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Assessment of Abnormal Process Conditions for Sr/TRU Removal Using a Waste Simulant

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ACCEPTED FOR
WTP PROJECT USE

for W. L. Tamosaitis
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Test Specification: 24590-WTP-TSP-RT-02-014
Test Plan: TP-RPP-WTP-218
Test Exceptions: None
R&T Focus Area: Pretreatment
Testing Scoping Statement: B-40

Battelle—Pacific Northwest Division
Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-WTP-TSP-RT-02-014 and Test Plan TP-RPP-WTP-218. 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

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

11/19/03
Date

Summary

The River Protection Project-Waste Treatment Plant (RPP-WTP) 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 sodium permanganate (0.05M), for TRU, at 50°C and 1M additional sodium hydroxide. Section 5 of the *Research and Technology Plan*, prepared by Bechtel National, Inc., identifies further research needs. One need shown is to determine optimal conditions for Sr/TRU precipitation reaction (SOW Ref.: Sec. C.6 Std.2(a)(3)(ii)(B) and WBS No.: 1.2.10.03 and .05). Abnormal process condition assessment for the Sr/TRU removal process is addressed in Scoping Statement B-40, which is included in Appendix C of the *Research and Technology Plan*. In accordance with Scoping Statement B-40, Test Specification 24590-WTP-TSP-RT-02-014, and Test Plan TP-RPP-WTP-218, studies were conducted with a tank waste simulant as part of the work to assess the impact of abnormal process conditions on the Sr/TRU removal process. In particular, tests were conducted with simulant to provide information to guide future tests with actual waste samples from Tank AN-102.

Objectives

The purpose of these studies was to determine the impact of various process conditions on the overall Sr/TRU removal process and define a subset of conditions for testing with actual waste samples. Experiments were conducted with a waste simulant prepared to mimic the waste composition in Tank AN-102. A test matrix was developed with a wide range of concentrations and reaction conditions. Of specific interest was the importance of varying initial waste concentration; added free hydroxide; reagent concentrations; precipitation temperature; reaction time; and deviation in process sequence, such as no mixing after reagent addition, reversing the order of reagent addition, and split reagent additions.

Conduct of Testing

Small-scale (nonradioactive) tests (~20 mL) were conducted with a waste simulant developed to represent waste from Tank AN-102. A matrix of experiments was developed with various test conditions to assess the impact of abnormal process conditions on the Sr/TRU removal process. The baseline process is the addition of 0.075M strontium followed by 0.05M permanganate to well-mixed waste heated to 50°C. The treated waste is mixed for 4h at 50°C then cooled to 25°C before filtration. In the waste treatment plant, the cooling is expected to take approximately 18h. The overall process time, from start of reagent addition to transferring the first waste to the filtration receipt vessel, would be approximately 24h. The initial sodium concentration of the waste simulant was varied, i.e., 4.5M, 5.5M, and 6.5M. The added free hydroxide level was none, 0.3M, and 1M. Samples were treated and digested at 15°C, 25°C, 35°C, and 50°C to assess the impact of temperature, but all samples were filtered at 25 ± 5°C (ambient room temperature). Varying amounts of both $Sr(NO_3)_2$ and $NaMnO_4$ reagents were added in all experiments, because earlier tests have demonstrated that additions of both reagents are required for Sr-90 and TRU removal. In the tests discussed here, reagent addition was reduced to 0.01M and 0.03M to assess the impact on Sr-90 and TRU decontamination. Other abnormal process conditions were examined by varying the sequence or timing of treatment. One variation of the baseline process conditions involved the addition of permanganate, followed by Sr addition. In two experiments, the reagents were added as separate additions of 0.01M; then 4h later, 0.02M more reagent was added. Three experiments were

conducted in which reagents were added without mixing for a period of 1, 4, and 24h after reagent addition, and then the mixtures were mixed well and sampled. Most experiments were sampled at 4h and 24h after reagent addition; sample times were modified for selected experiments because of the varied treatment schemes, and one experiment was sampled 4 days after treatment.

The [Sr] was examined as a function of time and treatment conditions to assess the impact of abnormal process conditions on Sr-90 removal. We have a good mechanistic understanding of the Sr removal process; Sr-90 removal is accomplished by isotopic dilution and $SrCO_3$ precipitation. It is known that reducing the amount of added nonradioactive Sr reduces the isotopic dilution; more Sr-90 would remain in solution and less decontamination would occur. Increasing the reaction time and temperature is known to result in significant reductions in [Sr], which would lead to less Sr-90 in solution and more decontamination. However, much of the [Sr] data from these simulant tests was confounded for unknown reasons. Consequently, abnormal process conditions based on [Sr] could not be assessed with the simulant data from these tests.

The impact of abnormal process conditions on TRU decontamination was assessed based on the percent removal of the surrogate TRU elements (lanthanide species, Ce, Eu, La, and Nd), and Fe, which have been found to correlate well with TRU removal in past studies. The percent removal of the lanthanide elements ranged from 60 to 80% for the reference tests, which is consistent with most of the other studies. The only test condition that appeared to have a significant reduction in surrogate TRU removal was reduced permanganate concentration (0.01M). When samples were taken immediately after initial mixing of the solids in the no-mix experiments, poor surrogate TRU element removal was noted. Other abnormal treatment conditions provided similar removal of the surrogate TRU elements as the reference conditions.

Results and Performance Against Objectives

The experimental data from these tests can be used to assess the impact of abnormal process conditions on Sr/TRU removal. Since a waste simulant was used for these tests, no direct measurement of Sr-90 or TRU decontamination was made. However, the assessment was based on the impact of process conditions on [Sr] and removal of the surrogate TRU elements (lanthanide elements). The [Sr] data from these simulant tests were not consistent with early studies and not used for any data analyses. However, the mechanism of Sr-90 removal is well understood, and important parameters to consider are time, temperature, and reagent concentration. Based on the percent removal of the lanthanide elements, the reagent concentration was determined to be important. Reduced permanganate addition of 0.01M significantly lowered the percent removal of the lanthanide elements. The no-mix experiments also showed significant impact on percent removal of the lanthanide elements. The percent removal of lanthanide elements showed a slight improvement as the reaction temperature was increased. The various other abnormal processing schemes had little or no impact.

Quality Requirements

Testing began in September 2002 and continued through December 2002 to assess the impact of abnormal process conditions using a waste simulant. Battelle—Pacific Northwest Division (PNWD) implemented the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. These quality requirements were implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP)*

Quality Assurance Requirements and Description Manual. The analytical requirements were implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs.*

PNWD addresses internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verified that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's WTPSP *Quality Assurance Requirements and Description Manual*.

Issues

None.

Contents

Figures

Table

1.0 Introduction

This report summarizes work performed by Battelle—Pacific Northwest Division (PNWD) in support of the River Protection Project-Waste Treatment Plant (RPP-WTP) at Hanford. Before the liquid (supernatant) fraction of Envelope C[(a)] wastes (Tanks AN-102 and AN-107) can be disposed of as low-activity waste (LAW), pretreatment is required to remove radioactive strontium (Sr-90) and transuranic (TRU) elements in addition to Cs-137 and the entrained solids. The Sr-90 removal process consists of isotopic dilution by nonradioactive $Sr(NO_3)_2$ addition and precipitation of $SrCO_3$. The TRU removal process involves addition of permanganate, stepwise manganese reduction, Mn(VII) to Mn(VI) to Mn(IV); precipitation of MnO_2; and concomitant TRU precipitation. Entrained solids and Sr/TRU precipitate are to be removed via crossflow filtration; Cs-137 is to be removed by ion exchange.

Optimized treatment conditions were identified in small-scale tests (20 mL) with AN-102 waste samples (Hallen et al. 2002a) and verified in small-scale (Hallen et al. 2002b) and bench-scale tests (Hallen et al. 2002c) with a waste blend consisting of AN-102 waste and C-104 high-level waste (HLW) pretreatment streams. These tests showed that minimized reagent addition (0.02M) and reduced process temperature (~25°C) provided adequate Sr-90 and TRU removal to meet immobilized low-activity waste (ILAW) requirements. However, the waste treatment plant's process baseline for the Sr/TRU remains as demonstrated in earlier work at PNWD (Hallen et al. 2000a,b) and the Savannah River Technology Center, SRTC (Nash et al. 2000a,b): addition of 0.075M $Sr(NO_3)_2$ followed by 0.05M $NaMnO_4$ at 50°C and precipitate digest time of 4h at 50°C.

The Sr-90 decontamination factors (DFs) have been shown to increase significantly with increased temperature (Hallen et al. 2002a) and time (Hallen et al. 2003a). However, this increased Sr-90 decontamination was not a result of increased isotopic exchange, but, rather, continued precipitation, i.e., reduction of total soluble Sr concentration. Isotopic exchange was found to be complete 18 min after reagent addition was complete (Hallen et al. 2002c). Therefore, the kinetics of the Sr precipitation reaction was shown to be important; more than 4h was required to approach the final equilibrium concentration.

Optimized treatment conditions provided adequate TRU removal from AN-102 diluted waste (Hallen et al. 2002a) and the AN-102/C-104 waste blend (Hallen et al. 2002b,c). The TRU decontamination only occurred after permanganate addition. The TRU removal exceeded the requirements for ILAW glass by a factor of 5. These results suggested that reaction temperature and time had much less impact on TRU removal than was observed for Sr-90. Additionally, experiments to examine the reaction mechanisms (Hallen et al. 2003a) showed that TRU removal was not impacted by not mixing for 1h after reagent addition.

After establishing an understanding of the reaction mechanisms for Sr/TRU removal, studies were conducted to determine the impact of abnormal or deviation of precipitation conditions from those proposed for plant operation. These studies were first conducted with a waste simulant (representing the composition of AN-102). The conditions that had the greatest impact on Sr-90 and TRU decontamination were then selected as the test conditions for the subsequent experiments with actual waste samples from AN-102. The testing with the waste simulant is reported here. Testing with the actual waste samples is reported in a separate document (Hallen et al. 2003b).

(a) Envelope designations are explained in DOE (2000).

In this report, the conditions and experimental procedures used for testing with the waste simulant are described in Section 2.0. Section 3.0 presents the results and discussion, with the conclusions and recommendations given in Section 4.0. The appendices contain the simulant recipe and the quantities of simulant and reagents used.

2.0 Test Conditions and Experimental Procedures

Experiments were conducted at various reagent concentrations and process conditions considered abnormal to the baseline Sr/TRU removal process with a waste simulant that represents diluted AN-102 waste. The waste simulant, test conditions, experimental procedures, and chemical analyses are described below. Additional details are provided in the appendices.

2.1 Description of Waste Simulant

PNWD prepared 1 L of AN-102 simulant following a recipe developed by SRTC. The quantities of reagents were adjusted such that the final solution contained a total sodium concentration of 5.5M. In addition, $Eu(NO_3)_3$ was added to the simulant as a surrogate TRU element, since it was not included in the initial recipe. The recipe used for preparation of the simulant is listed in Appendix A. Once prepared, the free hydroxide concentration was determine by titration, and adjusted to give approximately 0.1M free hydroxide in the initial simulant. The simulant was allowed to age for over 2 weeks before it was used for testing. Solids were noted in the simulant solutions and determined to contain phosphate, which corresponds to the observation made by SRTC that sodium fluorophosphates precipitate from solution for this recipe.

2.2 Development of Test Conditions

Experimental conditions were defined using the results from earlier tests with AN-102 (Hallen et al. 2002a), AN-102-C-104 blended waste (Hallen et al. 2002b,c) and reaction mechanism studies conducted with both AN-102 and AN-107 waste (Hallen et al. 2003a). The addition of 0.02M $Sr(NO_3)_2$ and permanganate showed adequate Sr-90 and TRU decontamination (Hallen et al. 2002a-c). Based on these studies, the minimum level of reagent addition was set at 0.01M. The mid-point concentration was defined as 0.3M reagent addition, and the baseline conditions were set at the maximum levels. Most previous tests have been conducted between 5M and 6M [Na] in the initial feed, so experiments were added to the matrix at 4.5M and 6.5M Na. Earlier tests showed that AN-102 could be treated with free hydroxide at the level present in the waste (~0.14M) or 0.3M added hydroxide with little impact (Hallen et al. 2002a). The tests conducted here were used to determine the impact of added free hydroxide at levels of none, 0.3M, and 1M. Four temperatures were evaluated, 15°C, 25°C, and 50°C; earlier studies only evaluated 25°C and 50°C (Hallen et al. 2002a).

The tests were designed to assess processing conditions such as no mixing during reagent addition, reverse reagent addition, and split reagent addition, as reflected in the test matrix shown in Table 2.1. Because these tests use nonradioactive solutions, analytical costs were greatly reduced and samples were collected at multiple times. For the reference case, Test R01 in Table 2.1, samples were taken until no solution remained. The target concentrations listed in the test matrix were based on the final composition after addition of all reagents. The quantity of each reagent added to the waste to achieve these values, as well as the actual quantities that were used, are listed in Appendix B.

Table 2.1. Test Matrix for Experiments Using Waste Simulant

Test	Temperature, (± 5°C)	OH$^-$	Sr^{+2}	MnO$_4^-$	Other/Comments	Stir	Sample Time
R01	25	0.3M	0.03M	0.03M	Proposed Optimized Conditions	Yes	1h; 4h; 8h; 24h; 48h; 96h
R02	50	1.0M	0.075M	0.05M	Current Baseline Filter at 25°C	Yes	4h; 24h
R03	50	0.3M	0.03M	0.03M	Filter at 25°C	Yes	4h; 24h
R04	50	1.0M	0.03M	0.03M	Filter at 25°C	Yes	4h; 24h
R05	50	1.0M	0.01M	0.01M	Filter at 25°C	Yes	4h; 24h
R06	50	AR[(a)]	0.03M	0.03M	Filter at 25°C	Yes	4h; 24h
R07	25	AR	0.01M	0.01M	None	Yes	4h; 24h
R08	25	AR	0.03M	0.03M	None	Yes	4h; 24h
R09	25	AR	0.075M	0.05M	None	Yes	4 h; 24h
R10	25	0.3M	0.03M	0.03M	None	No[(b)]	1h; 4h; 24h
R11	25	0.3M	0.03M	0.03M	None	No[(c)]	4h; 27h
R12	25	0.3M	0.03M	0.03M	None	No[(d)]	24h; 47h
R13	25	0.3M	0.03M	0.03M	Reverse Sr/Mn addition	Yes	4h; 24h
R14	25	1.0M	0.03M	0.03M	None	Yes	4h; 24h
R15	25	1.0M	0.03M	0.03M	Add OH$^-$ last	Yes	4h; 24h
R16	15	0.3M	0.03M	0.03M	Filter at 25°C	Yes	4h; 24h
R17	35	0.3M	0.03M	0.03M	Filter at 25°C	Yes	4h; 24h
R18	25	0.3M	0.01M	0.01M	None	Yes	4h; 24h
R19	25	1.0M	0.075M	0.05M	None	Yes	4h; 24h
R20	25	0.3M	0.03M	0.03M	Add Sr, stir 4h/sample, then add Mn	Yes	4h; 8h; 28h
R21	25	0.3M	0.03M	0.03M	Add Mn, stir 4h/sample, then add Sr	Yes	4h; 8h; 28h
R22	25	0.3M	0.01 + 0.02M	0.03M	Add 0.01M Sr 0.03M Mn, stir 4h/sample, then add 0.02M more	Yes	4h; 8h; 28h
R23	25	0.3M	0.03M	0.01 + 0.02M	Add 0.01M, stir 4h/sample, add 0.02M more	Yes	4h; 8h; 28h
R24	25	0.3M	0.03M	0.03M	Dilute to 4.5M Na[(e)]	Yes	4h; 24h
R25	25	0.3M	0.03M	0.03M	Evaporation to 6.5M Na[(f)]	Yes	4h; 24h
R26	25	0.3M	0.03M	0.03M	Repeat of R01	Yes	4h; 24h

(a) AR = as received, from simulant recipe.
(b) Mix sample after 1h of reaction.
(c) Mix sample after 4h of reaction.
(d) Mix sample after 24h of reaction.
(e) Dilute feed to approximately 4.5M from 5.5M.
(f) Evaporate feed to approximately 6.5M from 5.5M.

2.3 Experimental

The waste simulant was prepared at 5.5M [Na] and no additional hydroxide. The simulant was divided and composition adjusted for the respective tests. One sample was evaporated to 6.5M sodium, then adjusted with NaOH to give 0.3M additional hydroxide. Upon evaporation, a large increase in insoluble solids concentration was noted. One sample was diluted with deionized water to 4.5M [Na] and NaOH added to give 0.3M additional hydroxide. Upon dilution, the small amount of insoluble solids originally present in the simulant dissolved. Two other batches of simulant were prepared at 0.3M and 1M added hydroxide by addition of NaOH pellets.

The small-scale experiments were conducted in 60-mL sample jars using approximately 20 mL of the appropriate simulant. The reagents were added rapidly to the waste simulants with an adjustable pipette, in the order listed in Table 2.1 (from left to right, except as noted), at the specified temperature, and mixed with magnetic stir bars when specified. The 25°C experiments were conducted at room temperature, which ranged from 22°C to 25°C on the days of these tests. The experiments were conducted over a 1-week period. Samples were collected at the specified times, allowed to equilibrate to room temperature, and filtered with a 0.2-μm disposable syringe filter. The sample designation is the experiment number followed by the sample time in hours; for example, the 4h sample for Test R03 is designated R03-4. Samples of the initial waste simulants were also filtered and submitted for analyses as controls. The controls are designated as RC followed by the designation for the batch and time; for example, the control for the 0.3M added hydroxide experiments taken at 4h is RC-0.3-4.

Stock solutions of the reagents were prepared for addition to the waste simulant. The tests used 0.22M, 0.44M, or 1.65M solutions of $Sr(NO_3)_2$; and 0.22M, 0.44M, or 1.1M solutions of $NaMnO_4$. This allowed the addition of reagents to remain constant at 1 mL per 20 mL of initial waste for the various treatment levels. For the split reagent addition tests, the volume of reagents was adjusted to account for the removal of samples before the remaining 0.02M reagent was added. The specific quantities of waste and reagents used are given in Appendix B.

The test specification (Abodishish 2002) stated the temperature for these tests as 15, 25, 35, and 50 ± 5°C. For the 15°C, 35°C, and 50°C experiments, air-driven stir plates were mounted in a thermostatic water bath. No external heating or cooling was provided for the 25°C samples during this testing, because the room temperature (22°C to 25°C) was within the temperature requirement of 25 ± 5°C. All samples were filtered at room temperature, which was within the specified filtration temperature range, also 25 ± 5°C.

2.4 Chemical Analyses

All of the chemical analyses were conducted at PNWD. Metal ion concentration was determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES). Selected samples were analyzed by direct titration with 0.2M HCl to determine the free hydroxide concentration (free hydroxide in the sample corresponds to the first equivalence point).

2.5 Quality Assurance Requirements

2.5.1 Application of RPP-WTP Quality Assurance Requirements

PNWD implements the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual*. The analytical requirements are implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs.*

A matrix that cross-references the NQA-1 and 2a requirements with the PNWD's procedures for this work was given in Table 3 of approved test plan (TP-RPP-WTP-218). The test plan includes justification for those requirements not implemented.

2.5.2 Conduct of Experimental and Analytical Work

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System," assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified in the test specification (Abodishish 2002), BNI's QAPjP, PL-24590-QA00001 is not applicable since the work was not performed in support of environmental/regulatory testing, and the data will not be used as such.

2.5.3 Internal Data Verification and Validation

PNWD addressed internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's WTPSP *Quality Assurance Requirements and Description Manual*.

3.0 Results and Discussion

This section presents the results of the experiments with waste simulant conducted to help assess the impact of abnormal process conditions on the Sr/TRU removal process and determine the test conditions for experiments with actual waste.

3.1 Assessment of Abnormal Process Conditions on Strontium Concentration

The mechanism of Sr-90 removal is well understood, and extensive experimental data are available on the [Sr] as a function of temperature and time. Felmy and Mason (2003) report detailed thermodynamics on [Sr] as a function of [Na], [CO_3^{2-}], and temperature. All the data from past studies are consistent with the known retrograde solubility of $SrCO_3$. However, in the studies discussed here, the Sr solubility at temperatures less than 50°C was much lower than expected. Figure 3.1 shows results of these studies compared to previous experiments with actual waste and the expected behavior based on previous experiments with AN-102 waste conducted at 25°C and 50°C (Hallen et al. 2002a, 2003a). It appears that some competing Sr precipitate is formed at temperatures of 35°C and lower, resulting in much lower [Sr] than expected. The composition of the precipitate is not known, but appears to be unique to this simulant, since this behavior was not observed in past simulant studies (Lilga et al. 2003). Because of formation of this unknown Sr precipitate, the [Sr] data from the current simulant studies cannot be used to assess the impact of abnormal process conditions.

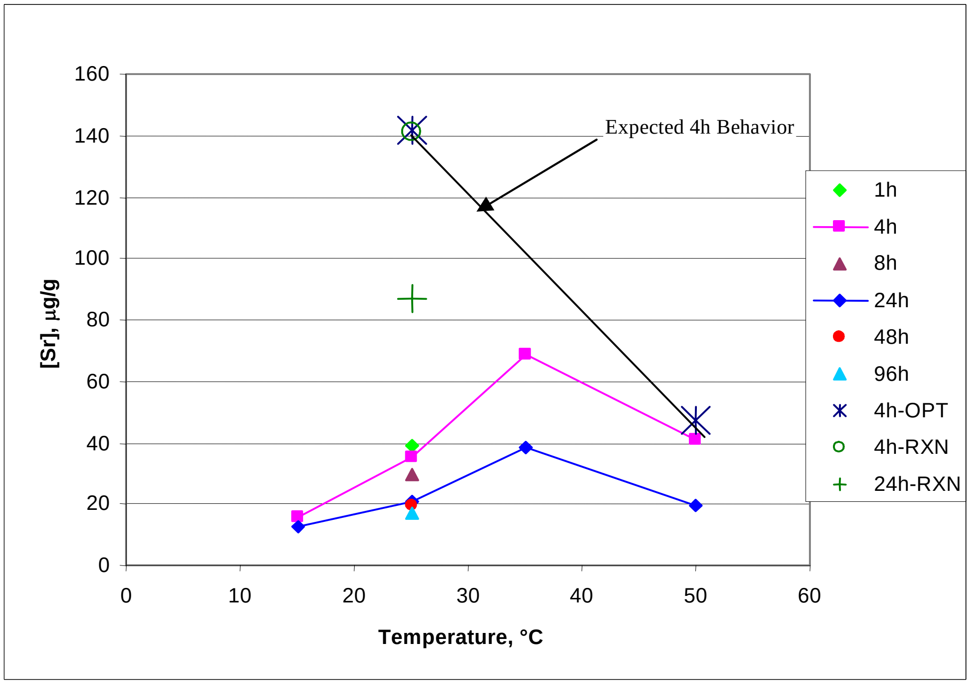

Figure 3.1. Strontium Concentration as a Function of Temperature and Time for This Study, and Expected Behavior Based on Past Tests with Actual Wastes (OPT=Hallen et al. 2002a, RXN=Hallen et al. 2003a)

3.2 Assessment of Abnormal Process Conditions on TRU Removal

The impact of the abnormal process conditions on TRU removal can be assessed by examining the percent removal of the various TRU surrogate elements (Ce, Eu, La, and Nd) and Fe. Data from selected experiments can be compared separately to assess the impact of TRU removal of each reaction parameter. Figure 3.2 shows data for treated, 0.3M added hydroxide, simulant at the same reagent concentrations (0.03M) and at the four different temperatures examined. The trend is a slight improvement in removal as the temperature is increased. However, the increase was generally small, and most element removal was still in the 60-80% range, which is consistent with earlier studies (Lilga et al. 2003 and Hallen et al. 2003a). Similar comparisons were made with data from the AR (no added hydroxide) and 1.0M added hydroxide levels and showed similar general trends for higher removal at increased reaction temperature. As well, experiments with the baseline reagent levels (1M added OH^-, 0.075M Sr, and 0.05M MnO_4^-) showed increased removal with increased temperature. The data in Figure 3.2 also show that an increased reaction time, comparing the 4h and 24h data, only results in a slight increase in removal.

The impact of free hydroxide concentration can be seen by examining the data in Figure 3.3 for treatment of waste with none (AR), 0.3M, and 1M added hydroxide. No significant impact was observed as the levels of free hydroxide were increased from AR to 0.3M (compare R08 to R01), and a slight reduction observed from 0.3M to 1M (compare R01 to R14). The figure also shows data for an experiment in which the Sr and permanganate reagents were added to the AR simulant first, then 1M hydroxide added after all other reagents (R15). The sequence of hydroxide addition last appears to have little impact on the treatment process, whereas when added initially (R14), it resulted in a slight reduction.

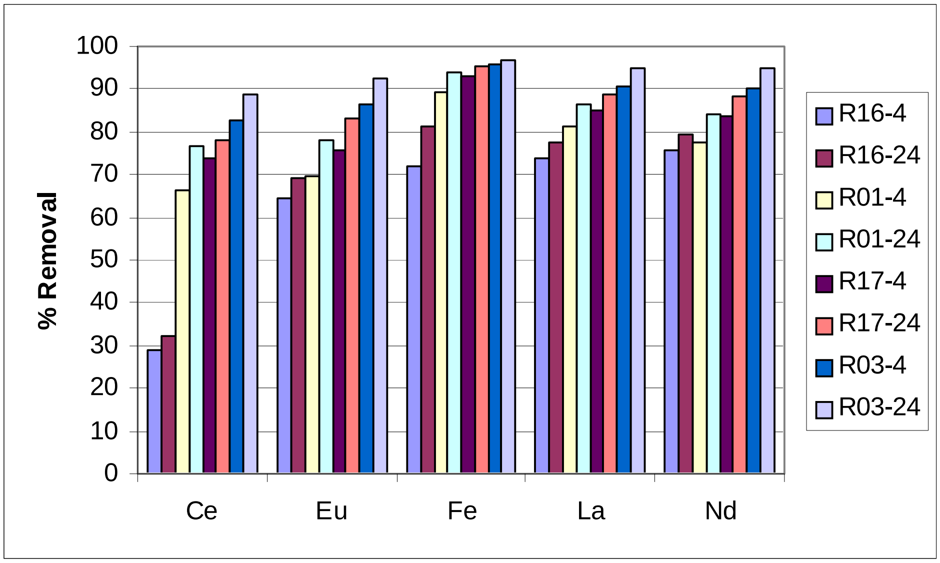

Figure 3.2. Impact of Temperature on Percent Removal of Metal Ions on Treatment. R16=15°C, R01=25°C, R17=35°C, and R03=50°C.

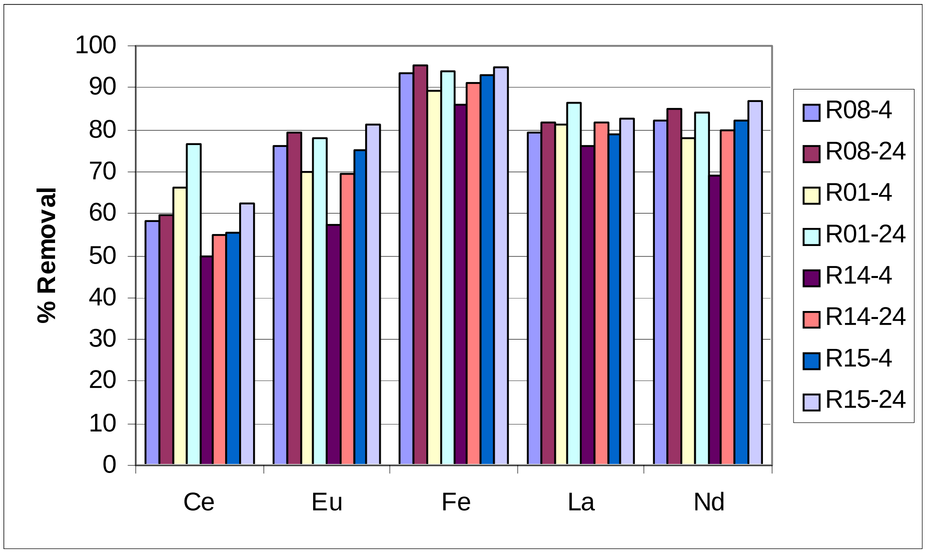

Figure 3.3. Impact of Free Hydroxide Concentration on the Removal of Metal Ions on Treatment. R08=AR, R01=0.03M, R14=1M added initially, and R15=1M added after Sr and MnO_4^-.

The impact of reagent concentration was determined for three different levels of added reagent. Figure 3.4 shows the removal of the surrogate TRU elements as a function of reagent concentration for treatment of the AR waste simulant at 25°C. TRU is removed by the added permanganate (Hallen et al. 2002a). The lowest reagent addition, 0.01M, showed a significant reduction in removal, compared to 0.03M, and 0.05M showed a slight increase in removal compared to 0.03M. Similar results were obtained for treatment of the 0.3M waste simulant at 25°C, but with 1M added OH^- and 50°C the differences between the various levels of reagent were less.

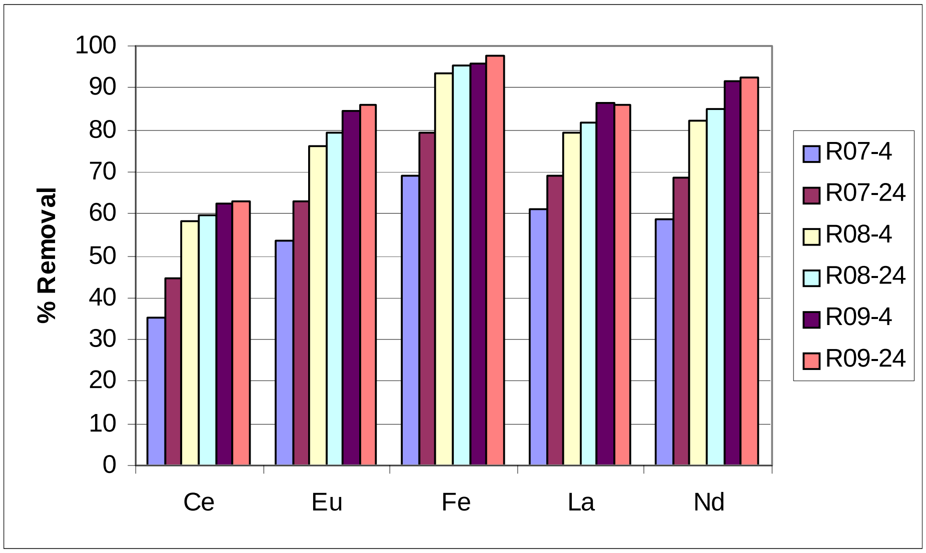

Figure 3.4. Impact of Reagent Concentration on the Removal of Metal Ions on Treatment. R07=0.01 Sr and MnO_4^-, R08=0.03M Sr and MnO_4^- , and R09=baseline**,** 0.075M Sr and 0.05M MnO_4^-.

The initial sodium concentration was varied from 4.5 to 6.5M, with other treatment conditions remaining constant. The removal of metal ions, shown in Figure 3.5, appears to be slightly better for the most dilute waste, decreasing slightly as [Na] is increased.

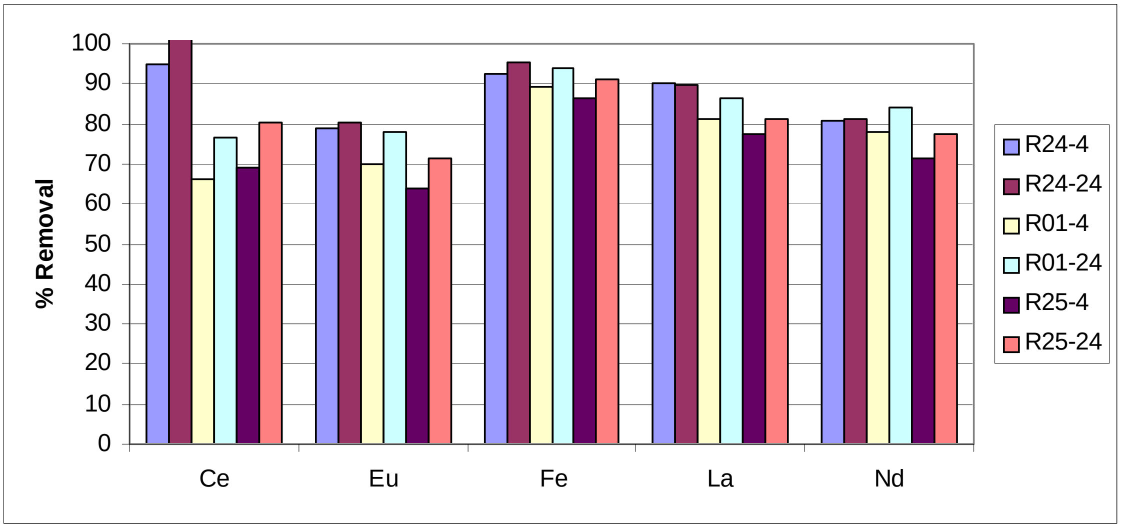

Figure 3.5. Impact of Initial Sodium Concentration on the Removal of Metal Ions on Treatment. R24=4.5M, R01=5.5M, and R25=6.5M.

A number of experiments were conducted in which the processing scheme was modified from the recommended baseline process. These modifications included adding reagents with no mixing, then after a period of time mixing the simulant well and collecting samples at various times. In Figure 3.6, the results from the various no-mix experiments are compared to the well-mixed experiment at the same

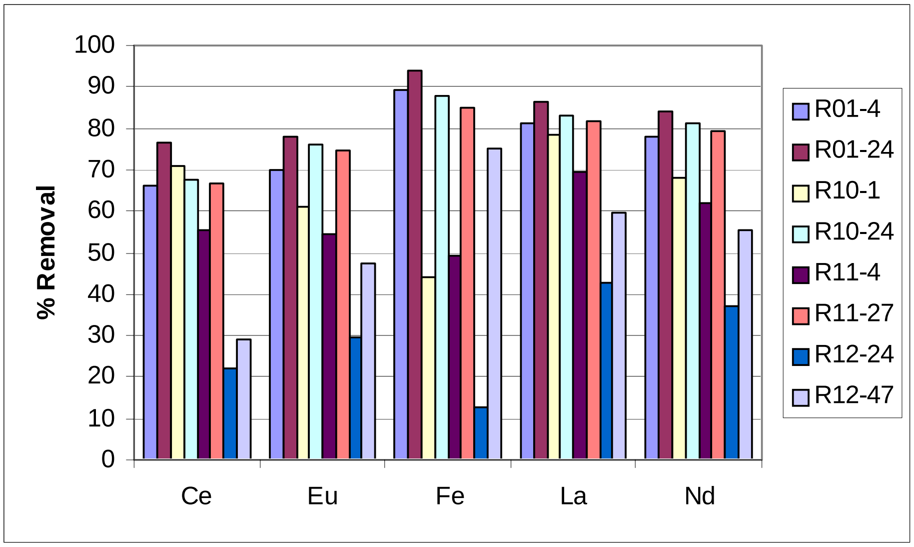

Figure 3.6. Impact of Not Mixing for Various Times on the Removal of Metal Ions. R01=Well Mixed, R10=No Mix for 1h, R11=No Mix for 4h, and R12=No Mix for 24h.

reagent levels. The first sample taken for each of the no-mix experiments was immediately after the waste was mixed for the first time. The results show that the longer mixing is delayed, the less removal that occurs. For the 1h and 4h no-mix experiments, after 24h of continued good mixing, the removal was quite similar to the well-mixed experiment. The 24h no-mix experiment improved with continued mixing, but never reached similar levels of removal.

Most of the abnormal processing schemes investigated had little or no impact on removal. In Figure 3.7, reversed reagent addition, Mn followed by Sr (R13-24), had no impact on removal or when adding in reversed order and waiting 4h between addition (R21-28). The 4h wait may have reduced removal slightly for the normal reagent addition sequence (R20-28). The split reagent addition, adding the reagent in increments with a 4h delay in-between (R22-28 and R23-28), had little or no impact on removal.

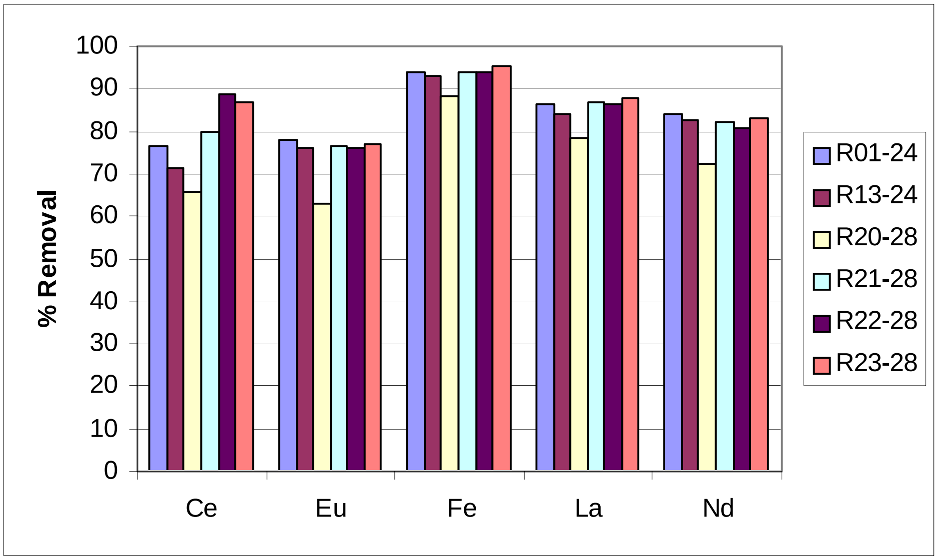

Figure 3.7. Impact of Reagent Addition Sequence on the Removal of Metal Ions at Equivalent Reaction Times, 24h After Addition of Both Reagents. R01=baseline conditions (Sr followed by MnO_4^-), R13=reversed order, R20=4h delay between Sr and Mn addition, R21=reversed order with 4h delay between Mn and Sr addition, R22=split Sr addition 0.01M then 0.02M 4h later, and R23=split Mn addition, 0.01M then 0.02M 4h later.

3.3 Change in Chemical Composition of Treated Supernatant

The change in chemical composition of the treated supernatant has been examined for tests with actual waste using AN-107 (Hallen et al. 2000b), AN-102 (Hallen et al. 2002a), and AN-102/C-104 waste blend (Hallen et al. 2002b,c) samples. The results from these wastes are quite similar and show little or no significant removal of most of the metal and inorganic ions from solution: Al, Cd, Co, Cu, K, Mo, Na, Ni, P, and Pb. Some Ca removal has been noted but usually around 20%. For the tests with simulant, some of the metal ions were not removed on treatment, Al, Cd, K, Mo, Na, and Ni, but a significantly higher removal from the treated simulant was noted for Ca, Co, Cu, P, and Pb. The data presented in Figure 3.8 show the percent removal of selected elements at the various reaction temperatures tested. At certain temperatures, as much as 80% of these elements were removed on treatment. Phosphorus removal showed the largest range, from 80% removal at 15°C to a 25% increase in P at 50°C (initial phosphorus-containing solids were dissolved at elevated reaction temperatures). These results suggest that the simulant composition does not accurately represent the actual waste, and the composition/concentration of the organic complexants may be the cause.

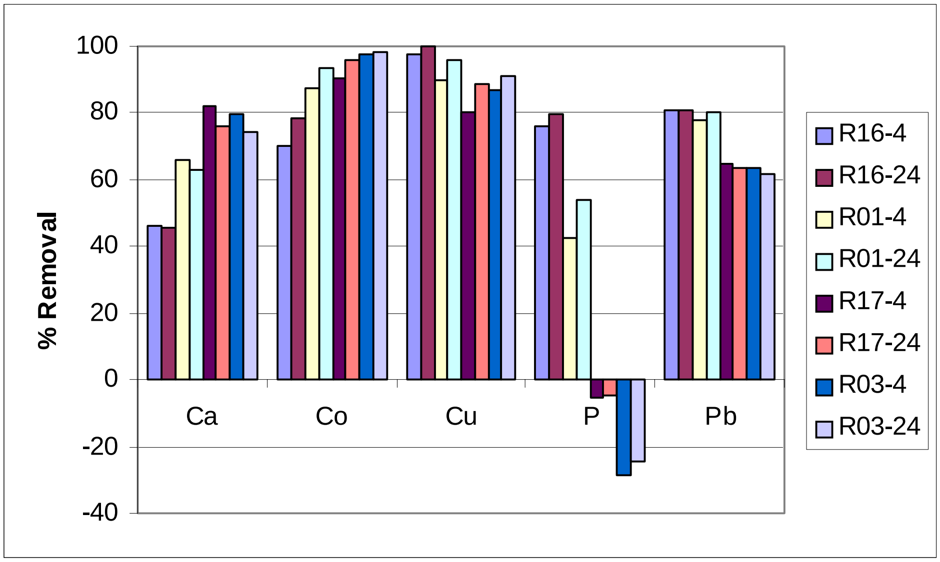

Figure 3.8. Impact of Temperature on Percent Removal of Selected Elements on Treatment. R16=15°C, R01=25°C, R17=35°C, and R03=50°C.

4.0 Conclusions and Recommendations

Experiments were conducted with a waste simulant that represents diluted AN-102 waste at various reagent concentrations and process conditions considered abnormal to the baseline Sr/TRU removal process. These experiments provided a better understanding of the important processing parameters for testing with actual AN-102 waste samples. Conclusions from this work and recommendations for the tests with actual waste are presented in this section.

The important factors for determining Sr-90 decontamination are the isotopic dilution ratio and the [Sr]. The impact of process conditions on Sr-90 removal can be evaluated with waste simulants by examining the change in [Sr] as a function of treatment condition. However, the [Sr] data from this series of simulant tests did not follow the known behavior of actual waste samples. Therefore, none of these data could be used to define the test conditions for the actual waste tests. Earlier studies did show that [Sr] and Sr-90 decontamination are greatly affected by temperature and reaction time. $SrCO_3$ has retrograde solubility, a higher solubility at lower temperature. Lower reaction temperatures also appear to slow the rate for equilibrium to be reached (Lilga et al. 2003). Tests with actual wastes should study a similar range of temperature and time as the simulant studies.

The impact of abnormal process conditions on TRU removal was assessed by examining the percent removal of the TRU surrogate elements (lanthanide elements) and Fe. Reducing the permanganate concentration to 0.01M resulted in a significant decrease in removal. A slight improvement in removal occurred as the temperature was increased over the temperature range examined, 15°C to 50°C. Increasing reaction time from 4h to 24h resulted in a slight increase in removal of the lanthanide elements and Fe. Added OH and initial [Na] had little to no impact on removal. The tests with actual wastes should use the middle levels for both of these variables, 0.3M added OH and 5.5M [Na]. Of the various abnormal process schemes examined, the no mix for 24h resulted in a significant decrease in removal. This suggests that to observe an impact from abnormal process schemes, the sample should be allowed 24h to react. It is recommended that an experiment be conducted with no mixing for the first 24h of reaction using an actual waste sample.

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Appendix A

Simulant Recipe

Table A.1. Compounds and Mass Quantities for Preparation of Waste Simulant Representing Tank AN-102 Waste (SRTC Recipe)

Compounds	Formula	Mass Added, g/L	Mass Fraction g Compound/ Total g
Aluminum Nitrate	$Al(NO_3)_3 \cdot 9H_2O$	117.6	9.38E-02
Bismuth Nitrate	$Bi(NO_3)_3 \cdot 5H_2O$	0.014	1.12E-05
Cadmium Nitrate	$Cd(NO_3)_2 \cdot 4H_2O$	0.115	9.17E-05
Calcium Nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	1.994	1.59E-03
Cerium Nitrate	$Ce(NO_3)_3 \cdot 6H_2O$	0.0187	1.49E-05
Cesium Nitrate	$CsNO_3$	0.017	1.36E-05
Cobalt Nitrate	$Co(NO_3)_2 \cdot 6H_2O$	0.0115	9.17E-06
Copper Nitrate	$Cu(NO_3)_2 \cdot 2.5H_2O$	0.0614	4.89E-05
Ferric Nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	0.2078	1.66E-04
Add Europium Nitrate ~10 ppm	$Eu(NO_3)_3 \cdot 6H_2O$	0.0171	1.36E-05
Lanthanum Nitrate	$La(NO_3)_3 \cdot 6H_2O$	0.0343	2.73E-05
Lead Nitrate	$Pb(NO_3)_2$	0.2051	1.64E-04
Magnesium Nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	0.568	4.53E-04
Manganous Chloride	$MnCl_2 \cdot 4H_2O$	0.0732	5.84E-05
Neodymium Nitrate	$Nd(NO_3)_3 \cdot 6H_2O$	0.0677	5.40E-05
Nickel Nitrate	$Ni(NO_3)_2 \cdot 6H_2O$	1.425	1.14E-03
Potassium Nitrate	KNO_3	3.479	2.77E-03
Rubidium Nitrate	$RbNO_3$	0.0111	8.85E-06
Strontium Nitrate	$Sr(NO_3)_2$	0.044	3.51E-05
Zinc Nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	0.0162	1.29E-05
Zirconyl Nitrate	$ZrO(NO_3)_2 \cdot H_2O$	0.0253	2.02E-05
Disodium Ethylenediaminetetraacetate	$Na_2C_{10}H_{14}N_2O_8 \cdot 2H_2O$	2.47	1.97E-03
n-(2-Hydroxyethyl)ethylenediaminetriacetic Acid	$C_{10}H_{18}N_2O_7$	0.2558	2.04E-04
Sodium Gluconate	$HOCH_2(CHOH)_4COONa$	1.135	9.05E-04
Citric Acid	$C_6H_8O_7 \cdot H_2O$	3.573	2.85E-03
Nitrilotriacetic Acid	$C_6H_9NO_6$	0.182	1.45E-04
Iminodiacetic Acid	$C_4H_7NO_4$	3.141	2.50E-03
Succinic Acid	$C_4H_6O_4$	0.0257	2.05E-05
Glutaric Acid	$C_5H_8O_4$	0.0468	3.73E-05
Adipic Acid	$C_6H_{10}O_4$	0.1718	1.37E-04
Azelaic Acid	$C_9H_{16}O_4$	0.719	5.73E-04
Suberic Acid	$C_8H_{14}O_4$	1.265	1.01E-03
Boric Acid	H_3BO_3	0.1451	1.16E-04
Ammonium Acetate	CH_3COONH_4	0.4346	3.46E-04
Sodium Chloride	$NaCl$	5.397	4.30E-03

Table A.1. (contd)

Compounds	Formula	Mass Added, g/L	Mass Fraction g Compound/ Total g
Sodium Sulfate	Na_2SO_4	12.88	1.03E-02
Potassium Molybdate	K_2MoO_4	0.0773	6.16E-05
Sodium Hydroxide	$NaOH$	68.18	5.44E-02
Sodium Phosphate	$Na_3PO \cdot 12H_2O$	15.24	1.22E-02
Sodium Tungstate	$Na_2WO_4 \cdot 2H_2O$	0.209	1.67E-04
Sodium Metasilicate	$Na_2SiO_3 \cdot 9H_2O$	0.07	5.58E-05
Sodium Glycolate	$HOCH_2COONa$	9.43	7.52E-03
Sodium Formate	$HCOONa$	8.769	6.99E-03
Sodium Acetate	$CH_3COONa \cdot 3H_2O$	0.464	3.70E-04
Sodium Oxalate	$Na_2C_2O_4$	0.486	3.88E-04
Sodium Chromate	Na_2CrO_4	0.542	4.32E-04
Sodium Carbonate	Na_2CO_3	78.19	6.23E-02
Sodium Nitrate	$NaNO_3$	72.87	5.81E-02
Sodium Nitrite	$NaNO_2$	68.31	5.45E-02
Sum of Compounds		483.3	3.85E-01
Water	H_2O	771.01	6.15E-01
Total Mass of 1 L		1254.35	--

Appendix B

Experimental Data

Table B.1. Mass Dilution Factors (MDF) Used in DF and Percent Removed Calculations for AN-102 Tests

	AN-102 added		**Sr added**		**MnO$_4^-$ Added**		**OH$^-$ Added**			
Exp. #	**Target, mL**	**Actual, wt (g)**	**Target, mL**	**Actual, wt (g)**	**Target, mL**	**Actual, wt (g)**	**Target, wt (g)**	**Actual, wt (g)**	**MDF**	**MDF 2**
Control 0.3	--	--	None	--	None	--	None	--	1	--
Control 1.0	--	--	None	--	None	--	None	--	1	--
Control AR	--	--	None	--	None	--	None	--	1	--
R-01	20	25.3557	1	1.1056	1	1.0713	None	--	1.0859	--
R-02	20	25.7122	1	1.2418	1	1.0918	None	--	1.0908	--
R-03	20	25.3508	1	1.0885	1	1.065	None	--	1.0849	--
R-04	20	25.6879	1	1.0769	1	1.0539	None	--	1.0829	--
R-05	20	25.6691	1	1.0073	1	1.0151	None	--	1.0788	--
R-06	20	25.2082	1	1.0848	1	1.0508	None	--	1.0847	--
R-07	20	25.2189	1	1.0280	1	1.0247	None	--	1.0814	--
R-08	20	25.2305	1	1.0989	1	1.0692	None	--	1.0859	--
R-09	20	25.1939	1	1.2519	1	1.1063	None	--	1.0936	--
R-10	20	25.3736	1	(a)	1	2.1857(a)	None	--	1.0861	--
R-11	20	25.3460	1	(a)	1	2.1701(a)	None	--	1.0856	--
R-12	20	25.4559	1	(a)	1	2.1738(a)	None	--	1.0854	--
R-13	20	25.3731	1	1.1117	1	1.0653	None	--	1.0858	--
R-14	20	25.6927	1	1.1042	1	1.0664	None	--	1.0845	--
R-15	20	25.1669	1	1.1006	1	1.0621	0.88	0.899	1.1217	--
R-16	20	25.3693	1	1.1040	1	1.065	None	--	1.0855	--
R-17	20	25.3409	1	1.0999	1	1.0647	None	--	1.0854	--
R-18	20	25.3612	1	1.0306	1	1.0235	None	--	1.0810	--
R-19	20	25.6748	1	1.2546	1	1.1129	None	--	1.0922	--
R-20	20	25.3340	1	1.1189	0.81	0.3837	None	--	1.0442	1.0629
R-21	20	25.3528	0.81	0.8919	1	1.059	None	--	1.0418	1.0854
R-22	20	25.3616	0.875	0.9766	1	1.0713	None	--	1.0568	1.0863
R-23	20	25.3549	1	1.1113	0.875	0.9323	None	--	1.0577	1.0860
R-24	20	24.5406	1	1.1042	1	1.0692	None	--	1.0886	--
R-25	20	26.5200	1	1.0999	1	1.0704	None	--	1.0818	--
R-26	20	25.3500	1	1.1042	1	1.0605	None	--	1.0854	--

(a) Individual weights of Sr and Mn reagents not determined.

Table B.2. Percent Removal of Metal Ions for All Samples Taken During Testing

Sample ID	Ce % Removed	Eu % Removed	Fe % Removed	La % Removed	Nd % Removed
R01-1	65	61	88	76	70
R01-4	66	70	89	81	78
R01-8	70	72	92	83	80
R01-24	76	78	94	86	84
R01-48	49	81	94	86	89
R01-96	59	82	95	86	90
R02-4	69	87	97	90	92
R02-24	70	92	97	93	97
R03-4	83	86	96	91	90
R03-24	89	92	97	95	95
R04-4	41	63	73	74	72
R04-24	68	90	96	92	95
R05-4	63	84	94	88	90
R05-24	60	82	90	88	90
R06-4	64	87	96	87	93
R06-24	70	92	98	91	97
R07-4	35	54	69	61	59
R07-24	45	63	79	69	69
R08-4	58	76	94	79	82
R08-24	59	80	96	82	85
R09-4	63	84	96	86	92
R09-24	63	86	97	86	92
R10-1	71	61	44	78	68
R10-4	62	68	79	80	75
R10-24	68	76	88	83	81
R11-4	55	54	49	70	62
R11-27	67	75	85	82	79
R12-24	22	29	12	43	37
R12-47	29	48	75	60	55
R13-4	66	68	90	80	77
R13-24	71	76	93	84	83
R14-4	50	57	86	76	69
R14-24	55	69	91	82	80
R15-4	55	75	93	79	82
R15-24	62	81	95	83	87
R16-4	29	64	72	74	76
R16-24	32	69	82	78	79
R17-4	74	76	93	85	84
R17-24	78	83	95	89	88
R18-4	44	56	38	69	63
R18-24	58	63	55	76	72
R19-4	59	66	93	83	77
R19-24	59	74	95	85	83

Table B.2. (contd)

Sample ID	**Ce % Removed**	**Eu % Removed**	**Fe % Removed**	**La % Removed**	**Nd % Removed**
R20-4	8	23	3	41	29
R20-8	53	54	82	72	64
R20-28	66	63	88	78	72
R21-4	76	66	88	80	72
R21-8	74	71	92	84	77
R21-28	80	77	94	87	82
R22-4	77	68	88	82	73
R22-8	78	71	92	84	77
R22-28	89	76	94	86	81
R23-4	42	44	69	62	54
R23-8	79	70	93	85	77
R23-28	87	77	95	88	83
R24-4	95	79	93	90	81
R24-24	102	80	95	90	81
R25-4	69	64	86	77	71
R25-24	80	71	91	81	78
R26-4	29	67	91	77	81
R26-24	40	76	94	82	86

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