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Annual Report, Fall 2016: Identifying Cost Effective Tank Waste Characterization Approaches

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December 2016

Savannah River
National Laboratory ™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

This report documents the activities that were performed during the second year of a project undertaken to improve the cost effectiveness and timeliness of SRNL's tank closure characterization practices. The activities performed during the first year of the project were previously reported in SRNL-STI-2015-00144.

The scope of the second year activities was divided into the following three primary tasks: 1) develop a technical basis and strategy for improving the cost effectiveness and schedule of SRNL's tank closure characterization program; 2) initiate the design and assembly of a new waste removal system for improving the throughput and reducing the personnel dose associated with extraction chromatography radiochemical separations; and 3) develop and perform feasibility testing of three alternative radiochemical separation protocols holding promise for improving high resource demand/time consuming tank closure sample analysis methods.

The technical basis for improving SRNL's tank closure characterization program assessed radionuclides being characterized in terms of the following attributes: a) relative activity dominance over time; b) relative analytical cost and time requirements; c) analytical detectability; d) contribution to long-term environmental risk; e) primary long-term source (current radionuclide inventory versus in-growth from parent nuclides); and f) potential applicability of alternative characterization approaches. Results of the assessment were used to identify areas of the characterization program where future potential changes should be considered - with the goals of making the characterization requirements commensurate with the importance of the data (higher focus on "high risk" constituents and lower focus on "low risk" constituents) and honing characterization methods where possible to reduce resource needs, while maintaining characterization integrity. Through this assessment, several potential characterization improvements were identified, along with the estimates of the savings that would be realized. The total expected cost savings are estimated to be on the order of two hundred thousand dollars per SRNL tank closure characterization campaign.

Prototypes of the new waste removal system associated with extraction chromatography radiochemical separations were designed and fabricated, in order to produce a system that was assured to be effective, economical, and practical. The final prototype consisted of two primary components, a column vacuum manifold device and a waste receipt and collection vessel. Preliminary testing of the system indicated that it was operable within the limited confines of the radiological hood and would increase throughput, significantly reduce the risk of laboratory contamination, and result in significantly decreased personnel dose. Plans over the next year include testing of the system with various tank sample analyses, optimization of the system, and implementation of the system into routine applications.

The alternative radiochemical separation protocols that were developed and tested included ones to replace the existing tank closure analyses that were deemed most costly and/or most time-consuming, due primarily to the low minimum detection limits required to support the performance assessment needs. Specifically, this included development of new methods for Ra-226 analysis, Th-229/Th-230 analysis, and Am/Cm/Cf isotope analysis. In the case of the Ra-226 analysis, the goal was to increase the radium chemical yield sufficiently that processing of large sample aliquots in the Shielded Cells would no longer be necessary. Similarly, in the case of the Th-229/Th-230 analysis, the goal was to find an alternate alpha spectrometry source preparation method, to improve energy resolution sufficiently to reduce the minimum detection limits to the point that processing of large sample aliquots in the Shielded Cells would no longer be necessarily. Elimination of the extensive Shielded Cells processing activities would significantly cut costs and time requirements, due to the efficiencies that working outside of the Shielded Cells (in the absence of deliberate robotic operation requirements) would bring.

In the case of the Am/Cm/Cf isotope analysis, the primary goal was to develop a radiochemical protocol that effectively separated the trivalent actinides (Am, Cm, and Cf) from the trivalent Y-90 isotope, following the Sr-90 removal step. The purpose of this was to allow rapid removal of the Am/Cm/Cf fraction from the Shielded Cells for completion of the analysis, without having to wait for the high dose-producing Y-90 to decay to safe levels. In the absence of such a separation, the typical "wait time" for decay of Y-90 is two weeks, which clearly extends the analysis turnaround time by two weeks.

Initial testing of the alternative methods for Ra-226, Th-229/Th-230, and the Am/Cm/Cf isotopes yielded promising results. In the case of the Ra-226 method, the chemical yield increased by an order of magnitude, suggesting that the new method offered the potential for eliminating the extensive Shielded Cells preparation activities. However, the testing was limited to the salt waste matrix, so confirmatory testing with the tank closure post-cleaning residue matrix is necessary to assure compatibility with the tank closure samples. The current plans include implementation testing of the new Ra-226 method during the next tank closure characterization campaign.

The alternative Th-229/Th-230 source preparation method significantly increases measurement resolution. However, as in the case of the new Ra-226 method, the Th-229/Th-230 tests were performed on the salt waste matrix, so additional testing will be necessary to assure the method is equally effective for tank closure sample matrices. Additionally, tests will be necessary to quantify the extent that the increased resolution reduces the minimum detection limits and to optimize the thorium source preparation such that the chemical yield sufficiently high to eliminate the need for the extensive Shielded Cells activities. Such optimization is planned for the next year, with the goal of honing the method sufficiently that it is ready for implementation testing during the next tank closure characterization campaign.

Results of the alternative Am/Cm/Cf separation protocol showed promise, but were contrary to the vendor literature indicating that a clean separation from yttrium would occur under certain acid concentrations. Additional testing over a greater range of acid conditions will be necessary to determine if the method is sufficiently selective and stable to provide effective, consistent removal of yttrium. Such additional testing is planned for next year, to determine if implementation of the method is practical.

Future potential scope that is recommended to be performed in FY17 includes development of a technical basis and strategy for improving SRNL's Salt waste characterization program, implementation of identified program improvements, and development and testing of additional radiochemical separation protocols holding promise for improving high resource demand radiochemical characterization methods.

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LIST OF ABBREVIATIONS

AMP	Ammonium molybdophosphate
DOE	Department of Energy
EM	Environmental Management
FWHM	Full width half max
HPGe	High purity germanium
MDL	Minimum detection limit
PA	Performance assessment
SA	Special analysis
SRNL	Savannah River National Laboratory
TAT	Turnaround time
TF	Tank Farm

1.0 Introduction

The U. S. Department of Energy (DOE) Office of Environmental Management (EM) has tasked the Savannah River National Laboratory (SRNL) with developing strategies and technologies to understand, optimize, scale, and speed up tank waste characterization.[a] This scope is part of a multi-year continuing project with the end goal of implementing programmatic changes that accelerate tank waste processing and tank closure schedules, and at the same time reduce characterization costs, while maintaining data integrity. The "second year" activities performed as part of this task include: a) identifying opportunities for improving characterization practices in the context of reducing cost and schedule; and b) developing and evaluating potential alternative characterization methodologies. This work is consistent with the path forward identified in the 2015 Annual Report detailing the "first year" project results.[b]

During the first year of the project, SRNL completed the following five activities: 1) identification of the characterization activities driving cost and schedule; 2) investigation of potential streamlining of characterization requirements based on the relative constituent risks (with the goal of reducing characterization requirements for "low risk" and "negligible risk" constituents); 3) determination of the relative usefulness of various potential characterization bases, including laboratory analyses, waste receipt history, process knowledge, scaling factors, and historic trends; 4) utilization of the differences between sludge, salt, and post-cleaning residue to hone characterization needs as a function of waste type; and 5) investigation of alternative characterization methods holding promise for being less costly and/or less time consuming.

Based on the results, conclusions were drawn regarding the aspects of SRNL's current characterization programs that are most costly and time consuming; the particular waste constituents that drive the costs, schedule, and program risks; recommended alternate characterization approaches (other than sampling and analysis) that are less expensive and more rapid; alternative laboratory methods that hold the greatest promise for reducing characterization costs and schedule; and in whole, the primary areas where the current characterization practices can be improved.

The "second year" scope is divided into the following three primary activities, per the path forward of the 2015 Annual Report:

- Develop technical basis and strategy for improving cost effectiveness and schedule of SRNL's tank closure characterization program

- Initiate design/assembly of hardware, plumbing, and software for automation of select radiochemical separation and their associated waste removal processes

- Develop and complete feasibility testing of at least two alternative radiochemical separation protocols holding promise for improving high resource demand/time consuming analysis methods

Details of each activity are presented in the sections below, by activity, with each section addressing the specific objectives, approach, results, conclusions, recommendations, and references associated with the

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[a] Office of Tank Waste and Nuclear Materials (EM-20), **Work Authorization/Task Change Request**, Project HQTD1001, Topical Area WP-1.2.1 (Cost Effective Characterization Approaches), February 2004.

[b] Reboul, S. H., R. H. Young, F. G. Smith, J. M. Pareizs, and D. P. DiPrete, *"Annual Report, Spring 2015: Identifying Cost Effective Tank Waste Characterization Approaches,"* SRNL-STI-2015-00144, April 2015.

particular activity. Following these sections, overall conclusions based on the "sum of the findings" and a path forward are presented.

Execution of these activities will provide the bases for developing more cost effective and practical characterization programs, for application at the Savannah River Site, Office of River Protection, and other DOE sites involved in tank waste processing, tank waste disposition, and tank closure operations.

Quality Assurance

This task was performed in accordance with the protocols identified in Task Technical and Quality Assurance Plan SRNL-RP-2014-00460 and Program Plan SRNL-RP-2014-00474. This report has been reviewed per the requirements established in Manual E7, Procedure 2.60. The extent and type of review has been identified using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

2.0 Technical Basis and Strategy for Improving Cost Effectiveness and Schedule of SRNL's Tank Closure Characterization Program

SRNL's current tank closure characterization program includes laboratory analysis of more than sixty radionuclides and stable waste constituents, with a nominal six month completion schedule beginning once all the samples have been received and the sample compositing protocols have been identified. The majority of the analytical cost and schedule is dedicated to activities supporting the radionuclide analyses (as opposed to the stable constituent analyses), due to the extensive matrix preparations, radiochemical separations, and hybrid measurements utilized to achieve the high analytical sensitivities necessary for effective Performance Assessment (PA) modeling of the radionuclides. As such, this activity focuses on the data needs, drivers, findings, and analysis attributes of the various radionuclides, on a nuclide-by-nuclide basis. Fifty-six nuclides are addressed,[c] to cover all radionuclides requiring characterization in one or more of the most recent six SRS tank closure campaigns (Tanks 18, 19, 5, 6, 16, and 12). Note that Tanks 18, 19, 5, and 6 are located in the F-area tank farm, while Tanks 16 and 12 are located in the H-area tank farm.

2.1 Objective

Development of a technical basis and strategy for improving cost effectiveness and schedule of SRNL's tank closure characterization program.

2.2 Approach

Radionuclides quantified in SRNL's current closure characterization program were assessed with respect to the following characteristics: a) relative activity dominance over time; b) relative analytical cost and time requirements; c) analytical detectability; d) contribution to long-term environmental risk; e) primary long-term source (current radionuclide inventory versus in-growth from parent nuclides); and f) potential applicability of alternative characterization approaches. Results of the assessment were used to identify areas of the program where future potential changes should be considered – this includes changes to sharpen the characterization practices for certain radionuclides, as well as changes to reduce requirements for other radionuclides.

2.3 Relative Activity Dominance over Time

Differences in the relative concentrations of radionuclides and their radiological decay rates produce a large variation in the extent that individual radionuclides contribute to the total radioactivity over time. Since the ability to detect radionuclides is a function of their activity, one criterion for gauging long-term radionuclide contribution from closed waste tanks is based upon the relative dominance of radionuclides driving activity at the present and into the future. Although there is considerable propagated uncertainty in projecting future environmental fate and transport of radionuclides, there is significantly less uncertainty in projecting temporal changes in radionuclide inventories, given the current high level of understanding of radiological decay and in-growth rates.

Radionuclide concentration data for the six most recent SRS tank closure characterization campaigns[1,2,3,4,5,6] were utilized to: a) project the total concentration of activity in each tank waste residue as a function of time; and b) identify the particular radionuclides dominating the activity inventory of

---

[c] This includes H-3, C-14, Al-26, Cl-36, K-40, Ni-59, Ni-63, Co-60, Se-79, Sr-90, Y-90, Zr-93, Nb-94, Tc-99, Pd-107, Sn-126, Sb-126, Sb-126m, I-129, Cs-135, Cs-137, Ba-137m, Sm-151, Eu-152, Eu-154, Pt-193, Ra-226, Ra-228, Ac-227, Th-229, Th-230, Th-232, Pa-231, U-232, U-233, U-234, U-235, U-236, U-238, Np-237, Pu-238, Pu-239, Pu-240, Pu-241, Pu-242, Pu-244, Am-241, Am-242m, Am-243, Cm-243, Cm-244, Cm-245, Cm-247, Cm-248, Cf-249, and Cf-251.

each tank waste residue as a function of time.   In doing so, it was assumed that no dilution and/or removal of constituents occurred, such that the maximum potential impact of each constituent was captured. In actuality, dilution and/or removal of constituents via environmental transport mechanisms would be expected to have a significant impact on the constituent concentrations over time, as has been demonstrated through the Tank Farm (TF) PAs performed at SRS.[7,8] Nonetheless, for the purposes of this particular assessment approach, the goal was to address the extent that individual nuclides contributed to the total activity inventories, as opposed to the extent that individual nuclides were impacted by environmental transport.

For each of the six recently closed SRS waste tanks (tanks 18, 19, 5, 6, 16, and 12), the total activity concentrations as functions of time were determined by entering the average measured concentration of each radionuclide into the RadCalc 4.1 decay/in-growth program,[9] and then using RadCalc 4.1 to calculate the total activity concentrations at times ranging from 1E+00 to 1E+05 years. Similarly, the RadCalc 4.1 output was utilized to determine the percentage of total activity contributed by each radionuclide over the 1E+00 to 1E+05 year timeframe. A minimum time of one year was used to ensure in-growth of short-lived decay products was taken into account when determining total activity concentrations and fractions of the total activity concentrations.

Plots of total activity concentrations versus time for the post-cleaning residues in the six recently closed SRS waste tanks are given in Figure 2-1. (Note that for Tank 16, only the annulus case was addressed, as the annulus residue contained significantly higher concentrations of most radionuclides than the tank interior residue, due to unintended leakage of waste into the annulus and the extreme level of cleaning that was performed on the tank interior). In each plot, the vertical axis identifies the total concentration of activity, in units of µCi/g, and the horizontal axis identifies the time, in years. As shown in the plots, the initial total activity concentrations (at a time of one year) ranged from a low of ~700 µCi/g for Tank 18 to a high of ~3E+04 µCi/g for Tanks 5, 6, and 12. In contrast, at 1E+05 years, the total activity concentrations ranged from a low of ~0.01 µCi/g for Tank 19 to a high of ~9 µCi/g for Tank 5. Over the 1E+05 year time period, the total activity concentrations dropped three to four orders of magnitude, depending on the distribution of radionuclides. Clearly, the reduction in activity was greater for residual material containing a higher fraction of short-lived nuclides and lower for residual material containing a higher fraction of long-lived nuclides or parent nuclides transforming to long-lived decay products.

Plots of the radionuclides dominating total activity in the six recently closed SRS waste tanks are given in Figure 2-2. Included in these plots are all radionuclides contributing a minimum of 5% of the total radioactivity at any time during the 1E+05 year period following closure of the tank. As shown in the figure, there are certain radionuclides that dominate activity in all of the closed tanks and other radionuclides that dominate activity in only a portion of the tanks. Short-term, over the first hundred years, the activity is dominated by Sr-90 and/or Cs-137, which is consistent with expectations based on the relatively high fission yields (on the order of 6%) and the relatively short half-lives (~30 years). Long-term, at times of 1E+04 to 1E+05 years, the dominant nuclides include Ni-59, Tc-99, Zr-93, and Pu-239, with half-lives ranging from 2.3E+04 to 1.5E+06 years. In the intermediate timeframe, from approximately 100 to 1000 years, the dominant nuclides include Ni-63, Sm-151, Pu-238, and Am-241, with half-lives ranging from approximately 90 to 400 years. Pu-240, although less dominant and shorter-lived than Pu-239, still contributes greater than 5% of the activity in multiple tanks over the timeframe of 1E+03 to 1E+04 years. In contrast, C-14 contributes significant activity over the timeframe of 1E+03 to 1E+04 years in only one tank (Tank 19).

Although variation in the dominance of the respective radionuclides in expected as additional tanks are closed, it is clear that certain radionuclides will tend to contribute the majority of activity under multiple circumstances. Due to the high relative activity concentrations, such radionuclides will have the highest likelihood of being detected and therefore should continue being characterized via high accuracy methods.

In contrast, radionuclides contributing negligible or undetectable activities may be candidates for alternative non-laboratory characterization methods.
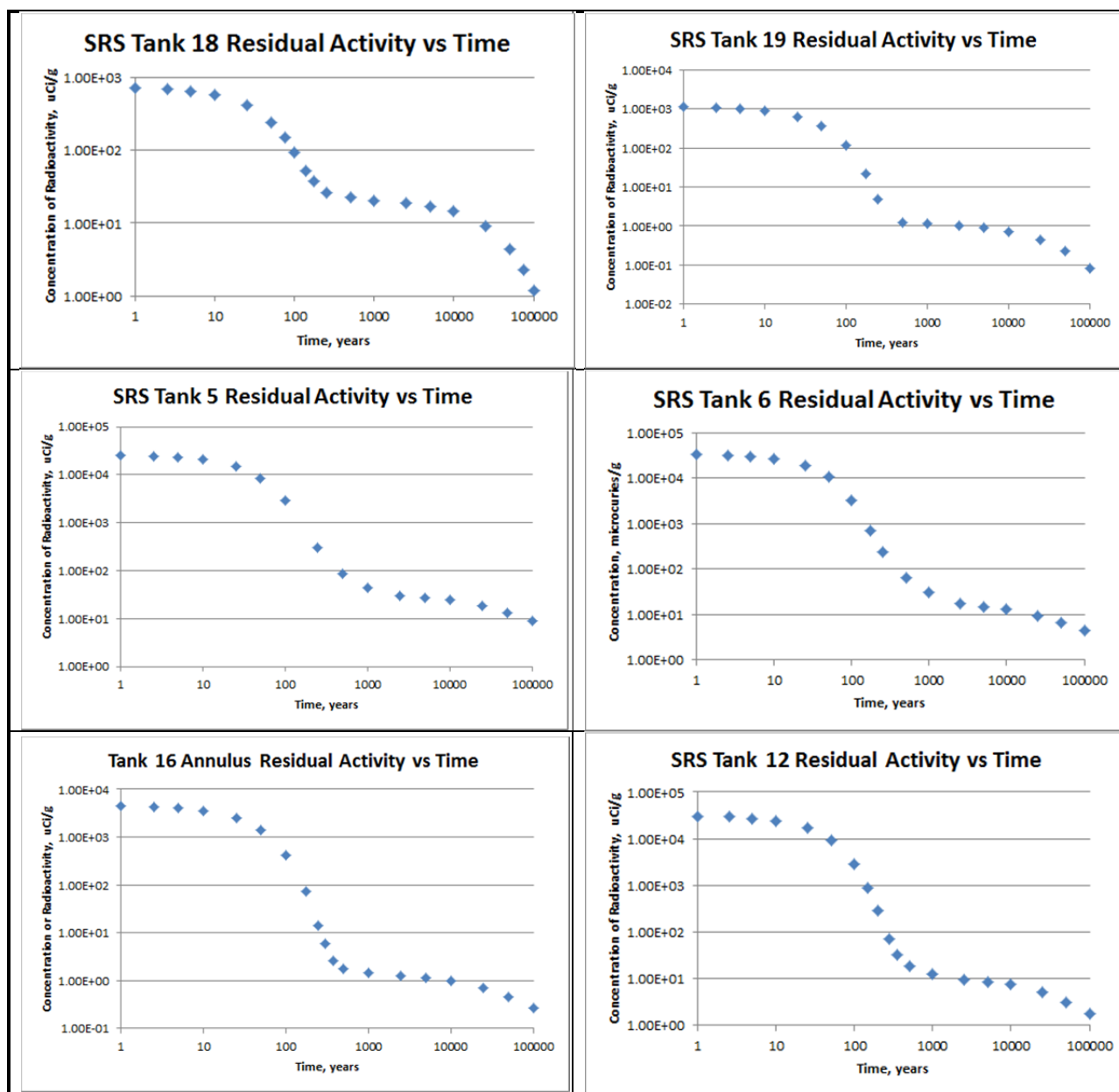

Figure 2-1. **Temporal Distribution of Residual Radioactivity in Closed SRS Waste Tanks**
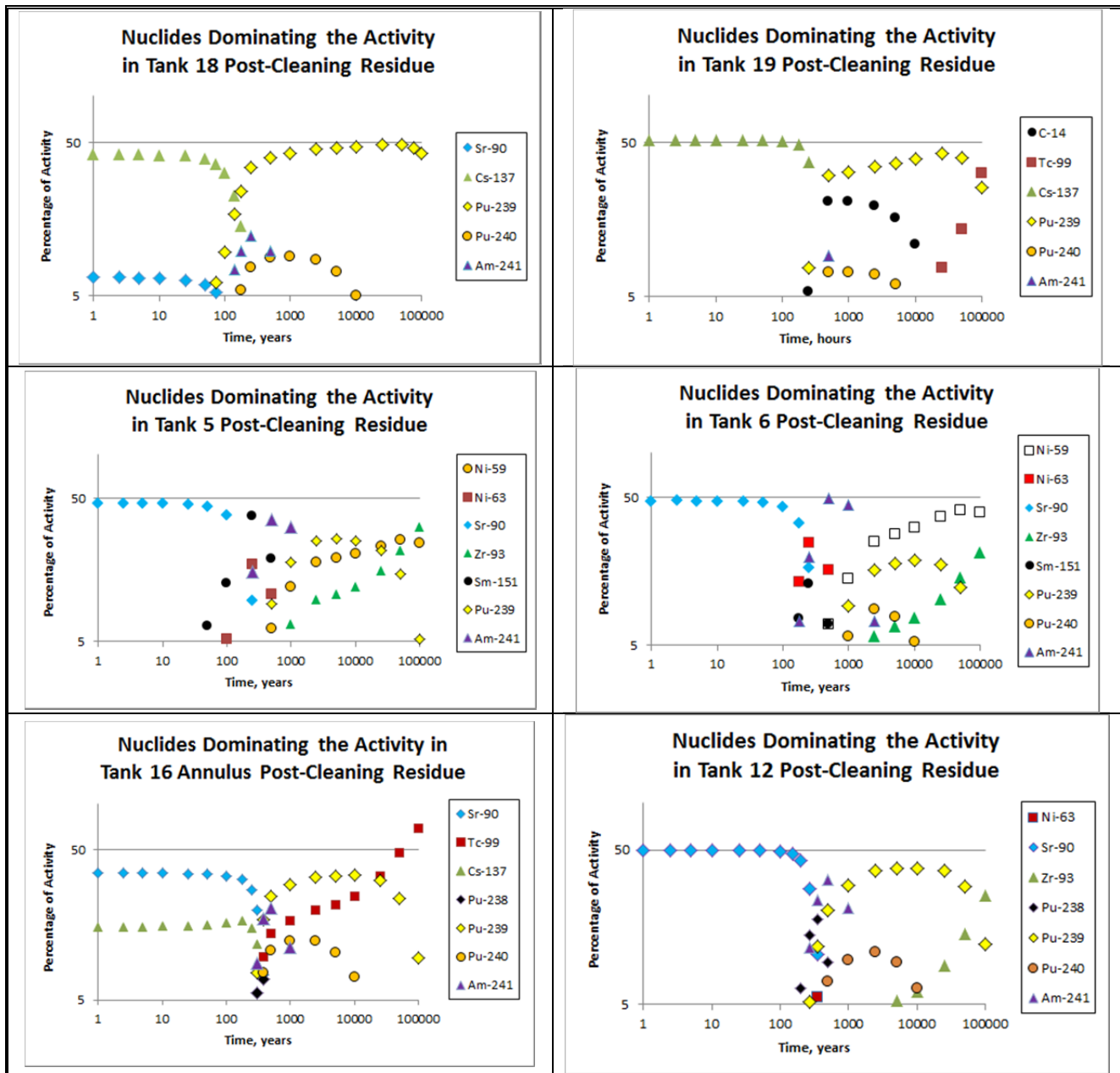
Figure 2-2. **Temporal Distribution of Nuclides Dominating Activity in Closed Waste Tanks**

2.4 <u>Relative Analytical Cost and Time Requirements</u>

Radionuclide analyses associated with the SRS tank closure campaigns tend to be labor intensive and costly due to the high radioactivity content of the samples, the complex and highly variable sample matrices, the extensive radiochemical processing that is required to remove interfering constituents from samples prior to measurements, and the hybrid measurement techniques that are typically needed to assure high quality analytical results. In addition, because the tank closure characterization work is typically being performed concurrently with multiple other site characterization projects (including those required to maintain operations at the SRS canyons, the Defense Waste Processing Facility, the salt waste processing facilities, and the Saltstone Production and Disposal Facilities), there is rarely the opportunity to focus solely on the tank closure scope. A consequence of this is that the completion times of the analyses tend to extend over several months, jeopardizing the ability to meet project deadlines when problems arise.

Most of SRNL's existing radioanalytical methods have not yet been optimized, as they were developed over short timeframes limited by funding restrictions and the need to meet aggressive reporting deadlines. As such, there is clearly the potential to improve methods with the objective of making them less labor intensive and/or more efficient, while still maintaining data integrity. Although there are many potential ways of making such improvements, a couple of the most likely possibilities include making changes that: a) minimize the need for performing extensive special preparatory processing steps in the Shielded Cells; b) utilize alternative radiochemical separation techniques that are simpler and/or produce higher analyte recoveries; and c) results in higher measurement resolution and/or lower minimum detection limits.

A first step in considering where characterization improvement efforts should be focused is identifying the current costs and time requirements associated with each of the individual analyses, and using the information to determine where the greatest potential savings exist. Clearly, there is little benefit in making changes to an established analytical method that has proven to produce good results and is already cost-effective and timely. In contrast, an existing method that is very labor intensive, costly, and lengthy offers a significant potential for improvement.

Utilizing the SRNL radionuclide characterization cost and schedule information presented in last year's Annual Report,[10] the typical SRNL labor costs and average completion times have been identified in Table 2-1. Note that the analyses in this table were ordered from most costly to least costly, with costs ranging from ~$20K to ~$60K per analysis per campaign. (The typical sample batch in a closure characterization campaign contains a minimum of one reagent blank, one matrix blank, and triplicate aliquots of three composite samples – thus, a total of eleven aliquots being individually analyzed). As shown in the table, the analysis for the Am/Cm/Cf isotopes is the most costly, while the analysis for Cs-137/Ba-137m is the least costly. Also identified in the table is whether the current analytical method requires "special preps" in the Shielded Cells, which significantly raises the analytical costs. (It is no coincidence that the seven most costly analyses – Am/Cm/Cf, Pa-231, Th-229/230, Cl-36, Ra-226, I-129, and Tc-99 – all require "special preps" in the Shielded Cells).

The farthest right hand column of the table identifies the average completion time of the set of analyses, in months. This value ranges from a high of 6.5 months for Pt-193 to a low of 1.8 months for Pm-147/Sm-151 and Cs-137/Ba-137m. As discussed before, the completion times for the individual analyses would be shorter if there were no competing characterization projects – however, given that several characterization projects are being performed simultaneously, the completion times become extended.

Table 2-1. Typical Labor Costs and Completion Times of SRNL Tank Closure Analyses

Radionuclide Analyses	Requires "Special Preps" in the Shielded Cells	Average Total Labor Costs per Campaign ($)	Average Completion Time in Months
Am/Cm/Cf isotopes	X	63K	5.8
Pa-231	X	56K	5.9
Th-229/230	X	52K	5.3
Cl-36	X	50K	6.3
Ra-226	X	47K	6.2
I-129	X	43K	2.3
Tc-99	X	42K	3.0
Ni-59/63		39K	3.4
Cs-135		35K	5.2
Pt-193		34K	6.6
Zr-93		33K	5.2
Pm-147/Sm-151		33K	1.8
Pd-107		33K	Not reported
Pu-239/240/242/244		31K	4.5
Np-237		31K	5.2
U-233/234/235/236		30K	2.8
Pu-238/241		30K	2.2
Se-79		29K	4.6
U-232		27K	4.1
K-40		27K	6.5
Sr-90/Y-90		27K	2.4
C-14		25K	5.5
Al-26/Co-60/Sb-126/Sn-126/Eu-152/Eu-154/Am-241		25K	3.6
Nb-94		25K	6.0
H-3		21K	2.7
Th-232/U-238		21K	2.5
Cs-137/Ba-137m		20K	1.8

(The information in this table was taken from Appendices D, F, and G of the Annual Report.[10])

With respect to reducing costs, the analyses that should initially be targeted include those for Am/Cm/Cf, Pa-231, Th-229/230, Cl-36, Ra-226, I-129, and Tc-99. One clear means of making the first five of these analysis methods more cost effective is to make changes to the protocols that will eliminate the need for the "special preps" in the Shielded Cells. An additional analysis that should be targeted near-term includes that for Ni-59/63, which is the most costly method that does not require "special preps" in the Shielded Cells.

With respect to reducing the time requirements, the analyses that should initially be targeted include those where the average completion time is currently five months or greater. From high to low completion times, this includes analyses for Pt-193, K-40, Cl-36, Ra-226, Nb-94, Pa-231, Am/Cm/Cf, C-14, Th-229/230, Cs-135, Zr-93, and Np-237. Given that the Pt-193, K-40, and Cl-36 nuclides are no longer part of the routine tank closure characterization list, the near-term focus should be on the other methods, particularly those that are currently both costly and time consuming, which includes Am/Cm/Cf, Pa-231,

Th-229/230, and Ra-226. Note that development of three of these methods (Am/Cm/Cf, Th-229/230, and Ra-226) was pursued this past year and is addressed in Section 4.0 of this report.

2.5 <u>Analytical Detectability</u>

The waste constituents that are characterized in a given tank closure campaign are identified in the contractor's Technical Task Request, along with the minimum detection limits (MDLs) that are to be targeted. The radionuclides requiring characterization have varied somewhat over the last six SRS waste tanks being closed, with a total of forty-two nuclides requiring quantification for Tanks 18 and 19, fifty-three nuclides requiring quantification for Tanks 5 and 6, thirty-nine nuclides requiring quantification for Tank 16, and thirty-five nuclides requiring quantification for Tank 12. Over these six tanks, a total of fifty-six different radionuclides have required characterization. (These fifty-six radionuclides are the ones identified in endnote c of page 3). The requested minimum detection limits have varied a bit from tank to tank and from nuclide to nuclide, but have been as low as 1.0E-05 µCi/g and as high as 3.0E+00 µCi/g. A primary driver in choosing an appropriate MDL target is the level of analytical sensitivity needed to demonstrate adequacy of the inventory projections utilized in the PAs.

For each tank being closed, several samples of the post-cleaning waste residue that remains in the tank after bulk waste removal and cleaning are collected and shipped to SRNL. Following receipt, the samples are air-dried, ground, and sieved, and then either analyzed individually or composited prior to analysis. For Tanks 18 and 19, the residue characterization was based on triplicate analyses of six individual samples taken from each tank. In contrast, for Tanks 5, 6, 16, and 12, the residue characterization was based on triplicate analyses of three composite samples, each generated from multiple individual samples.

In the majority of cases, the nuclide concentrations that are identified through the analyses are higher than the MDLs, which facilitate statistical assessment of the results, including averaging and calculation of upper concentration bounds at pre-defined confidence levels. In contrast, it is impossible to hone the average concentrations and judge the spread of the data when the measured concentrations are less than the MDLs. This is not to say that "less than MDL" data are useless, as they still may provide assurance that concentrations are within an acceptable range – however, there are clear limitations with utilizing "less than MDL" data, and with these limitations, the question arises as to whether such analytical results provide sufficient utility to meet data objectives. Particularly in the cases where non-detectability is consistent from tank to tank and from sample to sample, there may be a basis for reducing the number of analyses performed, changing the characterization approach to one that provides discrete values, and/or considering elimination of the analysis.

Table 2-2 provides a summary of the percentages of radioanalytical results that fall below the MDLs, as a function of the particular radionuclides and the past six SRS tank closure characterization campaigns. In this table, values of 100% indicate that all of the sample replicates produced analytical results below the MDLs (undetectable), values of 0% indicate that all of the sample replicates produced analytical results above the MDLs (detectable), and values between 0% and 100% indicate that some of the results were less than the MDLs (undetectable) and some were greater than the MDLs (detectable). Note that values of 100% have been highlighted in a light blue background, for ease of identification.

As shown in the table, about 20% of the nuclides were consistently less than the MDLs in every tank sample that was characterized (100% less than the MDLs). This includes H-3, Al-26, Cl-36, Pt-193, Ra-226, Ac-227, Pu-244, Cm-243, Cm-247, Cm-248, Cf-249, and Cf-251. An additional three nuclides were less than the MDLs in almost every case, with the exceptions being cases where the percentages of results less than the MDLs were still relatively high. These three nuclides are K-40, Nb-94, and Pa-231.

Table 2-2. Percentages of Radioanalytical Results Below the Minimum Detection Limits

Nuclide	Percentage of Radioanalytical Results Being Less than Minimum Detection Limits					
	Tank 18	Tank 19	Tank 5	Tank 6	Tank 16 ANN	Tank 12
H-3	100	100	100	100	NM	NM
C-14	0	0	100	0	100	100
Al-26	100	100	100	NM	NM	NM
Cl-36	100	100	100	NM	100	NM
K-40	72	100	100	NM	100	NM
Co-60	0	0	0	0	11	0
Ni-59	6	100	0	0	100	0
Ni-63	0	89	0	0	100	0
Se-79	100	100	0	0	NM	NM
Sr-90	0	0	0	0	0	0
Y-90	0	0	0	0	0	0
Zr-93	0	0	0	0	100	0
Nb-94	94	100	100	100	100	100
Tc-99	0	0	0	0	0	0
Pd-107	0	50	0	NM	NM	NM
Sn-126	0	0	100	100	NM	0
Sb-126	0	0	100	100	NM	0
Sb-126m	0	0	100	100	NM	0
I-129	17	67	11	0	0	0
Cs-135	0	0	0	0	0	100
Cs-137	0	0	0	0	0	0
Ba-137m	0	0	0	0	0	0
Sm-151	0	0	0	0	NM	NM
Eu-152	83	94	100	100	NM	0
Eu-154	0	0	0	0	0	0
Pt-193	100	100	100	NM	NM	NM
Ra-226	100	100	100	100	100	100
Ra-228	NM	NM	NM	NM	NM	0
Ac-227	100	100	100	100	NM	NM
Th-229	22	50	11	0	NM	100
Th-230	11	50	0	0	100	100
Th-232	NM	NM	NM	NM	NM	0
Pa-231	67	100	100	100	100	56
U-232	0	6	100	0	NM	0
U-233	17	17	100	0	100	89
U-234	0	0	11	0	0	0
U-235	0	0	0	0	0	0
U-236	0	0	0	0	0	0
U-238	0	0	0	0	0	0
Np-237	0	0	0	0	0	0
Pu-238	0	0	0	0	0	0
Pu-239	0	0	0	0	0	0
Pu-240	0	0	0	0	0	0
Pu-241	0	0	100	0	0	0
Pu-242	78	89	0	0	0	0
Pu-244	100	100	100	100	100	100
Am-241	0	0	0	0	0	0
Am-242m	50	100	0	0	100	22
Am-243	28	6	0	0	89	11
Cm-243	100	100	100	100	100	100
Cm-244	0	0	0	0	100	100
Cm-245	100	100	100	0	100	78
Cm-247	100	100	100	100	100	NM
Cm-248	100	100	100	100	100	NM
Cf-249	100	100	100	100	100	NM
Cf-251	NM	NM	100	100	100	NM

NM = not measured; ANN = annulus

Given the high resource demands associated with the radioanalyses, consistent non-detectability suggests that changes in the analytical approach may be warranted and should be considered. Note that thus far, five of the nuclides showing high non-detectability have already been removed from the routine characterization list. This includes H-3, Al-26, Cl-36, K-40, and Pt-193.

2.6 <u>Contribution to Long-Term Environmental Risk</u>

Quantification of long-term potential environmental risk due to emptied, closed DOE waste tanks is a complex undertaking, subject to numerous uncertainties and dependent upon many inputs identifying source terms, environmental transport mechanisms, uptake scenarios, and ultimate potential dose consequences. Formal projection of the long-term environmental risk consequences of closed SRS waste tanks has been performed and documented via the F and H-TF PAs[7,8] and Special Analyses (SAs).[11,12] In addition, a new experimental approach for modeling long-term environmental risks has been utilized to identify potential risk-driving waste constituents from individual closed SRS waste tanks.[10] Results of these various assessment approaches provide a tangible basis for identifying the primary radionuclides that drive the future potential environmental risks. Clearly, accurate characterization of the risk-driving nuclides (and of the parent nuclides contributing to the risk-driving nuclides) is a necessity, to assure source input values for environmental risk projections are appropriate.

This determination focuses on the relative projected long-term doses associated with residual radionuclides remaining in emptied tanks following waste removal and cleaning. Since the vast majority of future environmental risk will be contributed through the groundwater pathway, this is the pathway that is utilized in this assessment. Note that doses associated with groundwater include those from direct ingestion, inhalation, and exposure, as well as through ingestion of meat, vegetation, and milk that have been impacted by presence of the groundwater. For this particular assessment, dose projection results applicable to groundwater at a distance of 100 meters from the TFs are utilized.

The primary assessment period is 10,000 years following tank closure, since that is the PA compliance period. However, impacts over a 100,000 year period are also considered, as they provide a basis for comparison with impacts occurring during the compliance period. For the purposes of this assessment, the percentage of the total peak dose is one of the bases used for determining the extent that individual radionuclides contribute to dose, with a percentage of two or more being considered significant, and a percentage of less than two being considered "lost in the noise." For assessment of the F-TF results, dose projections for the Sector E case[d] were used, with the total peak doses for that sector being highest and a relatively large number of nuclides contributing significant dose. In contrast, for the H-TF comparisons, dose projections for the Sector C case were used, with the total peak doses for that sector being second highest, but with a larger number of nuclides contributing significant dose than in the case with highest peak dose. Note that the dose results of the SAs are considered to be more accurate than those of the PAs, as the SAs are based on improved source input data.

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[d] The 100 m boundary perimeters addressed in the PAs and SAs were divided into mulitple sectors to facilitate assessment of peak dose variability as a function of perimeter location. Five sectors were utilized in the F-TF PAs/SAs (Sectors A, B, C, D, and E), while six sectors were utilized in the H-TF PAs/SAs (Sectors A, B, C, D, E, and F).

PA and SA Results

Projected dose rates identified in the F-TF and H-TF PAs are given as functions of time in Figures 2-3 and 2-4, respectively. As shown in Figure 2-3, Ra-226 contributes the highest projected F-TF PA peak dose rate, 0.92 mrem/yr, at a time of 10,000 years. The second highest projected F-TF PA peak dose rate, 0.55 mrem/yr, is contributed by Np-237 at a time of approximately 6,000 years. The third highest projected F-TF PA peak dose rate, 0.38 mrem/yr, is contributed by Cs-135 at a time of approximately 6,000 years. Other radionuclides contributing sufficient F-TF PA dose rates to be included on the plot are Tc-99, U-233, U-234, C-14, I-129, Pa-231, and Th-229, with peak projected dose rates decreasing from 0.33 mrem/yr to 0.075 mrem/yr.

As shown in Figure 2-4, Ra-226 contributes the highest projected H-TF PA peak dose rate, 1.3 mrem/yr, at a time of 10,000 years. The second highest projected H-TF PA peak dose rate, ~0.4 mrem/yr, is contributed by Pa-231 at a time of 10,000 years. The third highest projected H-TF PA peak dose rates, at ~0.3 mrem/year each, are contributed by Tc-99 and I-129, at times of approximately 700 and 3,700 years, respectively. Other radionuclides contributing sufficient H-TF PA dose rates to be included on the plot are Np-237, Nb-94, C-14, Pb-210, and Cs-135, with peak projected dose rates decreasing from approximately 0.2 mrem/yr to approximately 0.05 mrem/yr.

In contrast to the PA dose projections, the F-TF and H-TF SA dose projections are given in Figures 2-5 and 2-6, respectively. As shown in Figure 2-5, Ra-226 contributes the highest projected F-TF SA peak dose rate, ~1.7 mrem/yr, at a time of 10,000 years. The second highest projected F-TF SA peak dose rate, ~1.3 mrem/yr, is contributed by Pa-231 at a time of approximately 6,000 years. The third highest projected F-TF SA peak dose rate, ~0.7 mrem/yr, is contributed by Np-237 at a time of approximately 6,000 years. Other radionuclides contributing sufficient F-TF SA dose rates to be included on the plot are C-14, Tc-99, and U-234, with peak projected dose rates of ~0.4 mrem/yr occurring at times of approximately 700, 4300, and 10000 years, respectively.

For times greater than 10,000 years, the F-TF SA identifies that three primary radionuclides contribute significantly to long-term peak dose: Pu-239 contributes the highest projected peak dose rate, ~500 mrem/yr, at a time of approximately 40,000 years; Nb-93m contributes the second highest projected peak dose rate, ~60 mrem/yr, at a time of approximately 75,000 years; and Pu-240 contributes the third highest projected peak dose rate, ~5 mrem/yr, at a time of approximately 40, 000 years. Although these doses are beyond the compliance period of the PAs, it is worthwhile knowing that these particular nuclides have the potential to contribute significant dose.

As shown in Figure 2-6, the two primary radionuclides contributing most of the H-TF SA dose include I-129, with a peak projected dose of ~2.0 mrem/yr at a time of approximately 4,000 yrs, and Ra-226 with a peak projected dose of ~1.7 mrem/yr at a time of approximately 10,000 years. The increased contribution of I-129 in the H-TF SA over that identified in the H-TF PA reflects an increase in the I-129 inventory associated with the Tank 12 post-cleaning residue. Other radionuclides contributing sufficient H-TF SA dose rates to be included on the plot are Tc-99, Pa-231, Np-237, Pb-210, C-14, and Cs-135.

Results of the PA and SA dose projections, in terms of percentage of the peak dose rates, are summarized in Table 2-3. This table provides ease of comparison between the nuclides contributing significant doses based on the various scenarios. As shown in the table, there are clear differences between the results observed for each TF, as well as clear differences between the results observed for the PAs and the SAs. These differences give some indication as to the variations and uncertainties that are applicable to the individual dose assessments. Also observed are some similarities, most notably those showing agreement

Figure 2-3. **Projected Groundwater Doses Identified in SRS F-TF PA (Sector E)[7]**

Figure 2-4. **Projected Groundwater Doses Identified in SRS H-TF PA (Sector C)[8]**

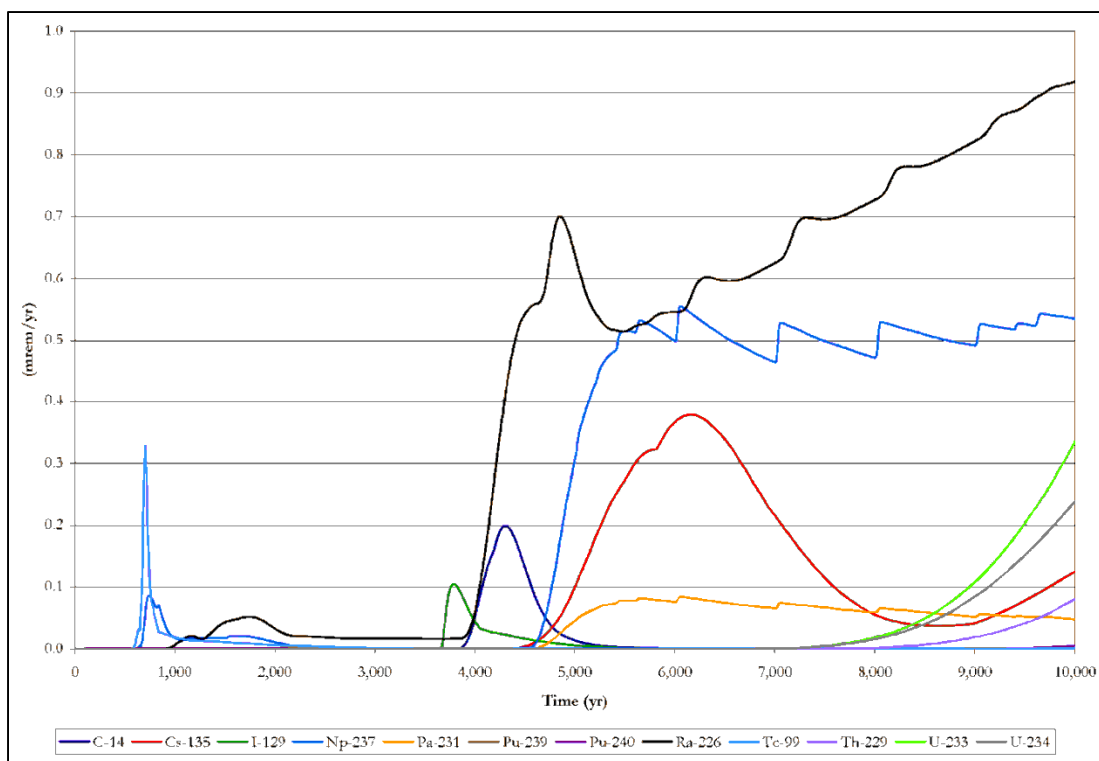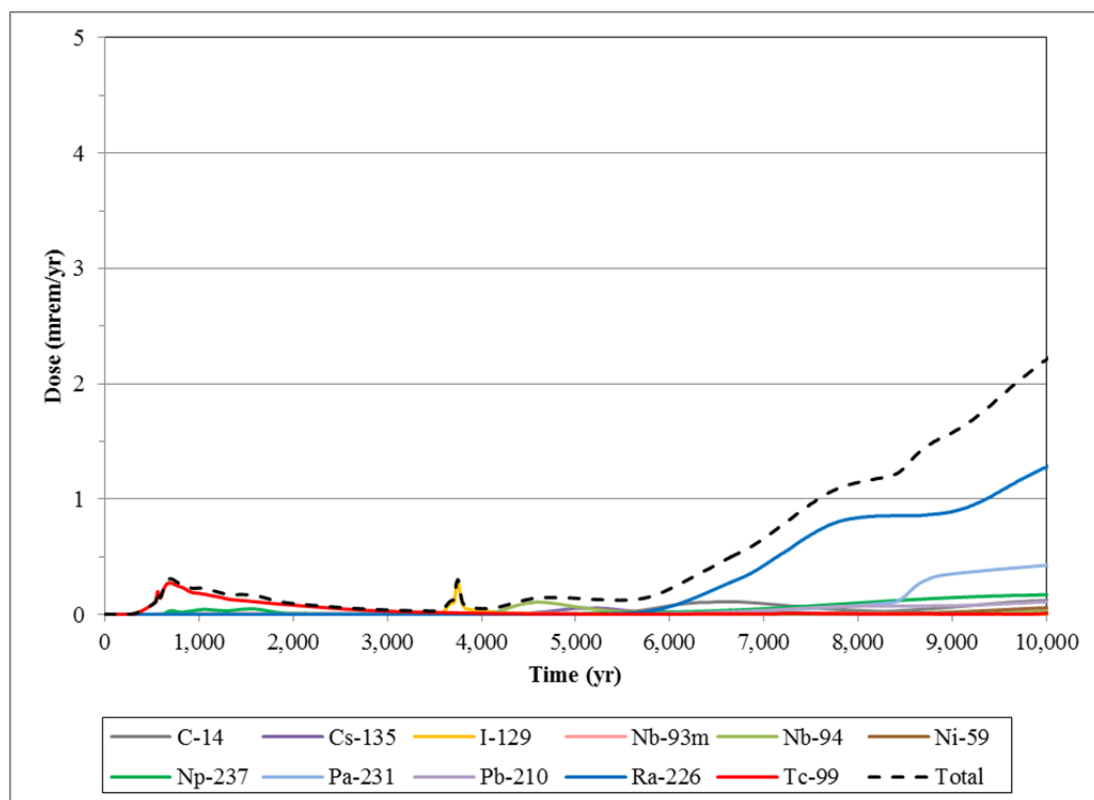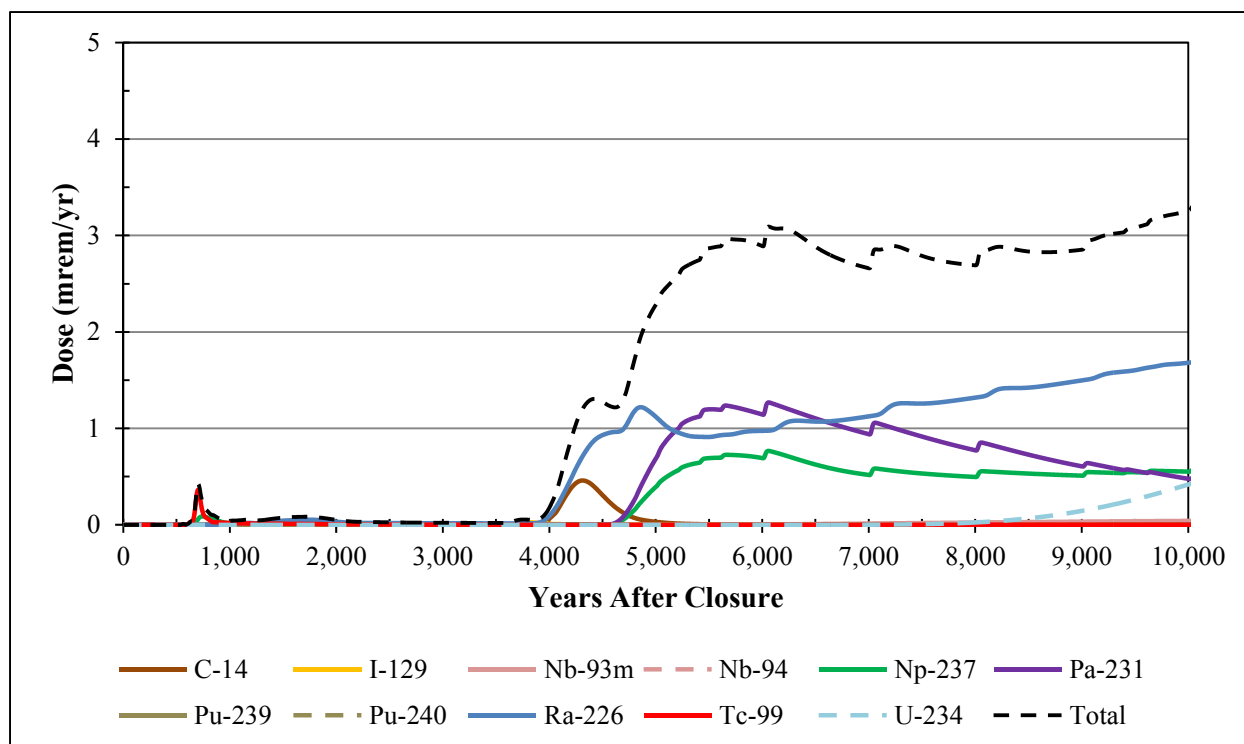**Figure 2-5**. **Projected Groundwater Doses Identified in SRS F-TF SA (Sector E)**[11]
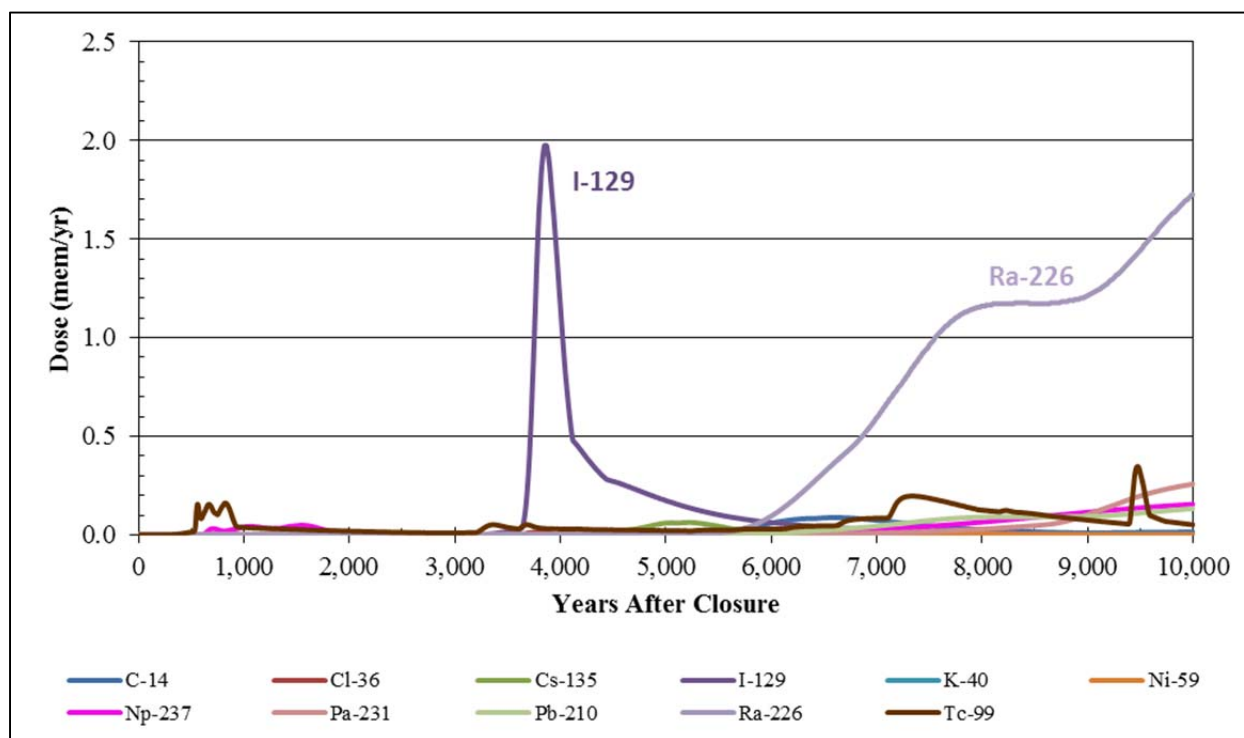

Figure 2-6. **Projected Groundwater Doses Identified in SRS H-TF SA (Sector C)**[12]

from case to case that there is a relatively small set of nuclides driving the total projected peak doses, and a slightly larger set of nuclides contributing lower, but still important doses (> 2% of the total peak doses). Specifically, the results make clear that Ra-226 is expected to be the greatest dose contributor over the 10,000 year period, with Pa-231 and Np-237 being the second biggest expected dose contributors. The next highest expected dose contributors include I-129, Tc-99, and C-14, with I-129 doses from H-TF being significantly greater than those from F-TF. Smaller, but still significant potential dose contributors include Cs-135, U-234, U-233, Pb-210, Nb-94, and Th-229. Although not expected to contribute significant doses during the first 10,000 years, Pu-239, Nb-93m, and Pu-240 are expected to contribute significant doses during the 40,000-75,000 year timeframe.

Table 2-3. Nuclides Driving Projected Well Water Doses Identified in SRS TF PAs and SAs

Nuclide	Percentage of Projected Peak Dose Over First 10,000 Years from Well Water at 100 m			
	F-TF PA (E)	H-TF PA (C)	F-TF SA (E)	H-TF SA (C)
C-14	9	7	10	2
Nb-94	< 2	7	< 2	< 2
Tc-99	10	10	10	7
I-129	4	10	< 2	40
Cs-135	20	4	< 2	< 2
Pb-210	< 2	7	< 2	4
Ra-226	40	60	70	40
Th-229	3	< 2	< 2	< 2
Pa-231	4	20	40	5
U-233	10	< 2	< 2	< 2
U-234	10	< 2	10	< 2
Np-237	20	9	30	4

Note: Only one significant digit is reported in the values above.

Doses from Recently Closed Tanks

Projected dose rates for the six most recently emptied and closed SRS waste tanks are given as a function of calendar year in Figure 2-7. This figure includes projected dose rates from Tanks 18 (closed September 2012), 19 (closed September 2012), 5 (closed December 2013), 6 (closed December 2013), 16 (closed September 2015), and 12 (closed April 2016).

As shown in the figure, the relative dose rates for the various nuclides differed from tank to tank, but several conclusions can be drawn based upon the results. The calendar years where the total peak doses were projected ranged from approximately CY3300 to CY6800, which corresponds to elapsed times ranging from approximately 1300 to 4800 years from today. Projected doses from a total of seven radionuclides contributed two percent or more of the total peak doses in at least one of the six closed tank cases. These seven nuclides included C-14, Nb-93m, Tc-99, I-129, Ra-226, Pa-231, and Np-237. In every one of the six closed tank cases, Ra-226, Pa-231, and Np-237 contributed significantly to the projected total peak doses, with their proportions ranging from approximately 7-70%, 3-70%, and 30-100%, respectively.

In contrast, the contributions from C-14, Nb-93m, Tc-99, and I-129 were each insignificant (< 2%) in at least two of the six closed tank cases and significant (> 2%) in at least one of the six closed tank cases. For example, the contribution from C-14 was very significant in the Tank 19 case, with a projected peak dose close to 100% of the total peak dose, while being insignificant in the other five closed tank cases. Another example is I-129, which contributed significantly to the projected doses in four of the closed tank
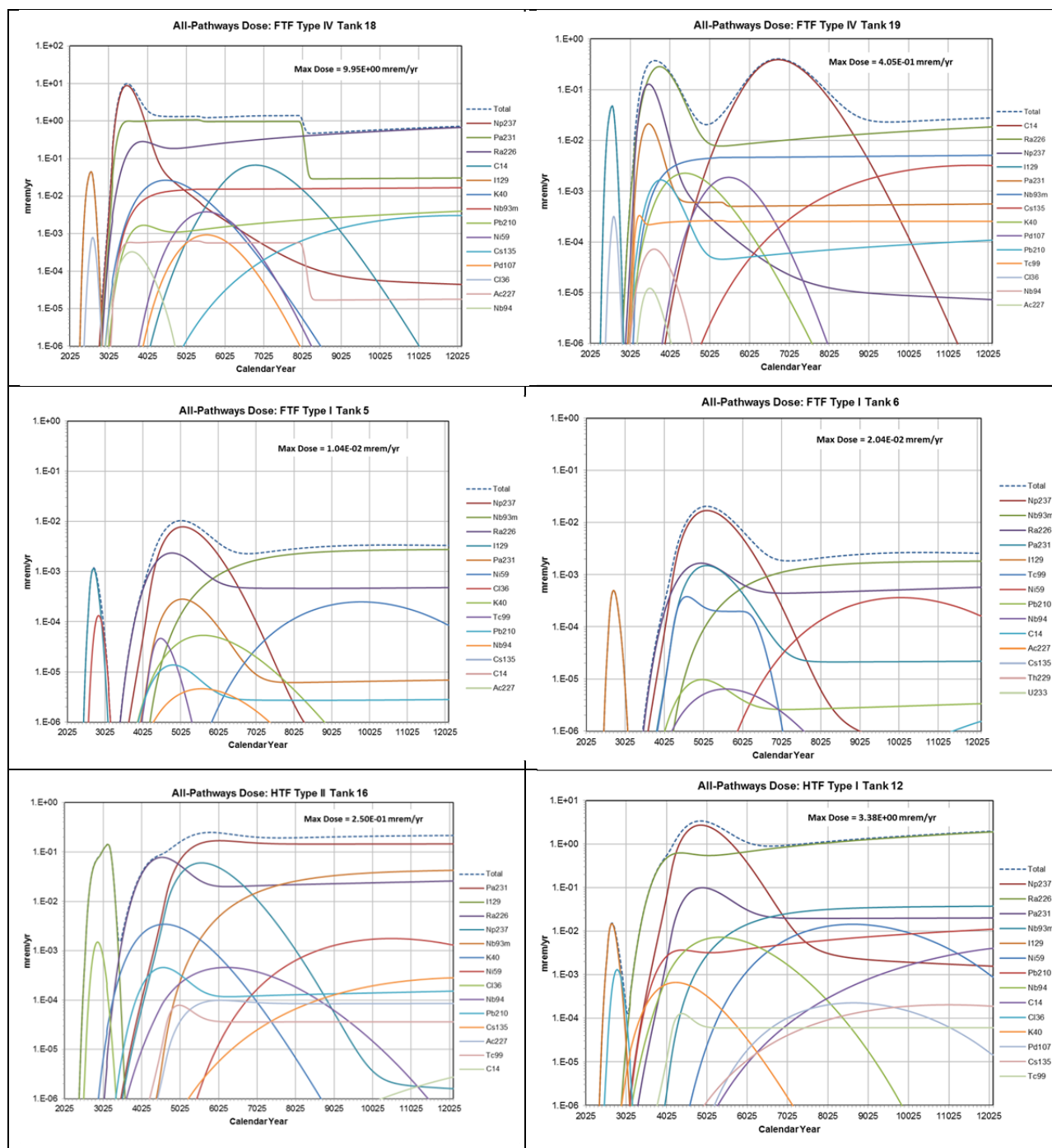
15

Figure 2-7. Projected All Pathways Doses From Most Recently Closed SRS Waste Tanks

16

cases (Tanks 19, 5, 6, and 16), but was insignificant in two of the closed tank cases (Tanks 5 and 12). Note that the Tank 12 case differed from the other cases in that the projected doses were modeled based on projected nuclide concentrations, as opposed to measured nuclide concentrations. This is important to understand, as the measured I-129 concentrations in the Tank 12 post-cleaning residue was higher than projected. As such, the projected dose rates due to Tank 12 I-129 (as shown in Figure 2-7) are clearly underestimates.

For ease of comparison, the percentages of the total peak doses contributed by the nuclides are summarized in Table 2-4, on a tank by tank basis. Looking at the percentages collectively, it is clear that the compositions of the different tank residues (post-cleaning residues) vary markedly and have a significant impact on the distribution of future potential doses. Worth noting is that all of the nuclides contributing significant projected doses based on the individual tank cases are ones also identified in the PAs and SAs as being significant contributors. This consistency is encouraging and lends credence to the alternative modeling approach utilized in the individual closed tank projections.

Table 2-4. Nuclides Driving Projected Doses from Most Recently Closed SRS Waste Tanks

Nuclide	Percentage of Projected Peak Dose Over First 10,000 Years from Well Water at 100 m					
	Tank 18	Tank 19	Tank 5	Tank 6	Tank 16	Tank 12
C-14	< 2	100	< 2	< 2	< 2	< 2
Nb-93m	< 2	< 2	30	10	10	< 2
Tc-99	< 2	< 2	< 2	2	< 2	< 2
I-129	< 2	10	10	3	60	< 2
Ra-226	7	70	70	7	30	60
Pa-231	10	5	3	6	70	3
Np-237	100	30	80	90	30	90

Note: Only one significant digit is reported in the values above.

Important Parent Nuclides

Given that the list of nuclides contributing significant potential future projected dose includes daughter products Nb-93m, Pb-210, Ra-226, Th-229, Pa-231, U-233, U-234, Np-237, Pu-239, and Pu-240, the impact of in-growth from the applicable parent nuclides must also be considered. The applicable parent nuclides are Zr-93 (for Nb-93m); Ra-226 (for Pb-210); Pu-238, U-234, and Th-230 (for Ra-226); U-233 (for Th-229); Pu-239 and U-235 (for Pa-231); Np-237 (for U-233); Pu-238 (for U-234); Am-241 (for Np-237); Cm-243 (for Pu-239); and Cm-244 (for Pu-240). Although Cm-243 is the parent of Pu-239, its contribution to the total activity of Pu-239 is expected to be insignificant, based on the relatively small quantity of Cm-243 that will be present (it has been undetectable in all the closure characterization campaigns thus far), the relatively large initial quantity of Pu-239 that will be present, and the long relative half-life of the Pu-239 compared to that of the Cm-243. For these reasons, the impact of in-grown Pu-239 from parent source Cm-243 is eliminated from consideration.

2.7 Primary Long-Term Sources of Nuclides

In gauging the long-term potential impact of in-growth from parent nuclides, it is necessary to understand the extent that parent nuclides contribute to inventories of the progeny nuclides over time. In order to gain such an understanding, plots have been developed that show in-growth of progeny nuclide activity over a 10,000 year period as a proportion of the initial parent activity. Plots applying to in-growth of Nb-93m, Pb-210, Ra-226, and Th-229 are given in Figure 2-8, and plots applying to in-growth of Pa-231, U-233, U-234, Np-237, and Pu-240 are given in Figure 2-9.
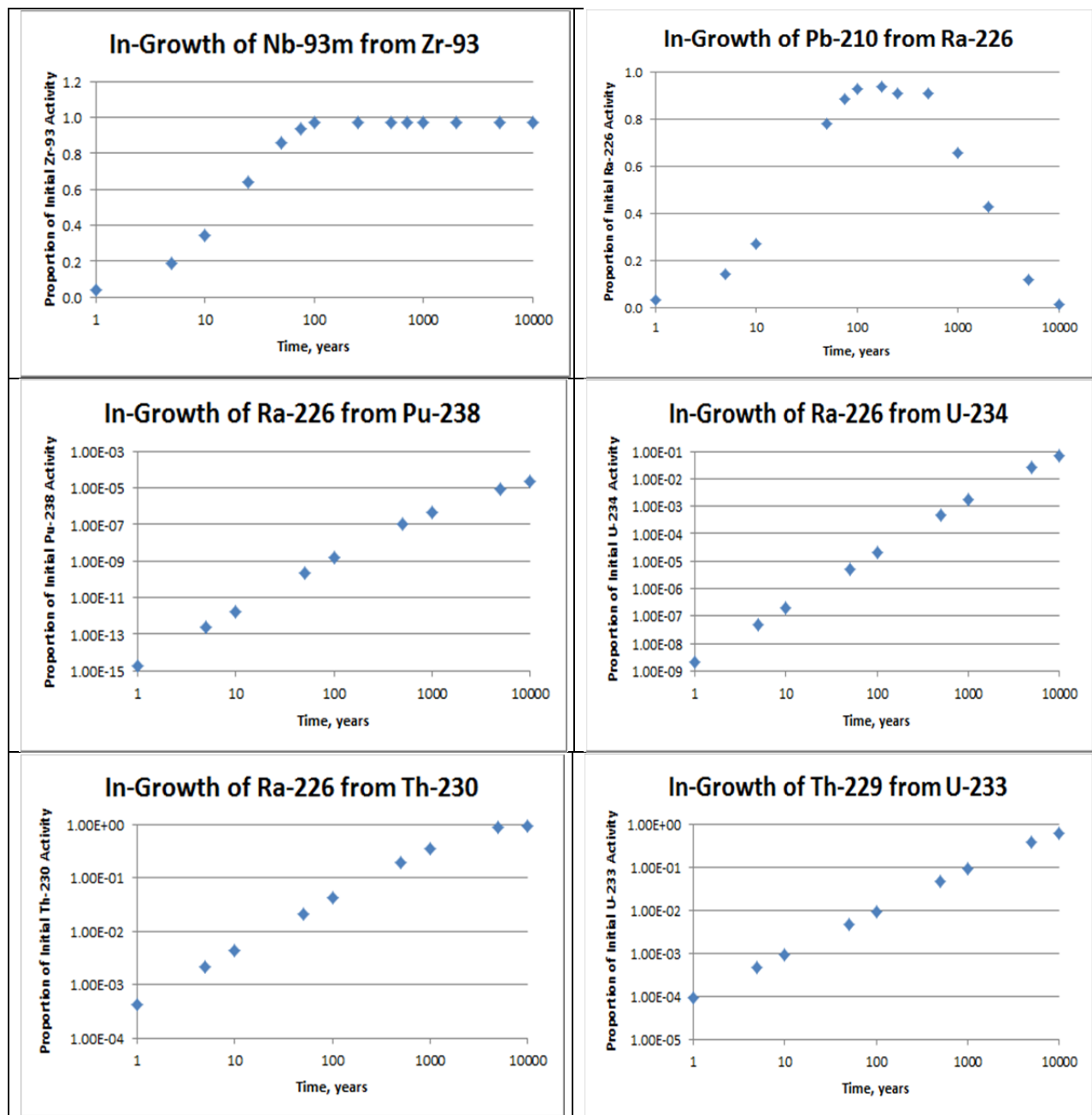
Figure 2-8. In-Growth of Nb-93m, Pb-210, Ra-226, and Th-229 from Parent Nuclides
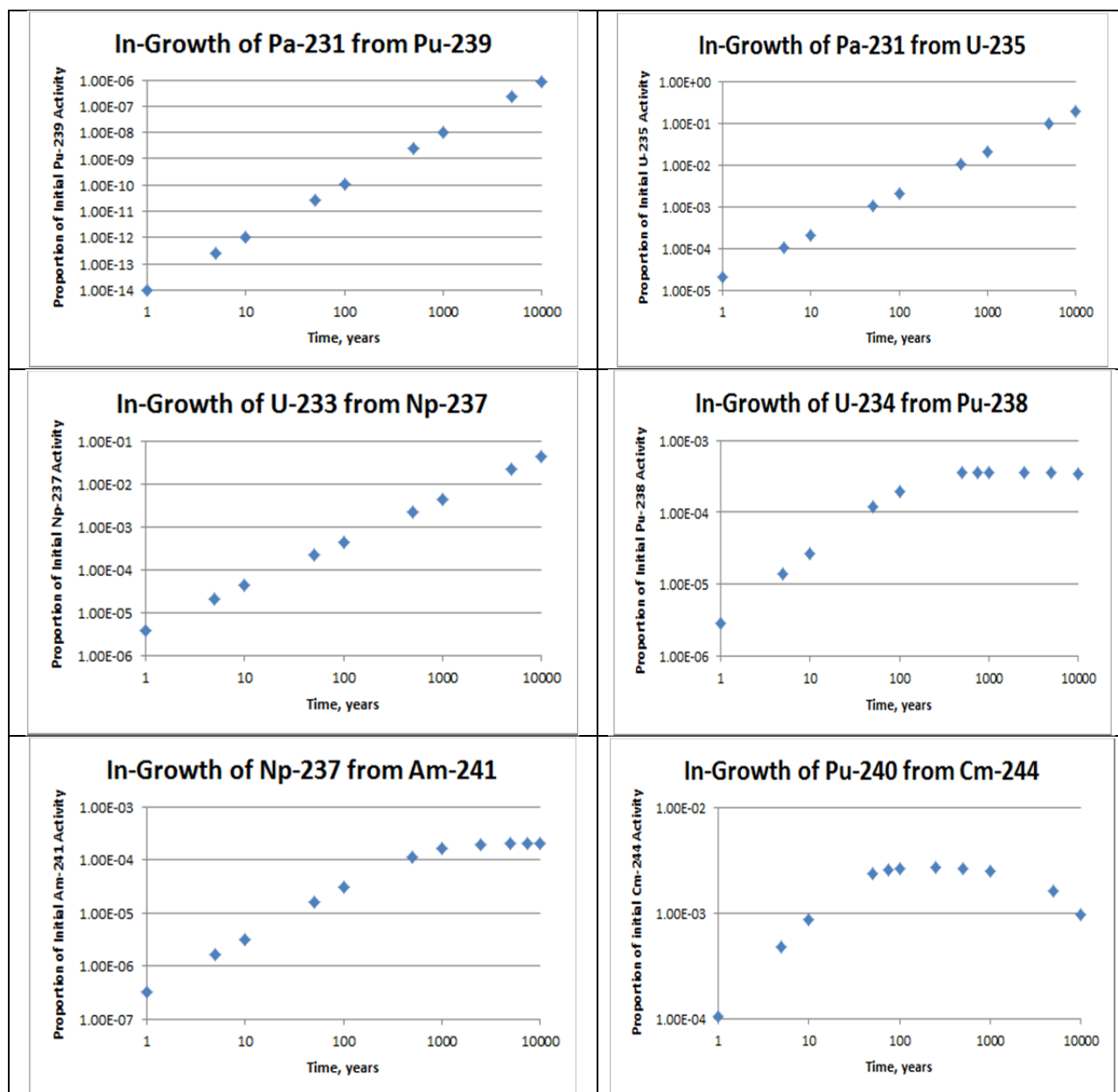
Figure 2-9. In-Growth of Pa-231, U-233, U-234, Np-237, and Pu-240 from Parent Nuclides

Nb-93m

The primary source of Nb-93m in waste is from decay of Zr-93, a fission product with long half-life (1.5E+06 years). As such, a good way of estimating the Nb-93m concentration is based on the Zr-93 inventory and the age of the waste. As the half-life of Nb-93m is relatively short (16.1 years), it grows-in relatively quickly and reaches a maximum after a period of approximately 100 years. This is illustrated in Figure 2-8, where the Nb-93m activity is approximately 97% of the initial Zr-93 activity for the period shown from 100 years to 10,000 years. In contrast, at times of 10, 25, and 50 years, the Nb-93m activity is approximately 34%, 64%, and 86% of the initial Zr-93 activity. For SRS tank waste, with a typical average age ranging from 30-50 years, the majority of the Zr-93 in-growth (> 50%) has already occurred. Clearly, the best way to estimate the current and future Nb-93m activity is through the current Zr-93 activity.

Pb-210

Pb-210 is a descendant of Ra-226, which is a long-term decay product of Pu-238, U-234, and Th-230 (a more detailed discussion of Ra-226 in-growth from these parent nuclides will be presented next in this section). Fresh tank waste is assumed to contain negligible Ra-226, with significant quantities of Ra-226 requiring thousands of years of in-growth, due to the long half-lives of U-234 and Th-230. Given this situation, the presence of significant activities of Pb-210 is not expected until significant activities of Ra-226 have accumulated (thousands of years) and sufficient additional time has elapsed to result in Pb-210 in-growth. As shown in Figure 2-8, the period of time for significant in-growth of Pb-210 to occur is in the 50-100 year timeframe. By 100 years, the Pb-210 activity is over 90% of the initial Ra-226 activity. In the figure, the Pb-210 activity is shown to decline after approximately 1,000 years – however, the case illustrated in the figure assumes that the original Ra-226 activity is not being replenished (through in-growth), which is not applicable for Ra-226 produced through in-growth from long-lived U-234 and Th-230, as occurs in tank waste. In tank waste, the Ra-226 will be accumulated and largely replenished for many tens of thousands of years into the future, due to in-growth from U-234 and Th-230, with half-lives of 2.5E+04 and 7.5E+04 years, respectively. The bottom line is that significant quantities of Pb-210 will be present after the passing of thousands of years and will continue to be present for many thousands of years into the future. Effective projection of Ra-226 concentrations into the long-term future will be necessary to effectively quantify future Pb-210 concentrations.

Ra-226

As identified above, the quantity of Ra-226 that is present in the waste will increase over time, as a function of the quantities of Pu-238, U-234, and Th-230 present in the fresh waste. Pu-238 and U-234 were present in the fresh waste, as Pu-238 was one of the nuclide products being generated, and U-234 was a natural constituent of the uranium fuel being processed. In contrast, Th-230 was only a significant constituent in the fresh waste if the waste was associated with a Thorex campaign, and in these cases, was present as a natural isotopic impurity. In the decay scheme, Pu-238 transforms to U-234, U-234 transforms to Th-230, and Th-230 transforms to Ra-226. Although the half-life of Pu-238 is relatively short (88 years), the half-lives of U-234 and Th-230 are relatively long (2.5E+04 and 7.5E+04 years, respectively), so the total time to produce significant quantities of Ra-226 is long (thousands of years), regardless of whether the starting nuclide is Pu-238, U-234, or Th-230.

As shown in Figure 2-8, the Ra-226 produced through in-growth from an initial source of Pu-238, U-234, or Th-230 continues to increase over the 10,000 year period presented in the various plots. For in-growth from Pu-238, the activity of Ra-226 after 10,000 years is approximately 2E-05 that of the initial Pu-238 activity. In contrast, for in-growth from U-234 and Th-230, the Ra-226 activities after 10,000 years are approximately 7% and 90% of the initial U-234 and Th-230 activities, respectively. The relatively low

proportion of initial Pu-238 that transforms to Ra-226 could incorrectly lead one to believe that Ra-226 in-growth from Pu-238 would be insignificant compared to that from U-234 and/or Th-230. However, in many tank waste cases, the initial Pu-238 activities are so much higher than those of the U-234 or Th-230 (many orders of magnitude higher) that Pu-238 decay may well be the largest contributor to long-term Ra-226 inventory. Nonetheless, tank waste compositions vary sufficiently that each case is different and Ra-226 in-growth tends to be a balance between contributions from initial Pu-238, U-234, and/or Th-230.

Regardless of the primary source of long-term Ra-226, it is clear that the current quantities of Ra-226 in tank waste are expected to be exceedingly small. This is consistent with sampling and analysis determinations, where 100% of the concentrations of Ra-226 in tank closure samples have been less than the MDLs. Based on this situation, it is worth considering whether quantification of the current Ra-226 concentrations is better served via sampling and analysis (where the result is expected to be less than an MDL) or via calculations based on the concentrations of Pu-238, U-234, and Th-230 associated with fresh waste (where concentrations in fresh waste would be estimated based on the current measured concentrations adjusted for back-decay). Regardless of the manner that the current concentration of Ra-226 is quantified, it is clear that future long-term concentrations of Ra-226 require determination based on in-growth from Pu-238, U-234, and Th-230.

Th-229

The primary source of Th-229 in waste is from decay of U-233, a long-lived nuclide (half-life of 1.6E+5 years) generated from neutron activation of Th-232 during the Thorex campaigns and produced through decay of Np-237. As shown in Figure 2-8, significant in-growth of Th-229 from U-233 occurs over a 10,000 year period, with the Th-229 activity at 10,000 years being approximately 60% of the initial U-233 activity. In contrast, at times of 10 years and 100 years, the in-grown activities are approximately 1E-03 and 1E-2 those of the initial U-233 activity, respectively. Using an analytical measurement technique with a very low MDL, Th-229 concentrations in tank closure samples have been measureable in some instances and undetectable in other instances. This is not unexpected, since only a limited number of Thorex campaigns were performed and only the wastes associated with the Thorex campaigns would be expected to contain measureable quantities of Th-229 (and U-233) at this time. As will be discussed below, long-term future quantities of U-233 can be impacted by in-growth from Np-237, but such impacts will require significant concentrations of Np-237 and thousands of years of Np-237 decay. Although sampling and analysis provides a means for quantifying the current Th-229 concentrations, projections based upon the U-233 concentrations are necessary for forecasting the long-term future Th-229 concentrations.

Pa-231

The primary source of Pa-231 in waste is not entirely clear at this time – one possibility is that it is due to natural impurities in the fuel and/or targets, ones that were not completely removed prior to fabrication of the fuel/targets – because the quantities of Pa-231 that have been measured in the tank waste samples are significantly higher than those that would be present due to in-growth from parent nuclides. The parent nuclides contributing to in-grown Pa-231 include Pu-239 and U-235, where Pu-239 decays to U-235, U-235 decays to short-lived Th-231 (half-life of 1.1 days), and Th-231 decays to Pa-231. Both Pu-239 and U-235 were present in the fresh waste, with Pu-239 being one of the nuclide products that was generated, and U-235 being one of the important uranium isotopes in the fuel being processed.

As shown in Figure 2-9, in-grown Pa-231 from parent nuclides Pu-239 and U-235 accumulates continuously over the first 10,000 years, with the Pa-231 activities at 10,000 years being approximately 1E-06 of the initial Pu-239 activity and approximately 20% of the initial U-235 activity. Although the contribution from Pu-239 is six orders of magnitude lower than that from U-235, both parent nuclides

have the potential to contribute comparable quantities of long-term in-grown Pa-231, as the initial Pu-239 activities are typically several orders of magnitude higher than those of the initial U-235.

Analyses of post-cleaning residue samples from two SRS tanks that are now closed (Tanks 18 and 12) indicated concentrations of Pa-231 two orders of magnitude higher than expected based upon in-growth from Pu-239 and U-235. Specifically, the measured Pa-231 concentrations were on approximately 2E-03 µCi/g, whereas the Pu-239 and U-235 were approximately 6E+00 and 5E-05 µCi/g, respectively. Assuming a waste age of 50 years, the expected Pa-231 from in-growth would have been approximately two orders of magnitude lower (on the order of 1E-06 µCi/g). This suggests that a more dominant source of short-term Pa-231 was present, such as the one identified above (impurities in the fuel/targets being processed). These results highlight the importance of performing specific sample analyses to identify the current Pa-231 concentrations. Use of the current concentrations, in combination with the in-growth relationships, will facilitate effective future Pa-231 projections.

U-233

The primary short-term source of U-233 in waste associated with the Thorex campaigns is neutron activation of Th-232. An additional source of U-233, particularly in non-Thorex waste, is decay of Np-237. With a half-life of 1.6E+05 years, U-233 in-growth from Np-237 is relatively slow, as shown in Figure 2-9, where the in-grown U-233 activity at 10,000 years is only about 4% of the initial Np-237 activity. Given that the Np-237 concentrations in fresh waste are typically relatively low, the impacts of in-grown U-233 over the first 10,000 years will likely be minor for Thorex waste, although primary for non-Thorex waste. Measurements of both U-233 and Np-237 provide the best means for projecting future long-term quantities of U-233.

Np-237

The primary short-term source of Np-237 in waste is through neutron activation of U-238, which occurs commonly in irradiated targets and fuel assemblies. A longer-term source of Np-237 is from decay of Am-241, which is typically prevalent in waste due to in-growth from short-lived Pu-241. As shown in Figure 2-9, the in-growth of Np-237 from Am-241 occurs primarily over the first 1,000 years, such that the in-grown Np-237 activity remains relatively constant from 1,000 to 10,000 years. During this time period, the activity of in-grown Np-237 is approximately 2E-04 that of the initial Am-241 activity. Because the Am-241 concentration of typical 40-50 year old tank waste is relatively high (approaching its maximum, due to near-full decay of Pu-241), the quantity of long-term Np-237 can be significantly impacted by in-growth from Am-241. Measurements of both Am-241 and Np-237 provide the best means for projecting future long-term quantities of Np-237.

Pu-240

The primary short-term source of Pu-240 in waste is from plutonium product generated in irradiated targets. An additional source of Pu-240, particularly in 50-1000 year old waste that received significant trivalent actinide inputs, is from relatively short-lived Cm-244 (half-life of 18 years). As shown in Figure 2-9, Pu-240 in-growth from Cm-244 reaches a maximum over the time period of approximately 50-1,000 years. In many cases, the Pu-240 contribution from Cm-244 in-growth will be minor compared to the quantity of Pu-240 contributed by the plutonium source, especially in wastes that contain little Cm-244. Nonetheless, measurements of both Pu-240 and Cm-244 provide a means for gauging future Pu-240 activities.

2.8 Potential Applicability of Alternative Characterization Approaches

Three primary categories of potential alternative characterization approaches are being considered – those that can be made more cost effective and/or timely through use of: 1) new laboratory methods that increase recoveries and/or reduce MDLs such that the extensive sample preparation steps performed in the Shielded Cells can be eliminated; 2) new laboratory methods that are significantly more efficient and/or significantly less labor intensive; and 3) efficient non-laboratory methods that provide technically defendable results. Although not an alternative characterization approach per se, another option worth considering is elimination of an existing analysis, particularly one that provides data for a constituent that has been demonstrated to have a negligible contribution to long-term risk and/or one that is consistently present at concentrations below the required MDL.

Tank closure laboratory analyses which currently require extensive sample preparation steps in the Shielded Cells include the SRNL methods for Cl-36, Tc-99, I-129, Ra-226, Th-229/230, Pa-231, and the Am/Cm/Cf isotopes. In each of these cases, the additional Shielded Cells preparation activities augment the analytical costs by a minimum of approximately $13K to a maximum of approximately $27K. The additional Shielded Cells activities also extend the turnaround times, typically by one to three work weeks. Given the higher costs and longer turnaround times of these analyses, developing new methods that eliminate the need for the additional Shielded Cells activities or reduce the scope of the additional Shielded Cells activities should be a priority.

Laboratory analyses that do not require additional Shielded Cells preparation activities, but are still particularly resource intensive and/or lengthy include the SRNL methods for Ni-59/63, Zr-93, Nb-94, and Cs-135. Although the existing methods have been demonstrated to be effective, there is the clear potential to hone these methods to make them more efficient.

Nuclides with concentrations consistently below the required MDLs, nuclides that accumulate over time due to in-growth from parent nuclides, and/or nuclides with negligible impacts on future environmental doses are ones that may be better quantified using theoretical relationships or process knowledge, as opposed to direct sampling and analysis. Included among this set of nuclides are H-3, Al-26, Cl-36, K-40, Nb-94, Pt-193, Ra-226, Ra-228, Ac-227, Th-229, Th-230, Pa-231, U-234, Pu-244, Cm-243, Cm-245, Cm-247, Cm-248, Cf-249, and Cf-251. In each of these cases, an assessment of the pros and cons of using an alternate characterization approach should be performed, to reach a decision of which approach provides the greatest potential benefit (in terms of data usability, characterization costs, and time requirements).

Estimates of the cost savings associated with implementing potential changes to SRNL's tank closure characterization program are summarized in Table 2-5. Note that some of the changes have already been made, some are in currently in progress, and some are planned for future pursuit. The total estimated cost savings for all changes identified in Table 2-5 is ~ $240,000 per tank closure characterization campaign. This is about 25% of the total radionuclide analysis labor cost per characterization campaign, based on the costing information presented in Table 2-1. (Note that the total radionuclide analysis labor cost does not capture the entire cost of SRNL's characterization campaign, as it does not includes costs associated with sample receipt, initial sample preparation, stable constituent analyses, statistical analysis of data, development of the characterization report, and laboratory waste disposition).

Approximately half of the savings associated with implementing changes to SRNL's radionuclide analysis program has already been achieved. Over the remaining 40+ SRS tank closure campaigns, implementation of all of the changes identified in Table 2-5 are expected to amount to a total savings of approximately ten million dollars. Of course, as SRNL's tank closure characterization program matures,

there is the expectation that additional improvements in the program will be made, leading to additional potential cost savings.

Table 2-5. Potential Cost Savings Per Tank Closure Characterization Campaign

Analysis	Potential Change	Estimated Cost Savings	Status
H-3	Eliminate due to low risk	$21K	Eliminated
Cl-36	Eliminate due to low risk	$50K	Eliminated
K-40	Eliminate due to low risk	$27K	Eliminated
Ni-59/63	Hone method	$15K	Future pursuit
Zr-93	Hone method	$5K	Future pursuit
Nb-94	Hone method	$5K	Future pursuit
Tc-99 I-129	Develop combined Tc-99/I-129 method reducing Shielded Cells prep effort	$10K	Future pursuit
Cs-135	Hone method	$10K	Future pursuit
Pt-193	Eliminate due to low risk	$34K	Eliminated
Ra-226	Improve recovery to eliminate need for extensive Shielded Cells prep	$20K	Development complete – planned implementation in next tank closure campaign
Ra-228	Calculate from Th-232 in-growth	$5K	Ready to implement
Th-229/230	Improve energy resolution to minimize need for extensive Shielded Cells prep	$25K	Development in progress – planned completion and implementation by next tank closure campaign
Pa-231	Hone method	$10K	Future pursuit

In most cases, the changes to make the analytical methodologies more cost effective also improve the turnaround times (TATs). Estimates of the time savings are more difficult to quantify than estimates of the cost savings, because competing priorities have a significant impact on the TATs, while only a minor effect on costs. Nonetheless, there is the expectation that in general, the improved methods will reduce TATs by an average of ~10-20%. For a program with a typical analytical duration on the order of six months, the changes are expected to reduce the duration by 2-4 weeks.

Although not included in Table 2-5, there are a couple of characterization method changes that should be mentioned. One is a potential new Am/Cm/Cf method that eliminates the waiting period for decay of Y-90 prior to removal of the processed samples from the Shielded Cells facility (see Section 4.5). Note that the decay waiting period is typically about two weeks. Although the potential new method is not expected to have a significant impact on the analysis cost, it is expected to reduce the TAT by two weeks.

In addition, a new waste removal system for use in numerous extraction chromatography radiochemical separations has been developed and is scheduled for testing and implementation in FY17 (see Section 3.0). The new waste removal system offers multiple potential benefits including reduced personnel dose, less chance of laboratory contamination, and reduced generation of radioactive solid waste. These changes will result in cost and time savings associated with waste management – however, the waste management costs are handled separately (outside of the customer characterization costs) and therefore are not addressed in Table 2-5.

2.9 <u>Strategy for Improving SRNL's Tank Closure Characterization Program</u>

A summary of the various attributes of SRNL's tank closure radionuclide analysis program, as discussed in this section, is provided in Table 2-6. In this table, check marks are used to identify radionuclides that should be considered when reaching a decision regarding the priority of how important a particular analysis is, and whether the existing method for characterizing the nuclide is a candidate for potential improvement or possible elimination. As mentioned before, this assessment addressed radionuclide characterization solely and ignored stable constituent characterization, as the resources that SRNL utilizes for tank closure radionuclide analyses currently far outweighs those utilized for stable constituent analyses. Note that this assessment focused on areas of the tank closure characterization program where the potential for improvement was greatest. As such, the assessment should not be considered complete – as additional improvement areas will surely be identified in the future, as the program matures and changes.

In considering improvements to the current characterization program, the general perspective was that characterization resources should be commensurate with the importance of the characterization data. In the past, this was not necessarily the case, as some of the very most resource intensive analyses were those for constituents that were identified as contributing negligible long-term environmental risks and those for constituents that were rarely or never detectable. Although non-detectability in itself is not a sufficient criterion to eliminate an analysis from the program, it is a consideration, particularly for those constituents that have negligible long-term risks, negligible chance of ever being detected, and high resource demands challenging effective and timely completion of analyses for higher potential impact constituents.

Identification of the characterization activities in greatest need of improvement requires consideration of many factors and agreement of multiple stakeholders who have the potential to be impacted by such programmatic changes. This includes the users of the characterization data, as well as the regulators who review the results and conclusions to reach an ultimate decision regarding conclusion integrity and acceptability.

The goal of the assessment presented in this section is to provide a basis for continuing improvement of the tank closure program, in a manner that maintains data integrity, but lowers the resource needs such that a greater portion of the resources is available for competing priorities, and the challenges of meeting regulatory milestones will be lessened.

2.10 <u>Conclusion</u>

Several potential means of making SRNL's tank closure characterization program more cost effective and timely are available, and are in the process of being implemented. Many of the approaches are based on analytical method improvements, including those to lessen the need for extensive Shielded Cells preparation activities, those to increase radiochemical yields, those to improve measurement resolution, those to reduce the analytical TATs, and those to speed-up commonly used waste removal processes. Other improvements are based on elimination of analyses for constituents contributing negligible long-term environmental risk or on using parent in-growth assumptions to estimate constituent concentrations. Although the laboratory changes resulting in higher cost effective characterization practices are just beginning for the tank closure program, they are already reducing costs on the order of $100K per characterization campaign, with the expectation that costs will be reduced by another $100K per campaign in the next one to two years. Over the life of the SRS tank closure program, the goal is to make changes that result in savings of several million dollars.

Table 2-6. Radionuclide Characterization Attributes for Tank Closure Applications

Attribute	H-3	C-14	Al-26	Cl-36	K-40	Co-60	Ni-59	Ni-63	Se-79	Sr-90	Y-90	Zr-93	Nb-94	Tc-99	Pd-107	Sn-126	Sb-126	Sb-126m	I-129	Cs-135	Cs-137	Ba-137m	Sm-151	Eu-152	Eu-154	Pt-193	Ra-226	Ra-228	Ac-227	Th-229	Th-230	Th-232	Pa-231	U-232	U-233	U-234	U-235	U-236	U-238	Np-237	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Pu-244	Am-241	Am-242m	Am-243	Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249	Cf-251
Dominant Activity (Typically >5% of Ci Inventory During the next 100,000 Years)							X	X		X	X	X		X						X	X	X																			X	X	X				X									
Analysis Typically Requires Extensive Shielded Cells Preparation Steps				X										X					X								X	X		X	X		X																X			X	X	X	X	X
High Analytical Cost and/or Long TAT		X		X	X		X	X								X	X		X								X	X		X	X		X																				X	X	X	X
Typically Unable to Detect (<MDL)	X		X	X	X								X														X	X	X																			X		X		X	X	X	X
Principal Contributor to Environmental Risk		X											X	X	X				X	X							X			X	X		X		X	X	X			X	X	X	X				X									
In-growth Potentially Increases the Long Term Source																											X	X		X	X		X		X	X				X			X													
Potential Alternative Characterization Approach(es)							X	X		X	X	X							X	X							X	X	X	X	X		X															X	X	X	X	X	X	X	X	X

2.11 <u>Recommendation</u>

Continue to focus on improving SRNL's tank closure characterization program, using technically-based decisions to understand characterization needs and optimize characterization methods such that future characterization approaches are appropriate, cost effective, and timely.

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3.0 Design/Assembly of Extraction Chromatography Waste Removal System

Many current radioanalytical separation methods utilize solid:liquid phase extraction chromatography for producing high purity analyte fractions to be used in measurements. In extraction chromatography, sample solutions are passed through columns packed with solid phase resin beads that have been activated with functional groups targeting extraction of one or more specific radioelements. Prior to passing the sample solutions through the columns, the extraction chromatography resins are conditioned with specific chemical solutions in a sequence that maximizes retention of the radioelement being purified. Following conditioning, the sample solutions are fed into the columns, the target radioelement is captured onto the surface of the resin (via reaction with the functional group), and then a series of chemical wash solutions are passed through the column to remove the interfering elements. Finally, the purified target radioelement is removed from the column, using a chemical solution chosen for effective radioelement elution. The purified radioelement aliquot is then utilized in the radioanalytical measurements.

Feeding and discharge of the conditioning solutions, the sample solution, and the wash solutions is currently performed in a manner that requires numerous manual manipulations of highly radioactive liquids in a limited workspace. The resin-containing columns are placed into holes on a vacuum manifold lid, and the lid is placed over reservoirs within a vacuum box. The radiological worker performing this type of analysis must, for every step of the multi-step separation, add reagent to each column, apply vacuum so the reagent is pulled through the resin column at an appropriate rate, disassemble the vacuum box by removing the lid of the vacuum box (which contains the columns), place the box in a stable configuration within a radiological containment unit, remove the filled collection reservoirs and dispose of the highly radioactive residue in the secondary vessel, replace the collection reservoirs in the vacuum box, replace the lid and columns, and continue to the next step. Such manipulations come with significant inherent contamination risks, dose consequences, and conditions impeding the processing throughput.

Commercial systems incorporating complex plumbing and computer interfaces to provide completely automated feed and removal of reagent solutions through columns are available, but are applicable to very limited set of extraction chromatography applications. Furthermore, they are expensive, require significant maintenance, and have a large footprint. Such systems are better suited to laboratories that perform a small range of routine analyses than those that perform a comprehensive range of analyses under a variety of complex matrix conditions.
With that in mind, development of an improved waste removal system for use with SRNL's wide range of extraction chromatography separations was undertaken.

3.1 Objective

Development of an extraction chromatography waste removal system that:

- Reduces contamination risk and personnel dose
- Improves processing throughout
- Is effective, economical, and practical

3.2 Approach

In developing an improved waste removal system, a couple of key attributes were targeted: a) a system that will accommodate the maximum number of columns utilized in a normal analytical batch; b) a column feed and discharge configuration that minimizes the potential for radionuclide contamination and

minimized worker dose exposure time; c) a waste collection system that accumulates all column waste into one aliquot, so the cumulative waste can be disposed in a single discharge, thus maximizing disposition efficiency; d) a system that will be inexpensive and simple to fabricate and operate; and e) a system with a small footprint and portability, to fit into a limited workspace and allow easy transport into and out of the workspace.

Initially, SRNL's plan was to design a system that included integration of hardware, plumbing, and software to produce a semi-automated process, much of which could be controlled remotely. However, early in the engineering phase of the project, it was determined that the advantages of a remotely operated system were clearly outweighed by the simplicity, cost-effectiveness, and small footprint of a manually-operated system. As such, integration of the software control was dropped from the design.

The waste removal system that was developed was designed to operate using two new primary components: 1) a Column Vacuum Manifold Device that holds the extraction chromatography columns and attaches to a vacuum source, to increase the liquid flow rate through the columns; and 2) a Waste Receipt and Accumulation Device that receives the effluent waste, accumulates it, and allows for cumulative discharge of the waste into the high activity waste drain. In FY16, three prototypes of the Column Vacuum Manifold Device and two prototypes of the Waste Receipt and Accumulation Device were developed. Details of the prototypes are provided below.

3.3 <u>Column Vacuum Manifold Device</u>

Figure 3-1 shows the first prototype of the device that holds the extraction chromatography columns and connects to the vacuum source (the Column Vacuum Manifold Device). As shown in the figure, the device holds twelve extraction chromatography columns, contains twelve individual control knobs for adjusting the strength of the vacuum through each column, and has half the control knobs located on one side of the device and half the control knobs located on the other side of the device. The footprint of the device has an area of 26 in^2, as the base which houses the column holders and knobs has a length of thirteen inches, a width of two inches, and a height of one and three-eighths inches.

In this first prototype, the height of the column ports is four inches. Note that in this figure, only the first column port (the one on the farthest left side) contains a column assembly loaded with an actual resin-filled column. This was done for illustrative purposes, to show the modular design of the column assemblies. A standard laboratory pipet tip provides the lower-most connection to the waste removal device (the pipet tip fits into a rubber stopper inserted into the top of the column port), the resin-filled column fits into the upper end of the pipet tip, and a 10 mL syringe tube attaches to the top of the resin-filled column. The syringe tube acts as the reservoir where the chemical reagents are added and then introduced to the column.

The vacuum port (the port where the vacuum source is attached) is shown on the lower right hand corner of the figure – it is the hole located on the end of the base. Although missing from the figure, a vacuum tube fitting is installed into the vacuum port to provide connection to the vacuum source.

Figure 3-1. **First Prototype of the Column Vacuum Manifold Device**

Operational testing of this prototype within the confines of the radiohood identified a clear limitation of the design – namely, that placement of the vacuum control knobs on both sides of the device made knob adjustment very clumsy, due to the need to either reach behind the device without full visibility of the knobs or to require 180 degree rotation of the device to visibly access the "rear" adjustment knobs. Neither of these options was considered acceptable, knowing the increased potential for contamination and/or other hood processing mistakes when performing such manipulations within the space and access limitations of the radiohood.

Because of this issue, a second prototype of the Column Vacuum Manifold Device was developed – one with all vacuum adjustment knobs on the same side of the device. As shown in Figure 3-2, the second prototype utilized the same base as the first prototype (13" x 2" x 1⅜"), but utilized alternating column port heights to accommodate all vacuum adjustment knobs on the same side of the device. Note that Figure 3-2 shows the vacuum tube fitting that was installed into the base (see lower right corner of the photograph), which was omitted from the figure of the first prototype (Figure 3-1).

Figure 3-2. **Second Prototype of the Column Vacuum Manifold Device**

With this new design, the heights of column ports 1, 3, 5, 7, 9, and 11 (from left to right) were all five inches, whereas the heights of column ports 2, 4, 6, 8, 10, and 12 (from left to right) were all four inches. Although this new design remedied the problems associated with having the knobs on both sides of the device, it created three new problems, which were not recognized until the second prototype was tested. The first problem was due to the alternating column heights, which impeded access to the openings of the "lower" syringe tubes. A possible solution to this issue was reduction of the length of the pipet tips connected to the "higher" column ports by one inch, to compensate for the taller port heights. Although plausible, this solution required additional handling of the pipet tips, as well as protocols to assure that adjustments to the pipet tips were appropriate and consistent. The second problem with the new design was the close proximity of the adjustment knobs, which hindered access to the knobs and adjustment control, particularly in the confines of the radiological hood, given the potential for contamination and for other hood processing mistakes. The third problem was instability due to the increased height in conjunction with the small footprint, which raised concerns associated with increased potential for laboratory and/or personnel contamination.

To address these issues, a third prototype of the Column Vacuum Manifold Device was designed and developed. The third prototype, pictured in Figure 3-3, eliminated all potential issues associated with vacuum adjustment knobs in the vicinity of the columns, as it removed them from the Column Vacuum

Manifold Device, with the expectation that vacuum control would be engineered into the Waste Receipt and Accumulation Device. This change made the Column Vacuum Manifold Device significantly simpler, which was a major advantage given the constraints of operations within the radiohood. In addition to being simpler, the third prototype did not suffer from the limitations of having different syringe tube heights, and the simple design facilitated a smaller footprint area (20 in^2) with significantly increased stability. This minimized the possibility of tipping (therefore minimizing risk of personnel contamination), due to the shorter length and a slightly increased width. Specifically, the dimensions of the third prototype base were 7¼" (length) x 2¾" (width) x 2" (height). Whereas the first and second prototypes utilized rubber stoppers to connect the pipets to the ports, pipet tips were attached directly to the base of the third prototype, via three-sixteenth inch diameter holes drilled into the polycarbonate base.

Figure 3-3. **Third Prototype of the Column Vacuum Manifold Device**

3.4 <u>Waste Receipt and Accumulation Device</u>

Figure 3-4 shows the first prototype of the Waste Receipt and Accumulation Device, which combines a one liter separatory funnel with a series of fittings to incorporate an enclosed waste receipt port, a vacuum source port, and a vacuum venting port. In this first prototype, the waste receipt and accumulation device is held in place with a standard laboratory ring stand. In operation, the white port on top (the one without the green actuation knobs) is the waste receipt port and is connected via tubing to the vacuum port on the base of the Column Vacuum Manifold Device. The left port (with the green actuation knob) is the vacuum source port and is connected via tubing to the vacuum source. The lower right port (with the green actuation knob) is the vacuum venting port, allowing easy control of vacuum actuation and termination. Whereas during the initial design of the Column Vacuum Manifold Device, there was a desire to install individual vacuum control to each column, it was later concluded that a single vacuum control for all columns was much more practical and advantageous from the standpoint of simplicity.

The total height of the device is 21", from the top of the waste receipt port to the bottom of the separatory funnel nozzle. Given the relatively high weight and large size of the device, it was determined that a standard ring stand did not provide sufficient stability to eliminate the possibility of tipping the device during use. Consequently, a second prototype of the device, one where the separatory funnel apparatus was merged with a specially-engineered, high stability stand, was designed and developed.

Figure 3-5 shows the second prototype of the Waste Receipt and Accumulation Device. The primary differences between the second and first prototype are: a) the holding ring for the separatory funnel is significantly more robust; b) the linkage between the holding ring and the stand is significantly more robust; c) the center of gravity of the device is much closer to the holding rod axis of the stand; d) the base of the stand has been supplemented with four relatively large diameter machined feet (1¼" each), for added stability; and e) the base of the stand has been supplemented with a special waste discharge aperture, for improved ergonomics during waste disposal operations.

3.5 <u>Status of Waste Removal System</u>

An invention disclosure has been submitted for the waste removal system (based on the third prototype of the Column Vacuum Manifold Device and the second prototype of the Waste Receipt and Accumulation Device).

3.6 <u>Conclusions</u>

1) The extraction chromatography waste removal system has been sufficiently developed to offer the potential of reducing contamination risk and dose, improving processing throughput, and being effective, economical, and practical.

2) Laboratory testing of the waste removal system during extraction chromatography separations of real world samples in a radiohood will be required to demonstrate the effectiveness of the system and/or determine any modifications needed to optimize use, prior to implementation.

3.7 <u>Recommendation</u>

Pursue testing, optimization, and implementation of the waste removal system during FY17.

Figure 3-4. **First Prototype of the Waste Receipt and Accumulation Device**

Figure 3-5. **Second Prototype of the Waste Receipt and Accumulation Device**

4.0 Alternative Radiochemical Separation Protocols Holding Promise for Improving High Resource Demand/Time Consuming Analysis Methods

Most of SRNL's existing radioanalytical methods have not yet been optimized, as they were developed over short timeframes limited by funding restrictions and the need to meet aggressive reporting deadlines. This has a particular impact in cases where the existing analytical approach is highly labor intensive, highly time consuming, subject to matrix interferences, and/or incapable of meeting the targeted minimum detection limits. Examples of methods fitting into this category include the analytical approaches that have recently been utilized for analyzing Tc-99, I-129, Ra-226, Pa-231, Th isotopes, and Am/Cm isotopes.

4.1 Objective

Develop and evaluate alternative radiochemical separation protocols holding promise for improving high resource demand/time consuming analysis methods. During the past year, the alternative radionuclide analysis methods targeted included those for:

- Radium-226

- Thorium-229 and thorium-230

- Specific trivalent actinide isotopes (such as americium-242m, americium-243, curium-243, curium-245, and curium-247)

4.2 Approach

The previously used radioanalytical methods for these isotopes suffered from one or more limitations impacting the ability to perform analyses effectively and efficiently – such limitations included low chemical yield, low measurement sensitivity, low measurement resolution, and/or a long holding time for radiological decay of interfering isotopes prior to measurement. Discussions of the previously used methodologies and the laboratory approaches utilized for developing the alternative separation and analysis protocols are provided below.

4.3 Ra-226 Separation and Analysis

4.3.1 Previously Used Ra-226 Radiochemical Separation Methodology

In the previously used Ra-226 analysis methodology, aliquots of tank waste samples were digested in the Shielded Cells using a sodium peroxide fusion dissolution method. The sample digestions were performed in the Shielded Cells, due to the high dose associated with the relatively large sample aliquot size required to obtain the low desired Ra-226 analytical minimum detection limit. The digest solutions were then decontaminated from interfering nuclides in the Shielded Cells with a series of extraction resins added in batch contact mode. Bio-Rad AMP (ammonium molybdophosphate) was added to reduce the Cs-137 concentrations. Eichrom Strontium resin was added to reduce the Sr-90 concentrations. Eichrom Diphonex resin was added to reduce the Y-90, actinide isotope, and lanthanide isotope concentrations.

The decontaminated sample solutions were then removed from the Shielded Cells and transferred to the radiohoods in the analytical laboratories, where they were treated again to the same batch contact decontamination steps as performed in the Shielded Cells. Radium was then extracted using cation exchange resin, and the radium chemical yields were traced with Ra-224 and Ra-226. Yields from this

methodology were low and erratic (the mean radium yields were on the order of 10%, but could be as low as 1-3%). Improvements in these yields were desired so that smaller aliquots of sample could be used to obtain the desired minimum detection limits – thus, eliminating the need for a specific Shielded Cells digestion dedicated to the Ra-226 analysis. Improvements in the yields would also eliminate the need for the specific decontamination steps performed in the Shielded Cells that were previously required for the Ra-226 analysis. The net result of such changes would be a significant reduction in analytical costs and turnaround times.

4.3.2 Evaluation of Potential New Ra-226 Radiochemical Separation Methods

Several extraction methods were evaluated for testing. Eichrom's Lanthanide resin shows affinity for radium per the information reported in the literature.[1] However, its selectivity for radium over the other elements that would be present in SRS high level waste matrices appears poor. Eichrom also produces a MnO_2 based resin which shows affinity for radium, but again, does not appear to have the selectivity necessary to effectively extract radium from tank waste samples. 3M produces a radium extraction technology called Empore Radium RAD Disks, with the claim that the technology is highly selective for radium, without retaining other alkaline earth metals such as strontium. This characteristic is essential for a radium extractive medium used for SRS tank samples, since strontium-90 is a dominant radioisotope in these samples and the driver for extremity dose associated with such samples. Available literature suggests that the active extractant in Empore Radium RAD disks is IBC Advanced Technologies Superlig 640.[2] The same reference source indicates that Superlig 640 co-extracts strontium with radium, which conflicts with the 3M literature.

4.3.3 Testing of Empore Radium Disks on SRS Supernatant Samples and Acid Blanks

Initial tests were performed using the 3M Empore Radium RAD disks to extract radium from SRS supernatant samples as well as from spiked acid blanks. Two milliliter aliquots of supernatant were acidified to 2 M nitric acid, with the total sample volume being ~38 mL after acidification. The supernatant samples were traced with Ra-224, while the acid blanks were traced with both Ra-224 and Ra-226. Cesium-137 concentrations in the samples were reduced using multiple Bio-Rad AMP batch contact strikes. In these strikes, 0.2 grams of AMP was added to 38 mL of sample solution and the combined material was agitated for 30 seconds. After each strike, the AMP solids were removed via 0.45 µm filtration. Following the AMP strikes, radium was extracted from the solutions by passing the solutions through the Empore Radium RAD disk at a nominal flow rate of one milliliter per second. The extractive medium was then rinsed with 150 mL of 2 M nitric acid, and the rinsed RAD disk was loaded into a 2.0 mL test tube for gamma analysis.

Radium recoveries for the two SRS tank waste samples were measured as 87% and 95%, while radium recoveries for the two acid blanks were measured as 84% and 87%. The similarity between the recoveries for the real waste samples and the acid blanks suggests that the additional constituents in the real waste samples did not reduce the radium recovery effectiveness.   Following the cesium removal step, the only measurable gamma emitting isotope present in the supernatant was Sn-126. The Empore Radium RAD disks had no measurable affinity for the Sn-126, as measurements identified that the Empore disk Sn-126 recoveries were <0.62% and <0.61%. This is a good thing, as it suggests that interference from Sn-126 is minimal or non-existent.

4.3.4 Assessment of Other Potentially Interfering Isotopes

A test was performed to evaluate the affinity of four common interfering isotopes found in SRS sludge matrices for the Empore disks. Twenty milliliter aliquots of 2 M nitric acid were spiked with Co-60, Sr-90, Eu-154, and Am-241. The test samples for each isotope were prepared in triplicate. The flow rates were adjusted to ~1 mL/second. The test samples were passed through the Empore disks, and then the disks were rinsed with 150 mL of 2 M nitric acid, with the final rinsate solutions being analyzed for the isotopes.

Recoveries for the cobalt, europium, and americium isotopes were all minimal (the Co-60 recoveries were <0.09%, <0.05%, and <0.05%; the Eu-154 recoveries were 0.1%, 0.08%, and 0.004%; and the Am-241 recoveries were <0.08%, <0.02%, and <0.04%). In contrast, the Sr-90 recoveries were quantitative, with measurements of 102%, 105%, and 105%. These high recoveries indicated that an alternative rinsing scheme (one significantly reducing the recovery of strontium) would be necessary for the Empore disk technology to be useful for tank waste radium purifications.

4.3.5 Reducing the Strontium Recovery While Maintaining the Radium Recovery

Test results showing quantitative recovery of Sr-90 indicated that an alternative rinsing scheme would be necessary (one that significantly reduces the strontium recovery) for the Empore disk technology to be useful for tank waste radium purifications. Clearly, quantitative recoveries for Sr-90 would be quite detrimental to the use of the Empore Radium disks for SRS tank closure samples. As such, a further review of the literature was conducted, to determine what options were available for reducing the strontium recovery during Empore disk use. A thesis focusing on a different Superlig extractant, Superlig 620, addressed using citrates to separate strontium from barium.[3] A test evaluating citrates as a possibility to separate Sr from Ra on the Empore Radium disk (suspected to be Superlig 640) was executed. Two 20 mL aliquots of 2 M nitric acid were spiked with Ra-226, and two were spiked with Sr-90. The samples were filtered through Empore Radium disks that had been conditioned with 50 mL of 2N nitric acid. The filters were rinsed with 150 mL of 2N nitric. One filter in each isotope set was also rinsed with 50 mL of 0.5 M sodium citrate. The Sr-90 spiked sample disks were placed in liquid scintillation counting (LSC) cocktail and analyzed by LSC after a period of 10 days ingrowth of the Y-90 daughter. The Ra-226 disks were then placed in test tubes and analyzed by gamma spectrometry.

As a citrate wash step showed promise in selectively reducing Sr-90 over Ra-226, a sodium citrate wash was evaluated with two sets of real waste samples of SRS Tank 50 salt feed spiked with radium tracers. Radium tracer was added to 2 mL of tank sample. The sample was acidified, resulting in a 38 mL solution of ~2 N nitric acid. Two blank samples spiked with radium were also run thru this process. The samples were run through a cesium-removal process, with each being treated with a batch addition of 0.2 g Bio-Rad AMP, contacted for 30 seconds, and then filtered. The filtrate was then passed through an Empore Radium disk that had been conditioned with 50 mL of 2 N nitric acid. The disks were rinsed with 150 mL of 2 N nitric. Then the disks were rinsed with 100 mL of 0.1 M sodium citrate. The disks were then loaded into 2 mL test tubes and assayed on a robotic high purity germanium (HPGe) well gamma spectrometer.

A more detailed study evaluating a range of concentrations of sodium citrate wash steps was than conducted. Six concentrations (0.1 M, 0.09 M, 0.08 M, 0.07 M, 0.06 M, and 0.05 M) were evaluated. One sample for each concentration was spiked with Sr-90 and one was spiked with Ra-226. Samples of 20 mL 2 N nitric acid were generated and spiked with the appropriate isotope. Empore Radium filters were set up for each sample, and were conditioned with 50 mL of 2 N nitric acid. The samples were added to their respective filters. The sample filters were rinsed with 150 mL of 2 N nitric acid. Each disk was then

rinsed with 100 mL of the appropriate concentration of sodium citrate wash. The Sr-90 disks were analyzed using LSC, while the Ra-226 disks were analyzed using gamma spectrometry.

As the Sr-90 recoveries appeared to be relatively flat over the range of the concentrations, while the Ra-226 recovery appeared to be increasing as the wash concentration decreased, the low end of the citrate waste concentration range was chosen to continue real waste tests. A 0.05 M sodium citrate wash was evaluated with another set of real waste samples of SRS Tank 50 spiked with radium tracers. Radium tracer was added to 2 mL of tank sample. The sample was acidified, resulting in a 38 mL solution of ~2 N nitric acid. Two blank samples spiked with radium were also run through this process. The samples were run through a cesium-removal process, each treated with a batch addition of 0.2 g Bio-Rad AMP, contacted for 30 seconds, and then filtered. The filtrate was then passed through an Empore Radium disk that had been conditioned with 50 mL 2 N nitric acid. The disks were rinsed with 150 mL 2 N nitric acid. Then the disks were rinsed with 100 mL 0.05 M sodium citrate. The disks were then loaded into 2 mL test tubes and assayed on a robotic HPGe well gamma spectrometer.

4.3.6 Test Results

On spiked acid aliquots, the 0.5 M sodium citrate wash reduced the recoveries of Sr-90 by a factor of 61 (to slightly less than 2%), while only reducing the recoveries for Ra-226 by a factor of 2.9 (to ~30%).

On spiked real waste salt feed samples that had been processed through cesium-removal, then passed through the Empore disk, rinsed with the 0.1 M sodium citrate, and then eluted, the radium recoveries were: a) 39%, 52%, and 52% for the first sample; and b) 46%, 52%, and 63% for the second sample. Under these conditions, on average, the radium recovery was ~50%.

On spiked acid blanks that had been processed through cesium-removal, then passed through the Empore disk, rinsed with the 0.1 M sodium citrate, and then eluted, the radium recoveries were: a) 62% and 44% for the first set; and b) 43% and 40% for the second set. Under these conditions, on average, the radium recovery was ~47%, which is approximately equal to that seen for the real waste salt feed samples.

For Empore disks eluted after being washed with rinses of 0.10 M, 0.09 M, 0.08 M, 0.07 M, 0.06 M, and 0.05 M sodium citrate: a) the Sr-90 recoveries from the spiked acid blanks were 1.6%, 0.9%, 1.8%, 0.3%, 1.9%, and 2.0% respectively; and b) the Ra-226 recoveries from the spiked acid blanks were 43%, 68%, 56%, 95%, 94%, and 72%, respectively. Given that the Sr-90 recoveries were relatively low ($\leq 2\%$) across the 0.05-0.10 M sodium citrate concentration range, while the Ra-226 recoveries generally appeared to increase as the citrate concentration dropped, it was thought that use of a 0.05 M sodium citrate rinse offered the greatest likely benefit. As such, final set of real waste tests was performed under this condition.

Using a 0.05 M sodium citrate rinse with spiked samples being processed through cesium removal and the Empore Radium disk, the Ra-226 recoveries were: a) 95%, 90%, and 86% for the three real waste samples; and b) 83% and 85% for the two spiked blanks. Such recoveries are significantly higher than those obtained using the previous radium method (the cation exchange method) and sufficiently high to pursue use of the new separation method for future tank closure Ra-226 analyses.

4.3.7 Conclusion

The radium separation scheme that has been developed using the Empore Radium Disks has increased the yields of radium by approximately an order of magnitude compared to what was previously being obtained using the cation exchange approach. This increase in yield will allow radiochemistry to be conducted on smaller aliquots of tank closure samples. Smaller aliquots of samples running through the procedure should allow the radiochemistry to be conducted entirely in the radiohoods of the analytical laboratories as opposed to performing the initial decontamination steps in the Shielded Cells. This will have the impact of reducing the costs and time requirements of future tank closure Ra-226 analyses.

4.3.8 Recommendation

During the next tank closure characterization campaign, perform comparative Ra-226 analyses using both the previous radiochemical separation method (the method utilizing initial decontamination chemistry in the Shielded Cells and final radium purification via cation exchange) and the new Empore disk method (where smaller sample aliquots are processed entirely in Analytical Development's routine radiochemical laboratories). Compare the analytical results derived from both approaches and use the comparison in combination with the applicable analytical costs and turnaround times to reach a conclusion on which method is most advantageous.

4.3.9 References

[1] Horwitz, E. P. et al., "Chemical Separations for Super-Heavy Element Searches in Irradiated Uranium Targets," Inorganic & Nuclear Chemistry 37, pp. 425-434, 1975.

[2] Izatt, S. R, R. L. Bruening, K. E. Krakowiak, and R.M. Izatt, "The Selective Separation of Anions and Cations in Nuclear Waste Using Commercially Available Molecular Recognition Technology (MRT) Products," WM'03 Conference, Tucson, AZ, February 23-27, 2003.

[3] Clements, J., "Characterization of the IBC Technologies Superlig 620 Solid Phase Extraction Resin with Applications for Automated Process Monitoring," Clemson University, Department of Environmental Engineering and Science, Masters Thesis, May 2007.

4.4 Th-229/Th-230 Source Preparation

4.4.1 Previously Used Th-229/230 Source Preparation Method and Analysis

In the previously used Th-229/230 analysis methodology, purified thorium fractions were prepared for alpha spectrometry measurements via cerium fluoride co-precipitation. (Prior to the co-precipitation step, two stages of quaternary amine based solid phase extraction were utilized to produce the purified thorium fractions, which were eluted in 10 mL of 9 M hydrochloric acid). Cerium fluoride co-precipitations were performed by adding 0.10 mg cerium to each purified thorium fraction, followed by one milliliter of concentrated hydrofluoric acid. The precipitated cerium fluoride was captured onto the surface of a 0.5 inch diameter 0.45 µm filter membrane, which was subsequently rinsed with 2 mL deionized water and then four drops of isopropanol, to displace the water. After drying, the filter membrane was transferred to a counting plate, for alpha spectrometry measurements.

Although the cerium fluoride co-precipitation approach was rapid and simple, it resulted in alpha counting spectra with limited energy resolution, due to the inherent thickness of the cerium fluoride layer

which facilitated energy straggling. Because of the limited energy resolution, the MDLs for the Th-229 and Th-230 isotopes were higher than targeted, particularly in cases where large amounts of Th-228 and Th-232 raised the baseline counting rates for the minor isotopes (such as in cases where tank waste contained material associated with thorium fuel cycle tests).

4.4.2 Evaluation of Alternative Th-229/230 Source Preparation Method and Analysis

In an effort to maximize energy resolution of the thorium isotopes (for the purpose of lowering Th-229 and Th-230 MDLs), assessment of an electroplating method for preparing purified thorium fractions for alpha spectrometry measurements was pursued. The primary benefit of an electroplated counting source over the previously used cerium fluoride source was the potential for making the source ultra-thin, thereby minimizing energy straggling impeding alpha spectrometry energy resolution. A secondary benefit of the electroplated counting source is that the thorium would now be securely fixed to the planchet, increasing safety of the analyses and reducing the opportunities for cross-contamination. In contrast, the co-precipitated source (the cerium fluoride precipitate) was present as a layer on the surface of the counting surface, in a form that was easily removable and thus more subject to personnel contact and/or laboratory cross-contamination.

A potential thorium electroplating protocol was identified based upon findings in the literature and was tested using aliquots of SRS Tank 50 salt feed waste spiked with Th-232. For evaluation purposes, the electroplating method was compared against the cerium fluoride co-precipitation method. In both cases, the thorium was extracted from 5 mL aliquots of the spiked salt feed using Eichrom TEVA extraction chromatography resin. In the case of the fractions being prepared for electroplating, the thorium extracts were dried, and then re-dissolved in 3.0 mL of 0.8 M sulfuric acid. Subsequently, the solutions were pH neutralized with 3.0 mL of 0.8 M sodium hydroxide, and then diluted with 12.5 mL deionized water.

Using these solutions, thorium was electroplated onto 0.5 inch diameter stainless steel planchets under a current of 0.5 A for 2.5 hours, via a Phoenix Technologies electroplater (see Figures 4-1 and 4-2). During the electroplating process, the stainless steel planchet served as the cathode and a platinum wire served as the anode, with voltage fluctuations from zero to approximately 20 volts.

Examples of thorium alpha spectra generated utilizing the electroplating source preparation method and the previously used cerium fluoride co-precipitation method are given in Figures 4-3 and 4-4, respectively. In each figure, number of counts is given on the vertical axis and alpha particle energy is given on the horizontal axis. With respect to thorium isotope measurements, it is important to note that: a) the large peak seen at an energy of ~3.9 MeV is attributed to Th-232; b) the small peak seen at an energy of ~4.6 MeV is attributed to Th-230; c) the small peak seen at an energy of ~4.8 MeV is attributed to Th-229; d) the large peak seen at an energy of ~5.4 MeV is attributed to Th-228; e) the small peak seen at an energy of ~5.6 MeV is attributed to Ra-224 (the short-lived progeny of Th-228 that has grown-in following the thorium purification), and f) the small peak seen at an energy of ~6.0 is attributed to Th-227.
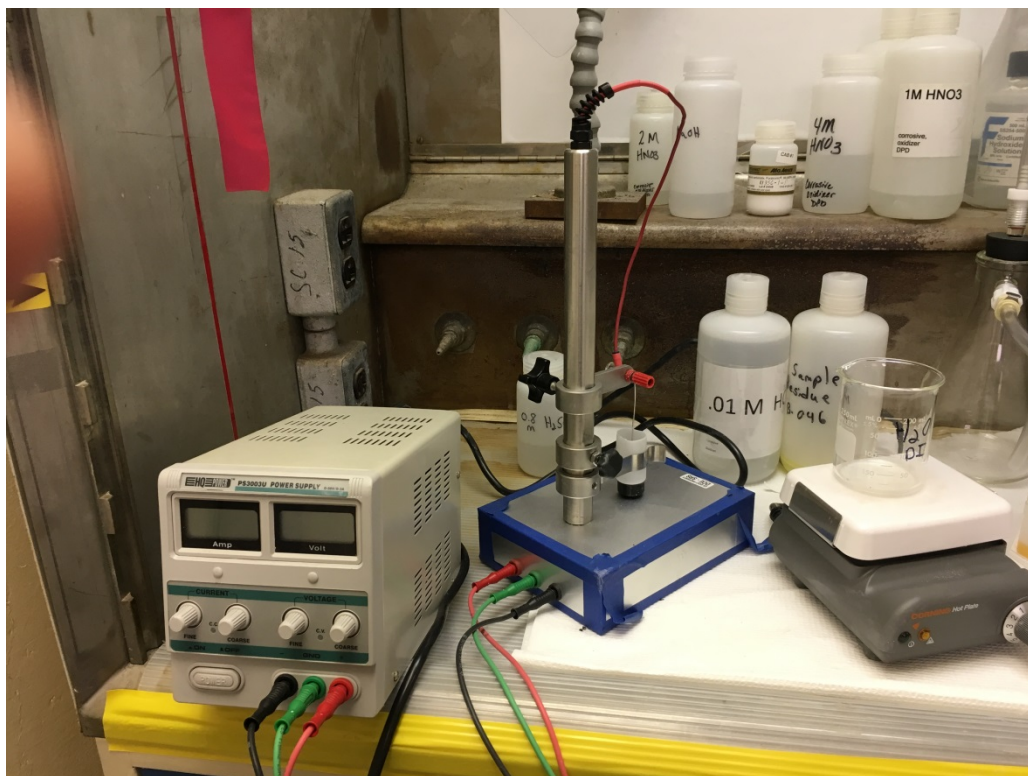
Figure 4-1. Electroplating Equipment in Hood

Figure 4-2. Electroplating Apparatus with Anode Extended into Vessel Holding the Cathode
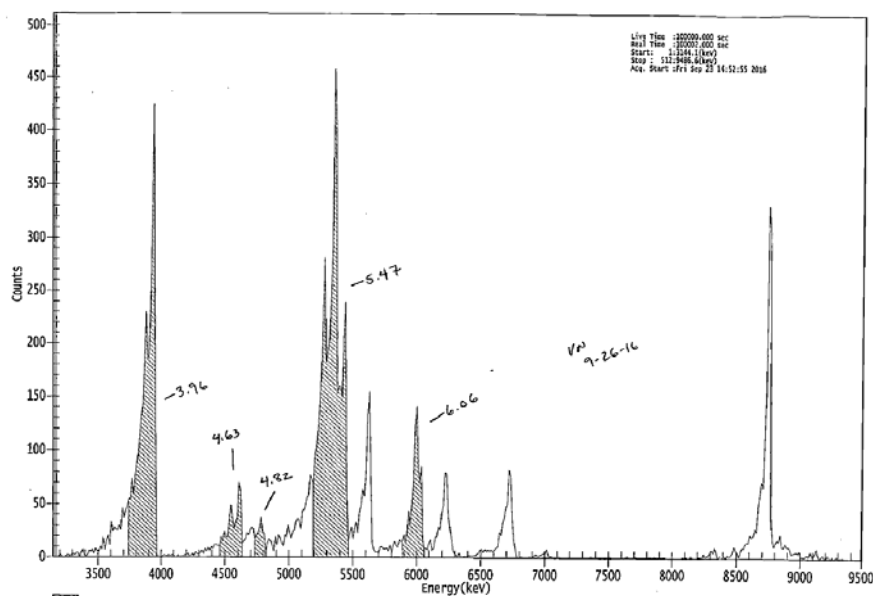
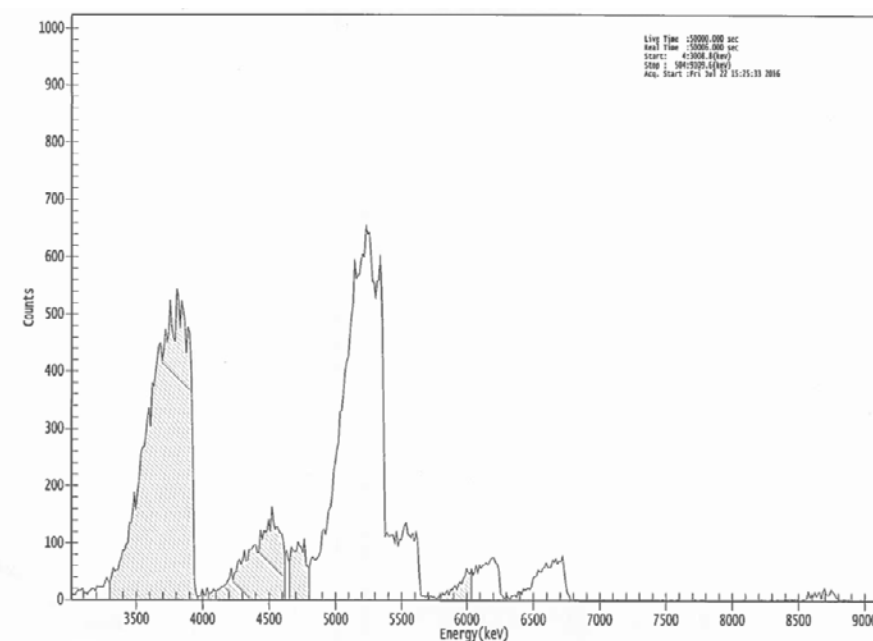**Figure 4-3. Electroplated Thorium Alpha Spectrum**

Figure 4-4. Co-Precipitated Thorium Alpha Spectrum

Clearly, the energy resolution of the electroplated source is significantly greater than that of the co-precipitated source. For instance, the full width half maximum (FWHM) for the Th-232 peak (~3.9 MeV) for the electroplated source is ~100 KeV, as compared to that of the co-precipitated source, which is ~500 KeV, approximately five times wider. Another example is the Th-227 peak (~6.0 MeV), which is completely resolved from the adjacent peak (~6.2 MeV) in Figure Z-1, but not resolved from the same adjacent peak in Figure Z-2. Although the higher resolutions associated with the electroplated source do not necessarily correlate with lower MDLs on a one-for-one basis, they clearly facilitate greater analytical sensitivity.

Optimization and implementation of the electroplating protocol into SRNL's routine analytical operations in the future will be advantageous, to provide a practical means of lowering MDLs associated with Th-229 and Th-230 analyses, without having to depend on labor-intensive processing of larger sample aliquots in the Shielded Cells.

4.4.3 Conclusion

Electroplating clearly improved the energy resolution obtained during alpha spectrometry Th-229 and Th-230 measurements over that encountered using the cerium fluoride co-precipitation source preparation method. The increase in resolution had the impact of lowering the MDLs for the Th-229 and Th-230 salt feed measurements. Additional experiments will be necessary to optimize the electroplating protocols on this type of sample matrix and to determine the extent the MDL can be improved. Although effectively demonstrated for analysis of examples of salt feed tank waste material, the electroplating method will still need to be evaluated for effectiveness in Th-229/230 measurements of other tank waste matrices, such as sludge and post-cleaning residue.

4.4.4 Recommendation

During the next tank closure characterization campaign, perform comparative Th-229/230 analyses using both the previous source preparation method (cerium fluoride co-precipitation) and the new electroplating method. Compare the analytical results derived from both approaches to quantify the extent that the improved resolution of the electroplating method lowers MDLs for the Th-229 and Th-230 isotopes. Quantify the chemical yields associated with the electroplating method and optimize the electroplating method to raise chemical yields to their maximum, so future tank closure thorium analyses can be performed without requiring "special preps" in the Shielded Cells.

4.5 Yttrium/Trivalent Actinide Separation Protocol

4.5.1 Previously Used Trivalent Actinide Purification Approach

The suite of radionuclides requiring analysis in the SRS tank closure characterization campaigns includes several trivalent actinides. While the specific set of trivalent actinides requiring characterization has varied somewhat from tank to tank, it has included Am-241, Am-242m, Am-243, Cm-243, Cm-244, Cm-245, Cm-247, Cm-248, Cf-249, Cf-251, and Cf-252. The current radiochemical separation scheme for these analyses includes an initial radiochemistry step in the Shielded Cells. During this step, the group of trivalent actinides is extracted from the sample matrix using an Eichrom Technologies extraction chromatography resin (RE resin), which consists of 1 M octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (abbreviated as CMPO) and tributyl phosphate (TBP) coated on an inert methacrylic polymeric support. The RE resin also co-extracts a number of other trivalent radionuclides, namely the lanthanides and Y-90.

The Y-90 (the short-lived progeny of Sr-90) that is co-extracted is particularly problematic as it is the primary contributor to the radiological contact dose associated with SRS High Level Waste sludge matrices, and is the primary contributor to the bremsstrahlung component of the whole body dose. Fortunately, the radiochemistry protocol used in the Cells does remove Y-90's parent radioisotope Sr-90, such that in-growth of Y-90 is terminated in the extracted fraction, allowing residual Y-90 in the extracted fraction to be removed via radiological decay. Given the 2.7 day half-life of Y-90, a nominal two week period is required (five Y-90 half-lives) for Y-90 to decay to a point where removal of the Am/Cm/Cf extract from the Cells becomes possible. The end result is that analyses of the trivalent actinide fractions

are delayed by two weeks, due to the presence of the Y-90. Given this situation, an alternate separation approach is desired – one that will remove Y-90, while maintaining effective extraction of the Am/Cm/Cf, thereby expediting the analyses by eliminating the need for the Y-90 decay step.

4.5.2 Alternative Trivalent Actinide Purification Approach

Two relatively new Eichrom Technologies extraction chromatography resins with potential application to trivalent actinide separations have become available. This includes Eichom's DGA Normal resin, utilizing N,N,N',N'-tetra-n-octyldiglycolamide extractant, and DGA Branched resin, utilizing N,N,N',N'-tetrakis-2-éthylhexyldiglycolamide extractant. Both of these extractants have high affinities for trivalent elements. A data set in the vendor's literature on DGA resin Normal suggested that the extractant showed promise for separating yttrium from americium in the low acid concentration region of 0.01 to 0.10 N nitric acid. As shown in Figure 4-5, the retention factors reported for yttrium in this concentration range (from ~60 at 0.01 N nitric acid to ~3000 at 0.10 N nitric acid) were about thirty times those of the americium (from ~2 at 0.01 N nitric acid to ~100 at 0.10 N nitric acid). Based on this information, it appeared that the extractant could potentially remove a large portion of the yttrium while removing a minimal portion of the americium (and other trivalent actinides).
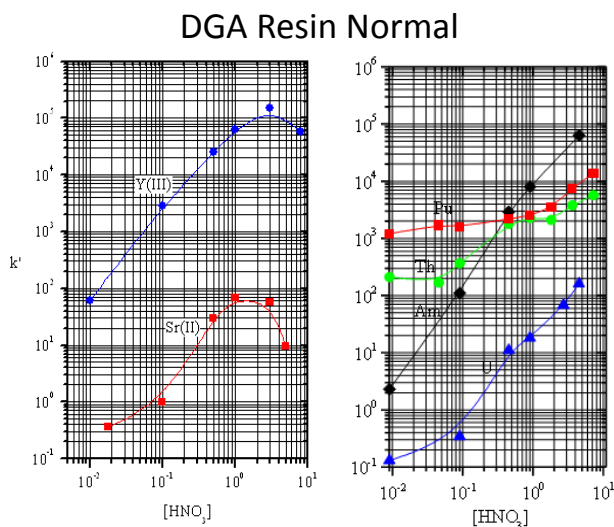

Figure 4-5. Retention Factors (k') of Select Elements on DGA Normal Resin

4.5.3 Experiments with DGA Normal Resin

Experiments were performed to determine if the Y/Am separation was feasible using the DGA Normal resin in the nitric acid concentration range of 0.01 to 0.10 N. In this experiment, Y-90 tracer solutions were generated by extracting Sr-90 from an aliquot of a NIST traceable Sr-90 standard. The Sr-90 was extracted using Eichrom Technologies Sr Resin, leaving the Y-90 daughter to be used as a tracer for yttrium performance. 0.2 mL aliquots of the Y-90 tracer (which had been re-constituted in 0.01 N nitric acid) were added to ten different 20 mL aliquots of nitric acid solutions ranging in concentrations from 0.01 to 0.10 N. The minimum Y-90 tracer concentration was ~4,000 dpm/mL, which corresponded to a minimum Y-90 activity of ~800 dpm added via each 0.2 mL aliquot.

Ten cartridges of DGA normal resin were mounted on an Eichrom vacuum extraction box and conditioned with 5 mL of the applicable acid (0.01 to 0.10 N nitric acid). The vacuum was adjusted so

the solutions would flow through the cartridges at a rate of approximately 1 mL/minute and the spiked acid solutions were then passed through the cartridges. Two milliliter aliquots of each solution that passed through the cartridges were added to liquid scintillating cocktail and analyzed for breakthrough of yttrium. A liquid scintillation counting (LSC) vial of the Y-90 tracer was also analyzed by LSC. An identical experiment was set up using an Am-241 tracer, with the Am-241 recoveries being determined via gamma spectrometry analyses.

Over the nitric acid concentration range of 0.01 to 0.10 N, the DGA Normal resin had high affinity for both yttrium and americium. Specifically, greater than 98% of each element was removed over the entire nitric acid range. While high removal was expected for yttrium, it was not expected for americium, based on the vendor literature. Given that high removal was desired for yttrium, but not desired for americium, use of the DGA Normal resin does not appear to provide an effective means for separating yttrium from americium.

4.5.4 Experiments with DGA Branched Resin

Experiments were also performed to study the behavior of the branched form of the extractant (DGA branched resin), for which no yttrium data were available. The first set of DGA Branched resin experiments was conducted using the same experimental approach as the previous DGA Normal resin experiments (targeting retention of yttrium and americium over the 0.01 to 0.10 N nitric acid range). The second set of DGA Branched resin experiments were performed similarly to the first set, except that the nitric acid concentrations were higher, ranging from 0.10 to 1.0 N.

Over the nitric acid concentration range of 0.01 to 0.10 N, the DGA Branched resin had minor affinity for yttrium, while having no measurable affinity for americium. Specifically, the results indicated that retention of the Y-90 ranged from 4-16%, with no clear correlation with acid concentration, and with analytical uncertainties typically greater than the differences between the respective results, limiting the ability to make definitive conclusions (see Table 4-1). However, given the low Y-90 retention values, use of the DGA Branched resin over the 0.01 to 0.10 N nitric acid range did not appear to provide sufficient Y removal for high effectiveness Y/Am separations.

Over the nitric acid concentration range of 0.2 to 1.0 N, the DGA Branched resin did appear to show differences in the relative retentions of yttrium and americium, particularly at the lower end of the nitric acid range (see Table 4-2). At 0.2 N nitric acid, Y-90 appeared to completely pass through the resin with no measurable retention, while clear retention of Am-241 was now being observed (52% retention). In contrast, at 0.3 N nitric acid, the Y-90 retention was now measurable at 27% and the Am-241 retention increased slightly to 64%. However, at 0.4 N nitric acid, the difference between the Y-90 retention and the Am-241 retention was significantly less, with 73% of the Y-90 retained and 96% of the Am-241 retained. Not surprisingly, at nitric acid concentrations from 0.5 to 1.0 N, complete or near complete retention of both yttrium and americium was observed.

Given the relative yttrium and americium retention differences seen at 0.2 and 0.3 N nitric acid, it is likely that the DGA Branch resin holds potential for development of a yttrium/trivalent actinide separation method. One possibility is making use of the retention difference at 0.2 N nitric acid, where approximately half of the americium is captured on the resin, while all or nearly all of the yttrium passes through. Under this circumstance, subsequent elution of the captured americium could produce an americium fraction essentially free of yttrium. However, additional testing will be necessary to prove the concept, optimize the approach, and establish whether the other trivalent actinides behave similarly to the americium.

Table 4-1. Y-90 Breakthrough and Retention for 0.01 to 0.10 N Nitric Acid

Nitric Acid Concentration, N	Y-90 % Breakthrough	1 σ % Uncertainty of Breakthrough Results	Y-90 % Retention
0.01	96	10	4
0.02	88	11	12
0.03	89	12	11
0.04	92	11	8
0.05	91	11	9
0.06	84	12	16
0.07	89	10	11
0.08	85	11	15
0.09	93	11	7
0.10	96	11	4

Table 4-2. Y-90 and Am-241 Breakthrough/Retention for 0.20 to 1.0 N Nitric Acid

Nitric Acid Concentration, N	Y-90 % Breakthrough	1 σ % Uncertainty of Y-90 Breakthrough Results	Am-241 % Breakthrough	1 σ % Uncertainty of Am-241 Breakthrough Results	Y-90 % Retention	Am-241 % Retention
0.2	100%	7.8%	48%	5%	0	52
0.3	73%	9.7%	36%	5%	27	64
0.4	27%	22%	3.6%	7.5%	73	96
0.5	<8%	MDA	3.2%	6.7%	>92	97
0.6	<8%	MDA	3.9%	8.1%	>92	96
0.7	<8%	MDA	< 2.1%	MDA	>92	>98
0.8	<8%	MDA	< 0.52%	MDA	>92	>99
0.9	<8%	MDA	< 0.53%	MDA	>92	>99
1.0	<8%	MDA	< 1.3%	MDA	>92	>99

4.5.5 Conclusion

A closer study of the DGA Branched resin towards yttrium and americium separation in the 0.2 to 0.3 N nitric acid range is warranted. In contrast, further evaluation of the DGA Normal resin does not seem warranted at this time. The DGA Branched resin vendor literature had described a resin that appeared to be capable of removing yttrium, while allowing americium to flow through unretained under a range of low nitric acid concentrations. SRNL's testing did not support that conclusion. However, in the study of the DGA Branched resin, for which the vendor had no data available addressing yttrium behavior, the experiments demonstrated the potential for the resin to do the opposite – extract americium to a significant degree while not extracting yttrium.

4.5.6 Recommendation

Perform additional Y/Am separation tests utilizing DGA Branched resin over the nitric acid concentration range of 0.2 to 0.3 N. Once a definitive separation path is established for yttrium and americium, perform experiments to confirm that the other trivalent actinides of interest (curium and californium) behave similarly to americium.

5.0 Overall Conclusions

1) Multiple options are available for making SRNL's tank closure characterization program more cost effective and timely, without compromising data integrity. Some of these options have already been implemented, some are in the process of being implemented, and some are slated for future development and implementation. The total expected cost savings associated with the changes identified in this document are on the order of $200,000 per SRS tank closure characterization campaign, which corresponds to the expectation of saving several million dollars over the entire SRS tank closure program. Reductions in TATs resulting from these changes are expected to be on the order of 2-4 weeks per characterization campaign. Additional options for improving the SRS tank closure characterization program should be identified and pursued in the future, as the program continues to evolve over the coming years.

2) The new waste removal system for use with all routine extraction chromatography separations has been sufficiently developed that it is ready for testing, optimization, and implementation. In its final design, the system has two primary components, the Column Vacuum Manifold Device and the Waste Removal and Accumulation Vessel. Preliminary testing of the system indicates that it will be effective, economical, and practical. Although the system will ultimately provide increased processing throughput and save significant waste management time, the system will also provide several other benefits, including reduced personnel dose, reduced risk of laboratory contamination, and reduced generation of radioactive solid waste. The current goal is to complete testing and optimization during FY17 such that implementation can occur at the beginning of FY18.

3) The three new radiochemical separation protocols that were investigated showed promise for lessening the resource demands and/or time requirements associated with future tank closure sample analyses. Summaries of the findings and status of each of these new potential methods are given below.

- New Ra-226 radiochemical separation method: In testing with SRS salt supernatant samples, the new method effectively increased the radium chemical yield by an order of magnitude, offering the potential for smaller sample aliquot requirements. This provides the possibility of eliminating the extensive Shielded Cells preparation steps that have been needed for the previous SRS tank closure Ra-226 analyses. Elimination of the Shielded Cells preparation steps would reduce the costs of the analysis by approximately $20K per campaign, and result in a shorter TAT. Plans include optimizing the new radiochemical separation approach in FY17, and implementing it during the next tank closure characterization campaign.

- New Th-229/230 source preparation method for alpha spectrometry: In testing with SRS salt feed solution, the new source preparation method produced a significant increase in alpha spectrometry resolution, offering the potential for significantly reduced MDLs. This provides the possibility of eliminating the extensive Shielded Cells preparation steps that have been needed for the previous SRS tank closure thorium analyses. Elimination of the Shielded Cells preparation steps would reduce the costs of the analysis by approximately $25K per campaign, and result is shorter TAT. Plans include optimizing the new source preparation method in FY17, with the goal of maximizing chemical yield such that the new approach can be implemented during the next tank closure characterization campaign.

- New yttrium/trivalent actinide separation approach: In testing with a range of spiked acid solutions, the new separation method showed promise although the behavior was contrary to the information reported in the literature. Additional tests over a different acid range will be necessary to determine potential applicability. Plans are to perform the additional tests in FY17, to determine if the new

approach will be effective for the tank closure characterization campaigns. If effective, the new method will reduce the TAT of the method by approximately two weeks, since decay of Y-90 will no longer be necessary.

6.0 Path Forward

1) Develop technical basis and strategy for improving the cost effectiveness and timeliness of SRNL's Salt characterization program.

2) Develop and test alternative radiochemical separation approaches holding promise for improving high resource demand tank closure analyses.

- Simultaneous Tc-99/I-129 Shielded Cells separation protocol

- Improved Zr-93 radiochemical separation protocol

- Yttrium/trivalent actinide separation protocol (continuation of FY16 effort)

3) Test, optimize, and implement use of the new waste removal system that was developed for the extraction chromatography radiochemical separations.

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