PNWD-3141
WTP-RPT-029

Optimization of Sr/TRU Removal Conditions with Samples of AN-102 Tank Waste

R. T. Hallen
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D. R. Weier

June 2002

Prepared for
Bechtel National, Inc.
under Contract 24590-101-TSA-W0000-0004

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By
Battelle—Pacific Northwest Division
Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification TSP-W375-00-00033 and Test Plan CHG-TP-41500-019. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

______________________________________ __________________

Gordon H. Beeman, Manager Date
WTP R&T Support Project

Approved for RPP-WTP Project Use:

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Research and Technology

Summary

The River Protection Project-Waste Treatment Plant baseline for pretreating Envelope C low-activity waste (LAW) at Hanford includes a precipitation step for removing radioactive strontium (Sr-90) and transuranic (TRU) isotopes before the waste is vitrified. The current design basis for the Sr/TRU removal process is the addition of strontium nitrate (0.075M) for isotopic dilution and permanganate (0.05M) for TRU removal at 1M additional sodium hydroxide. Section 5 of the *Research and Technology Plan* (BNI 2002) identifies further research needs, which are illustrated in Figure 5-14, Precipitation Test Matrix. One need shown in this matrix is optimization of the Sr/TRU precipitation reaction conditions [SOW Ref.: Sec. C.6 Std.2 (a)(3)(ii)(B) and WBS No.: 1.2.10.03 and .05]. The optimization of the Sr/TRU precipitation process is also addressed in Scoping Statement B-35, which is included in Appendix C of the *Research and Technology Plan*. In this context "optimization" refers to conditions that promote adequate decontamination to meet LAW requirements with a minimum of added reagents.

This report summarizes testing performed in accordance with Scoping Statement B-35 and Test Specification TSP-W375-00-00033. The purpose of this testing was to determine the effects of temperature and low levels of reagent on Tank AN-102 waste liquids and to identify the conditions for later integrated process testing with a mixture of Tank AN-102 waste and high-level waste (HLW) pretreatment streams (filtrate, wash, and leach solution from HLW pretreatment of Tank C-104 wastes). These conditions include determining the minimum amount of strontium and permanganate needed for decontaminating the liquid waste to meet LAW requirements for vitrification. The success criteria include demonstrating that the treated waste meets Specification 2 of the Bechtel National, Inc. contract (BNI 2001) for removing Sr-90 and TRU elements from the LAW solution; i.e., 20 Ci/m^3 for Sr-90 and 100 nCi/g for TRU. Target decontamination levels were established at 50% below the LAW requirements, which corresponds to a Sr-90 decontamination factor (DF) of 10 and a TRU DF of 2 for AN-102 waste. The decontamination factor is defined as the amount of the contaminant in the waste before treatment divided by the amount present after treatment.

For the experiments, a sample of Tank AN-102 supernatant was decanted from a sample bottle of waste received from Hanford's 222-S Laboratory. The supernatant was diluted to 5M sodium for testing. Test conditions were varied over limited ranges, sufficient to complete statistical analysis of the sensitivity of the dependent variable of interest (decontamination factor) as a function of the independent variables. A total of eight experiments were conducted in the Radiological Processing Laboratory hot cells in the Hanford 300 Area: five at ambient hot cell temperature (~26°C) and three at 50°C. The nonradioactive strontium addition ranged from zero to 0.02M. The permanganate addition ranged from zero to 0.02M. The total hydroxide content ranged from the as-received (after dilution) molarity of 0.14M to 0.5M. The samples were digested for 4 hours following reagent addition.

Decontamination factors were determined by comparing the Sr-90 and Am-241 (greater than 90% of the TRU content in the AN-102 sample is from Am-241) concentrations in the filtered, treated supernatant with the concentration of these isotopes in the starting diluted waste. The DFs for precipitation of Sr-90 varied between 5 and 7 at 26°C. At the elevated temperature (50°C), DFs ranged from 15 to 30. The DFs for Am-241 were relatively independent of temperature and ranged between 5 and 6 with permanganate addition. Without permanganate addition, no TRU removal occurred. The addition of free hydroxide resulted in a decrease in DF for Sr-90 and had little impact on the DF for Am-241.

The test results indicate that addition of strontium nitrate to a molarity of 0.02M is sufficient to exceed the LAW contract requirement for Sr-90. If further reduction of Sr-90 is desired, additional strontium nitrate should be added. Addition of permanganate to a molarity of 0.02M is sufficient to exceed the LAW contract requirement for TRU. Addition of hydroxide beyond that contained within the original sample is not recommended, as the tests showed it reduced the Sr-90 DF. These levels of reagent addition are significantly less than the project baseline. Higher-temperature precipitation is not recommended, because it would require the crossflow filtration system to be run at the same elevated temperature. Conducting the filtration at elevated temperature increases the risk of downstream post-filtration precipitation.

The reduced reagent loading, if incorporated into the project baseline, will result in cost savings related to procurement of reagents. Reduced reagent addition will also decrease solids loading on the filtration system, and may reduce the filter size. Reduced reagent loading will decrease the quantity of solids from Sr/TRU precipitation that must be incorporated into the immobilized high-level waste. Finally, eliminating the addition of sodium hydroxide will allow higher waste loading in the immobilized low-activity waste (ILAW), reducing the total volume of ILAW produced.

References

Bechtel National, Inc. (BNI). 2001. *Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant*. Contract DE-AC27-01RV14136, U.S. Department of Energy, Office of River Protection, Richland, WA.

Bechtel National, Inc. (BNI). 2002. *Research and Technology Plan*. 24590-WTP-PL-RT-01-002, Rev. 1, U.S. Department of Energy, Office of River Protection, Richland, WA.

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1.0 Introduction

This report summarizes work performed in support of the River Protection Project-Waste Treatment Plant (RPP-WTP) at Hanford. Before the liquid (supernatant) fraction of Envelope C wastes (Tank AN-107 and Tank AN-102 waste) can be disposed of as low-activity waste glass, pretreatment is required to remove radioactive strontium (Sr-90) and transuranic (TRU) elements in addition to Cs-137 and Tc-99. Because of the high concentration of organic complexants in this waste, conventional separation processes (e.g., ion exchange) are not effective for Sr-90 or TRU removal. Under earlier work for the RPP-WTP contractor, Battelle—Pacific Northwest Division (PNWD) and Savannah River Technology Center (SRTC) conducted technology development and demonstration of the Sr-90 and TRU (Sr/TRU) removal process with waste samples from Envelope C tanks (Hallen et al. 2000a,b; Nash et al. 2000a,b). The baseline Sr/TRU process was identified as addition of nonradioactive strontium for precipitation/ isotopic dilution and addition of permanganate for precipitation of TRU elements.

The Sr/TRU removal process was based on earlier work at the Pacific Northwest National Laboratory by Orth et al. (1995), who examined the removal of Sr-90 and TRU from complexant-containing (citrate, glycolate, EDTA, HEDTA, and NTA) tank waste by the addition of metal cations and chemical oxidant. Permanganate was examined as a chemical oxidant to promote destruction/defunctionalization of the complexing agents and, possibly, promote flocculation by the manganese solids. Permanganate was found to oxidize chromium first; then organic carbon; and last, nitrite. A sample of 3:1 diluted waste from Tank SY-101 was treated with 0.15M permanganate, and decontamination factors (DFs)[a] of >143 were obtained for Sr and 28.5 for Pu. Orth et al. recommended permanganate doses of 0.1M for treating complexant-containing wastes. For wastes such as in Tank SY-101, the chromium in the sludge consumes as much as half the permanganate. Waste in Tanks AN-102 and AN-107 do not have the high chromium values in the sludge, so permanganate was expected to be effective at lower concentrations.

The objective of the work reported here was to determine the optimal conditions and minimal reagent addition that would provide adequate Sr/TRU decontamination of Tank AN-102 waste. SRTC conducted Sr/TRU removal tests with samples of AN-102 waste at relatively high concentrations of added hydroxide, strontium, and permanganate (Rosencrance et al. 1999; Nash et al. 2000a,b). The larger-scale SRTC tests (Nash et al. 2000b) were also conducted at 50°C, whereas PNWD had shown that ambient temperature was adequate for Sr/TRU removal from Tank AN-107 waste (Hallen et al. 2000a). The AN-102 waste samples used in the SRTC tests were inadvertently contaminated with Cm-244 and, possibly, Am-241 and Pu isotopes. This contamination may have accounted for the higher reagent concentration needed to decontaminate the SRTC waste samples.

The optimization experiments discussed in this report were performed in radioactive hot cells using approximately 20-mL samples of waste with various amounts of strontium, permanganate, and/or hydroxide. Experiments were conducted with 4-hour solids digest time at ambient temperature and 50°C. Supernatant decontamination data were obtained from the test data. The Sr-90 and TRU DFs were compared to determine the efficiency of the Sr/TRU removal process. Preferred conditions were identified for future testing.

(a) The decontamination factor is defined as the amount of the contaminant in the waste before treatment divided by the amount present after treatment.

The results from a series of small-scale Sr/TRU decontamination tests are described. Test conditions and experimental procedures are described in Section 2.0. Experimental results from the tests are described in Section 3.0. The major conclusions and recommendations from this work are given in Section 4.0. The appendices contain the test instructions, data sheets, logbook entries, analytical data, calculations, and staff roles/responsibilities.

2.0 Test Conditions and Experimental Procedures

This section describes the conditions used for the optimization tests and the procedures used for the experiments and analyses.

2.1 Description of AN-102 Waste Samples

PNWD received 27 bottles of tank waste from Hanford's 222-S Laboratory that were taken by grab sampling of AN-102 from riser 022 over the period August 7 through 11, 2000. Eight of the samples were designated for process testing. This material was originally collected from the tank and shipped to the 222-S Laboratory in Hanford's 200 West Area. The sample material was transferred to 500-mL bottles before being shipped to the Radiological Processing Laboratory (RPL) in the 300 Area, where the samples were inspected on receipt. All of the samples contained a settled layer of light brown solids with a dark brownish/black standing liquid. Sample inspection and Sr/TRU feed preparation were documented through Test Instruction 41500-009, "AN-102 Sample Inspection" (Appendix A of this report). Approximately 137 grams of supernatant were removed from bottle 2AN-00-25 (25th grab sample taken on August 11, 2000, 76 inches from the bottom of the tank), and diluted with approximately 74 grams of 0.01M sodium hydroxide. The target sodium concentration of the diluted waste was 5.3M.

SRTC received a sample of AN-102 waste for characterization and process testing in FY 1999 (Hay et al. 2000). PNWD also characterized the as-received waste prior to the scheduled integrated process testing (Urie et al. 2002). Both analyses confirmed the samples had elevated levels of Sr-90 and TRU components, primarily Am-241. There appeared to be no significant difference in the composition of the supernatant samples shipped to SRTC for the earlier tests and the new samples received at RPL, even though the samples were collected at a different height in the tank and contained different levels of solids. The major difference was the Cm-244 contamination that had occurred with the SRTC samples. However, the free hydroxide concentration in the as-received waste was in question based on three different values reported by SRTC and the value reported in the Hanford TWINS database. Urie et al. reported a concentration of 0.25M free hydroxide in the as-received waste. This value was consistent with the results from this optimization study, which found the diluted waste had 0.14M free hydroxide (Appendix D).

2.2 Development of Test Conditions

The RPP-WTP contract (WTP 2001) requires that the immobilized low-activity waste (ILAW) product contain less than 100 nCi/g TRU and that the average Sr-90 be less than 20 Ci/m^3. However, shielding for the LAW vitrification facility now requires that every ILAW container be less than or equal to 20 Ci/m^3 Sr-90. Supernatant from Envelope C waste contains levels of Sr-90 and TRU too high to meet ILAW requirements. At the design basis waste oxide loading of 15 wt% for Envelope C tanks, waste from AN-102 needs DFs of approximately 10 for Sr-90 (90% removal) and 2 for TRU (50% removal) to meet a target that is 50% below the ILAW disposal requirements. Since over 90% of the TRU in AN-102 is Am-241, a target DF of 2 was established for Am-241.

Experimental conditions were defined using the results from earlier studies with AN-107 waste (Hallen et al. 2000a,b). Based on these studies, a strontium and permanganate treatment level of 0.02M was expected to yield good decontamination results. AN-102 waste was reported to have a free hydroxide concentration of >0.1M, enough to give good decontamination of Sr-90 and TRU. This information was used to construct the test matrix shown in Table 2.1. The target concentrations listed in the test matrix

Table 2.1. Test Matrix for Experiments Using Tank AN-102 Waste Samples

Sample Number	Target $[OH^-]$	Target $[Sr^{2+}]$	Target $[MnO_4^-]$	Digest Temperature	Comment
HD-01	AR[(a)]	0	0	Ambient	Initial waste-filtered
HD-02	AR[(a)]	0	0	Ambient	Initial waste-filtered, duplicate
HD-03	AR[(a)]	0.02M	0	Ambient	Sr only at ambient temperature
HD-04	AR[(a)]	0.02M	0	50°C	Sr only at 50°C
HD-05	AR[(a)]	0.02M	0.02M	Ambient	Sr and Mn at ambient temperature
HD-06	AR[(a)]	0.02M	0.02M	50°C	Sr and Mn at 50°C
HD-07	0.5M	0.02M	0.02M	Ambient	Increased $[OH^-]$ at ambient temperature
HD-08	0.5M	0.02M	0.02M	50°C	Increased $[OH^-]$ at 50°C
(a) As received ~0.14M.					

are based on the final composition after addition of all reagents. The quantity of each reagent to add to the waste to achieve these values, as well as the actual quantities that were used, can be found in Test Instruction 41500-008 (Appendix B of this report).

The test specification lists temperatures of 25 ± 5°C and 50 ± 5°C for the experiments. The ambient hot cell temperature was 26°C on the day of the test and was within the temperature requirement of 25 ± 5°C for the lower-temperature experiments. Selected experiments were heated to 50 ± 5°C and held for 4 hours after reagent addition. The 4-hour solids digest time was expected to allow more isotopic exchange of Sr-90 with added nonradioactive strontium. The 50°C treatment temperature is the system design basis for the Sr/TRU removal process, but is a holdover of the earlier Sr/TRU removal process that used iron precipitation instead of permanganate. Subsequent studies showed that ambient temperature resulted in adequate Sr-90 and TRU decontamination (Hallen et al. 2000a).

2.3 Experimental

The decanted AN-102 supernatant was diluted with 0.01M sodium hydroxide in the High Level Radiochemistry Facility hot cells (in the RPL). The waste was transferred to the Shielded Analytical Laboratory hot cells (in the RPL) for these tests. The small-scale experiments were conducted in 60-mL sample jars with approximately 20 mL of the diluted tank waste. The reagents were rapidly added to the wastes with an adjustable pipette, in the order listed in Table 2.1 (from left to right), at ambient hot cell temperature, and mixed with magnetic stir bars. The ambient hot cell temperature was 26°C on the day of the test. All reagents were added before the samples were heated in a hot water bath that had been preheated to the set temperature. The samples were held for the prescribed time, 4 hours, at this temperature, removed, cooled, and filtered with a 0.45-µm disposable syringe filter for analyses. Duplicate samples of initial waste, HD-01 and HD-02, were filtered, along with the other samples, but no chemical reagents were added. The samples for chemical and radiochemical analyses were acidified and diluted to the appropriate levels for the analytical method.

Stock solutions of the reagents were prepared for addition to the waste. The experiments used 0.4M strontium nitrate and 0.4M sodium permanganate as the stock solutions. Although the process design basis specifies 1M strontium nitrate and 1M sodium permanganate solutions, more dilute solutions were used to provide more accurate dispensing and better mixing/distribution of the reagents. Before the experiments were started, sodium hydroxide was added as a 10M solution to the diluted waste to increase the total hydroxide level to 0.5M. The actual quantities of waste and reagents used are given in the test instructions (Appendices A and B).

2.4 Chemical Analyses

All of the chemical analyses were conducted at PNWD. The test specification designated the analytes of interest and minimum reportable quantities (Reynolds 2000). Separation and alpha energy analysis (AEA) were required for Am-241 because of the high Cs-137 concentration. The Sr-90 concentration was determined by chemical separation followed by beta counting. Sodium concentration was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), as were the other metals listed in the test instructions. Selected samples were also analyzed by titration to determine the free hydroxide concentration. All of the analytical results are included in Appendix D.

3.0 Results and Discussion

These experiments focused on treatment at two different reaction temperatures with strontium nitrate alone and in combination with permanganate and at two hydroxide concentrations. The results are discussed below.

3.1 Decontamination of Sr-90 and TRU

The series of experiments involved multiple samples, and all samples were analyzed as a single analytical batch to determine the change in waste composition upon treatment. Duplicate samples of the starting diluted waste were analyzed after filtration to determine the initial composition of the supernatant. The radionuclide composition of the treated samples was compared with the initial composition to determine the extent of decontamination. The DF for a specific radionuclide is defined as the concentration of the component in the initial waste divided by the concentration after treatment, corrected by the amount of dilution that occurred during sample treatment:

$$DF = [A]_i/([A]*MD)$$

where $[A]_i$ is the concentration of component A per mass in the initial sample; [A] is the concentration of component A per mass in the treated sample; and MD is the mass dilution, final mass of treated solution divided by the initial mass of solution. The final mass is determined by summing up the mass of initial waste and all dilutions, adjustments, and/or reagent additions.

The decontamination factors for Sr-90 are shown in Figure 3.1. The Sr-90 DFs were greatly increased by the solids digest and filtration at 50°C. Addition of permanganate increased the Sr-90 DFs regardless of temperature. The added free hydroxide resulted in a slight reduction in the Sr-90 DFs. Only the experiments with the 50°C digest and filtration resulted in DFs above the target of 10, but all treatment conditions were adequate to meet the ILAW glass requirements for Sr-90 (DF=5, derived from Table 3.3 in Section 3.4).

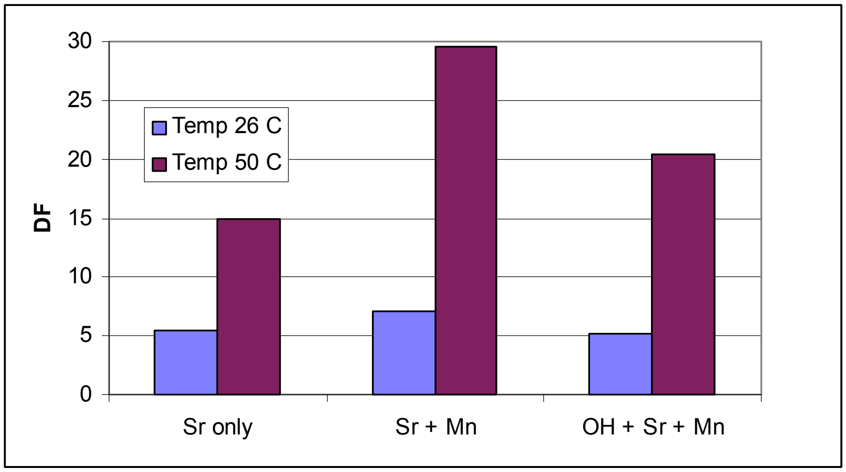


Figure 3.1. Strontium-90 Decontamination Factors for Treated Samples as a Function of Digest Temperature. Sr only: 0.02M Sr^{2+}; Sr + Mn: 0.02M Sr^{2+} and 0.02M MnO_4^-; and OH + Sr + Mn: 0.5M OH^-, 0.02M Sr^{2+}, and 0.02M MnO_4^-.

SRTC (Rosencrance et al. 1999) conducted a statistically designed set of beaker experiments to determine the impact of strontium addition at three different levels, 0.02, 0.05, and 0.075M, but all experiments were run at 50°C. Those experiments cannot be directly compared to the experiments in this report, because different levels of permanganate and hydroxide were used. The closest test conditions to those reported here, EXP-24 (50°C, 0.02M Sr, 0.03M Mn, and 1M OH), had a Sr-90 DF of 14.9. The Sr-90 DF determined here for "close" conditions (50°C, 0.02M Sr and Mn, 0.5M OH) was 20.4. The other difference is that SRTC added the reagents with the samples heated to 50°C, whereas in this study the reagents were added at ambient temperature and then the precipitate was digested at 50°C.

Examining the ICP-AES data for total soluble strontium provides an understanding of the Sr-90 decontamination mechanism. The total soluble strontium in the initial waste is very low (~1 µg/g) and well below the saturation limit for strontium carbonate. On addition of nonradioactive strontium nitrate, the total strontium increases to levels around 150 µg/g. In examining the total strontium concentration as a function of temperature and reagent addition, Figure 3.2, it is clear the temperature has the largest impact on total strontium solubility. The elevated digest temperature reduces the strontium solubility because of the retrograde solubility of strontium carbonate. Therefore, the reduction of total strontium solubility is directly linked to the high Sr-90 decontamination. The permanganate addition also reduces the total strontium levels, but has much less of an effect than the temperature. The reduction in total strontium by permanganate treatment is likely a result of partial oxidation of the chelating agents, EDTA and HEDTA. The increased hydroxide level did not reduce the total strontium solubility and, therefore, did not increase the Sr-90 decontamination.

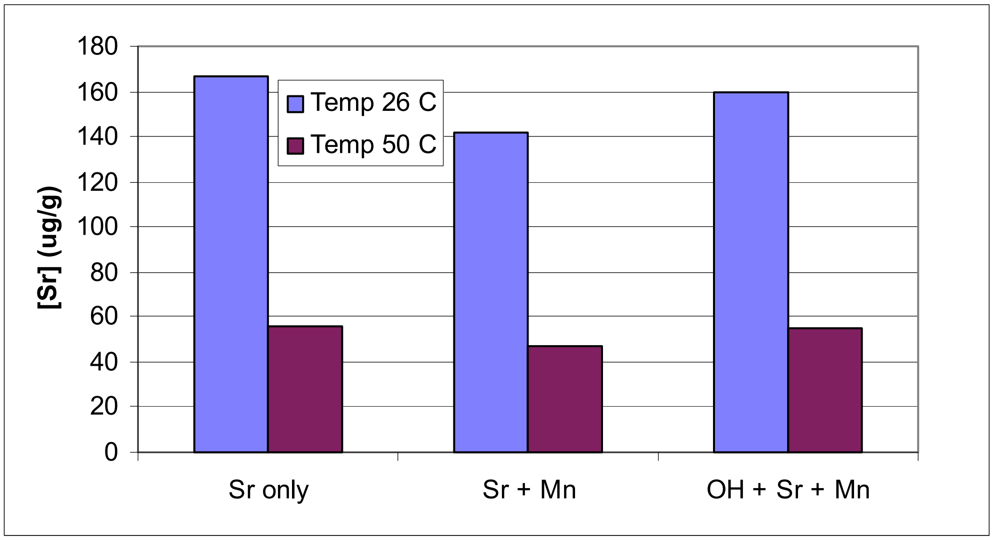


Figure 3.2. Total Strontium Solubility in the Treated Samples as a Function of Digest Temperature. Sr only: 0.02M Sr^{2+}; Sr + Mn: 0.02M Sr^{2+} and 0.02M MnO_4^-; and OH + Sr + Mn: 0.5M OH^-, 0.02M Sr^{2+}, and 0.02M MnO_4^-.

In comparison, the extreme sensitivity to temperature on Sr-90 removal (DF) was not reported as significant for the earlier AN-102 samples (Rosencrance et al. 1999) or for samples of AN-107 waste (Hallen et al. 2000a). Rosencrance et al. concluded that the Sr/TRU removal process was robust with respect to temperature, but reported Sr-90 DFs of 23 ± 5 at 25°C and 37 ± 7 at 50°C. It is noted in the

SRTC study that the Sr-90 DF is typically more than adequate and the conditions used for the experiments were non-optimum. Strontium solubility was not reported, but this DF variation with temperature is consistent with the temperature variation observed here. The total soluble strontium levels were similar for treated AN-107 waste. However, AN-107 waste was treated with very high levels of strontium nitrate, 0.075M, and higher permanganate, 0.05M. The isotopic dilution in AN-107 waste was much higher. The total strontium solubility for AN-107 at ambient temperature (~160 µg/g) resulted in high decontamination because of the higher reagent addition; 95% (DF=20) of the Sr-90 was removed at ambient temperature. With a high Sr-90 removal at ambient temperature, the increase in temperature to 50°C would only increase the Sr-90 removal by approximately 3%. Thus, the temperature effect on Sr-90 is most significant and noticeable at low reagent addition, such as 0.02M used for these studies.

The system design temperature for operation of the crossflow filtration equipment is 25°C. The high Sr-90 removal at 50°C is a result of the decreased total strontium solubility. As the waste is cooled to 25°C for filtration, the total strontium solubility will increase and result in a loss of Sr-90 decontamination. If a higher DF is desired for Sr-90, more nonradioactive strontium should be added to the waste (for example, increase strontium addition to 0.03M), or the temperature will need to be increased in the filtration system to match the precipitation temperature. Because of the concern for post-filtration precipitation, the filtration temperature should remain 25°C for the plant.

The effectiveness of the various treatment conditions for TRU removal can be seen by examining the DFs for Am-241 shown in Figure 3.3. The target DF of 2 was obtained for samples when permanganate was added. The elevated temperature digest resulted in better TRU decontamination, but with 0.02M permanganate at ambient temperature, the DFs greatly exceeded the target of 2. TRU decontamination was not increased with added hydroxide to the AN-102 waste sample. This is in contrast to results from AN-107, which required additional hydroxide because the waste as received was hydroxide deficient (Hallen et al. 2000c).

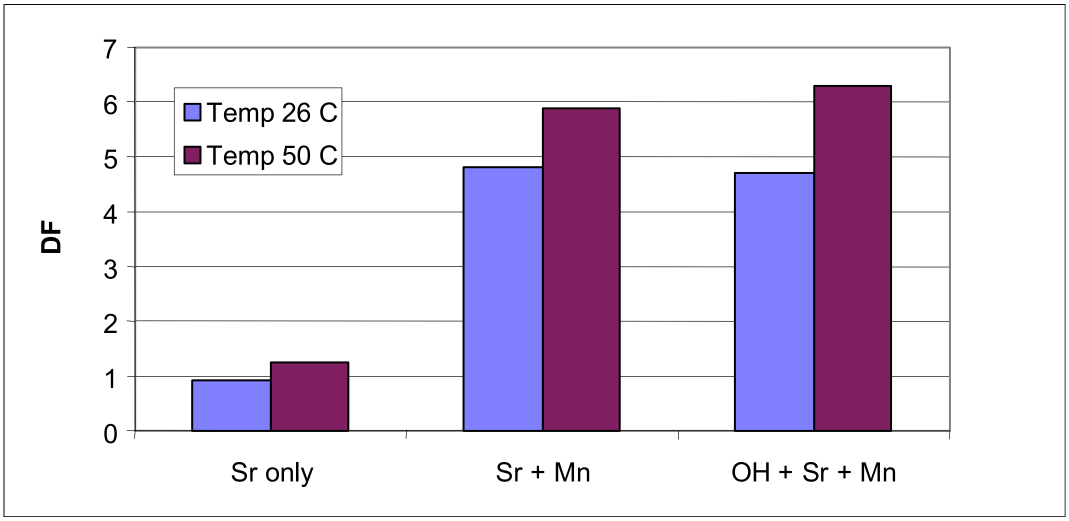


Figure 3.3. Americium-241 Decontamination Factors for Treated Samples as a Function of Digest Temperature. Sr only: 0.02M Sr^{2+}; Sr + Mn: 0.02M Sr^{2+} and 0.02M MnO_4^-; and OH + Sr + Mn: 0.5M OH^-, 0.02M Sr^{2+}, and 0.02M MnO_4^-.

The curium isotopes, primarily 243 and 244, account for approximately 5% of the total TRU and are analyzed as part of the Am-241 analytical method. Figure 3.4 shows a comparison of the DFs for the curium isotopes and Am-241. The DFs for the curium isotopes follow the same trends as found for Am-241, but have greater variability due to increased analytical error associated with the very low concentrations of these isotopes.

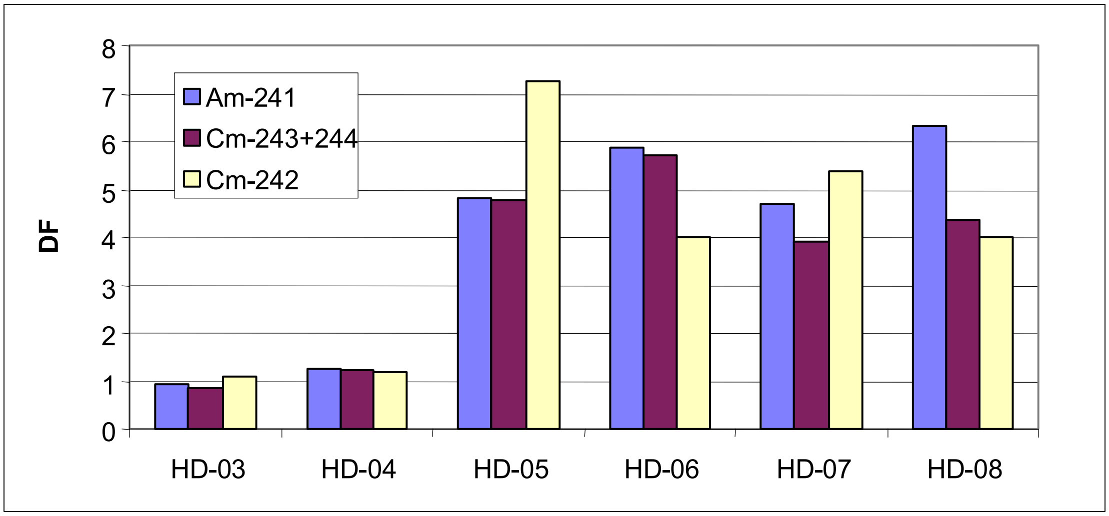


Figure 3.4. Comparison of Decontamination Factors for Am-241, Cm-243+244, and Cm-242

3.2 Statistical Analyses of Data

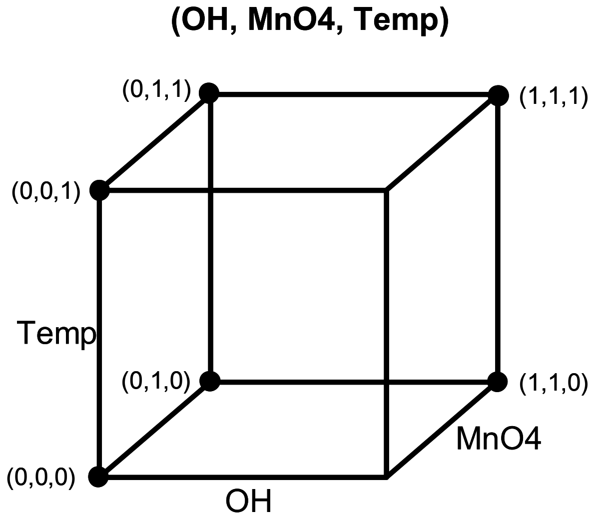
The experimental test matrix is represented by the variables listed in Table 3.1, where the strontium addition is held constant at 0.02M for all tests. For OH^-, the level 0 represents no additional hydroxide, and the level 1 represents 0.5M added OH^-. For MnO_4^-, the level 0 represents no permanganate addition, and the level 1 represents 0.02M addition. For temperature, level 0 represents ambient temperature (26°C), and level 1 represents 50°C. The responses, as percent removal relative to the starting solution, are given for Sr-90, Am-241, Cm-243+244, and Cm-242.

Table 3.1. Test Matrix and Response of Variables

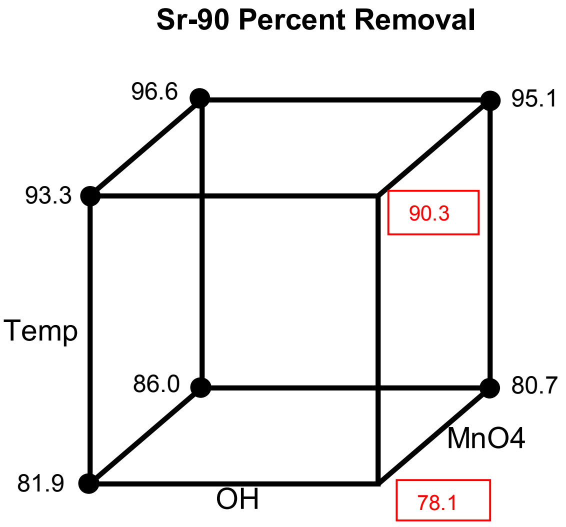
	Variable			Response			
Test No.	**OH^-**	**MnO_4^-**	**Temp.**	**Sr-90**	**Am-241**	**Cm-233+244**	**Cm-242**
HD-03	0	0	0	81.9	-6.8	-19.1	8.2
HD-04	0	0	1	93.3	20.7	18.3	16.4
HD-05	0	1	0	86.0	79.3	79.1	86.3
HD-06	0	1	1	96.6	83.0	82.5	75.0
HD-07	1	1	0	80.7	78.7	74.4	81.5
HD-08	1	1	1	95.1	84.2	77.1	75.0

This experimental matrix can be expressed graphically by the cube below. The six corners covered by dots represent the experimental combinations of the factors that were included in the study. The lower left corner, at the junction of the left, bottom, and front faces of the cube, represents the (0,0,0) experimental trial, that is, with all three factors at their respective zero levels. Like an X, Y, Z coordinate system with points represented by (x, y, z), the triples shown at the corners represent the respective levels of the factors in the form (OH^-, MnO_4^-, Temp.). The levels of OH^- are thus displayed, respectively, on the left and right faces of the cube; for MnO_4^-, the levels are on the front and back faces, respectively; and for temperature, the levels are on the bottom and top faces, respectively.

The percent removal results for each analyte are given adjacent to the corresponding corners of the cube in this same pattern on the following pages. Given a fitted model, one could predict the responses at the "missing" corners of the cube, that is, for those combinations of factors not run in the experiment. While such estimates are provided on the following pages, caution should be exercised in using these values. Considerable uncertainty is associated with these values, especially since little information is available to estimate experimental or measurement error due the minimal number of trials.



Sr-90 Removal – Experimental results for the percent removal of Sr-90 are given by the cube diagram below. The value at each of the dotted vertices, representing the six experimental combinations, is the resulting percent removal. The boxed values at the other two vertices are discussed below. The analysis summary that follows the cube can be interpreted as statistical multiple linear regression.



Summary of Fit

RSquare	0.98
Significance	0.0248
Root Mean Square Error	1.4
Mean of Response	88.9
Observations	6

Parameter Estimates

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob >|t|**
Intercept	81.5	1.16	70.49	0.0002
OH^-	-3.4	1.42	-2.40	0.1384
MnO_4^-	3.7	1.42	2.61	0.1206
Temp.	12.1	1.16	10.49	0.0090

The r-square value given on the first line above is the proportion of variability in the six Sr-90 responses that can be explained by the changing levels of the factors OH^-, MnO_4^-, and Temp. The closer this value is to 1.0, the stronger the relationship between the percent removal responses and the levels of the factors. The value on the second line, labeled "Significance," is a statistical measure of the significance of this r-square value relative to the number of trials run. The smaller this significance value, the more significant the r-square value and the stronger the relationship between percent removal and the factor levels. Generally, significance levels less than 0.05 can be taken to indicate "statistical significance."

The third line, with the value 1.4 labeled "Root Mean Square Error " (RMSE), gives an estimate of variability, analogous to a standard deviation, which would be expected if repeated values were run at a particular set of factor levels. Prediction limits for an individual future value, or for the underlying mean value, at that set of factor levels, depend on the magnitude of the RMSE, the experimental design used, and the amount of data available for estimating error. In these applications, such prediction limits can be extremely wide due to the minimal number of trials run and relatively large RMSE values for some of the response analytes.

In the second section of results above, labeled "Parameter Estimates," the first line, labeled "Intercept," represents the expected percent removal when the zero level of each factor is used. Therefore, with no OH^- or MnO_4^- addition, and at ambient temperature, average percent removal is estimated at 82. The dominant influence on Sr-90 removal in the study is temperature, since its increase from ambient to 50°C improves the percent removal by the estimate indicated, that is, by about 12.1 percentage points. The final value on this temperature line, 0.0090, is again a measure of the statistical significance of this particular factor. The smaller the value, the more significant, so the importance of temperature is clearly indicated.

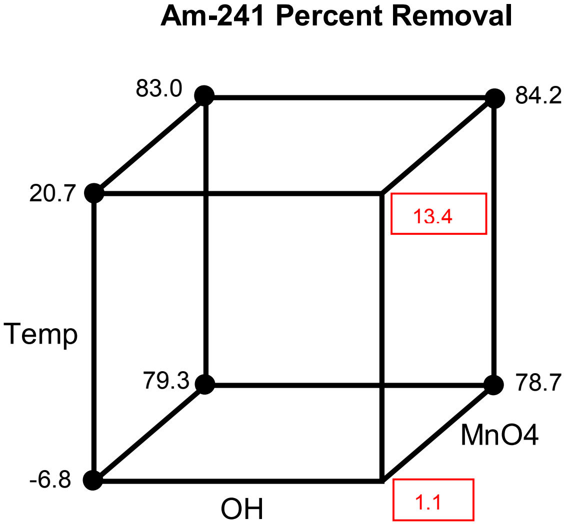
By comparison, the two additives are only marginally influential relative to this temperature change. OH^- addition actually lowered removal by 3.4 percentage points, while MnO_4^- addition raised it by about 3 percentage points. The statistical significances of these two factors are, respectively, 0.1384 and 0.1206, which indicate a relatively modest contribution in explaining the variability of the percent removal.

The importance of temperature can be observed on the cube diagram, where the results for the elevated temperature are on the top face of the cube. They considerably exceed their corresponding results on the bottom face of the cube by 12.1 percentage points on the average. Given this substantial temperature impact, the relatively modest improvement obtained with the addition of MnO_4^- can then be seen in the slightly larger values on the back of the cube relative to those on the front. Similarly, the slightly lower values on the right face, relative to the left, show the decrease in percent removal resulting from the OH^- addition.

The boxed values on the other two vertices are predictions based on the estimated model for the cases that were not run. They are simply point estimates of what might be expected if that set of conditions were used. Again, they should not be used without considering the substantial uncertainties associated. For example, a 95% prediction interval for the underlying mean value at the combination of levels corresponding to the 90.3 value is actually (82.4, 98.1).

Similar analyses for the other analytes are given on the following pages.

Am-241 Removal – Results for the percent removal of Am-241 are given below:



Summary of Fit

RSquare	0.97
Significance	0.0337
Root Mean Square Error	9.4
Mean of Response	56.5
Observations	6

Parameter Estimates

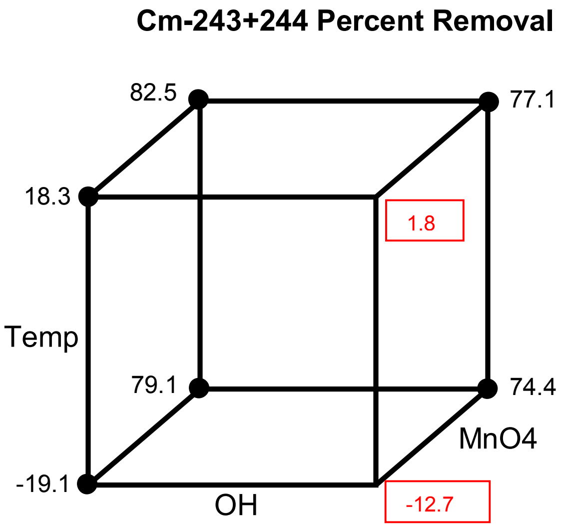
Term	**Estimate**	**Std Error**	**t Ratio**	**Prob >|t|**
Intercept	0.8	7.7	0.11	0.9232
OH^-	0.3	9.4	0.03	0.9774
MnO_4^-	74.2	9.4	7.92	0.0156
Temp.	12.2	7.7	1.60	0.2510

Again, the percent removal variation is explained by the changing factor levels. With no OH^- or MnO_4^- addition and ambient temperature, average percent removal is estimated at less than 1. The dominant influence is then MnO_4^- addition, since this improves the percent removal on the average by about 74.2 percentage points. This is considered to be statistically significant, as indicated by the associated significance level 0.0156. Increasing the temperature then gives additional marginal improvement that is not statistically significant (relative to error in the model) by increasing the removal percentage by another 12.2 percentage points. OH^- addition had virtually no impact.

This impact of MnO_4^- addition is observed in the cube diagram, where the higher percent removals all lie on the back face of the cube, which represents the experiments that included this additive. Also, the relatively marginal increase associated with the higher temperature can be seen by comparing the top and bottom faces of the cube.

Boxed values are again predictions based on the estimated model for the cases that were not run. Due to the greater variability in the results than for Sr-90, these predicted estimates have even more uncertainty. Given the variability, again indicated by the now considerably larger RMSE (9.4), and again the minimal amount of data, the questionable utility of the 13.4 predicted mean value is indicated by considering the associated prediction interval (-38.7, 65.4).

Cm-243+244 Removal – Results for the percent removal of Cm-243+244 are given below:



Summary of Fit

RSquare	0.96
Significance	0.0649
Root Mean Square Error	14.0
Mean of Response	52.1
Observations (or Sum Wgts)	6

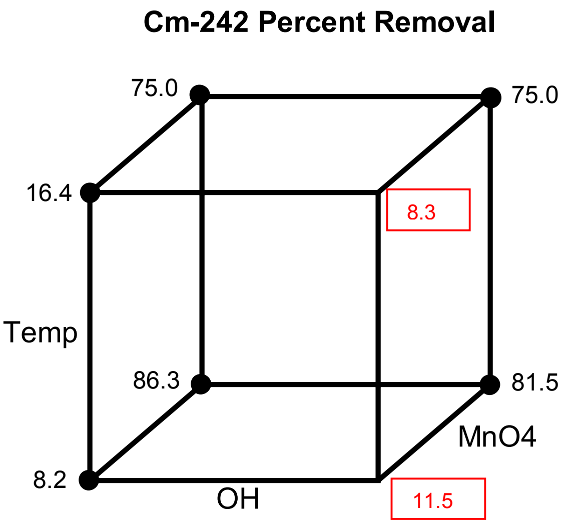
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob >|t|
Intercept	-7.7	11.6	-0.67	0.5729
OH^-	-5.2	14.0	-0.36	0.7533
MnO_4^-	81.2	14.0	5.79	0.0286
Temp.	14.5	11.5	1.27	0.3330

A slightly less significant proportion of the variability in percent removal is explained (significance level 0.0649). With no OH^- or MnO_4^- addition and ambient temperature, average percent removal is predicted to be negative due to the combined effect of measurement error and our inability to perfectly model the relationships with this modest amount of data. The dominant influence is again MnO_4^- addition, since this improves the percent removal by about 81.2 percentage points. Increasing the temperature then gives marginal improvement (relative to error) by increasing the percent removal by another 14.5 percentage points. OH^- addition appears to have no significant impact and, if anything, its addition decreases the percent removal. Again, the higher percent removals all lie on the back face of the cube diagram, which represents the experiments that included MnO_4^-.

Extremely large uncertainties are again associated with the predictions based on the estimated model for the cases that were not run. They are presented primarily for completeness and consistency in the analyses.

Cm-242 Removal – Results for the percent removal of Cm-242 are given below:



Summary of Fit

RSquare	0.98
Significance	0.0251
Root Mean Square Error	7.2
Mean of Response	57.1
Observations (or Sum Wgts)	6

Parameter Estimates

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob >|t|**
Intercept	13.9	5.9	2.37	0.1413
OH^-	-2.4	7.2	-0.33	0.7701
MnO_4^-	68.5	7.2	9.51	0.0109
Temp.	-3.2	5.9	-0.55	0.6401

A significant proportion of percent removal is again explained. With no additives and ambient temperature, average percent removal is predicted to be about 13.9. The dominant influence is again MnO_4^- addition, since this improves the percent removal by about 68.5 percentage points. Temperature increase and OH^- addition do not have a significant impact and, if anything, appear to decrease the percent removal slightly. Again, the impact of MnO_4^- addition is observed on the cube diagram, where the higher percent removals all lie on the back face of the cube (which represents the experiments that included the additive).

The statistical analysis of the curium isotopes should have been the same, but because of very low curium concentrations and Cm-242 concentrations, an order of magnitude lower than Cm-243 and Cm-244, differences were seen. However, conclusions from these analyses are the same; i.e., permanganate addition has the dominant impact on curium removal.

The boxed values are again given for completeness of the analyses, but very large uncertainties are associated with them.

3.3 Change in Chemical Composition

Chemical analyses of each sample were performed by ICP-AES. The ICP data of the various samples can be used to determine the impact of the various process conditions on the chemical composition of the supernatant. The impact of the process condition on the chemical composition of the treated supernatant is calculated as a percent removal relative to the starting waste. Table 3.2 shows the composition of the starting waste (HD-02) in µg/g, and the percent change that occurred for the various treated samples. A number of the analytes show little or no significant change on treatment: Al, Cd, Co, Cu, K, Mo, Ni, and P. It is important that Al and P both stay in the supernatant and go to the low-level glass melter. Chromium is also an important element that is preferred in the supernatant. The Cr showed little removal with strontium addition only (HD-03, -04), but some removal when both strontium and permanganate were added. The Cr removal is significant because Cr can be a glass-limiting element in high-level waste (HLW) treatment; the less Cr removed from the supernatant, the better for the overall treatment plant. The Cr data also showed higher removal at the elevated temperature. In comparison, the Cr removal from AN-107 was significantly higher than that for AN-102, ranging from 50% to as high as 90% removal. AN-107 treatment involved higher permanganate dosages and higher digest temperatures. Consequently, the reduced level of permanganate and lower digest temperature used in treatment of AN-102 have resulted in less Cr in the Sr/TRU precipitate (HLW).

Table 3.2. Percent Removal of ICP Metals for the Treated Samples

Analyte	HD-02 (µg/g)	HD-03 (%)	HD-04 (%)	HD-05 (%)	HD-06 (%)	HD-07 (%)	HD-08 (%)
Al	5670	-2	3	5	1	1	0
Ca	183	13	24	17	26	15	24
Cd	24.2	-1	3	3	-1	-1	0
Co	[1.6]	[9]	[2]	[-2]	[5]	[-1]	[-1]
Cr	101	1	8	34	38	23	36
Cu	9.5	-1	3	4	1	2	0
Fe	29.4	45	60	[90]	[76]	68	[89]
K	844	-1	1	0	-2	-2	-2
La	[6.3]	[27]	[52]	[71]	[>76]	[>75]	[>75]
Mn	[9.3]	[3]	[13]	[60(a)]	[47(a)]	[75(a)]	[78(a)]
Mo	20.6	-1	3	2	0	-1	-2
Nd	[13]	[12]	[25]	[74]	[>77]	[67]	[>76]
Ni	162	-1	3	2	0	-1	-2
P	735	-1	3	5	3	1	0
Pb	68	1	3	8	11	15	25
Zn	[2.1]	[-29]	[10]	[>30]	[>29]	[>26]	[>26]
Zr	[4.2]	[3]	[8]	[53]	[>64]	[48]	[>63]

Note: Values in brackets are in low concentration, values less than 10 times the detection limit, and error likely to exceed 15%. > before the number denotes the sample was below the detection limit, and percent removal was calculated assuming the concentration was at the detection limit.

(a) Manganese was added as a reagent in Tests HD-05 through -08.

As discussed in Section 3.1, strontium addition caused a large increase in strontium concentration in the treated supernatant. The strontium addition removed Ca from solution. The Ca removal is dependent on temperature; Ca has lower solubility at higher temperature. However, the Ca removal was not significantly impacted by the addition of permanganate and hydroxide. Strontium-only addition (HD-03, -04) also resulted in some Fe, La, and Nd removal. Much more Fe, La, and Nd were removed when both strontium and permanganate were added. The iron removal was surprisingly high with the strontium-only addition and higher than La and Nd removal. The Nd percent removals were very similar to those obtained for radioactive Am and Cm. This supports the use of Nd as a surrogate for Am and Cm in waste simulant studies. Appreciable Mn removal only occurred when permanganate was added, and its removal is also very similar to those for Am and Cm.

3.4 Estimated Sr-90 and TRU Levels in ILAW Glass

The data from these experiments can be used to estimate the Sr-90 and TRU loadings that would be expected in ILAW glass made from the treated supernatant. The TRU activity is calculated by adding Am-241, Cm-242, and Cm-243+244. This sum represents 95% of the TRU radioisotopes in AN-102 waste. The calculated glass loadings are listed in Table 3.3 for the current baseline design waste glass concentration of 15 wt% waste Na_2O. The results show that all treated samples were below the contract limits for ILAW glass. However, the target level of 50% below the limit was only met for Sr-90 at the higher temperature. Thus, 0.02M added strontium nitrate and ambient temperature (26°C) are adequate to meet the contract requirement. TRU loadings of 50% below the contract limit were met when permanganate was added.

Table 3.3. Sr-90 and TRU ILAW Glass Loadings for 15 wt% Waste Na_2O

Digest Temperature	Target $[Sr^{2+}]$	Target $[MnO_4^-]$	Additional $[OH^-]$	Sr-90 Loading (Ci/m^3)	TRU Loading (nCi/g)
ILAW limits				**20**	**100**
Ambient	none	none	none	89	74
Ambient	0.02M	none	none	17	84
50°C	0.02M	none	none	7	66
Ambient	0.02M	0.02M	none	14	17
50°C	0.02M	0.02M	none	3	14
Ambient	0.02M	0.02M	0.5M	18	16
50°C	0.02M	0.02M	0.5M	4	11

4.0 Conclusions and Recommendations

Experiments were conducted with actual samples of diluted AN-102 waste at various modified Sr/TRU removal process conditions. The results of these experiments have demonstrated the potential for optimizing the Sr/TRU removal process. Reduced reagent addition and simplified process conditions provided adequate Sr-90 and TRU decontamination.

Experiments were conducted to examine a solids digest temperature of 25 ± 5°C and 50 ± 5°C, strontium nitrate addition at 0.02M with and without permanganate at 0.02M, and hydroxide levels as received (>0.1M) and with 0.5M additional hydroxide. These experiments also provided a better understanding of mechanisms for Sr-90 decontamination. The decontamination factors for Sr-90 from all of the experimental conditions evaluated resulted in a Sr-90 DF of 5 or higher, which is an adequate decontamination to meet ILAW requirements. However, the Sr-90 DFs were very temperature sensitive and greatly increased by the solids digest and filtration at 50°C. The addition of permanganate slightly increased the Sr-90 decontamination at both temperatures tested. The added free hydroxide resulted in a slight reduction in the Sr-90 DF. These results demonstrate that, for Sr-90 removal, hydroxide addition is not recommended; the precipitation temperature in the treatment plant can be reduced from 50°C to 25°C; and the strontium nitrate addition can be reduced from 0.075M to 0.02M to meet ILAW glass requirements.

When the total soluble strontium data (by ICP-AES) are correlated to the Sr-90 DFs, the decontamination mechanism becomes clearer. The primary mechanism for Sr-90 removal is isotopic dilution with the added nonradioactive strontium nitrate. The total soluble strontium in the initial waste is very low (~1 µg/g) and well below the saturation limit for strontium carbonate in the complexant-containing tank waste (AN-102 and AN-107). On addition of nonradioactive strontium nitrate, the total soluble strontium increases to levels around 150 µg/g. The total strontium concentration is extremely sensitive to the digest temperature, reduced by nearly half at 50°C, which correlates directly to the increased Sr-90 DF at 50°C. The reduction of total strontium solubility is directly linked to the increase in Sr-90 decontamination. An increase in temperature reduces the strontium solubility because of the retrograde solubility of strontium carbonate. The permanganate addition also reduces the total strontium levels, but has much less of an effect than the temperature. The reduction in total soluble strontium by permanganate treatment is likely a result of partial oxidation of the chelating agents, EDTA and HEDTA. The increased hydroxide level did not reduce the total strontium solubility and, therefore, did not increase the Sr-90 decontamination.

The system design temperature for operation of crossflow filtration equipment is 25°C. The high Sr-90 removal at 50°C is a result of the decreased total strontium solubility. As the waste is cooled to 25°C for filtration, the total strontium solubility will increase and result in a loss of Sr-90 decontamination. If a higher DF is desired for Sr-90, more nonradioactive strontium should be added to the waste. The precipitation and filtration temperature should be the same. Because of the concern for post-filtration precipitation, the precipitation and filtration temperature should be 25°C.

The TRU decontamination in AN-102 waste only occurred when permanganate was added. The TRU removal exceeded the requirements for ILAW glass by a factor of >5. The digest at 50°C only provided a slight increase in TRU decontamination. TRU decontamination was not increased with added hydroxide to the AN-102 waste sample. These results show that, for TRU removal, the precipitation and digest temperature should be 25°C; the permanganate can be reduced from the baseline concentration of 0.05M to 0.02M; and no additional hydroxide is needed before the waste is treated.

The recommended Sr/TRU removal process conditions for waste from Tank AN-102 are listed below:

1. Dilute/evaporate to a final target sodium concentration of 5M and do not add additional sodium hydroxide.

2. Then, at a temperature of 25 ± 5°C with the waste stirring, add 0.02M strontium nitrate followed by 0.02M sodium permanganate.

3. After both reagents are added, stir/digest the precipitate at 25 ± 5°C for 4 hours.

4. Next, filter the waste at 25 ± 5°C.

These conditions are much lower than the current baseline Sr/TRU removal conditions of 0.075M strontium, 0.05M permanganate, 1M additional sodium hydroxide, and treatment/digest at 50°C. The recommended conditions would result in substantial savings in procurement costs for the reagents; less precipitation and filter cycle time; fewer solids to filter, hence less filter capacity required and fewer wash streams for recycle; and fewer HLW solids that need to be stored and incorporated into HLW glass. Eliminating the additional sodium hydroxide will allow higher waste loadings in ILAW glass, which will reduce the total volume of low-activity waste glass.

5.0 References

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Appendix A

Test Instruction
TI-41500-009

# PNNL Test Instruction	**Document No.:** TP-41500-009 **Rev. No.:** 0

Title: AN-102 Sample Inspection

Work Location: HLRF	Page 1 of 7
Author: Paul Bredt **Use Category Identification:** Reference	**Effective Date:** Upon final signature **Supersedes Date:** New
Identified Hazards: _ Radiological _ Hazardous Materials _ Physical Hazards _ Hazardous Environment _ Other:	**Required Reviewers:** X Technical Reviewer __Building Manager _ Radiological Control _ ES&H _ Quality Engineer _ Project Manager _ RPL Manager _ Client

Are One-Time Modifications Allowed to this Procedure?
X Yes _ No

NOTE: If Yes, then modifications are not anticipated to impact safety. For documentation requirements of a modification see SBMS or the controlling Project QA Plan as appropriate.

On-The Job Training Required? ____ **Yes or** __X__ **No**
FOR REVISIONS:
Is retraining to this procedure required? ___ Yes _X__ No
Does the OJT package associated with this procedure require revision to reflect procedure changes? __ Yes__ No X N/A

Approval	signature	Date
Author		12/4/00
Technical Reviewer		12/4/00

Applicability

This test instruction describes work to be performed under Project 41500 Tasks 2.1, 2.6 and 9.0. Samples of actual Hanford waste from Tank AN-102 were received in the 325 HLRF for testing. This test instruction provides a method for documenting the condition of the as-received samples in accordance with Technical Procedure 41500-004, "Sample Compositing". This document is a mechanism for the cognizant scientist to communicate to technical staff and the client specifics on procedure implementation. Therefore, this Test Plan qualifies as a test instruction under Part B Section 16 of the RPL Operations Manual.

Work will be performed by RPL staff under the direction a cognizant scientist.

Work with actual tank material will be performed in radiological hot cells.

Justification/Test Objectives/Success Criteria

The initial objective of this test instruction is to document to condition of the samples shipped from the Hanford 222-S laboratory to the 325 HLRF. Information to be documented includes the following:

1) Jar numbers
2) Condition of the jars and lids
3) Jar masses
4) Appearance of the solids (color, texture, gel, and/or other observations)
5) Appearance of the liquids (color, turbidity, and/or other observations)
6) Inspection for a separable organic layer

The second objective of test instruction is to obtain a subsample of AN-102 supernatant for Sr/TRU removal under task 2.6 . This supernatant will be decanted from one or more jars as needed to collect the required sample volume. Any remaining settled solids must be left with at least 10 ml of standing liquid to prevent drying of the solids. This supernatant will then be diluted to ~5.3M [Na] using 0.01M NaOH.

Quality Control

This work is to be conducted to the quality requirements in "Conducting Analytical Work in Support of Regulatory Programs." This quality program can be found on the PNNL internal web site at http://quality.pnl.gov/Guidance/QualityAssurancePlanning.

Changes to the test instructions can be made only by cognizant scientist and will be documented by crossing out the original information with a single line, and recording, initialing, and dating the changes.

The results of all measurements will be recorded in an LRB, test instruction, or bench sheet. Copies of the completed test instructions, bench sheets, and LRBs will be transferred to the project file upon completion of the project.

Spill Mitigation

When working with liquids and slurries, there is a risk of sample loss through inadvertent spills. During hot cell work, spills primarily result from dropped or tipped sample bottles, broken glassware, and the failure of transfer equipment. In most cases, spills can be controlled and material losses minimized through the use of secondary containment and other good laboratory practices. The cognizant scientist is responsible for working with hot cell staff to reduce the potential and programmatic impact of spills. Specific examples include:

1) Bottle holders to stabilize jars during sample transfers
2) Catch pans below homogenization vessels and primary sample containers
3) Safety coated jars and bottles (when this does not interfere with analytical requirements)
4) Plastic centrifuge liners

If a spill does occur, every practical effort will be made to recover as much of the sample as possible.

AN-102
Fos; Sr-TRU Aliquot

M&TE List

Balance: Calibration ID 362-06-01-049 388-06-01-020

Expiration Date 8-2001 8/2001

Balance Location HLRF-"B" cell HLRF-"C" Cell

Record daily balance check information below:

Date	Actual (g)	Measured (g)	Tolerance (g)	Acceptable (Y/N)	Balance Location
12/4/00	200 g	199.999 g	±.02	y	"C" cell
12/5/00	1000.0 g	999.99	±.02	y	"B" cell

Data entered by R.G. Swoboda - 5/28/02

Work Instructions

1) The following table contains a list of samples received from the 222-S laboratory. Video tape each of the bottles and complete the Table.

Tape Label: AN-102 Sample Inspection 12/4/00

** Jar ID	222-S ID	Gross Mass (g)	Bottle and Lid in good Condition (a)?	Organic Layer? (b)	* Appearance of Solids	* Appearance of Liquid	Order Viewed
2AN-00-01	S00T001626	964.64	Yes	?	None observed (light Brown Small Layer Likely)	Very Dark ~500 mL Dark Brown/Black.	5)
2AN-00-02	S00T001668	954.25	Yes	?	None observed (Small Layer Likely)	~500 mL Mostly All Dark Brown/Black	4)
2AN-00-03	S00T001627	960.08	Yes	?	None observed (Small Layer Likely)	~500mL Very dark Solution	12)
2AN-00-04	S00T001649	955.51	Yes	?	None observed (Small Layer Likely)	↓	13)
2AN-00-05	S00T001652	962.00	Yes	?	None observed (Small Layer Likely)	↓	24)
2AN-00-06	S00T001628	958.80	Yes	?	None observed (Small Layer Likely)	~500 mL Very Dark Solution	21)
2AN-00-07	S00T001669	945.01	Yes	?	None observed (Small Layer Likely)	~500mL Very Dark Solution	6)
2AN-00-08	S00T001629	909.01	Yes	?	None observed (Small Layer Likely)	<500mL ↓	7)
2AN-00-10	S00T001670	957.27	Yes	?	None observed (Small Layer Likely)	~500mL ↓	8)
2AN-00-11	S00T001631	963.40	Yes	?	Little Layer light Brown ppt	~500mL Very Dark Solution	17)
2AN--00-12	S00T001632	948.76	Yes	?	None observed (Small Layer likely)	~500mL ↓	11)
2AN-00-13	S00T001647	960.82	Yes	?	↓ ↓	↓ ↓	19)

* Very Dark supernate makes color differentiation and/or possible organic Layer virtually impossible to appraise

**- JAR ID's were engraved on Bottles

12/4/00 rgs

10) At this point, TAPE RAN thru Lunch ~45 min.

Jar ID	222-S ID	Gross Mass (g)	Bottle and Lid in good Condition (a)?	Organic Layer? (b)	Appearance of Solids *	Appearance of Liquid *	Order Viewed
2AN-00-14	S00T001648	974.32	yes	?	None observed (possible small layer)	~500 mL Very Dark. Solution	10)
2AN-00-15	S00T001650	957.99	yes	?	None observed (possibly Very small Layer)	~500 mL Very Dark	27)
2AN-00-16	S00T001651	966.65	yes	?	None observed (possibly Very small layer)	~500 mL Very Dark	25
2AN-00-17	S00T001653	972.04	yes	?	None obServed (possible very Small Layer)	~500 mL Very Dark	7)
2AN-00-18	S00T001671	972.00	yes	?	↓ ↓	↓	26)
2AN-00-19	S00T001672	970.39	yes	?	Small Layer of Light Brown ppt	~500 mL Very Dark	22)
2AN-00-20	S00T001673	978.66	yes	?	None observed (Possibly a Small Layer)	~500 mL Very dark	15)
2AN-00-21	S00T001598	967.05	yes	?	~100 mL of Light Brown ppt	Dark Brown/Black ~400 mL	3)
2AN-00-24	S00T001602	964.41	yes	?	~275 mL of Lite Brown ppt, some Cracking of ppt	Dark Brown/Black Solution ~225 mL	23)
3) 2AN-00-25	S00T001664	817.29 + 137.02 = 954.31	yes	?	~100 mL of Light Brown ppt	Dark Brown/Black ~400 mL	11)
2AN-00-26	S00T001665	983.90	yes	?	~300 mL of light Brown ppt	~200 mL Dark Brown/Black Solution	20)
2AN-00-27	S00T001666	965.42	Yes	?	~200 mL Light ~~Dark~~ rgs Brown/~~Black~~ Solids	Dark Brown/Black ~300	1)
2AN-00-28	S00T001667	973.15	yes	?	~200 mL of Light Brown Solids	" ↓	2)
2AN-00-29	S00T001662	973.~~97~~ 973.47 rgs 12/5/00	yes	?	~300 mL of Light Brown ppt	~200 mL Dark Brown/Black Solution	16)

* Dark Supernate makes actual color difficult, possible organic Layer virtually impossible to Appraise. 12/4/00 rgs

3) Removed 137.02 g upfront for AN-102 Sr-TRU.

Jar ID	222-S ID	Gross Mass (g)	Bottle and Lid in good Condition (a)?	Organic Layer? (b)	Appearance of Solids	Appearance of Liquid
2AN-00-30	S00T001663	989.07	y	?	~250 mL of Light Brown	Dark Brown/Black ~250 14)

(a) If bottle and lid are not in good condition, describe the condition below including sample ID. Replace lids as needed, and transfer material to new bottles if needed. Label any new lids or bottles with the old sample number and document the new tare for the bottle.

(b) If organic layer is found, describe below. Include depth of layer, appearance, and bottle ID

Comments and Additional Observations (add additional pages if necessary):

Data entered by rgs – on 12/4/00 – continuation of table on pages 4 and 5. 5/28/02

2) Decant 137 g (±0.5) of supernatant into a 250 ml glass jar of known mass from one or more of the AN-102 samples already inspected starting with jar 2AN-00-25. Consult the cognizant scientist on which jars to use if there is insufficient material in 2AN-00-25. Leave at least 10 ml of standing liquid on any remaining settled solids. Record the mass of material collected below. outside Cell

Balance # 1113120467
Cal Date 2/2001

AN-102 SR/TRU – Bottle Tare = 219.55g

in "C" cell

Total 356.572 g
Tare 219.550 g
Liquid 137.022 g

Bal # 388-06-01-020
Cal. Expires: 8/2001

3) Record which bottles were used, and how much material was decanted in the following table. Removed 137.02g of 2AN-00-025

817.29 + 137.02 g = 954.31 (rgs)

Jar ID	Initial Mass (g)	Final Mass (g)	Net Removed (g)
2AN-00-25	954.31	817.29	137.022

4) Weigh a stir bar.

Stir bar 3.807 g → Stir Bar 3.80692 g

Balance #
360-06-01-035
Cal Date 2/2001

5) Add the stir bar to "AN-102 SR/TRU".

6) Obtain at least 75 g of 0.01M NaOH from Rich Hallen. Record any data on the material label.

Label: See Attached 7a page on prep of 0.01m NaOH rgs 12/4/00

7) While stirring, add 75 (±0.5) grams of 0.01M NaOH to sample "AN-102 SR/TRU". Record the weight before and after caustic addition. Record any observation on dilution (are solids formed?). SEE AN-102 Sample Inspection TAPE 12/4/00

Due to end of tape, I inserted stirring video after Jar 14 inspection.

AN-102 SR/TRU

Stir bar

Final 434.41 g ← offscale - Balance only weighs to 400+g; therefore weighed on "B" cell Balance on 12/5/00 rgs

356.572 ~~137.022~~ + 3.807 = Initial 360.379 g

0.01 M NaOH 74.03 g

rgs 12/5/00

Observation on dilution: None – except it went from Dark Brown to a Little lighter (See video starting after 2AN-00-14 inspection) No ppt formed.

8) Replace cap tightly to keep "AN-102 SR/TRU" from picking up CO_2 from the air.

12/5/00

PSL 1425

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Pg 7a of 7

Balance ID# 380-06-01-006 380-06-01-013
Calibration Date 2/2001 2/2001

Prep of 75 mL of 0.01M NaOH

Target Concentration of NaOH 0.01 M

Tare a 100 mL volumetric flask + Stopper 65.3515 grams

Lot# Aldrich 04608MY

In a 100 mL volumetric add 1.0142 mL of 0.986 M NaOH

set 1.01 mL = 66.5993 grams

Dilute to mark and reweigh 164.9062 grams

164.9064

calculate density 0.995 ⇒ 1.00 g/mL

tare 100 mL storage bottle 160.34 grams
transfer 75 mL to a bottle and label: 0.01M NaOH
bottle plus NaOH 235.34 grams
weight of 0.01M NaOH 75.00 grams

0.01 M NaOH
for AN-102
SR/TRU
PREP

Prepared by:
Date: 12/04/2000

Appendix B

Test Instruction
CHG-TI-41500-008

Rich Hallen

PNNL Test Instruction

Document No.: CHG-TI-41500-008
Rev. No.: 0

REFERENCE COPY

Title: Sr/TRU Removal from AN-102: Small Scale Active Tests to Evaluate Temperature Effect on Decontamination

Work Location: RPL SFO HLRF and SAL	**Page** 1 of 11
Author: RT Hallen	**Effective Date: New**
Use Category Identification: Reference	**Supersedes Date: New**

Identified Hazards:
x Radiological
x Hazardous Materials
___ Physical Hazards
___ Hazardous Environment
___ Other:

Required Reviewers:
x Author
x Technical Reviewer
__RPL Manager
__Project Manager
__RPG Quality Engineer
__CHG

Are One-Time Modifications Allowed to this Procedure? x Yes ___ No

NOTE: If Yes, then modifications are not anticipated to impact safety. For documentation requirements of a modification see SBMS or the controlling Project QA Plan as appropriate.

On-The Job Training Required? _____ Yes or x No

FOR REVISIONS:
Is retraining to this procedure required? _____Yes x No

Does the OJT package associated with this procedure require revision to reflect procedure changes?
_____Yes _____No x N/A

Approval	**Signature**	**Date**
Author	Richard T. Hallen Richard T. Hallen	12/06/00
Technical Reviewer	Ingrid Burgeson Ingrid Burgeson	12/6/00

Concurrence	**Signature**	**Date**
SAL-RPL Representative	Not Required 12/6/00 Rick T. Steele	
RPL Representative	Randy Thornhill	
CHG Reviewer	Dan Reynolds	

I. Applicability

This test instruction describes how to implement the RPL Routine Research Operations Procedure, RPL-OP-001, for experiments with actual tank waste to determine the effect of heating the Sr/TRU precipitate after reagent addition is completed. These tests will use AN-102 waste that was recently delivered to PNNL and is currently in HLRF. Approximately 95 mL of supernatant will be decanted from one sample container and diluted with 0.01M NaOH to approximately 170 mL. The precipitation tests described herein will be performed in the Shielded Analytical Laboratory (SAL) hot cells located in the Radiochemical Processing Laboratory (RPL).

Work is to be performed by hot cell technicians under the supervision of a cognizant scientist. The cognizant scientist shall be responsible for implementation and adherence to this test instruction. This instruction is specific to:

- Sr/TRU removal by chemical addition to an envelope C waste; AN-102 decanted supernatant
- strontium nitrate addition with and without sodium permanganate addition for precipitation of active wastes in RPL hot cell facilities, and
- tests performed at PNNL in the RPL, by staff in the Environmental Technology Division.

II. DRD Reference

Task 9.2.2 of the Development Requirements document identifies activities for Active Integrated Pretreatment Testing (i.e., mixing AN-102 and C-104 HLW permeate and subsequent process verification testing).

III. Schedule Reference

The RPP WTP Research and Technology schedule for Y2001 identifies this activity as R20850, RTPT Integration of Pretreatment systems (PNNL). The corresponding activities on the PNNL schedule are 02.05.01.02.01 and 02.08.04.

IV. Justification

Sr/TRU removal tests at Savannah River last year were successful in demonstrating adequate Sr and TRU decontamination. The prior tests did not fully explore the effect of temperature on the solids digest nor the situation of minimizing reagent addition. The temperature of the solids digest will have a major impact on plant design if heat is needed to obtain adequate decontamination. These tests will use diluted AN-102 supernatant to test certain conditions at low levels of reagent treatment to allow an informed decision as to how to proceed with testing the AN-102/C-104 waste later. This test will take advantage of the time delay in homogenization of the AN-102 waste, mixing with C-104 wash/leach solutions, and evaporation to further our understanding of the optimum process.

V. Objective

The objectives of this task are to:

- Prepare approximately 170 mL of diluted AN-102 supernatant.
- Perform a series of Sr/TRU precipitation test on the diluted AN-102 waste as shown in Table 1.
- Filter and analyze a portion of each test solution for sodium, total strontium, ^{90}Sr, and ^{241}Am. And determine free hydroxide on selected samples.
- Evaluate and report the results.

VI. Success Criteria

The success criteria are to demonstrate that the treated waste meets specification 2 of RFP solicitation DE-RP27-00RV14136 for removal of ^{90}Sr and TRU elements from the LAW solution.

VII. Spill Protection/Response

Hot cell technicians shall conduct tests in a manner to minimize the impact of a spill. In the event of a spill, all practical efforts will be made to recover the test material. Recovered material will be segregated and retained pending a decision by the cognizant scientist on how to proceed.

VIII. Feed Description

These Sr/TRU removal tests will use diluted AN-102 supernatant. This material will be prepared for testing by the implementing following steps:

1. Decant supernatant from a single bottle of AN-102 waste. Approximately 95 mL will be needed.
2. Dilute the AN-102 waste using 0.01M NaOH solution until the waste is approximately 5.3 M sodium assuming original supernatant is 9.5M.

IX. Equipment Description

These tests will be conducted on a small scale, approximately 20 mL each. Appropriate glass vials will be used, such that the selected samples can be heated to a temperature of 50°C and held at this temperature for 4 hours. Good mixing of the samples during chemical addition must be provided, small magnetic stir bars for each sample vial are recommended. Reagents will be added slowly as liquids, and stirred after each reagent is added. Some experiments will require two different reagents to be added in the proper sequence as detailed in the test matrix.

X. Work Instructions

1.0 Relevance

This test instruction is to be used to perform tests for Sr/TRU removal from diluted AN-102 supernatant. Supernatant from one bottle of AN-102 tank waste currently located in HRLF will be used. Dilution of the supernatant with 0.01M NaOH will occur in HLRF before transfer to SAL under Test Plan 41500-004 and according to Test Instruction 41500-009.

2.0 Supporting Documents

This test instruction is to be used with the Routine Research Operations Procedure, RPL-OP-001. Sr/TRU removal test conditions and analytical requirements were designated in Test Specification TSP-W375-00-00### from CHG. These are follow-on studies of work performed at Battelle and SRTC for the RPP-WTP Contr4actor (BNFL-TI-29953-037, -040, -041. -043, -052, and -063).

3.0 Responsible Staff

The staff responsible for executing this test plan are as follows.

- Task Manager – Rich Hallen
- SFO Manager – Randy Thornhill (Rick Steele)
- Test Scientists – Sandy Fiskum, Ingrid Burgeson, and/or Paul Bredt
- Hot Cell Technician – list names/location/work performed

  ____

- Radiological Control Technician

4.0 Materials, Equipment, Supplies and Reagents Needed

4.1 Materials Required

1. Eight 20 mL glass vials for rad chem samples, 8 plastic vials for ICP samples, and 4 vials for hydroxide samples, pre-labeled as follows: HD-01 through HD-08. And 8, 40-mL glass scintillation vials or similar bottles for conducting experiments labeled 1, 3-8, with a 20 mL volume mark on each vial (one extra vial for additional sampling if necessary).
2. 8 - disposable syringes and 0.45 micron syringe filters. With extras on hand if filtering is difficult.
3. One bottle of diluted AN-102 supernatant moved from HLRF, sample bottle name "AN-102 SR/TRU."
4. 60 mL storage bottle with 2.37 mL of 10M NaOH for caustic adjustment (test 7 and 8)
5. Magnetic stir bars
6. Disposable pipettes and volumetric pipette tips.
7. Two 10 mL volumetric flasks for determining the density of the diluted AN-102 supernatant.

4.2 Equipment

1. 160 gram capacity analytical balance
2. Clock/Stop-watch
3. Calculator
4. Stir plate(s)
5. Hot plate(s)
6. Volumetric Pipette(s)
7. Thermometer or temperature reading device

4.3 Reagents Needed In Hot Cell (see prep sheet)

1. 10 mL of 0.4M $Sr(NO_3)_2$
2. 10 mL of 0.4M $NaMnO_4$

4.4 Other Supplies

1. Copy of this TI to record data
2. Laboratory Record Book (use yellow bound lab notebook, record book, BNW-57651)

5.0 Instructions

The laboratory record book (LRB) shall be used to record observations and other testing information as required by this test instruction. All test conditions shall be recorded on a copy of this test instruction or in the lab notebook.

Cross-contamination between samples and contamination of samples from outside sources must be minimized at each step. Use new supplies and bottles for each sample as much as practical.

Keep lids on containers to minimize the potential for spills and to prevent evaporation.

5.1 Prestart

✓ JB **5.1.1** Prepare strontium and permanganate solutions according to the attached preparation sheet. Calculate solution densities and record these values. All vials should be labeled and marked with the 20 mL line before they are taken into the hot cell. NOTE: Tare weigh bottle/vials with caps/lids

✓ JB **5.1.2** Inventory materials, equipment, supplies, and reagents to ensure all required items are available. Modified materials/equipment as needed for remote handling.

Record Unique ID # of reagents:

0.4M $Sr(NO_3)_2$ 0.4m ~~MnO~~ $Sr(NO_3)_2$ JB 12/7/00

0.4M $NaMnO_4$ 0.4m MnO_4.

5.1.3 Review the test matrix (Table 1) in this test instructions. Note the calculation worksheet, which gives quantities of reagents to be added. Reagents can be added as volume but always record the mass added.

5.1.4 Obtain the following information:

M&TE List: Note Balance Location, HLRF/SAL and cell

✓ Balance(s) : (record for each balance used)

Calib ID 360-06-01-016 Calib Exp Date 2/01

Location SAL/cell 2 100g wt = 99.9991 g

✓ temperature reading device (thermometer or thermocouple/reader):

Calib ID 03256 Calib Exp Date 8/2002

Location cell 5 SAL

entry by Ingvild Burgeson 12/7/00

5.2 Operation

5.2.1 Obtain diluted AN-102 supernatant from SAL. Record diluted AN-102 ID.

AN-102 Sample Bottle ID AN-102 Sr/TRU

Document the appearance of the diluted waste, noting the color and clarity of the supernatant, presence/absence of solids and color/characteristics of the solids if present.

Diluted Supernatant light brown color, no visible cloudiness or solids

Solids Present ? none visible / whole sample 200mR/hr contact + 110 mR at 30 cm

If solids are present and readily settle to the bottom, allow solids to settle and pipette supernatant from above the solids layer. It solids remain suspended, mix well before pipetting supernatant for the density determination. Use a volumetric flask (ball flask) to determine the density of this solution. Record the density of the diluted waste, and use this density to determine the weight of 20 mL of waste.

Record Cell Temperature 26°C (thermometer in cell 2) verified to within 1°C of calibrated thermocouple

tare flask 12.8361 g, flask + waste — g, waste mass 12.6477 g, flask volume 10.0 mL

density of diluted AN-102 supernatant 1.264 g/mL

Repeat in clean volumetric.

tare flask 12.8368 g, flask + waste — g, waste mass 12.5437 g, flask volume 100 mL

density of diluted AN-102 supernatant 1.254 g/mL

Average density 1.259 ~1.26g g/mL 20 mL of diluted supernatant = 25.2 grams

Pour the waste out of the volumetric flasks back into the original bottle of diluted AN-102 supernatant.

[illegible] 12/6 125 large mouth, plastic

Tare ~~60~~ mL sample bottle for caustic adjustment –

tare + 10M addition done in PSC 1425
Balance # 380-06-01-013
Cal. 2/2001 [illegible] 12/6/00

tare weight bottle 21.7674 g

pipette 2.37 mL of 10M NaOH into sample bottle, reweigh 24.9486 g in cell wt 24.9478 g
Fisher Sci. Lot# 953618-24

Use the density to calculate the weight of 45 mL of diluted supernatant 45 mL x 1.22 g/mL = 56.7 g

Add 45 mL or 56.7 g of diluted supernatant to ~~60~~ 125 [illegible] 12/6/00 mL storage bottle for caustic adjustment

Total weigh after waste added 81.2692 g (81.2692 − 24.9478 = 56.3214 g sample added)

Save this caustic adjusted waste for test 7 and 8.

Review the test matrix shown below, Table 1. Record data in Table 2. Note to check each activity when complete. This should be done and verified by the cognizant scientist.

Table 1. Test Matrix.

Test #	Additional [OH]	Target [Sr]	Target [MnO4]	Digest Temperature	Comment
1	none	none	none	ambient	control-filtered
2	none	none	none	ambient	control-filtered, dup
3	none	0.02 M	none	ambient	temp effect on Sr
4	none	0.02 M	none	50	temp effect on Sr
5	none	0.02 M	0.02 M	ambient	temp effect on TRU
6	none	0.02 M	0.02 M	50	temp effect on TRU
7	0.5M	0.02M	0.02M	ambient	temp and [OH] effect
8	0.5M	0.02 M	0.02 M	50	temp and [OH] effect

The permanganate oxidation reaction generates very little heat at these low reagent additions, thus the sample is not expected to be above ambient cell temperature. All samples need to be digested for 4 hours. After the chemical additions are complete to all of the vials, the vials 4, 6 and 8 should be heated to 50°C and held at this temperature for 4 hours. All vials should be treated the same, with the exception of heating vials 4, 6 and 8. So stir/mix all vials the same over the 4-hour period. Tests 1 and 2 are duplicate control/blanks, and only need to be stirred. Sample will not generate significant gas, or built up pressure when heated to 50°C but vial caps do not need to be overly tight during heating.

5.2.2 Record the weights (and volumes where appropriate) of all vials, samples, additions, and dilutions. After the precipitate digest time of 4 hours, the samples held at 50°C need to be allowed to cool to ambient temperature, which should occur in 15 minutes. Use the syringe and disposable filters to filter each sample into the corresponding "analytical vial." Follow ASR instruction for sample preparation and distribution. Note that 4 samples, 1, 2, 5, 7, and 8 need an additional sample collected for [OH] measurement by autotitration (do not add acid to these samples, PNL-ALO-101).

6.0 Sample Analysis

All subsequent sample dilution to achieve instrument or ALARA conditions are to be recorded noting both volume and mass. The data for preparation of the samples for analyses shall be recorded in a table format, or on an analytical lab data sheet. The point of contact for the sample preparation and distributions from these tests is Rick Steele.

6.1 Chemical and Radiochemical Analysis

Table 3 below shows the sample analysis list. The table lists the analyses to be performed on samples generated from this test instruction. An Analytical Services Request (ASR) will be completed by the cognizant scientist/task leader and submitted to the CMC with the samples.

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BDM

Data Sheet

PSC 1425

Preparation of Stock Solution
Record all information and observations on prep sheet or in lab notebook.
Balance number: 360-06-01-013.
Balance calibration: 2/2001.

Makeup stock NaMnO4 solu 0.4 M
use NaMnO4.1 H2O, 97+%, ACS Reagent Grade
159.94 grams/mole (FW) (lot # A010675901) Acros Organics
Tare 10 mL volumetric flask 11.9547 grams
add 0.63976 grams NaMnO4 flask + NaMnO4 ________ grams
actual weight of NaMnO4 added 0.6425 grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
fill to volumetric line with Milli-Q water. Record total weight: 22.2784 grams
calculate actual [MnO4] = actual weight/159.94/volume in Liters = 0.4017 M
calculate density of solution, weight of solution/volume = 1.032 grams/mL
Transfer stock solution to bottle and label unique ID # 0.4M MnO4

Makeup Sr(NO3)2 solution 0.4 M
use Sr(NO3)2
211.63 grams/mole (FW) (lot # 984987)
Tare 10 mL volumetric flask 11.2790 grams
add 0.84652 grams Sr(NO3)2 flask + Sr(NO3)2 ________ grams
actual weight of Sr(NO3)2 added .8483 grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
fill to volumetric line with Milli-Q water. Record total weight: ~~0.4~~ RDM grams
calculate actual [Sr] = actual weight/211.63/volume in Liters = 0.4008 M
~~calculate~~ determine density of solution, weight of solution/volume = 1.064 grams/mL
Transfer stock solution to bottle and label unique ID # 0.4M $Sr(NO_3)_2$
2.00mL = 2.1389 2.1291 2.1253 2.1260 2.1199
AVE = 1.0638
std dev = 0.0035
Date prepared: 12/04/2000
Prepared by:
Work Package Number: F20748

Table 2. Data Sheet.

Test #	Analytical Vial ID	Vial Tare Weight, g	Number Indicates Order of Addition						Test Complete (initial)
			Target 1		Target 2		Target 3		
			25.2 AN-102 added		1.12g Sr added		1.08g MnO_4^- added		
			target mL	actual g	target mL	actual g	target mL	actual g	
1	HD-01		20		0	×	0	×	JEB
2	HD-02		20		0	×	0	×	JEB
3	HD-03	86.1586	20	24.89	1.05	IB 12/5/00 ~~1.12~~ 1.13 ①	0	×	JEB
50°C 4	HD-04	86.0190	20	25.06	1.05	1.13	0	×	JEB
5	HD-05	85.1598	20	24.88	1.05	1.13	1.05	1.11	JEB
50°C 6	HD-06	85.0103	20	25.02	1.05	1.12	1.05	1.10	JEB
7*	HD-07*	84.7890	20*	25.50	1.05	1.14	1.05	1.11	JEB
50°C 8*	HD-08*	84.8065	20*	25.26	1.05	1.13	1.05	1.14	JEB

* make sure to use caustic adjusted waste for tests 7 and 8, additional 0.5M NaOH - verified 7+8 were w/ [OH] added IB 12/7/00

Record Times

preheated bath 50°C

Test #	Reagent Addition Started	Reagent Addition Completed	Heating/Stirring Started	Heating/Stirring Completed	Analytical Sample Removed ie Filtered
1	×	×	—	—	filters easily
2	×	×	—	—	"
3	8:36	8:36	8:37	12:38	12:55
50°C 4	8:25	8:25	8:30	12:33	1:03 - easier than 3 to filter
5	8:41	8:58	8:58	1:00	1:12 - stiff filtering
50°C 6	8:29	8:49	8:50	12:51	1:25 slightly easier than #5
7	8:44	9:01	9:01	1:00	1:38 filters easily
50°C 8	8:33	8:53	8:54	12:56	1:32 filters easily

allowing to settle for ~15 minutes did not result in appreciable settling/clarity

① recording error IB 12/5/00

Table 3. Samples and Their Required Analyses

Process Variable	Vial ID	Sample Type	Sample Preparation	Analysis Description[(a)]
Diluted AN-102 supernatant	HD-01	Filtrate	0.45 um disk	Sr/Am, ICP, [OH$^-$]
Duplicate feed, HD-01	HD-02	Filtrate	0.45 um disk	Sr/Am, ICP, [OH$^-$]
0.02 M Sr only, low temp	HD-03	Filtrate	0.45 um disk	Sr/Am,ICP
0.02 M Sr only, high temp	HD-04	Filtrate	0.45 um disk	Sr/Am, ICP
Sr and Mn, low temp	HD-05	Filtrate	0.45 um disk	Sr/Am, ICP, [OH$^-$]
Sr and Mn, high temp	HD-06	Filtrate	0.45 um disk	Sr/Am, ICP
Sr/Mn/OH, low temp	HD-07	Filtrate	0.45 um disk	Sr/Am, ICP, [OH$^-$]
Sr/Mn/OH, high temp	HD-08	Filtrate	0.45 um disk	Sr/Am, ICP, [OH$^-$]

(a) Descriptions of analyses are contained in Table 4.

Table 4. Description of Analyses

Constituent	Analysis Method	PNNL Procedure No.
Acid digestion for Am-241, Sr-90 and ICP		PNL-ALO-101
Strontium-90	Separations and Beta Counting	PNL-ALO-476/408
Americium-241 (Cm)	Separation, plating and AEA	PNL-ALO-417, 496 422
Hydroxide	EPA SW-846 Modified Method, 310(3)	PNL-ALO-228
Na and total Sr (report all ICP metal listed in Table 5)	ICP-AES	PNL-ALO-211/280

Table 5. Minimum Reportable Quantities for Liquid Samples (supernatant/filtrate).

Analyte	Minimum Reportable Quantity (μg/mL)
Al	7.5E+01
Ba	2.3E+00
Ca	1.5E+02
Cd	7.5E+00
Cr	1.5E+01
Cs	1.5E+00
Fe	1.5E+02
K	7.5E+01
La	3.5E+01
Mg	3.0E+02
Na	7.5 E+01
Ni	3.0E+01
P	6.0E+02

Analyte	**Minimum Reportable Quantity (μg/mL)**
Pb	3.0E+02
Sr	8.7E+01
^{241}Am	7.2E-04 μCi/mL
^{90}Sr	1.5E-01 μCi/mL
OH	0.05**M**

7.0 Calculation and Important Information

Estimated density of starting AN-102 sample = 1.47 g/mL

Estimated density of diluted AN-102 supernatant = estimated 1.2 g/mL

Density of 0.4M $NaMnO_4$ solution = 1.032 g/mL

Density of 0.4M $Sr(NO_3)_2$ solution = 1.064 g/mL

Mass of Solutions based on above density data. Densities (and masses) need to be verified based on actual solution densities. This will be performed after solutions are prepared in Step 4.3.

Test #	Waste (mL)	Added [OH] (M)	Target [Sr] (M)	Volume of Sr (mL)	Target [Mn] (M)	Volume of Mn (mL)
1	20	0	0	0	0	0
2	20	0	0	0	0	0
3	20	0	0.02	1.05	0	0
4	20	0	0.02	1.05	0	0
5	20	0	0.02	1.05	0.02	1.05
6	20	0	0.02	1.05	0.02	1.05
7	20*	0.5	0.02	1.05	0.02	1.05
8	20*	0.5	0.02	1.05	0.02	1.05

* Use caustic adjusted waste for tests 7 and 8.

8.0 References

Reynolds, Dan. 2000. River Protection Project – Waste Treatment Plant Test Specification "Sr/TRU Removal Testing of AN-102 Waste," TSP-W375-00-00###, December 6, 2000, CH2M Hill Hanford Group, Inc.

Appendix C

Laboratory Record Book

BNW- 57651
10-19-00

PACIFIC NORTHWEST LABORATORY
ISSUED
OCT 1 9 2000
BATTELLE RECORDS MGMT.

[illegible]
[illegible]
U.S. [illegible] LABORATORIES
[illegible] 1830

F17197

	LABORATORY RECORD BOOK NUMBER BNW- 57651	This document consists of .... pages, copy no. ....
	TITLE (INDICATE SUBJECT CONTENT) Sr/TRU Removal - Active Tests	
AUTHOR - DIVISION AND DEPARTMENT		
PERIOD COVERED FROM	TO	

Route To	P. R. No.	Location	Route Date	Signature & Date
RT Hallen	39230	K2-12	10/19/00	Richard T. Hallen 10/26/2000

Authorized Users

Printed Name	Signature	Date	Initials
Richard T. Hallen	Richard T. Hallen	10/26/2000	RTH
Ingrid Burgeson	Ingrid Burgeson	12/5/2000	IEB

TABLE OF CONTENTS

Density $NaMnO_4$ (pg 2) = 1032 g/mL

Experiment Volume Addition of $NaMnO_4$

m $NaMnO_4$ = 0.4017
Volume $NaMnO_4$ needed = 1.05 mL (0.4017)(x) = (0.20)(20+x) x = 1.0486 IB 12/7/00
mass of $NaMnO_4$ needed = ~~1.12~~ 1.08 ① IB 12/7/00 g (1.048 mL) * (1.032 g/mL) = 1.08 g
6 IB 12/7/00

Density $Sr(NO_3)_2$ = 1.064 g/mL (pg 2)

Experiment Volume Addition of $Sr(NO_3)_2$

m $Sr(NO_3)_2$ = 0.4008 m
Volume $Sr(NO_3)_2$ needed = ~~1.12 g~~ 1.048 mL IB 12/7/00 (0.4008)(x) = (0.20)(20+x) x = ~~1.115~~ 1.048 IB 12/7/00
Mass of $Sr(NO_3)_2$ needed = 1.12 g (1.048 mL) × (1.064 g/mL) = 1.115 g

ρ of AN102 -liquid is clear + light brown in color - Diluted w/ NaOH in HLRF
-no solids, very consist coloring throughout depth

10 mL vol flask MT 12.8361 g w/lid + 10 mL AN102 12.6477 g ρ = 1.26 g/mL
chg density tared flask + then added 10 mL supernate = 12.5437 ρ = 1.25 g/mL
Balance ID 360-06-01-016 cal due 2/01 100 g wt = 99.9991 g

Bottle of NaOH w/ lid = 24.9478 g
" + AN102 = 81.2692
Mass AN102 = 56.3214 g
volume AN102 = 44.69 mL (56.3214 / 1.26 g/mL)

verified density to be 1.26 g/mL

cell temp #2 w/ thermometer 26 °C (not calibrated)
#5 thermocouple 25 °C (channel 4) - calibrated

① recording error IB 12/7/00

Project No.________ Date of Work________
Entered By Ingrid Burgeson Date 12/7/00
Disclosed To and Understood By
Signed 1.________ Date________
2.________ Date________

12/7/00
IB

Bottle #7 w/ stir bar	= 84.7890 g	tared wt of sample	25.4998
#8	= 84.8065 g		25.2575
#3	= 86.1586 g		24.8927
#4	= 86.0190 g		25.0648
#5	= 85.1598 g		24.8813
#6	= 85.0103		25.0246

AN102 Diluted Sample + bottle > 160 g exceeds balance capacity ∴ no SAL mass

Dose info from transfer from HLRF to SAL
Top @ contact 200 mR γ no β
@ 30cm 110~~0~~ mR γ no β IB 12/7/00 ①
Bottom @ contact 1000 mR no β

Balance ID 360-06-01-016 cal due 2/01 100 g block = 99.9990 g IB 12/8/00

12-8-00

Addition of Reagents - while stirring gently (?) - yes

	Rxn #	mass $Sr(NO_3)_2$	time	mass MnO_4	time	To preheated bath
50°C	4	1.1277	8:25	—	—	8:30
	6 ~~5~~ IB 12/8/00	1.1267	8:29	IB 12/8/00 1.1020	8:49	8:50
	8	1.1347	8:33	1.1390	8:53	8:54
RT	3	1.1309	8:36	—	—	—
	5	1.1459	8:41	1.1106	8:58	—
	7	1.1396	8:44	1.1080	9:01	—

} on stir plate @ 9:05

- using 5 mL pipet 1.05 mL check; 1.1636 1.00 mL = 1.0574

gentle stirring during addition of $Sr(NO_3)_2$ - white ppt formed on top layer
stirred more vigorously to dispel ppt homogeneously (takes only few minutes)
-even distribution of white solids results in murky
addition of MnO_4 - uniform darkening of solution due to color of reagent
-no other visible changes
@ 9:02 rxn 5 is darker than rxn 7. Rxn 7 just had MnO_4^- addition ∴ appears as if solution darkens during reaction

cell temp in #5 = 25°C

① recording error IB 12/7/00

Project No. ____ Date of Work 12-7 + 12-8 00

Entered By Ingrid Burgeson Date 12/7/00 + 12/8/00

Disclosed To and Understood By

Signed 1. ____ Date ____

2. ____ Date ____

Water Bath

	8:30	50°
100 ~~came off~~ *	8:55	60° - added more H_2O
	9:05	48°-
	9:25	44° - increased heat
	10:00	50°
	11:00	50°
	11:30	52°
	12:20	~51°
	12:58	50°

Time to Perform Filtering (remove from bath)

Vial	target time	actual time	
3	12:36	12:55	(tried to settle ~15 min - no help)
✩ 4	12:30	1:03	easier than 3 to filter
5	12:58	1:12	stiff filtering
✩ 6	12:50	1:25	slightly easier than #5
7	1:01	1:38	easy filtering
8	12:54	1:32	easy filtering

Filtered 8-9 mL of solution, Those reactions containing MnO4 makes the filtration very stiff (just like AN107)

#6, first 3 mL was appreciably clearer than remainder sample (settling does occur to slight extent)

#8 ditto. Marked difference in sol - dark thick (ie more ρ liquid) comes up at ~3mL. Purple colored "2nd" liquid

cm γ 3 Check of sample activity 500μl filtered rxn #1 reads 190β (1 inch), 15γ (1 inch), 2γ (30 cm)
- discussed w/ CZS to determine if levels are acceptable to hood prep. Agreed to do hood prep w/o reservation (option of m-cell was discussed + discarded) - hood prep will provide better data

	Analytical Vial	filtered solution	wt w/solution	comments
1	17.0263 (17.0300 out of cell)	AN-102 stock bottle	38.4017	filters easily
~ anodise 3	17.1227*	rxn #3 vial	32.0766	
Jum 4	17.1848*	rxn #4 vial	27.4474	easy to filter
5	17.1457*	rxn #5 vial	26.6713	stiff filtering
6	17.0387*	rxn #6 vial	26.7168	slightly easier than #5
7	17.1021*	rxn #7 vial	28.0088	easy filtering
8	17.0636*	rxn #8 vial	27.4815	easy filtering

* mass of vials weighed outside of cell balance ID 360-06-01-036 20.0g wt check = 19.9997 (prep lab)
Above information is recorded to provide approximate info on the volume available in those archive vials.

✩ inner seal of lid came (#4 & #6) off when preparing for filtering IB 12/8/00

Project No.________________ Date of Work 12-8-00

Entered By Ingrid Burgeson Date 12/8/00

Disclosed To and Understood By

Signed 1.________________ Date________

2.________________ Date________

Appendix D

Analytical Data

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Processing Group

filename 01-0169
1/25/01

Client : I. Burgeson

Cognizant Scientist: C Soderquist Date : 1-25-01

Concur : LRGreenwood Date : 1-25-01

Procedures
RPG-CMC-476, -408 (Sr-90)
RPG-CMC-417, -496, -422 (Am, Cm)

Measured Activities, μCi/g ± 1s total uncertainty

ALO ID Client ID	Sr-90 ± 1s	Am-241 ± 1s	Cm-243 + Cm-244 ± 1s	Cm-242 ± 1s
01-00169 HD-01	2.94E+1 ± 3%	6.40E-2 ± 5%	2.33E-3 ± 8%	2.15E-4 ± 23%
01-00169 DUP HD-01	3.07E+1 ± 3%	6.80E-2 ± 4%	2.08E-3 ± 7%	2.01E-4 ± 19%
RPD	4%	6%	11%	7%
01-00170 HD-02	3.00E+1 ± 3%	6.06E-2 ± 14%	2.04E-3 ± 18%	1.58E-4 ± 25%
01-00171 HD-03	5.21E+0 ± 3%	6.56E-2 ± 5%	2.45E-3 ± 8%	1.68E-4 ± 25%
01-00172 HD-04	1.92E+0 ± 5%	4.87E-2 ± 15%	1.68E-3 ± 19%	1.53E-4 ± 25%
01-00173 HD-05	3.86E+0 ± 4%	1.22E-2 ± 15%	4.13E-4 ± 19%	2.41E-5 ± 32%
01-00174 HD-06	9.35E-1 ± 8%	1.00E-2 ± 15%	3.45E-4 ± 19%	4.39E-5 ± 22%
01-00175 HD-07	5.04E+0 ± 4%	1.19E-2 ± 25%	4.78E-4 ± 27%	3.08E-5 ± 19%
01-00176 HD-08	1.28E+0 ± 6%	8.83E-3 ± 6%	4.27E-4 ± 8%	4.15E-5 ± 20%
Matrix Spike*	108%	(129 ± 65)%		
Blank Spike	100%	100%		
Blank	<2.E-3	1.28E-4 ± 23%	<4.E-5	<4.E-5

*The Am-241 matrix spike result has high uncertainty because the spike was too small for the sample activity.

Analysis of AN102 Filtrate

1/24/01

Eight samples of AN-102 filtrate were submitted for analysis of strontium-90, americium-241, metals by ICP, and alkalinity by titration. The samples for the strontium and americium analyses were prepared in a hot cell by acid digestion according to procedure PNL-ALO-101. Direct samples were delivered to the laboratory for the hydroxide measurements.

Strontium-90 Analysis

The sample material, as received by the lab, was diluted and mounted for a gross alpha-gross beta count. The gross alpha and gross beta results were used to estimate the stronium-90 and americium-241 activity for calculating aliquot sizes. (No gamma count was requested for these samples.)

Strontium-90 was measured by chemically separating the strontium, then counting it for beta emission (procedures RPG-CMC-476 and -408). Strontium-85 was used as a tracer and all the results were corrected for tracer recovery. The tracer recovery averaged about 0.93.

The lab blank had no detectable strontium-90. The blank result was well below the required MRQ. Two spikes were run with the samples, a matrix spike and a reagents-only spike. Both spike results were well within expected uncertainty. The duplicates agreed within 4%.

After the beta counting was done, we discovered that the strontium-90 spike solution used for this work had increased in concentration, apparently from evaporation. Using the expected strontium-90 concentration, the two spikes gave results 25% and 16% high, far outside analytical uncertainty. We accurately assayed the strontium-90 spike solution and found that its concentration had increased about 15% over what it originally had been. Using the true strontium-90 concentration, the spike results came out 100% for the reagents-only spike and 108% for the matrix spike. (The assay of the spike solution is included in the project file. That strontium-90 spike solution will not be used again.) .

Americium-241 Analysis

Americium-241 was chemically separated from the sample solution, then mounted for alpha spectroscopy by coprecipitation with a rare earth fluoride onto a membrane filter (procedures RPG-CMC-417, -496, and -422). Curium accompanies the americium. The alpha emitters were measured by alpha spectroscopy, using americium-243 as a tracer to correct the counting results for chemical recovery.

The aliquot sizes used for americium were too large, which compromised analytical precision. The gross alpha count used to estimate the aliquot sizes apparently gave low results (probably from mass loading, which absorbs alpha emission). Also, we assumed that 30% of the alpha would be americium, but americium turned out to be more than that. The result of such a large aliquot size was that the americium-241 peak tail added to the americium-243 peak area, artificially increasing the tracer recovery. On several samples, the measured tracer recovery is probably slightly high, and on one sample we estimate it is 20% high. The high bias in the tracer causes a **low bias in the final analytical results** for both americium and curium. We have increased the total uncertainty on the affected samples to include the uncertainty in the tracer recovery. There is no practical way to deconvolute the alpha spectra. If more accurate results are needed, then the samples should be rerun with smaller aliquot sizes.

The lab blank was slightly contaminated with americium, but it was 800 times lower than the lowest sample. (The lab blank result given on the result has been corrected for typical sample dilutions.) The activity in the lab blank was below the required MRQ. The duplicates agreed well within expected uncertainty (within 6% for Am-241). The reagents-only spike gave a 100% recovery. The matrix spike was too small, compared to the americium already in the sample, to give a meaningful result. (The matrix spike yield is 1.29 ± 0.65 at 1s. The sample aliquot was too big for the spike we used. A large number with good precision minus another large number with good precision gives a small number with high uncertainty.)

Hydroxide Analysis

Sample aliquots, as received by the lab, were titrated for bases according to procedure PNL-ALO-228, using a Brinkman 636 Auto-Titrator. A 0.1 N NaOH solution was standardized in triplicate against NIST standard reference material potassium acid phthalate, and used as a standard and spike. The titrant was 0.2 M HCl, standardized in triplicate against the 0.1N NaOH. The autotitrator takes a complete titration curve for each sample and marks the inflection points. Each sample was run in duplicate. The titration curves are included with the report.

The titration curves all showed three inflection points, generally attributed to hydroxide, carbonate, and bicarbonate. The duplicate results were in good agreement, with RPD values less than 12%. The hydroxide blank spike recovery averaged 113% and two sample spikes both recovered at 106%. No hydroxide was detected in a reagent blank. (The blank had no inflection point.) The sample hydroxide concentrations were all far above the required MRQ.

Review:
1-25-01

Project / WP#:	/F17197
ASR#:	6004
Client:	I. Burgesen
Total Samples:	8 (liquids)

	From	To
RPL#:	01-00169	01-00176
Client ID:	"HD-01"	"HD-08"

Sample Preparation: Samples acidified with 2M HNO_3.
AOIs: Al, Ba, Ca, Cd, Cr, Fe, K, La, Mg, Na, Ni, P, Pb, and Sr.

Procedure: PNNL-ALO-211, "Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry" (ICPAES).

Analyst: D.R. Sanders

Analysis Date (File): 01-05-2001 (A0632)

See **Chemical Measurement Center 98620 file:** ICP-325-405-1
(Calibration and Maintenance Records)

M&TE Number:	WB73520	(ICPAES instrument)
	360-06-01-029	(Mettler AT400 Balance)

3-15-02
Reviewed by

Renée Russell 3-15-02
Concur

Eight caustic samples from Analytical Service Request (ASR) 6004 were received and diluted with 2M nitric acid by the Sample Receiving and Preparation Laboratory (SRPL) and analyzed. Sample aliquots of 0.300 mL were added to 10.0 mL of 2M nitric acid. No other sample preparations were performed.

The attached ICPAES Results (4 pages) presents the final sample and QC results. The ICPAES measurement results are reported in µg/mL of as-received liquid sample.

In the ASR, Al, Ba, Ca, Cd, Cr, Fe, K, La, Mg, Na, Ni, P, Pb, and Sr were identified as analytes of interest for this work. The quality control (QC) results for each of these analytes have been evaluated and are presented below. Analytes other than those detected as part of the ICPAES analysis are reported, but have not been fully evaluated for QC performance.

The following is a list of quality control measurement results relative to ICPAES analysis requirements of the controlling QA plan. Since the samples were prepared by the client, no duplicates, process blanks, matrix spikes, or processing laboratory control samples were analyzed. Selected samples from each day's runs were post spiked with the analytes of interest.

Process Blank:

Not applicable.

Duplicate Relative Percent Difference (RPD):

Not applicable.

Laboratory Control Sample (Montana Soil SRM 2710):

Not applicable.

Matrix Spiked Sample:

Not applicable.

Post-Spiked Samples:

All post-spiked analytes of interest in samples analyzed were recovered within the acceptance criteria of 75% to 125%, except Na. The post spike analysis uses a general spiking solution intended to be usable on the majority of sample analyzed by ICPAES. However, for the sample selected for post spiking, the spike concentration for Na was greater than the upper measurement limit. For Na, the use of serial dilution results is used to evaluate potential matrix interferences.

Serial dilution:

Serial dilution was required for Na, since the post spike concentrations were greater than the upper measurement limit (i.e., recoveries could not be evaluated). The percent difference (%Diff) for the serial dilutions for Na were within the acceptance criteria of ±10% after correcting for dilution.

Other QC Standards:

The K failed the high calibration check. The acceptance criterion was 95% to 105% and K was measured at 108% and 109%. Therefore, the reported results for K may be slightly biased high.

Comments:

1) "Final Results" have been corrected for all laboratory dilution performed on the sample during processing and analysis unless specifically noted.
2) Detection limits (Det. Limit) shown are for acidified water. Detection limits for other matrices may be determined if requested. Method detection limits (MDL) can be estimated by multiplying the 'Multiplier' times the Detection Limit.
3) Routine precision and bias is typically ± 15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations greater than ten times detection limit up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within ten times instrument detection limit (adjusted for processing factors and laboratory dilutions) and have a potential uncertainty much greater than 15%.
4) Absolute precision, bias and detection limits may be determined on each sample if required by the client.
5) The maximum number of significant figures for all ICP measurements is 2.

Battelle PNNL/RSE/Inorganic Analysis.... ICPASE Report

	Run Date=	1/5/2001	1/5/2001	1/5/2001	1/5/2001	1/5/2001	1/5/2001	1/5/2001
	Multiplier=	132.7	26.7	133.7	27.3	136.7	27.2	135.8
	RPL/LAB #=	01-00169 @5	01-00170	01-00170 @5	01-00171	01-00171 @5	01-00172	01-00172 @5
Det. Limit	*Client ID=*	*HD-01*	*HD-02*		*HD-03*		*HD-04*	
(ug/mL)	(Analyte)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)
0.060	Al	6,280	5,670		5,510		5,250	
0.010	Ba	--	[0.65]		[1.1]		[0.69]	
0.250	Ca	[200]	183		153		133	
0.015	Cd	26.9	24.2		23.3		22.5	
0.020	Cr	114	101		95.9		89.1	
0.025	Fe	[20]	29.4		15.5		11.3	
2.000	K	[930]	844		816		800	
0.050	La	[6.7]	[6.3]		[4.4]		[2.9]	
0.100	Mg	--	--		--		--	
0.150	Na	95,000	>	90,400	>	90,200	>	84,100
0.030	Ni	186	162		156		151	
0.100	P	805	735		706		678	
0.100	Pb	[78]	68.0		64.5		63.4	
0.015	Sr	--	[1.0]		166		55.6	
Other Analytes								
0.025	Ag	--	--		--		--	
0.250	As	--	--		--		--	
0.050	B	394	350		366		331	
0.010	Be	--	--		--		--	
0.100	Bi	--	--		--		--	
0.200	Ce	--	--		--		--	
0.050	Co	--	[1.6]		[1.4]		[1.5]	
0.025	Cu	[9.9]	9.47		9.16		8.76	
0.050	Dy	--	--		--		--	
0.100	Eu	--	--		--		--	
0.030	Li	--	--		--		--	
0.050	Mn	[10]	[9.3]		[8.6]		[7.7]	
0.050	Mo	[23]	20.6		19.8		19.2	
0.100	Nd	[14]	[13]		[11]		[9.3]	
0.750	Pd	--	--		--		--	
0.300	Rh	--	--		--		--	
1.100	Ru	--	--		--		--	
0.500	Sb	--	--		--		--	
0.250	Se	--	--		--		--	
0.500	Si	[460]	410		443		403	
1.500	Sn	--	--		--		--	
1.500	Te	--	--		--		--	
1.000	Th	--	--		--		--	
0.025	Ti	--	--		--		--	
0.500	Tl	--	--		--		--	
2.000	U	--	--		--		--	
0.050	V	--	--		--		--	
2.000	W	--	--		--		--	
0.050	Y	--	--		--		--	
0.050	Zn	--	[2.1]		[2.6]		[1.8]	
0.050	Zr	--	[4.2]		[3.9]		[3.7]	

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.

2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.

3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

	Run Date=	1/5/2001	1/5/2001	1/5/2001	1/5/2001	1/5/2001	1/5/2001	1/5/2001	1/5/2001
	Multiplier=	27.1	135.4	27.5	137.6	27.2	135.9	26.9	134.5
	RPL/LAB #=	01-00173	01-00173 @5	01-00174	01-00174 @5	01-00175	01-00175 @5	01-00176	01-00176 @5
Det. Limit	*Client ID=*	*HD-05*		*HD-06*		*HD-07*		*HD-08*	
(ug/mL)	(Analyte)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)
0.060	Al	4,910		5,130		4,900		4,900	
0.010	Ba	[0.31]		[0.87]		[0.76]		[0.63]	
0.250	Ca	139		124		135		121	
0.015	Cd	21.6		22.4		21.2		21.1	
0.020	Cr	60.7		57.3		67.3		56.0	
0.025	Fe	[2.8]		[6.5]		8.23		[2.7]	
2.000	K	776		788		748		747	
0.050	La	[1.7]		--		--		--	
0.100	Mg	--		--		--		--	
0.150	Na	>	79,900	>	83,600	>	84,000	>	89,200
0.030	Ni	145		149		143		143	
0.100	P	639		656		634		637	
0.100	Pb	57.3		55.3		50.3		44.1	
0.015	Sr	142		47.0		160		54.5	
Other Analytes		Other Analytes							
0.025	Ag	--		--		--		--	
0.250	As	--		--		--		--	
0.050	B	335		347		386		358	
0.010	Be	--		--		--		--	
0.100	Bi	--		--		--		--	
0.200	Ce	--		--		--		--	
0.050	Co	[1.5]		[1.4]		[1.4]		[1.4]	
0.025	Cu	8.33		8.62		8.08		8.23	
0.050	Dy	--		--		--		--	
0.100	Eu	--		--		--		--	
0.030	Li	--		--		--		--	
0.050	Mn	[3.4]		[4.5]		[2.0]		[1.8]	
0.050	Mo	18.4		19.0		18.1		18.3	
0.100	Nd	[3.1]		--		[3.7]		--	
0.750	Pd	--		--		--		--	
0.300	Rh	--		--		--		--	
1.100	Ru	--		--		--		--	
0.500	Sb	--		--		--		--	
0.250	Se	--		--		--		--	
0.500	Si	407		416		451		443	
1.500	Sn	--		--		--		--	
1.500	Te	--		--		--		--	
1.000	Th	--		--		--		--	
0.025	Ti	--		--		--		--	
0.500	Tl	--		--		--		--	
2.000	U	--		--		--		--	
0.050	V	--		--		--		--	
2.000	W	--		--		--		--	
0.050	Y	--		--		--		--	
0.050	Zn	--		--		--		--	
0.050	Zr	[1.8]		--		[1.9]		--	

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.

2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.

3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

QC Performance 1/5/01

Criteria>	<20%	80% - 120%	75%-125%	75%-125%	75%-125%	< +/-10%	< +/-10%
QC ID=	Duplicates (none)	LCS/BS (none)	MS (none)	01-00169 + Post Spike A	01-00169 + Post Spike B	01-00169 @5/@25 Serial Dil	01-00170 @1/@5 Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff	%Diff
Al				nr		2.9	5.9
Ba				104			
Ca				97			
Cd				91			7.7
Cr				nr		2.7	7.7
Fe							
K							
La							
Mg				103			
Na				>		8.6	
Ni				nr		1.0	8.6
P				nr		-3.1	5.8
Pb							
Sr				105			

Other Analytes

Ag							
As							
B				nr		1.7	6.4
Be							
Bi				97			
Ce							
Co				105			
Cu							
Dy					95		
Eu					101		
Li				95			
Mn							
Mo							
Nd							
Pd							
Rh							
Ru							
Sb							
Se							
Si							
Sn							
Te							
Th					99		
Ti				95			
Tl							
U							
V							
W							
Y				103			
Zn				110			
Zr				107			

Shaded results exceed acceptance criteria

Bold results for information only; LCS or Serial Dilution concentration less than EQL

n.r. = not recovered; spike concentration less than 20% of sample concentration

> = value greater than upper measurement limit

R. Hallen

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

ASR # 6004

WP# K17197

Hydroxide and Alkalinity Determination
Procedure: PNL-ALO-228 Equip # WB76843

Analyst: 1/15/01

Reviewer: LRGreenwood 1/16/01

RPG #	Client ID		Concentration, moles/liter		
			First Point	Second Point	Third Point
01-00169	HD-01		0.14	1.21	0.85
01-00169	HD-01	Rep	0.13	1.21	0.83
		RPD	7%	0%	2%
01-00170	HD-02		0.13	1.24	0.83
01-00170	HD-02	Rep	0.14	1.25	0.84
		RPD	11%	1%	1%
01-00173	HD-05		0.12	1.08	0.73
01-00173	HD-05	Rep	0.11	1.08	0.74
		RPD	12%	0%	1%
01-00175	HD-07		0.48	1.14	0.70
01-00175	HD-07	Rep	0.53	1.05	0.76
		RPD	10%	8%	7%
01-00176	HD-08		0.45	1.17	0.68
01-00176	HD-08	Rep	0.46	1.12	0.73
		RPD	2%	4%	7%
Reag. Blk.			0		
Standard 1			114%		
Standard 2			112%		
01-0169MS	Matrix spike		106%		
01-0176MS	Matrix spike		106%		

Note: Results are presented for the first, second, and third inflection points on the titration curves, as applicable. The first inflection point is generally associated with the hydroxide concentration. The second and third points generally represent the carbonate and bicarbonate concentrations.

Appendix E

Calculations

See TI-41500-009
137.022 grams of supernate from Jar ID: 2AN-00-25
74.03 grams of 0.01M NaOH solution
211.052 grams of diluted AN-102 solution for tests

See TI-41500-008

Density Determination:	10 mL =	12.6477 grams	1.26477 g/mL	
	10 mL =	12.5437 grams	1.25437 g/mL	
		Average	1.260 std dev.	0.007

Caustic Adjustment: for 7 and 8
3.1812 grams (2.37 mL) 10M NaOH
56.3214 grams diluted AN-102
59.5026 grams caustic adjusted solution

Note these tests used 0.4M Sr and MnO4-

Test #	Analytical Vial ID	Number Indicates Order of Addition						Mass Dilution Factor (MDF)
		1		2		3		
		AN-102 added		Sr added		MnO_4^- added		
		target mL	actual g	target mL	actual g	target mL	actual g	
1	HD-01	20	×	0	×	0	×	1
2	HD-02	20	×	0	×	0	×	1
3	HD-03	20	24.89	1.05	1.13	0	×	1.0454
4	HD-04	20	25.06	1.05	1.13	0	×	1.045092
5	HD-05	20	24.88	1.05	1.13	1.05	1.11	1.090032
6	HD-06	20	25.02	1.05	1.12	1.05	1.1	1.088729
7*	HD-07*	20*	25.5	1.05	1.14	1.05	1.11	1.149702
8*	HD-08*	20*	25.26	1.05	1.13	1.05	1.14	1.151424

* caustic adjusted waste

Calculations by 5/28/02

Reviewed by RJ 5/28/02

Client ID	Sr-90 (uCi/g)	Am-241 (uCi/g)	Cm-243+ Cm-244 (uCi/g)	Cm-242 (uCi/g)	
HD-01	2.94E+1	6.40E-2	2.33E-3	2.15E-4	
HD-01	3.07E+1	6.80E-2	2.08E-3	2.01E-4	Sum of
HD-02	3.00E+1	6.06E-2	2.04E-3	1.58E-4	Alpha
AVE	3.00E+1	6.42E-2	2.15E-3	1.91E-4	6.65E-2
STDV	6.51E-1	3.70E-3	1.57E-4	2.97E-5	Mass
					Dilution
HD-03	5.21E+0	6.56E-2	2.45E-3	1.68E-4	1.0454
HD-04	1.92E+0	4.87E-2	1.68E-3	1.53E-4	1.04509
HD-05	3.86E+0	1.22E-2	4.13E-4	2.41E-5	1.09003
HD-06	9.35E-1	1.00E-2	3.45E-4	4.39E-5	1.08873
HD-07	5.04E+0	1.19E-2	4.78E-4	3.08E-5	1.1497
HD-08	1.28E+0	8.83E-3	4.27E-4	4.15E-5	1.15142

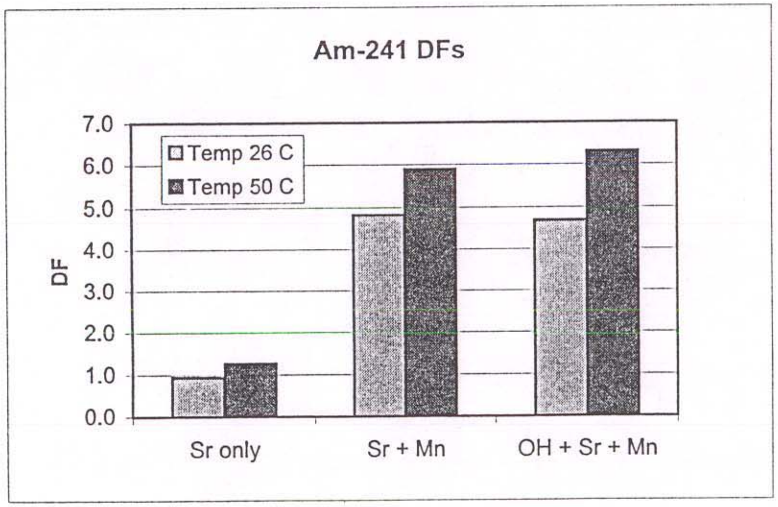
Calculation by D T Hale 5/28/02

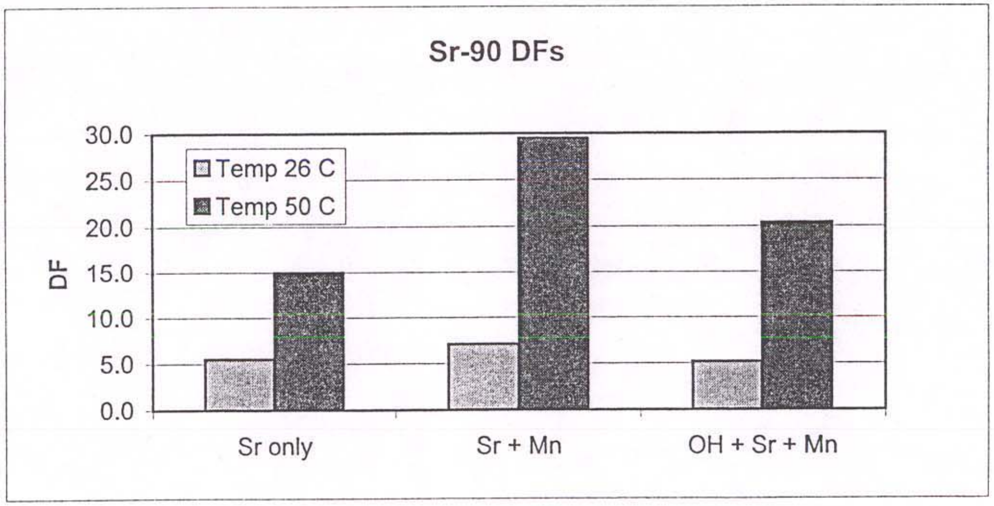
Reviewed by RJ 5/28/02

Decontamination Factor (Corrected for Dilution)				Percent Removal (Corrected for Dilution)			
Sr-90	Am-241	Cm-244	Cm-242	Sr-90	Am-241	Cm-244	Cm-242
5.5	0.9	0.8	1.1	81.9	-6.8	-19.1	8.2
15.0	1.3	1.2	1.2	93.3	20.7	18.3	16.4
7.1	4.8	4.8	7.3	86.0	79.3	79.1	86.3
29.5	5.9	5.7	4.0	96.6	83.0	82.5	75.0
5.2	4.7	3.9	5.4	80.7	78.7	74.4	81.5
20.4	6.3	4.4	4.0	95.1	84.2	77.1	75.0

	Temp 26 C	Temp 50 C
Sr only	0.9	1.3
Sr + Mn	4.8	5.9
OH + Sr + Mn	4.7	6.3

	Temp 26 C	Temp 50 C
Sr only	5.5	15.0
Sr + Mn	7.1	29.5
OH + Sr + Mn	5.2	20.4





	d=1.28		density		density		density		density		density		density
Multiplier=	26.75	27.35	1.25	27.18	1.26	27.09	1.26	27.54	1.24	27.18	1.26	26.91	1.28
RPL/LAB #	01-00170	01-00171	MDF	01-00172	MDF	01-00173	MDF	01-00174	MDF	01-00175	MDF	01-00176	MDF
Client ID=	HD-02	HD-03	1.0453998	HD-04	1.0450918	HD-05	1.0900322	HD-06	1.088729	HD-07	1.1497021	HD-08	1.1514242
			dilution corrected		dilution corrected		dilution corrected		dilution corrected		dilution corrected		dilution corre
(Analyte)	ug/g	ug/g	% removed	ug/g	% removed	ug/g	% removed	ug/g	% removed	ug/g	% removed	ug/g	% removed
Al	5670	5510	-2	5250	3	4920	5	5130	1	4900	1	4910	0
Ca	183	153	13	133	24	139	17	124	26	135	15	121	24
Cd	24.2	23.3	-1	22.5	3	21.6	3	22.4	-1	21.2	-1	21.1	0
Co	1.6	1.4	9	1.5	2	1.5	-2	1.4	5	1.4	-1	1.4	-1
Cr	101	96	1	89.1	8	60.7	34	57.4	38	67.4	23	56	36
Cu	9.47	9.16	-1	8.76	3	8.33	4	8.62	1	8.09	2	8.24	0
Fe	29.4	15.5	45	11.3	60	-2.8	90	6.5	76	8.23	68	2.7	89
K	844	816	-1	800	1	776	0	788	-2	748	-2	747	-2
La	6.3	4.4	27	2.9	52	1.7	71	--	BDL	--	BDL	--	BDL
Mn	9.3	8.6	3	7.7	13	3.4	60	4.5	47	2	75	1.8	78
Mo	20.6	19.9	-1	19.2	3	18.5	2	19	0	18.1	-1	18.3	-2
Nd	13	11	12	9.3	25	3.1	74	--	BDL	3.7	67	--	BDL
Ni	162	156	-1	151	3	145	2	149	0	143	-1	143	-2
P	735	707	-1	679	3	640	5	656	3	634	1	638	0
Pb	68	64.6	1	63.4	3	57.3	8	55.4	11	50.3	15	44.1	25
Sr	1	167	17558	55.6	5911	142	15578	47	5217	160	18495	54.6	6387
Zn	2.1	2.6	-29	1.8	10	--	BDL	--	BDL	--	BDL	--	BDL
Zr	4.2	3.9	3	3.7	8	1.8	53	--	BDL	1.9	48	--	BDL

"-" means below detection limit. The detection limit can be calculated by multipling the individual element instrument detection limit by the dilution factor.
values in red have higher uncertainty due to low level of analyte, within 10 times the detection limit

Calculations by 5/28/02

Reviewed by 5/28/02

Calcuations from Mike Johnson, Waste Loading in ILAW

I used the data you sent me to determine the Sr-90 and Am-241 concentrations in the ILAW glass. I had to assume the sodium oxide loading in the ILAW glass would be 20 wt%, since the sulfate concentration in the sample was not reported. The actual sodium oxide loading in the ILAW glass will probably be less than 20wt% (based on the formula I sent in the earlier message).

For the Sp-03 sample, the Sr-90 and Am-241 concentrations in the ILAW glass are:

Sr-90: 10.5 Ci/m3 of glass
Am-241: 57.5 nCi/gram of glass

Na molarity = [(Sodium ug/gm) * (sample density gm/ml) *(1E-06 gm/ug) * (1000 ml/L) / (23 gm /mole)]
Na molarity = [(104,000 ug/gm) * (1.269 gm/ml) * (1E-06 gm/ug) * (1000 ml/L) / (23 gm /mole)]
Na molarity = 5.74 M

Grams of ILAW glass / liter of sample = [Na molarity * (62 grams Na2O / mole)] / [(moles Na / mole Na2O) * 0.2]
Grams of ILAW glass / liter of sample = 5.74 M * (62)/(2 * 0.2)
Grams of ILAW glass / liter of sample = 889.4 grams of glass / liter of sample
m3 of ILAW glass / liter of sample = (889.4 grams of glass / liter of sample) * (1E-06 MT/gm) / (2.66 MT/m3)
m3 of ILAW glass / liter of sample = 3.34E-04 m3 / liter of sample

Am-241 concentration in glass = (4.03E-02 uCi/gm) * (1.269 gm/ml) * (1E+03 nCi/uCi) * (1000 ml/L)/ (889.4 grams of glass / liter of sample)
Am-241 concentration in glass = 57.5 nCi/gm of glass

Sr-90 concentration in glass = (2.76 uCi/gm) * (1.269 gm/ml) * (1E-06 Ci/uCi) * (1000 ml/L)/ (3.34E-04 m3 / liter of sample)
Sr-90 concentration in glass = 10.47 Ci/m3

Similarly, for the Sp-04 sample, the Sr-90 and Am-241 concentrations in the ILAW glass are:

Sr-90: 12.3 Ci/m3 of glass
Am-241: 68.4 nCi/gram of glass

For the Sp-05 sample, the Sr-90 and Am-241 concentrations in the ILAW glass are:

Sr-90: 8.01 Ci/m3 of glass
Am-241: 28.0 nCi/gram of glass

For the Sp-06 sample, the Sr-90 and Am-241 concentrations in the ILAW glass are:

Calculations by 5/28/02
Reviewed by 5/28/02

ILAW Glass Loading Calculations

									ILAW Glass Loading at 20% Na2O		ILAW at 15wt% Na2O		ILAW at 10wt% Na2O	
Sample #	density	[Na], ug/mL	[Na], M	Sr-90	Am-241	Cm-243 + Cm-244	Cm-242	Sum of Alpha	Sr-90 Ci/m^3 of glass	Sum of Alpha nCi/gram of glass	Sr-90	Sum of Alpha	Sr-90	Sum of Alpha
HD-01/02	1.25	125000	5.43	3.00E+1				0.06654	118.6	99	89.0	74.1	59.3	49.4
HD-03	1.25	113000	4.913	5.21	0.0656	0.00245	0.00017	0.06822	22.7	112	17	84	11.4	56.0
HD-04	1.25	106000	4.6087	1.92	0.0487	0.00168	0.00015	0.05053	8.9	88	7	66	4.5	44.2
HD-05	1.25	101000	4.3913	3.86	0.0122	0.000413	2.4E-05	0.01264	18.9	23	14	17	9.4	11.6
HD-06	1.25	104000	4.5217	0.935	0.01	0.000345	4.4E-05	0.01039	4.4	19	3	14	2.2	9.3
HD-07	1.25	106000	4.6087	5.04	0.0119	0.000478	3.1E-05	0.01241	23.5	22	18	16	11.7	10.9
HD-08	1.25	114000	4.9565	1.28	0.0088	0.000427	4.2E-05	0.0093	5.5	15	4	11	2.8	7.6
		ug/mL		uCi/g										

Calculations by 5/28/02

Reviewed by RJ 5/28/02

Appendix F

Staff Roles and Responsibilities

Table F.1. Staff Roles and Responsibilities

Staff Member	Role/Responsibility
Richard Hallen	Scientist/Technical Leader - Sr/TRU Removal
Ingrid Burgeson	Scientist/Hot Cell Experiments - lead and direct hot cell experiments
Vaughn Hoopes	Technician/Hot Cell Experiments- conduct experiments and sample prep.
Dennis Weier	Scientist/Statistician - Data Analysis

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