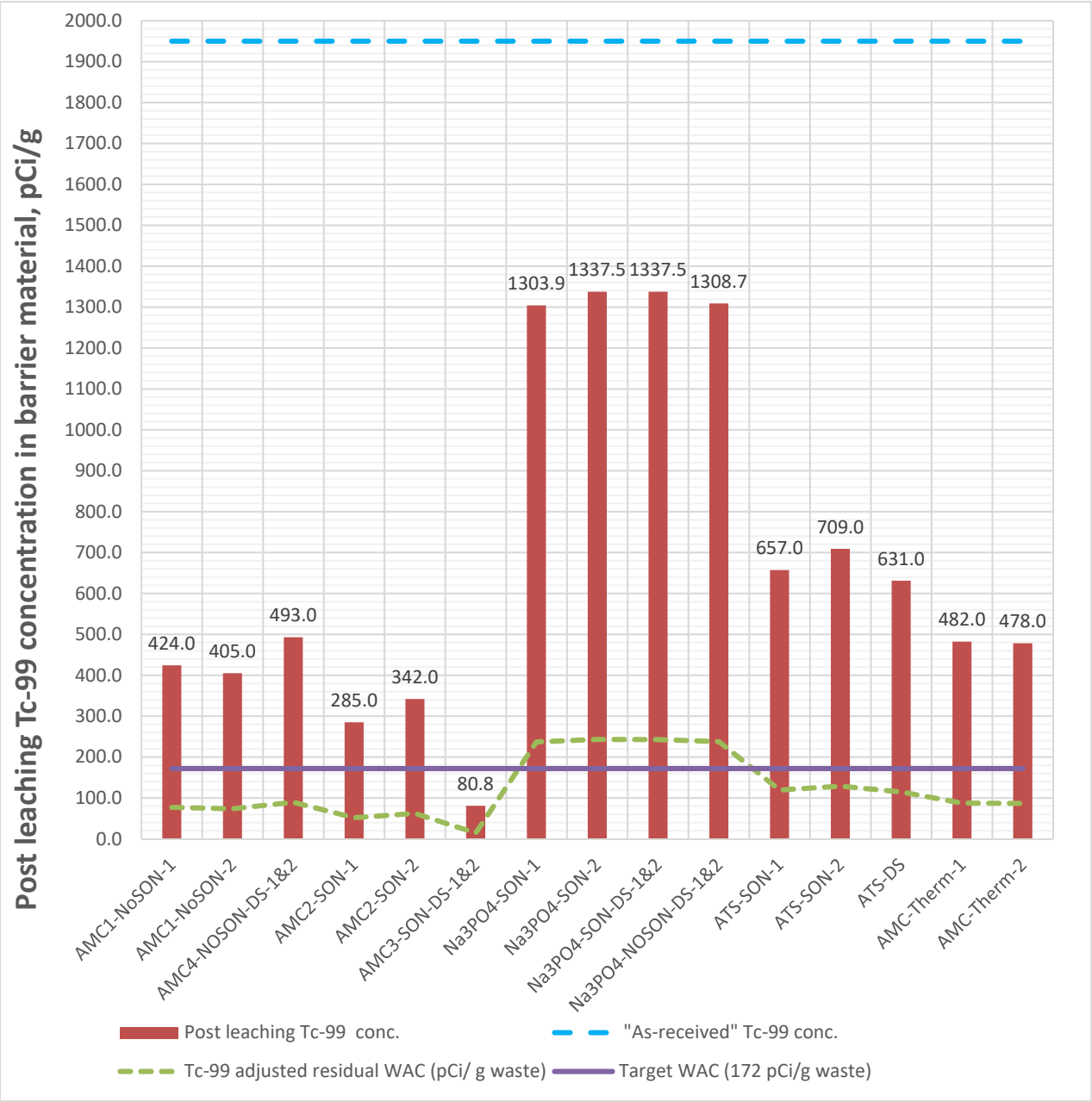


Figure 4-13 Tc-99 concentration on barrier materials after leaching with ammonium carbonate tris-sodium phosphate and ammonium thiosulfate relative to Tc-99 concentration in the "as-received" barrier material: a comparative overlay plot.

The best results for leaching of the barrier material to remove Tc-99 was achieved with ammonium carbonate (AMC) as the lixiviant. Leaching with AMC produced the desired WAC for Tc-99 disposal with or without sonication treatment. Sonication, especially double strike sonication in AMC, removes the most Tc-99 from the barrier material.

Thermally induced leaching (heating of the AMC lixiviant solution) did not improve the removal efficiency of Tc-99 from the barrier material when compared with sonication treatment. In fact, Tc-99 removal results obtained from AMC leaching without sonication is comparable to the results obtained with heating of AMC solution at 53 ° C for the same test duration time of two hours. The calculated average Tc-99 adjusted disposal WAC obtained with thermally induced leaching in AMC was 87.3 ±0.5 pCi /g of waste (Table 4-28). This AMC leaching with heating adjusted Tc-99 disposal WAC value, although about the same order of magnitude as Tc-99 WAC for leaching in AMC without sonication, it is still higher than the Tc-99 adjusted disposal WAC obtained with AMC leaching without sonication, which was 75.4 ± 2.4 /g of waste (see overlay plots in Figure 4-13 and Table 4-2).

Leaching with ammonium thiosulfate (ATS), with sonication, results in the removal of appreciable amounts of Tc-99 from the barrier material but the Tc-99 disposal WAC limit obtained is not comparable to leaching with AMC with or without sonication. ATS leaching with sonication results in Tc-99 disposal WAC below the Oak Ridge WAC of 172 pCi / g converter waste, as shown graphically above in Figure 4-13. ATS single strike leaching with sonication resulted in an average Tc-99 adjusted disposal WAC of 124.3 ± 6.7 pCi /g of waste and ATS leaching with double lixiviant strike with sonication produced a Tc-99 adjusted disposal WAC limit of 114.7 pCi /g of waste.

In general, it was observed that without sonication only Tc-99, uranium isotopes and Np-237 bound on the surface of the barrier material were removed and those embedded in the barrier material can only be dislodged with sonication. It is worth noting that both AMC and ATS removed more than 90% of the uranium isotopes in the barrier material at all treatment conditions, however, tri-sodium phosphate was the only lixiviant which consistently removed less than 50% of both uranium isotopes and neptunium-237 from the barrier material after leaching.

Possible technetium compounds formed with ammonium carbonate and ammonium thiosulfate lixiviants leaching of the barrier material may include ammonium pertechnitate ($NH_4Tc\text{-}O_4$) salts with other technetium compounds.

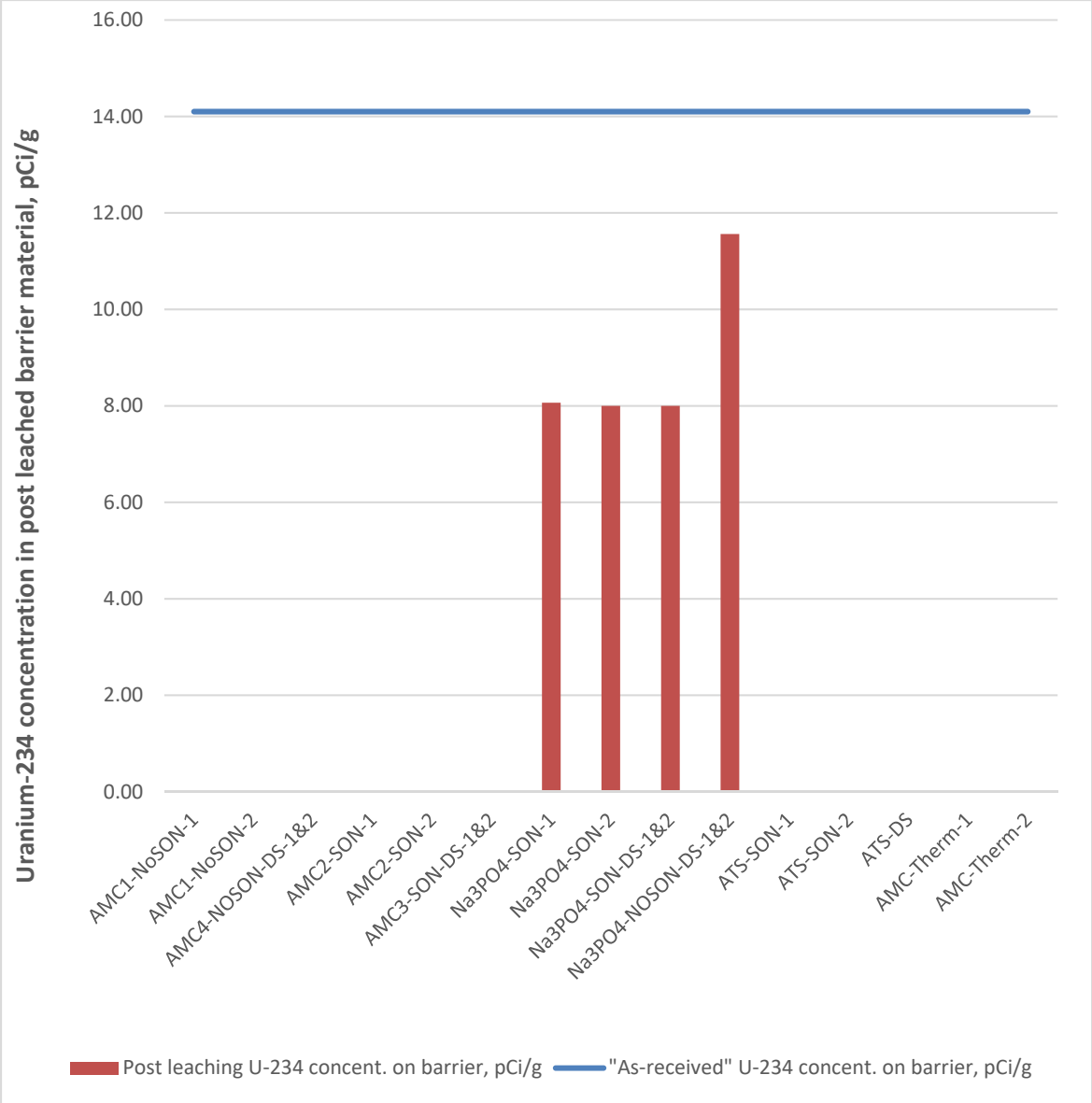


Figure 4-14 Uranium-234 concentration on barrier materials after leaching with ammonium carbonate and tris-sodium phosphate and ammonium thiosulfate relative to U-234 concentration in the "as-received" barrier material: a comparative overlay plot.

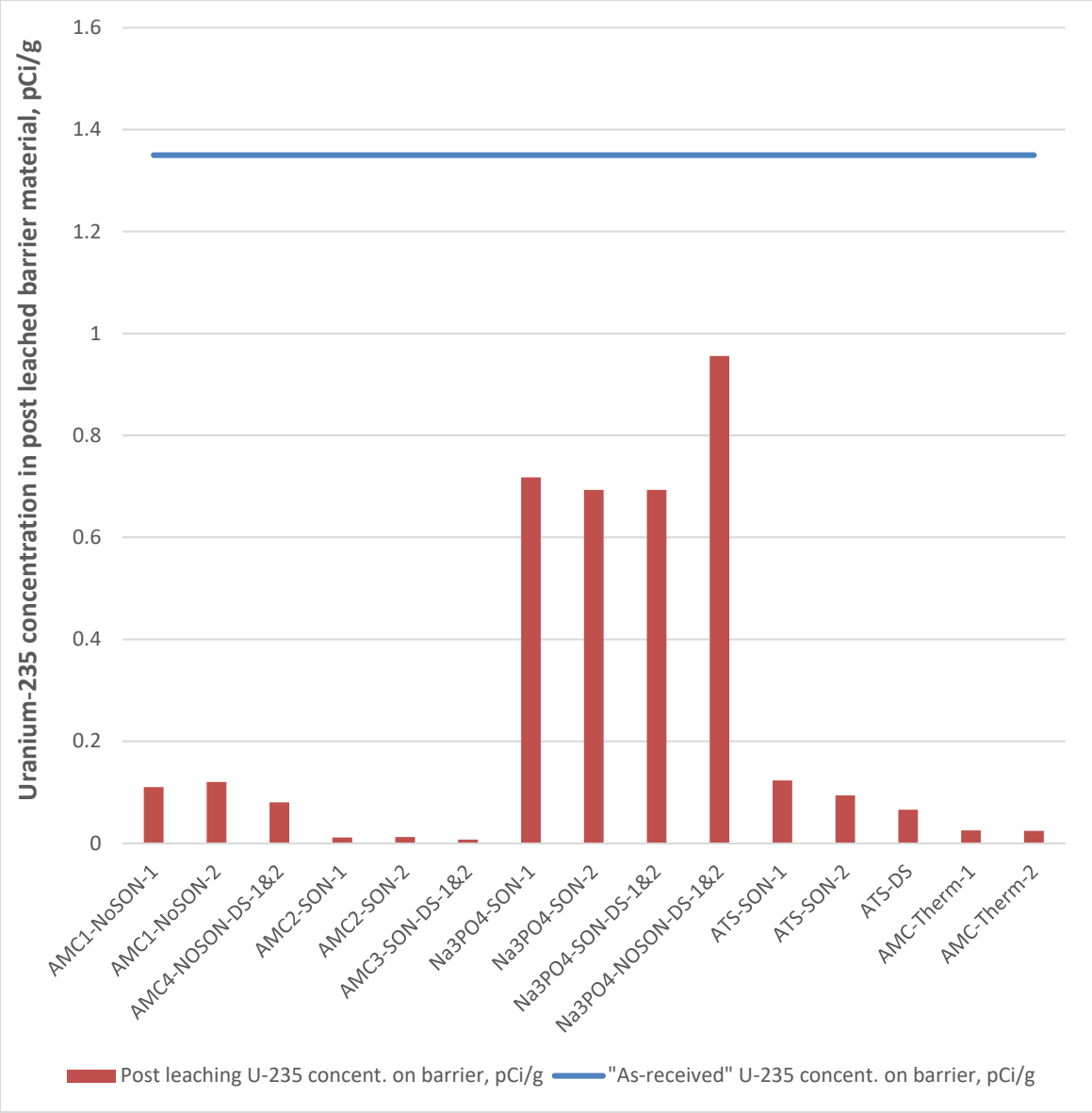


Figure 4-15 Uranium-235 concentration on barrier materials after leaching with ammonium carbonate and tris-sodium phosphate and ammonium thiosulfate relative to U-235 concentration in the "as-received" barrier material: a comparative overlay plot.

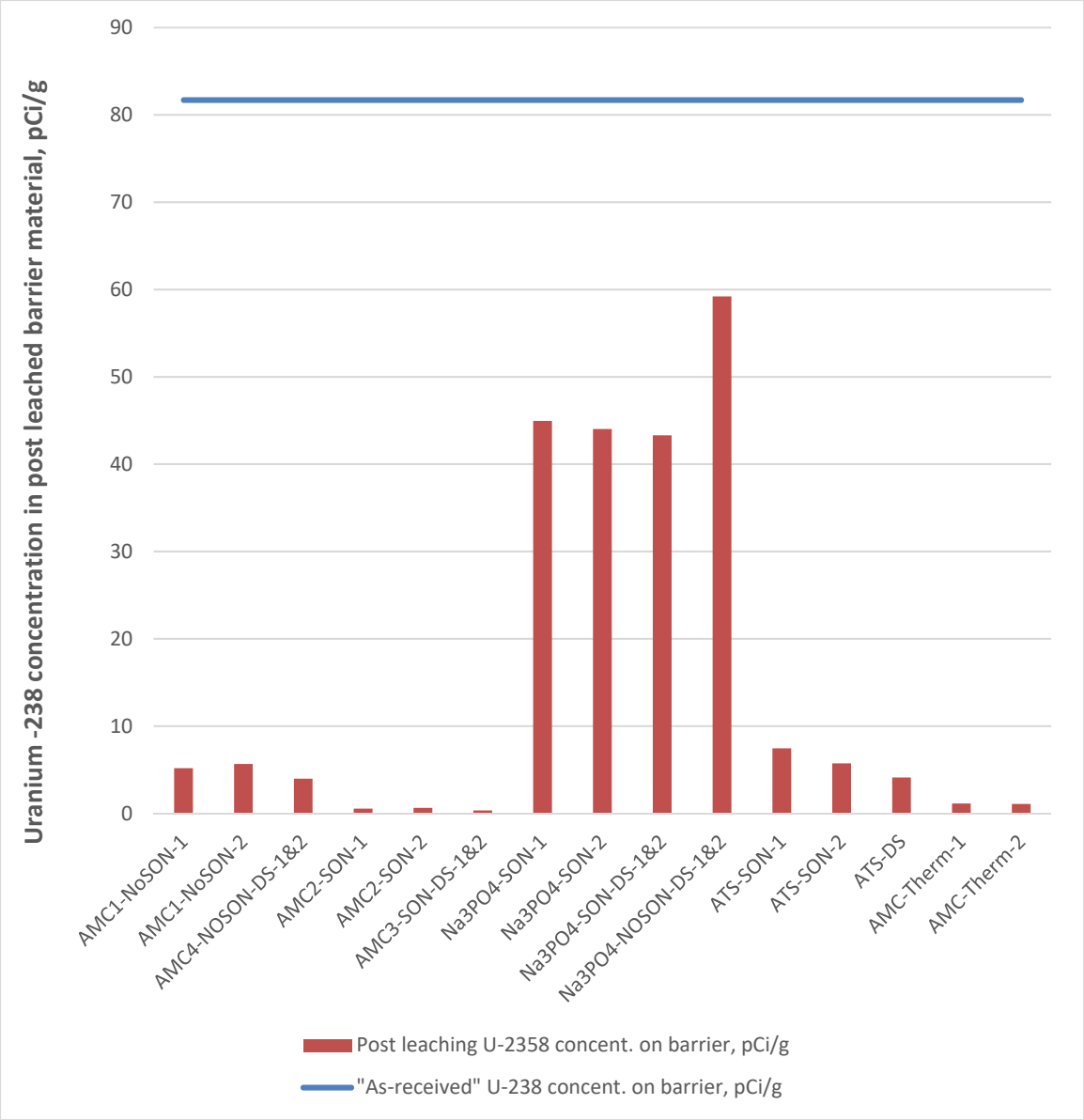


Figure 4-16 Uranium-238 concentration on barrier materials after leaching with ammonium carbonate and tris-sodium phosphate and ammonium thiosulfate relative to U-238 concentration in the "as-received" barrier material: a comparative overlay plot.

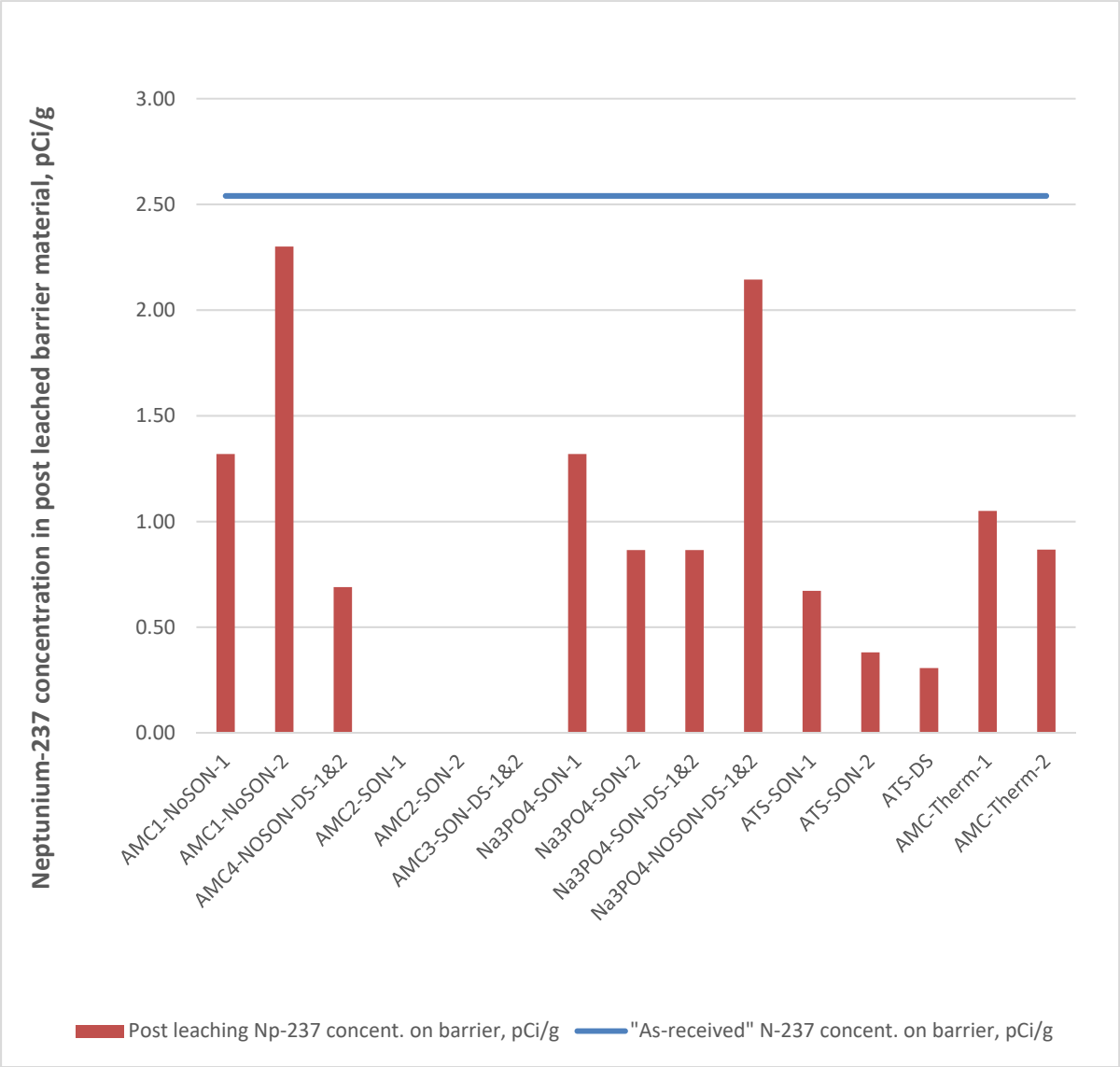


Figure 4-17 Neptunium-237 concentration on barrier materials after leaching with ammonium carbonate, tris-sodium phosphate and ammonium thiosulfate relative to Np-237 concentration in the "as-received" barrier material: a comparative overlay plot.

5.0 CONCLUSIONS AND RECOMMENDATIONS

As part of ongoing efforts by the Department of Energy's Portsmouth/Paducah Project Office to decommission the uranium enrichment gaseous diffusion plant at Paducah, Kentucky, research efforts have been focused on removing the remaining kilogram quantities of Tc-99 gaseous diffusion plant process impurities from the diffusion cascades to meet Tc-99 Waste Acceptance Criteria (WAC) disposal requirements. With the goal being to develop and deploy an in-situ Tc-99 decontamination process for the cascades, we have been looking at the use of lixiviants like ammonium carbonate to leach Tc-99, uranium isotopes and neptunium from gaseous diffusion membranes from the Paducah cascades.

In our current laboratory bench top studies, using actual cascade membrane materials, we have investigated whether leaching of the barrier materials in an aqueous media of ammonium carbonate, sodium phosphate or ammonium thiosulfate, with and without sonication treatment, will result in a significant removal of Tc-99 as well as uranium isotopes and neptunium from the barrier material.

These results show that leaching with ammonium carbonate or ammonium thiosulfate lixiviants, with or without sonication, removed appreciable quantities of these radionuclides to guarantee meeting or exceeding the Oak Ride Tc-99 waste disposal reference WAC of 172 pCi/g of converter[5]. Double strike leaching with ammonium carbonate gave the best Tc-99 adjusted WAC for disposal result; the Tc-99 adjusted WAC for disposal by this method was 15 pCi/g of barrier material waste which corresponds to about 96% Tc-99 removal from the barrier material. Ammonium carbonate leaching of barrier material under room temperature conditions, without sonication or thermal treatment, also resulted in effective removal of Tc-99 and other radionuclides. Under these conditions, about an average of 78.7 ± 0.7% of the Tc-99 in the barrier material was removed and the corresponding calculated Tc-99 adjusted WAC for disposal is 75.4 ± 2.4 pCi/g of barrier material waste. Therefore, with or without sonication, ammonium carbonate leaching of the barrier material results in the meeting of the Oak Ride Tc-99 waste disposal reference WAC.

Ammonium thiosulfate single strike leaching with sonication resulted in an average Tc-99 adjusted disposal WAC of 124.3 ± 6.7 pCi /g of barrier material waste and corresponds to an average of 65.0 ± 1.9 % Tc-99 removal from the barrier material. Ammonium thiosulfate leaching with double lixiviant strike produced a Tc-99 adjusted disposal WAC of 114.7 pCi /g of barrier material waste.

Tri-sodium phosphate leaching, even with sonication of the barrier material inside the leaching media, did not result in sufficient removal of Tc-99 from the test barrier materials. Only an average of about 30-41 % of the radionuclides were removed from the barrier material. The adjusted Tc-99 WAC for disposal, based on the post tri-sodium phosphate leaching of barrier material, averaged 240.3 ± 3.2 pCi/g of barrier material waste; hence the reference Oak Ridge Tc-99 waste disposal WAC of 172 pCi/ g converter waste was not met with tri-sodium phosphate leaching of the barrier material. The leaching results with tri-sodium phosphate did not produce the desired goals of minimizing the amount of uranium isotopes leached out of the barrier material while at the same time enhancing Tc-99 removal from the barrier material to meet the disposal WAC.

However, laboratory leaching of the barrier material in an ammonium carbonate or ammonium thiosulfate lixiviants resulted in the accumulation of significant quantities of uranium isotopes, which in practice, may

lead to criticality problems if neutron absorbers/poison agents are not employed with the leaching of the barrier material.

Thermally raising the lixiviant temperature beyond room temperature conditions during the leaching process did not enhance the leaching out of radionuclides (Tc-99, uranium isotopes and Np-237) from the barrier material. Only leaching with sonication treatment of the lixiviants produced extra measurable Tc-99, uranium isotopes and Np-237 decontamination of the barrier material.

The following recommendations are provided:

- Ammonium carbonate-based lixiviant or other leaching agents, doped with neutron poison agents to address criticality concerns which may result from the accumulation of uranium isotopes with leaching of the barrier material, should be considered for further studies. Such a leaching study should also include the evaluation of other Tc-99 target lixiviants, leaching time duration, lixiviant concentrations, pH, solid/liquid ratio (phase ratio), effects of the use of higher input wattage ultrasonic device (200-360 Watts/40KHz ultrasonic frequency) on barrier material Tc-99 decontamination and higher temperature effects on Tc-99 and uranium isotope removal efficiency with and without sonication.

- It may be possible to completely remove nearly all the residual radionuclides, including Tc-99, which are embedded in the barrier material after double strike leaching with ammonium carbonate and a follow up leaching with an oxidizing agent such as a solution of dilute nitric acid (0.5-2 molar). It is therefore recommended that additional experiments be conducted to evaluate the impact of such post double ammonium carbonate strike with nitric acid or other oxidizing agents.

- Identify and evaluate other lixiviants which may selectively remove Tc-99 without necessarily removing all uranium isotopes from the barrier material; this approach will minimize the accumulation of uranium isotopes and reduce criticality concerns.

- Thermal decontamination of both Tc-99 and uranium isotopes from the Paducah barrier materials should be evaluated using electromagnetic induction melting or microwave heating of the barrier material.

- The use of fluorinating agents, such as environmentally compatible nitrogen trifluoride, which under thermal conditions will convert the technetium compounds in the barrier material into more volatile technetium compounds, should also be considered as an alternative means of attaining the desired Oak Ridge Tc-99 waste disposal reference WAC.

6.0 QUALITY ASSURANCE

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

The Task Technical and Quality Assurance Plan (TTQAP) details the planned activities and associated quality assurance implementing procedures for the Tc-99 Decontamination of a Gaseous Diffusion Membrane - Phase I (TTQAP, SRNL-RP-2016-00180, Rev. 0, April 30, 2016) task. The documents referenced in the TTQAP include the following: Laboratory Notebook SRNL-NB-2016-00005. Various AD notebooks contain the analytical data and the Laboratory Information Management System (LIMS) numbers for tracking the AD analytical results for this study are presented in Table 3-1.

7.0 REFERENCES

[1] W. R. Golliher, R. A. LeDoux, S. Bernstein, and V. A. Smith, "Separation of Technetium-99 from Uranium Hexafluoride," TID-1 8290, April 1963

[2] W. D. Bostock, "Chemical and Radiological Properties affecting the Control of ^{99}Tc Contamination during K-25 and K-27 D&D Activities, K25-10-050, March 2010.

[3] PE-TC99, Estimate of Technetium-99 Quantity and Distribution Remaining in the Paducah Gaseous Diffusion Plant Cascade, Pro2Serve under contract to DOE contract No. DE-DT0005139, July 2017.

[4] DOE/OR/01-1909&D3, Attainment Plan for Risk/Toxicity-Based Waste Acceptance Criteria at the Oak Ridge Reservation, Oak Ridge, Tennessee, October 2001, Appendix A, Final Waste Acceptance Criteria, Page A-4.

[5] P2S-15-198, Submittal of Paducah Technetium-99 Sampling Results Graph, Professional Project Services, Inc., September 21, 2015.

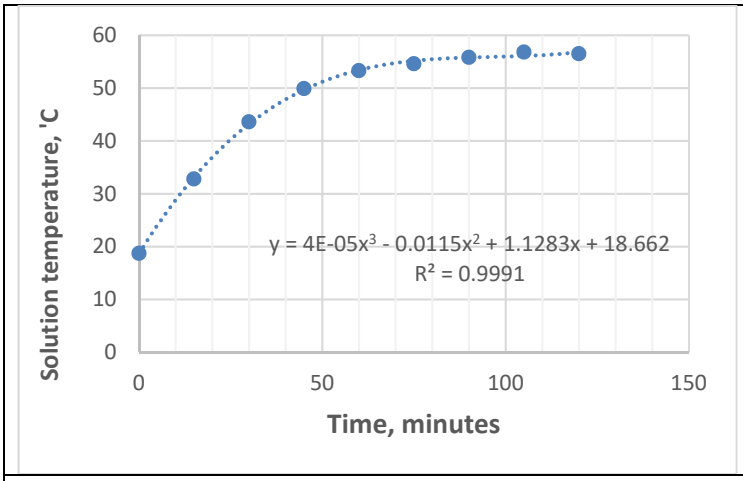
[6] Oji, L.N., Wilmarth, W.R., Restivo, M.L., M.R. Duignan, 2017, "Tc-99 Decontamination from Heat-treated Gaseous Diffusion Membrane - Phase I, Part B," SRNL Report No. SRNL-STI-2017-00380, November 2017.

[7] DOE/OR/01-1909&D3, Attainment Plan for Risk/Toxicity-Based Waste Acceptance Criteria at the Oak Ridge Reservation, Oak Ridge, Tennessee, October 2001, Appendix A, Final Waste Acceptance Criteria, Page A-4.6

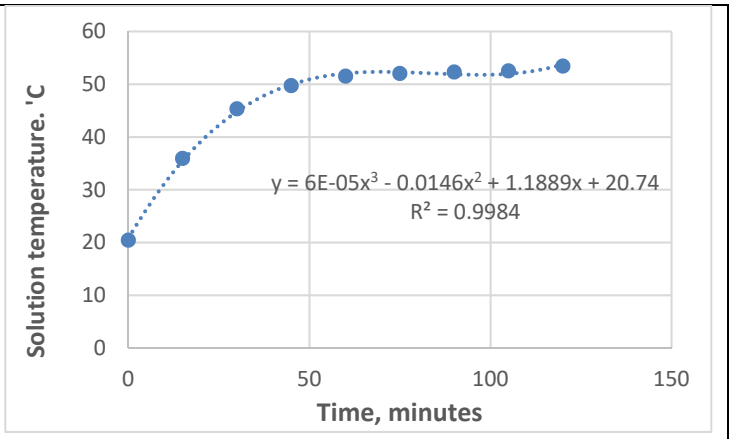
[8] P2S-15-198, Submittal of Paducah Technetium-99 Sampling Results Graph, Professional Project Services, Inc., September 21, 2015.

APPENDIX A

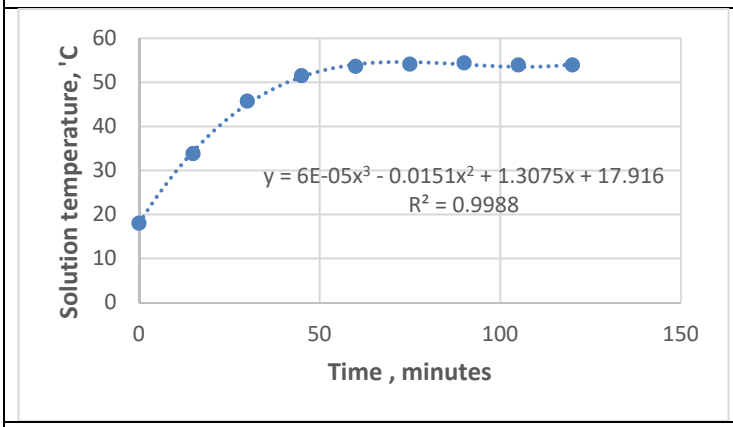
Temperature profiles for ammonium carbonate leaching with sonication (Single and double strikes)



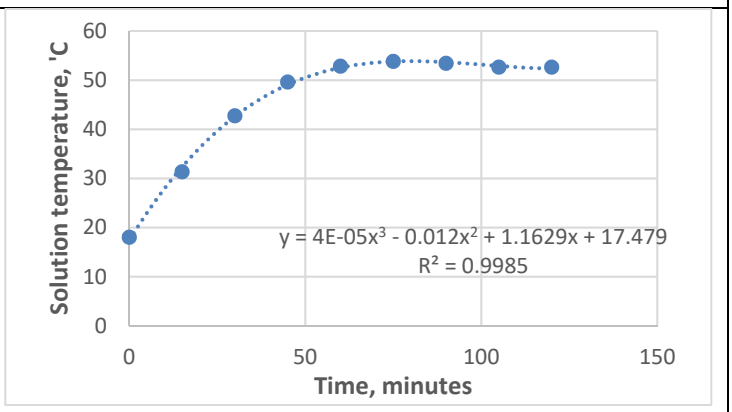
Insert $A_1$1: Ammonium carbonate leaching with sonication-1



Insert $A_1$2: Ammonium carbonate leaching with sonication-2



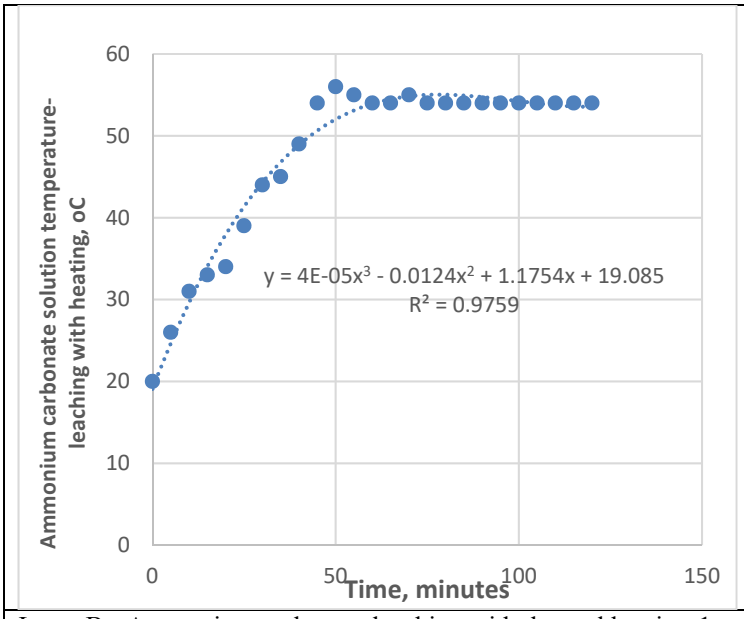
Insert $A_1$3: Ammonium carbonate leaching with sonication- strike-1 (DS-1)



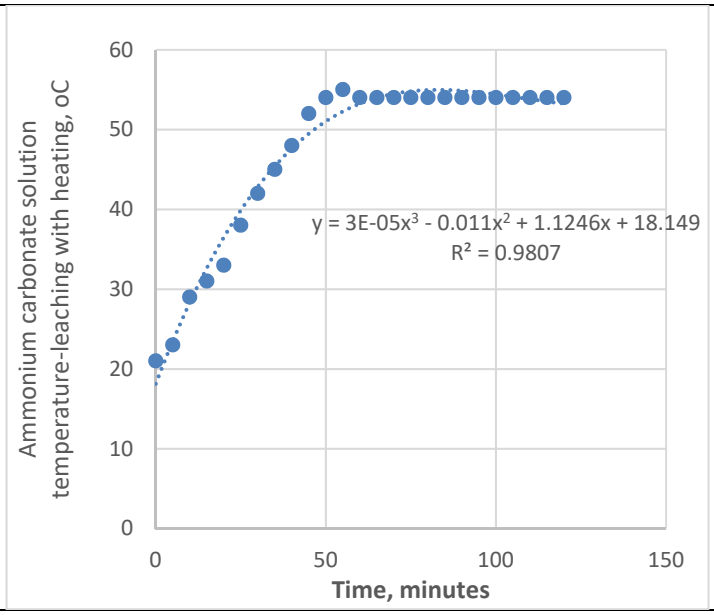
Insert $A_1$4: Ammonium carbonate leaching with sonication- strike 2 (DS-2)

APPENDIX B

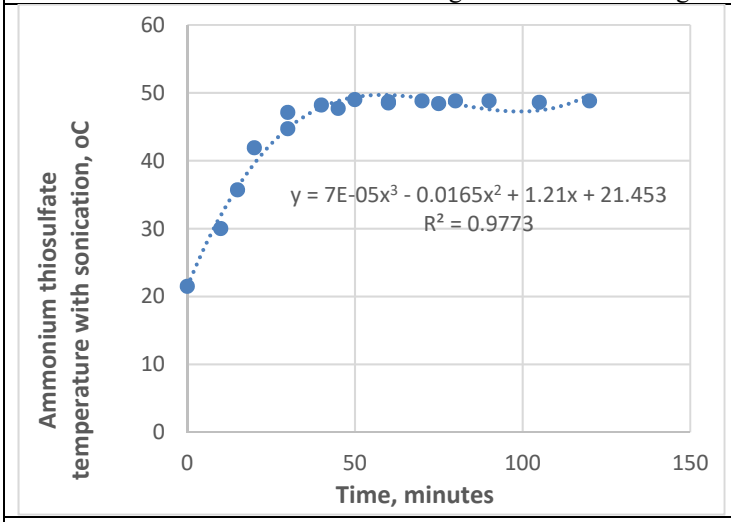
Temperature profiles for ammonium carbonate (thermal heating) and ammonium thiosulfate leaching with sonication (single and double strikes).



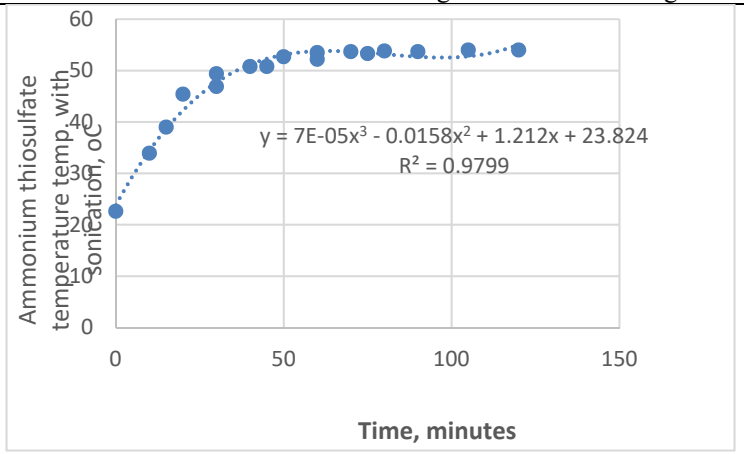
Insert B_1: Ammonium carbonate leaching with thermal heating-1



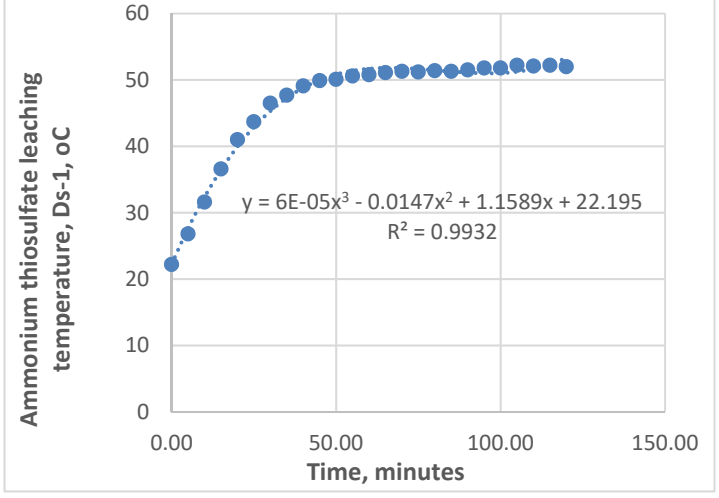
Insert B_2: Ammonium carbonate leaching with thermal heating-2



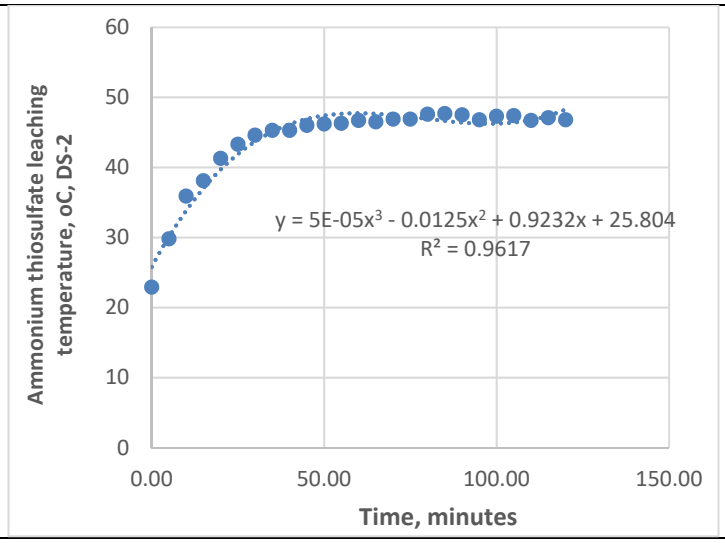
Insert B_3: Ammonium thiosulfate leaching with sonication- test-1



Insert B_4: Ammonium thiosulfate leaching with sonication- test-2



Insert B_5: Ammonium thiosulfate leaching with sonication- first strike (DS-1)

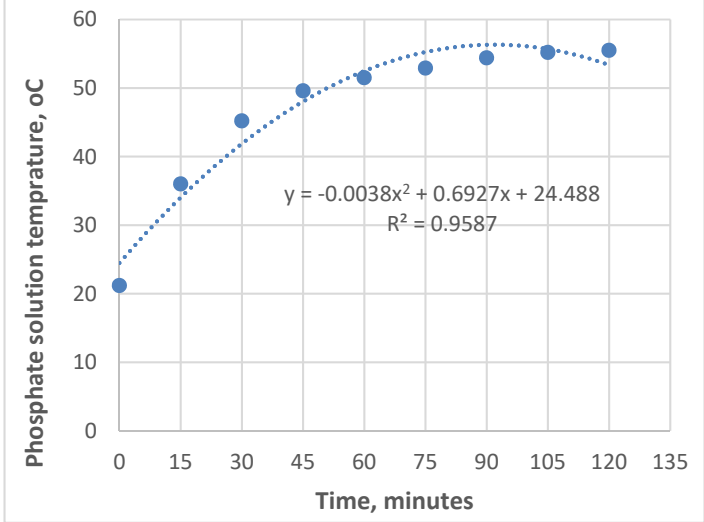


Insert B6: Ammonium thiosulfate leaching with sonication-second strike (DS-2)

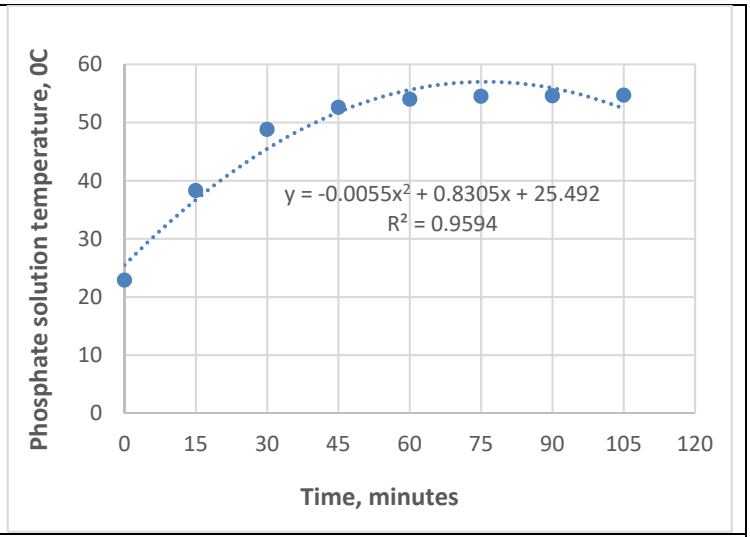
Figure B 1 Temperature profiles: Leaching with ammonium carbonate and ammonium thiosulfate lixiviants: Inserts B_1 and B_2, ammonium carbonate leaching with thermal heating, inserts B_3 and B_4 ammonium thiosulfate leaching with sonication and inserts B_5 and B_6 ammonium thiosulfate leaching with sonication-double strike.

APPENDIX C

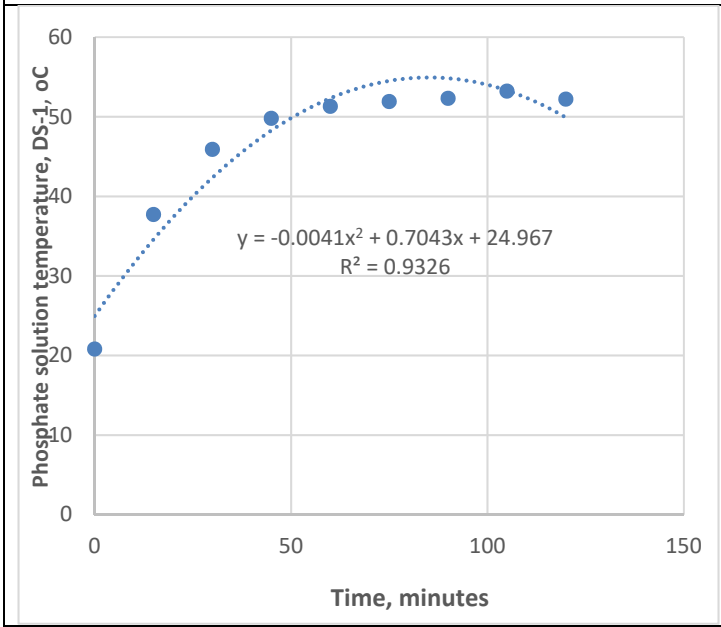
Temperature profiles for Tri-sodium phosphate Leaching with sonication



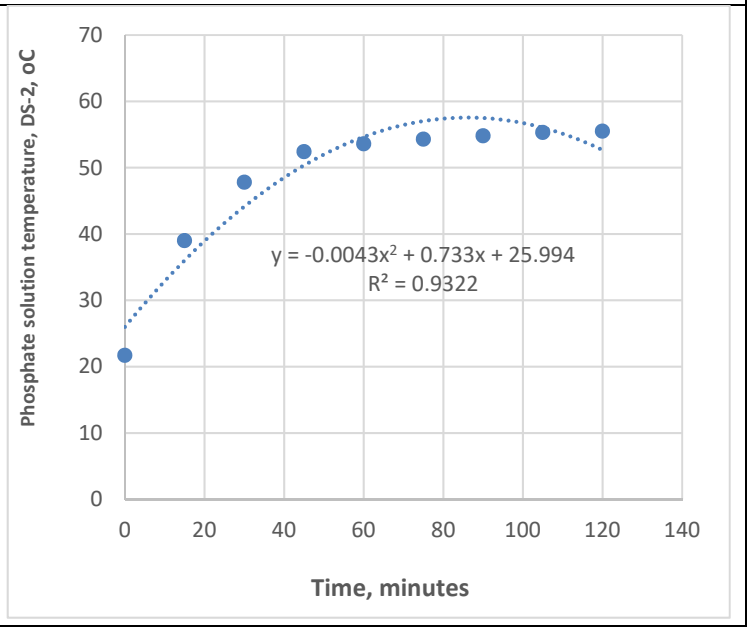
Insert C1: Tri-sodium phosphate leaching with sonication-1



Insert C2: Tri-sodium phosphate leaching with sonication-2



Insert C_3: Tri-sodium phosphate leaching with sonication-strike-1 (DS-1)



Insert C_4: Tri-sodium phosphate leaching with sonication-strike-2 (DS-2)

Figure C 1 Temperature profiles: Tri-sodium phosphate leaching with sonication; Inserts C_1, C_2 (duplicate single strike tests), Inserts C_3, C_4 (one sample; double leaching strike tests)

APPENDIX D:

Comparative amounts of Tc-99, uranium and neptunium in ammonium carbonate, tri-sodium phosphate and ammonium thiosulfate leachates

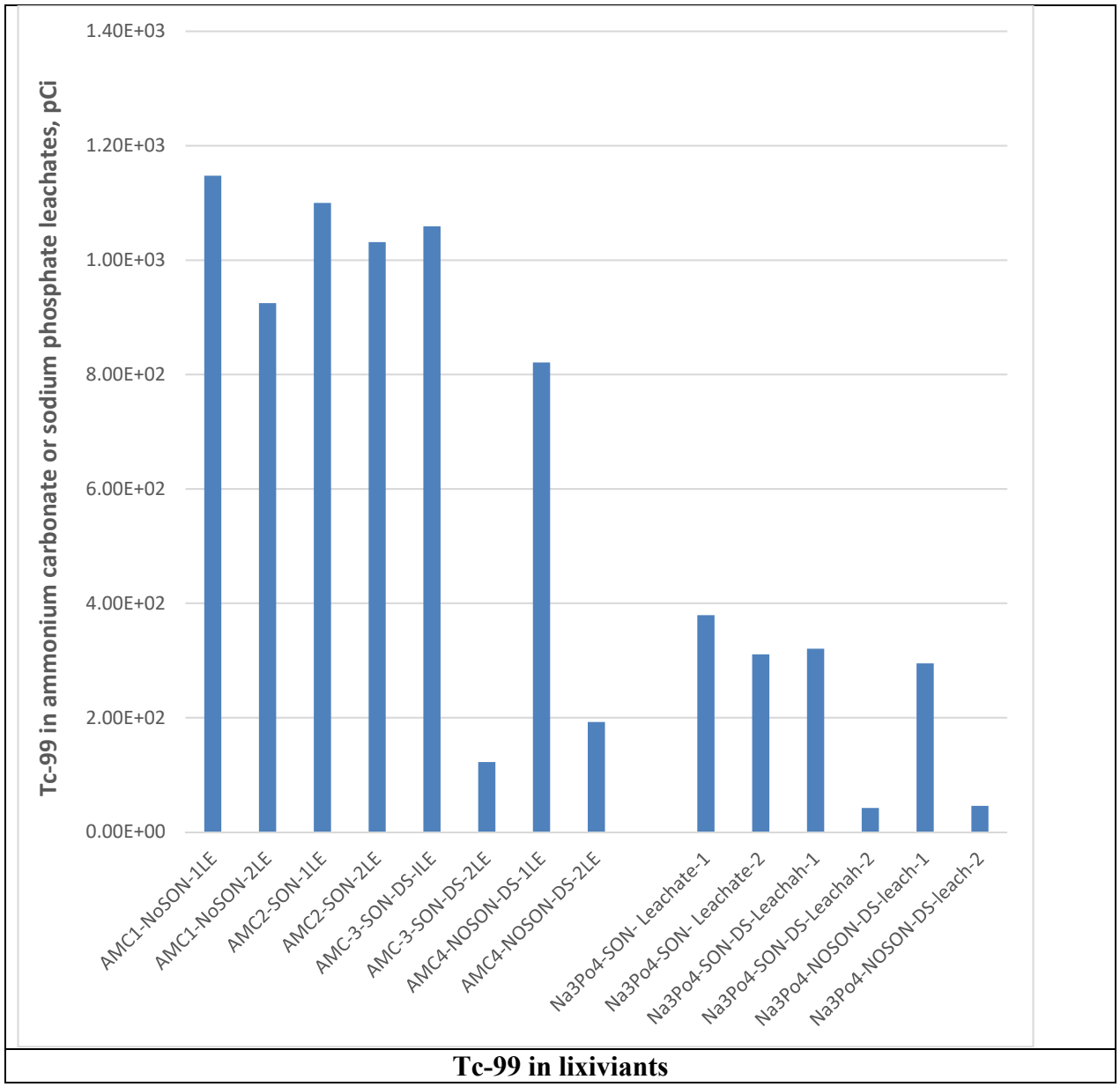


Figure D 1 Overlay plots of relative amounts of Tc-99 in ammonium carbonate or tri-sodium phosphate lixiviant solutions

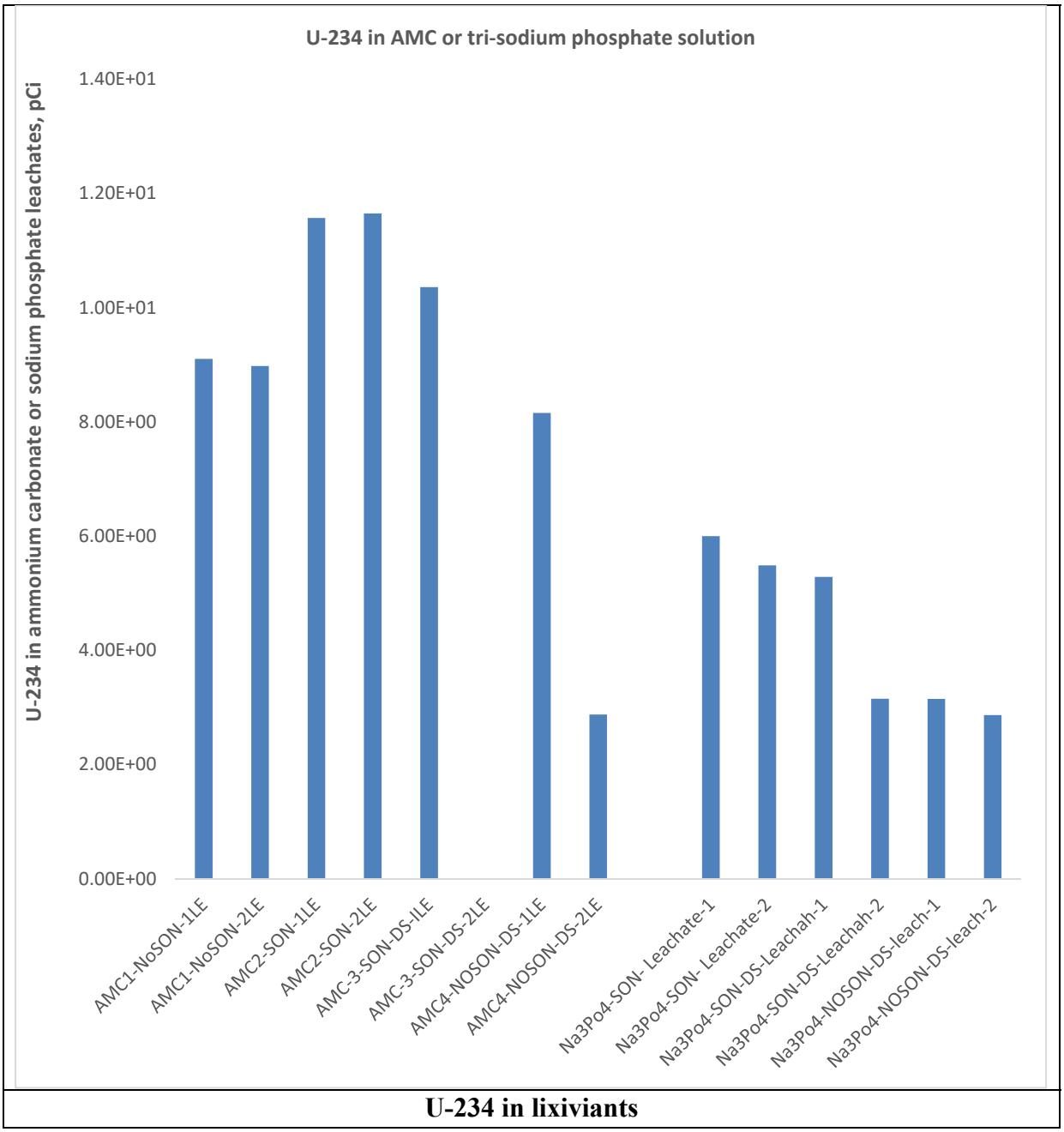


Figure D 2 Overlay plots of relative amounts of U-234 in ammonium carbonate or tri-sodium phosphate lixiviant solutions

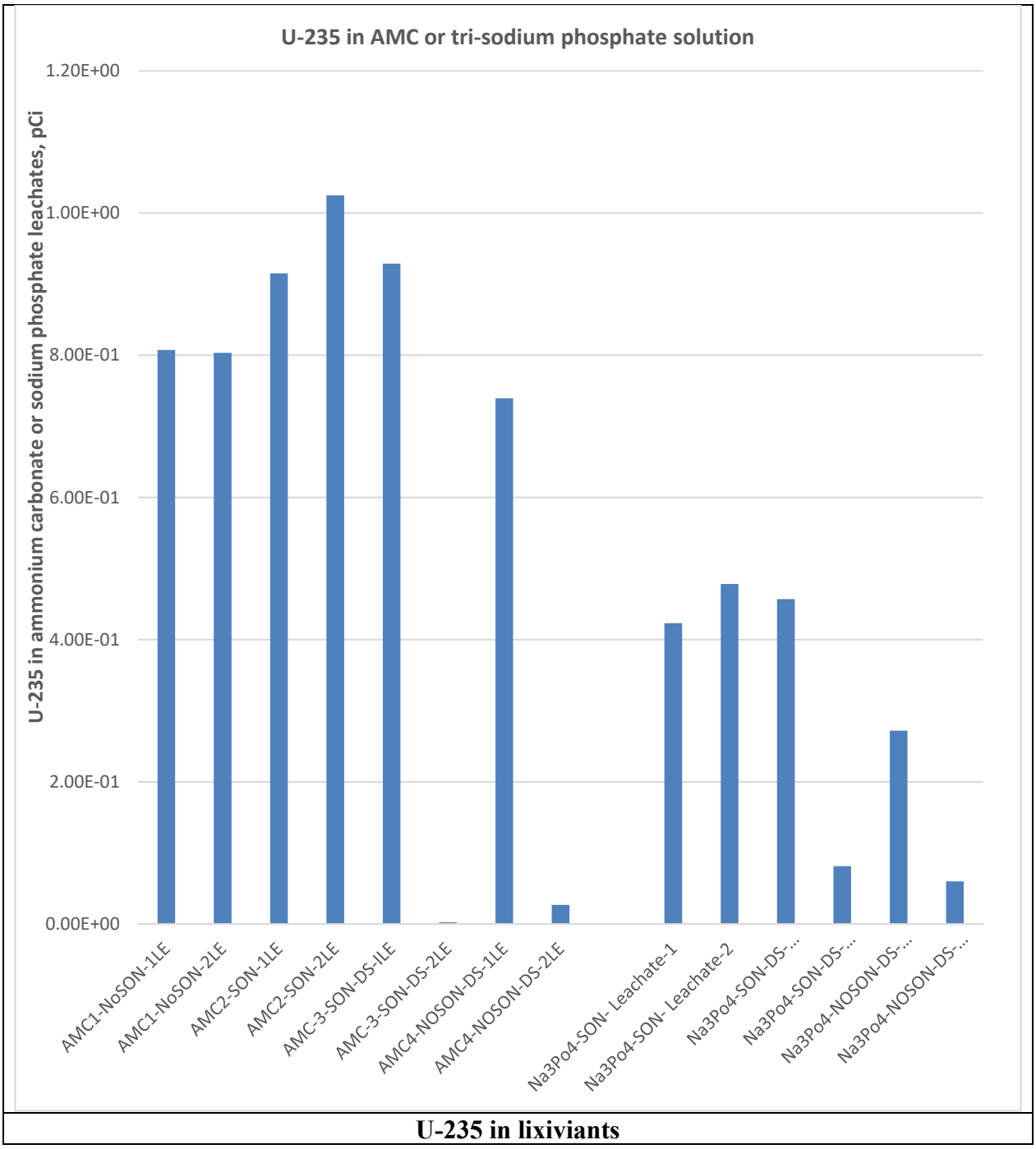


Figure D 3 Overlay plots of relative amounts of U-235 in ammonium carbonate or tri-sodium phosphate lixiviant solutions

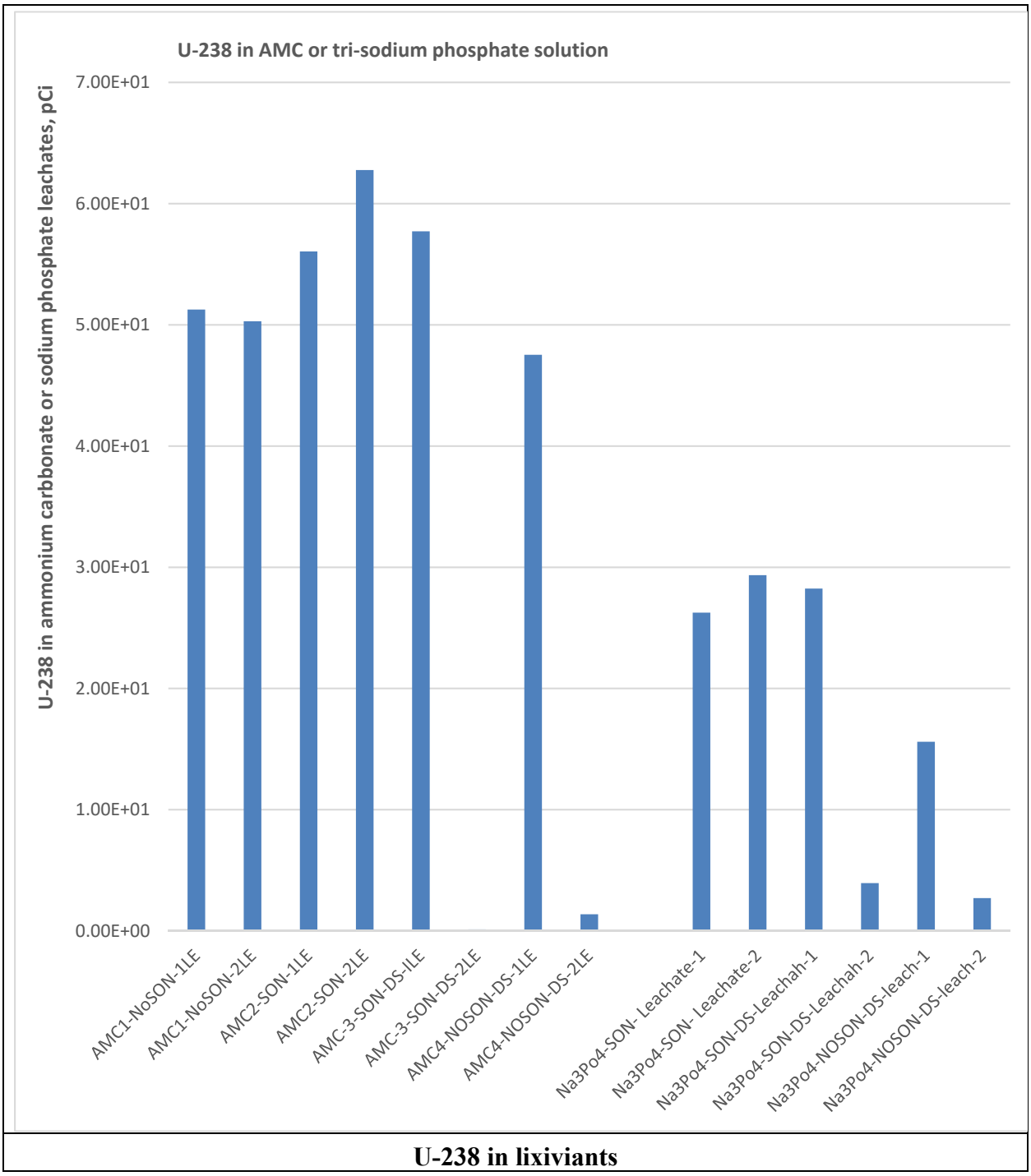


Figure D 4 Overlay plots of relative amounts of U-238 in ammonium carbonate or tri-sodium phosphate lixiviant solutions

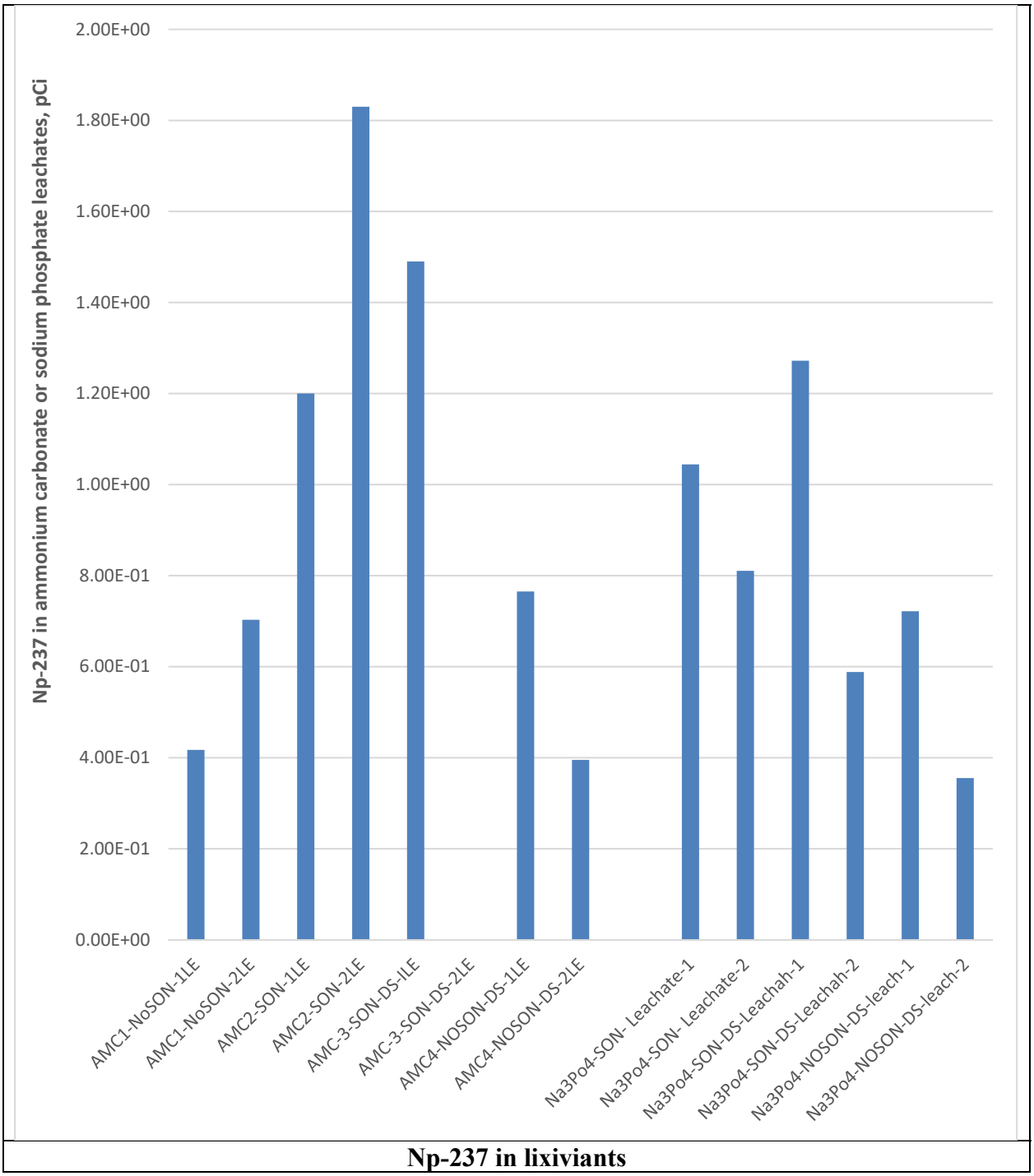


Figure D 5 Overlay plots of relative amounts of Np-237 in ammonium carbonate or tri-sodium phosphate lixiviant solutions.