PNWD-3263
WTP-RPT-068 Rev. 0

Assessment of the Sr/TRU Removal Precipitation Reaction Mechanisms Using Waste Simulant Solutions

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Report

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Test Specifications:
TSP-375-01-00003, Process Description;
24590-WTP-TSP-RT-02-013, Test Matrix
Test Plan: CHG-TP-41500-019
Test Exceptions: None
R&T Focus Area: Pretreatment
Testing Scoping Statement(s): B-38

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-02-013 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 WTP R&T Support Project	Date
G. Todd Wright, Manager Research and Technology	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 (0.075 *M*) for isotopic dilution and sodium permanganate (0.05 *M*) for TRU removal at 50°C and 1 *M* additional sodium hydroxide. Section 5 of the *Research and Technology Plan* (BNI 2002)(a) identifies further research needs, which are illustrated in that document in Figure 5-14, Precipitation Test Matrix.

One need shown in this matrix is to determine the mechanism of the Sr/TRU precipitation process (SOW Ref.: Sec. C.6 Std.2(a)(3)(ii)(B) and WBS No.: 1.2.10.01 and .02). Reaction mechanism assessment for the Sr/TRU precipitation process is addressed in Scoping Statement B-38, which is included in Appendix C of the *Research and Technology Plan*. In accordance with Scoping Statement B-38, Test Specification TSP-375-01-00003, Process Description, and 24590-WTP-TSP-RT-02-013, Test Matrix; and Test Plan CHG-TP-41500-019, studies were conducted with simple mixtures of organic complexants and simulated supernatant solutions to develop a better understanding of the TRU decontamination mechanisms.

This report discusses investigations into the mechanism of the strontium/permanganate treatment process for removal of Sr-90 and TRU from tank supernatant destined for immobilization as LAW. Experiments were conducted with simple mixtures of organic complexants and an inactive, simulated supernatant based on the composition of AN-102 waste mixed with C-104 sludge pretreatment solutions. This mixture is referred to as the "AN-102/C-104 waste blend." The purpose of these mechanistic studies was to determine the importance of oxidation, absorption, precipitation, and ligand displacement on TRU decontamination. Previous studies, supported by additional results from these investigations, have demonstrated isotopic dilution and $SrCO_3$ precipitation of Sr-90 by added nonradioactive $Sr(NO_3)_2$. In addition, results from these tests will guide future tests with actual waste samples from Tanks AN-102 and AN-107.

The investigation conducted for this report provided a better understanding of manganese reaction behavior relevant to waste processing. In the oxidation of organics, permanganate ($Mn^{VII}O_4^-$) is reduced to various observable Mn species, including manganate ($Mn^{VI}O_4^{2-}$); manganese dioxide (MnO_2, or its hydrated form); and, when the reductant is gluconate, a manganese(IV) gluconate complex. The reactivity, stability, and methods of preparation of these species were investigated. The Mn(IV) gluconate complex becomes more stable as the hydroxide concentration increases and was likely present in earlier waste simulant filtration testing.

(a) 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.

The inactive AN-102/C-104 waste blend simulant was spiked with about 20 ppm nonradioactive Ce, Eu, Fe, La, Mn, and Nd; filtered; and treated with a variety of reagents under a variety of reaction conditions. The optimized Sr/TRU precipitation treatment conditions—no added hydroxide, addition of Sr (0.02 *M* target concentration) followed by sodium permanganate (0.02 *M* target concentration) with mixing at ambient temperature—were used as a reference for comparison. The removal of the spike elements (i.e., Ce, Eu, Fe, La, Mn, Nd) was used as an indication of the extent/effectiveness of treatment. Strontium was added to all of the experiments except for one, in which only MnO_4^- was added. One experiment was conducted in which only Sr was added. Variations of the optimized conditions were conducted in which Sr and MnO_4^- reagents were added in inverse order, simultaneously, with no mixing, or with added base. In other experiments, sodium permanganate was replaced by other manganese reagents, including sodium manganate, Mn(VI); manganese dioxide, Mn(IV); and manganese chloride, Mn(II). Other oxidants in place of MnO_4^- were added, such as Ce(IV), Fe(VI), and IO_4^-, and other precipitants were also studied, such as Ce(III), Fe(III), and Zr(IV). Experiments ran for 24h at ambient laboratory conditions with samples taken at 4h and 24h. Samples were filtered, acidified, and analyzed by inductively coupled plasma-atomic emission spectroscopy for metals content.

Results indicated that experiments involving an oxidant generally had higher levels of spike element removal than those in which only precipitation or absorption occurred. For example, Mn(VII) and Mn(VI) reagents showed similar performance that was better than when Mn(IV) or Mn(II) was added. Fe(VI) performed better than Fe(III) [but not as well as Mn(VII)]. Ce(IV) gave better removal than Ce(III) for most elements. Not mixing the MnO_4^- treatment until after 1h had very little effect; essentially the same removal of spike elements was observed as in the optimized condition treatment. Likewise, inverse addition and simultaneous addition of the Sr and MnO_4^- reagents, or addition of extra base, gave the same results as the optimized condition treatment.

Ligand displacement appeared to be important for some of the treatments. Added Zr(IV) resulted in similar removal as the MnO_4^- treatment for most of the spike elements. The concentration of Zr in the 4h and 24h samples was high. Presumably, Zr(IV) competed well for ligands, remaining soluble, while displacing other metal ions that precipitate in the basic solution. Similarly, the performance of Ce(IV) with added base was comparable to the optimized condition treatment with almost half the added Ce remaining in solution. The high Ce concentration suggests that it successfully competes for organic ligands in solution, displacing other metal ions that then precipitate. Ce(IV) was especially efficient at decreasing the Sr concentration. Experiments with Ce(IV) contained only about one-fourth the amount of soluble Sr found when treated using the optimized conditions.

The greatest difference between the 4h and 24h samples was the concentration of soluble Sr. The soluble Sr was typically twice as high at 4h as 24h. This would translate to a twofold increase in Sr-90 decontamination factor (DF) between the 4h and 24h samples. The overall Sr-90 DF is determined by the amount of isotopic dilution and final Sr concentration. Increasing the Sr-90 DF by waiting 24h to filter would have the same effect as doubling the initial nonradioactive Sr addition if filtration were to occur at 4h. These results suggest that the treated waste should be filtered more than 4h after reagent addition.

Good mixing during the Mn reduction reactions was not as important as earlier expected, as long as the resulting precipitate was well mixed with the supernatant before the sample was filtered. This was expected for Sr-90 removal but surprising for permanganate treatment, since a large fraction of the waste was not directly contacted/oxidized with Mn(VII) or Mn(VI). However, the addition of preformed Mn(IV) solids or Mn(IV) solids from the air oxidation of Mn(II) was not as effective in decontamination, so oxidation reactions in the waste solution appear to be important for maximum decontamination. These results suggest that oxidation, absorption, precipitation, and ligand displacement are all important processes in the TRU decontamination mechanism.

The data presented in this report were generated in experiments conducted from August 2001 through August 2002 to assess the reaction mechanisms of Sr/TRU removal by added $Sr(NO_3)_2$ and permanganate. RPP-WTP quality assurance (QA) requirements changed during this period. The QA requirements were addressed by Battelle—Pacific Northwest Division (PNWD) through implementation of quality assurance project plans (QAPjP) approved by the RPP-WTP quality assurance organization. PNWD's quality assurance project plan, CHG-QAPjP, Rev. 0, invoked PNWD's Standards Based Management System (SBMS), compliant with DOE Order 414.1A Quality Assurance and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A—Quality Assurance Requirements. Due to a change in the contract QA requirements, PNWD's quality assurance project plan, RPP-WTP-QAPjP, Rev. 0, was prepared, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description (WTPSP) Manual. Report preparation and collection of analytical data associated with test matrix experiments (primarily reported in Sections 3.2 and 3.3) were conducted under RPP-WTP-QAPjP, Rev. 0. All other experiments and data collection (primarily reported in Section 3.1) were conducted under the earlier CHG-QAPjP, Rev. 0. The quality of the data gathered during the earlier experiments was not impacted by the change in requirements.

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. The review procedure is part of PNWD's WTPSP Manual.

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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 (e.g., Tanks AN-107 and AN-102) 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, Tc-99, and the entrained solids. The Sr-90 removal process consists of isotopic dilution and precipitation of $SrCO_3$ by nonradioactive $Sr(NO_3)_2$ addition, and the TRU removal process involves addition of permanganate, stepwise manganese reduction [Mn(VII) to Mn(VI) to Mn(IV)], precipitation of MnO_2, and subsequent TRU precipitation. This TRU decontamination method is based on work conducted at Pacific Northwest National Laboratory (PNNL) by Orth et al. (1995). Entrained solids and Sr/TRU precipitate are to be removed via crossflow filtration; Cs-137 and Tc-99 are to be removed by ion exchange. In previous work for the RPP-WTP contractor, PNWD and the Savannah River Technology Center (SRTC) demonstrated Sr/TRU removal with actual waste samples from Envelope C (Hallen et al. 2000a,b; Hallen et al. 2002a,b,c; Nash et al. 2000a,b) by added nonradioactive Sr and permanganate.

The WTP proposed process flowsheet for Envelope C waste includes the potential for mixing the incoming tank waste with recycle streams and high-level waste (HLW) sludge pretreatment streams (supernatant, sludge wash, caustic leach, and rinse solutions). These streams would be blended and processed through the Sr/TRU removal process. Optimized treatment conditions were identified in tests with AN-102 waste samples (Hallen et al. 2002a), and were used for small-scale (20 mL) process verification testing (Hallen et al. 2002b) on a specified blend of AN-102 waste samples and C-104 sludge pretreatment solutions. This blend is referred to as the "AN-102/C-104 waste blend." The Hallen et al. (2002b) tests verified that optimized process conditions, which minimized reagent addition and reduced the process temperature to ambient temperature (25 ± 5°C), provided adequate Sr-90 and TRU removal to meet immobilized low-activity waste (ILAW) requirements.

Further work established the mechanism of Sr-90 removal and showed that treatment of a larger, 1-L, batch of AN-102/C-104 waste blend also gave adequate Sr-90 and TRU decontamination factors (DFs)[(b)] (Hallen et al. 2002c). Treatment and digest were conducted at the ambient hot cell temperature of approximately 31°C and at the initial free hydroxide level (0.33 *M*) with $Sr(NO_3)_2$ addition at 0.02 *M* followed by permanganate addition at 0.02 *M*. Before Sr addition, the waste was undersaturated with Sr. Upon treatment, the DFs for Sr-90 for all of the samples taken were higher than 5, which is an adequate decontamination to meet ILAW disposal requirements.

A primary mechanism for Sr-90 removal was isotopic dilution with the added nonradioactive $Sr(NO_3)_2$, a process that was complete at 18 minutes. The addition of permanganate increased the Sr-90 decontamination, likely a result of oxidation of the chelating agents. The Sr-90 DFs increased

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

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

significantly with time. However, this increased Sr-90 decontamination was not a result of increased isotopic exchange or ligand oxidation, but rather continued precipitation, i.e., reduction of total soluble Sr concentration. Therefore, the kinetics of the Sr decontamination reaction are important; more than 4h are required to approach the final concentration. Upon introduction and simultaneous cooling of the sample to 22-25°C in the cells unit filter (CUF) for filtration testing, the Sr concentration increased (Sr-90 DF decreased) as a result of the retrograde solubility of $SrCO_3$. Therefore, in addition to isotopic dilution, the other important factor in decontamination is the total Sr concentration (distribution of Sr between the solution and solid phases), which is a function of the degree of ligand oxidation, temperature, and time.

The TRU decontamination in the AN-102/C-104 waste blend occurred after the permanganate was added (Hallen et al. 2002b,c). The TRU removal exceeded the requirements for ILAW glass by a factor of 5. The TRU removal from the AN-102/C-104 waste blend (Hallen et al. 2002c) was consistent with actual AN-102 diluted waste (Hallen et al. 2002a). This result suggested that blending had no impact on TRU removal. The initial concentrations of TRU elements were also significantly decreased with the waste blending, such that the waste without treatment was below the ILAW levels. However, permanganate treatment has the added benefit of reducing gamma levels in the LAW feed, i.e., through the removal of Eu-154 from solution.

Previous work has shown that permanganate addition to waste results in reduction to a variety of Mn species (Gauger and Hallen 2001). Oxidation of formate and organics in the waste reduces Mn(VII) to Mn(VI) then to Mn(IV). Depending on the organic compounds present, soluble Mn(IV) complexes can form, but eventually Mn(IV) precipitates as MnO_2.

The objective of the work reported here was to further investigate Mn reaction chemistry relevant to waste processing and to perform tests with an inactive AN-102/C-104 waste blend simulant to investigate treatment reaction mechanisms and to scope experiments to be performed on actual, active, waste. The purpose of these mechanistic studies was to determine the importance of oxidation, absorption, precipitation, and ligand displacement on decontamination.

The results from reaction mechanism tests are presented in this report. Test conditions and experimental procedures are described in Section 2.0. Experimental results from the tests are discussed in Section 3.0. The major conclusions and recommendations are given in Section 4.0. The appendix contains sample data, concentration data for key elements, and calculated DFs for the nonradioactive spike elements.

2.0 Test Conditions and Experimental Procedures

Experiments investigating the reaction chemistry of Mn species were conducted using simple mixtures of organic compounds in 0.1 *M* NaOH (50 mL) with a typical Mn concentration of 0.0005 *M*. This Mn concentration was chosen because reaction solutions could be analyzed directly by UV/Vis spectroscopy without dilution and because reaction rates were slow enough to easily follow reaction progress using the UV/Vis technique. Experiments were conducted by first combining the organic material and hydroxide in a 50-mL volumetric flask, then adding a $KMnO_4$ solution, diluting to the mark, mixing, and pouring into a 100-mL bottle. Samples were taken via syringe and filtered through a 0.2-µm syringe filter into a cuvette. UV/Vis spectra were recorded on a Cary 3E spectrophotometer. 18.2 MΩ-cm water was used for preparation of all solutions.

Experiments probing the mechanism of TRU removal used a simulated supernatant of the AN-102/C-104 waste blend originally prepared for inactive CUF filtration tests (Geeting et al. 2002). Two sets of tests were conducted in order to repeat certain experiments. Tables 2.1 and 2.2 show the experiments conducted in each set of these tests (Tests 1 and 2, respectively). In each test, the simulant was prefiltered through a 0.2-µm filter, then spiked with nonradioactive Ce, Eu, Fe, La, Mn, and Nd as the digluconate complexes at approximately 20 ppm each, immediately before testing was initiated. Because the spiked simulants for Tests 1 and 2 were prepared separately, the concentrations of spike elements in each are different. Comparisons, therefore, are made only between experiments in the same test.

The starting simulant volume in each of the treatment experiments was 20 mL, and reagents were added to give target concentrations of 0.02 *M*, except where noted. Reagents were typically added as aqueous solutions, but, in some cases, the solid reagent had to be added (see Tables 2.1 and 2.2). Strontium was added to all experiments, except one (Experiment 4). All experiments were conducted at ambient laboratory temperature and stirred with magnetic stir bars, except for the no-mix experiments (Experiments 6 and 27), in which stirring was started 1h after reagents were added as a layer on top of the simulant. Samples were taken at 4h and 24h, filtered through 0.2-µm syringe filters, acidified, and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Results are corrected for mass dilution caused by reagent addition.

Table 2.1. Reagent Concentrations for Sr/TRU Removal Test 1. Sample times were 4h and 24h for all experiments.

Experiment Number	Sr^{+2}	Mn(VII)	Mn(VI)	Mn(IV)	Mn(II)(a)	Other(b)	Stir	Added OH^-
1	--	--	--	--	--	--	No	AR(c)
2	--	--	--	--	--	--	No	AR
3	0.02 *M*	0.02 *M*	--	--	--	--	Yes	AR
4	--	0.02 *M*	--	--	--	--	Yes	AR
5	0.02 *M*	0.02 *M*	--	--	--	--	Yes	0.3 *M*
6	0.02 *M*	0.02 *M*	--	--	--	--	No(d)	AR
7	0.02 *M*	--	0.02 *M*	--	--	--	Yes	AR
8	0.02 *M*	--	--	Solid(e)	--	--	Yes	AR
9	0.02 *M*	--	--	--	0.02 *M*	--	Yes	AR
10	0.02 *M*	--	--	--	--	Ce(IV)(f)	Yes	AR
11	0.02 *M*	--	--	--	--	Ce(III)	Yes	0.09 *M*
12	0.02 *M*	--	--	--	--	Ce(IV)	Yes	0.09 *M*
13	0.02 *M*	--	--	--	--	IO_4^-(g)	Yes	AR
14	0.02 *M*	--	--	--	--	Zr(IV)(h)	Yes	AR
15	0.02 *M*	--	--	--	--	Ce(III)	Yes	AR
16	0.02 *M*	--	--	--	--	--	Yes	AR
17(i)	0.02 *M*	0.02 *M*	--	--	--	--	Yes	AR
18(j)	0.02 *M*	0.02 *M*	--	--	--	--	Yes	AR
19	--	--	--	--	--	--	Yes	AR
20	0.02 *M*	--	--	--	--	Fe(III)	Yes	AR
21	0.02 *M*	--	--	--	--	Fe(VI)(k)	Yes	AR

(a) Mn^{+2} precipitates as $Mn(OH)_2$, which air oxidizes to Mn(IV).
(b) Periodate (IO_4^-) is a non-precipitating oxidant, and zirconium, Zr(IV), is a non-oxidizing precipitant.
(c) AR = as received, 0.3 *M* OH^-; no added hydroxide.
(d) Mix sample after 1 hour of reaction.
(e) Solid reagent, freshly precipitated $MnO(OH)(ONa) \cdot xH_2O$, same number of Mn equivalents added as Experiment 3.
(f) Solid reagent, $(NH_4)_2Ce(NO_3)_6$.
(g) Solid reagent, KIO_4.
(h) 0.028 *M* $Zr(NO_3)_4$.
(i) Reverse addition, Mn(VII) then Sr^{+2}.
(j) Simultaneous addition of Mn(VII) and Sr^{+2}.
(k) Solid reagent, K_2FeO_4.

Table 2.2. Reagent Concentrations for Sr/TRU Removal Test 2. Sample times were 4h and 24h for all experiments.

Experiment Number	Sr^{+2}	Mn(VII)	Mn(VI)	Mn(IV)	Mn(II)[(a)]	Other	Stir	Added OH^-
22	--	--	--	--	--	--	No	AR[(b)]
23	0.02 *M*	0.02 *M*	--	--	--	--	Yes	AR
24	0.02 *M*	--	0.02 *M*	--	--	--	Yes	AR
25	0.02 *M*	--	--	Solid[(c)]	--	--	Yes	AR
26	0.02 *M*	--	--	--	0.02 *M*	--	Yes	AR
27	0.02 *M*	0.02 *M*	--	--	--	--	No[(d)]	AR
28	0.02 *M*	0.02 *M*	--	--	--	--	Yes	AR
29	0.02 *M*	--	--	--	--	Fe(III)[(e)]	Yes	AR
30	0.02 *M*	--	--	--	--	Fe(VI)[(f)]	Yes	AR
31	0.02 *M*	--	--	--	--	Fe(VI)[(g)]	Yes	AR
32	0.02 *M*	--	0.02 *M*	--	--	--	Yes	AR
33	0.02 *M*	--	--	--	--	Fe(III)[(h)]	Yes	AR
34	--	--	--	--	--	--	No	AR

(a) Mn^{+2} precipitates as $Mn(OH)_2$, which air oxidizes to Mn(IV).
(b) AR = as received.
(c) Solid reagent, freshly precipitated $MnO(OH)(ONa) \cdot xH_2O$, same number of Mn equivalents added as Experiment 23.
(d) Mix sample after 1 hour of reaction.
(e) [Fe(III)] = 0.038 *M*.
(f) Solid reagent, K_2FeO_4, 0.025 *M*.
(g) Solid reagent, K_2FeO_4, 0.031 *M*.
(h) [Fe(III)] = 0.02 *M*.

3.0 Results and Discussion

The results of Mn reaction sequence investigations and reaction mechanism testing with inactive AN-102/C-104 simulant spiked with nonradioactive elements are discussed in this section.

3.1 Manganese Reaction Sequence Results

The reaction of permanganate with reducing agents in basic solutions is complex. At least three oxidation states of Mn are involved, and complexes with organic ligands are important. Fortunately, each species is highly colored and has a distinctive UV/Vis spectrum that can conveniently be used to monitor reaction progress and determine relative kinetics and reaction mechanisms. Spectra of the purple $Mn^{VII}O_4^-$ and green $Mn^{VI}O_4^{2-}$ are shown in Figure 3.1.

Early reaction mechanism work (Gauger and Hallen 2001) determined that formate is rapidly oxidized by MnO_4^-, but that nitrite and oxalate do not react:

$$2\ MnO_4^- + HCO_2^- + 3\ OH^- \rightarrow 2\ MnO_4^{2-} + CO_3^{2-} + 2\ H_2O$$

The course of the formate reaction can be monitored by UV/Vis spectroscopy, as shown in Figure 3.2. The intensity of the MnO_4^- absorbance decreases, while that of the MnO_4^{2-} species simultaneously increases. The solution color changes from purple to dark green. At longer reaction times, the intensity of the MnO_4^{2-} species slowly decreases; the solution becomes lighter; and brown MnO_2 precipitates.[a]

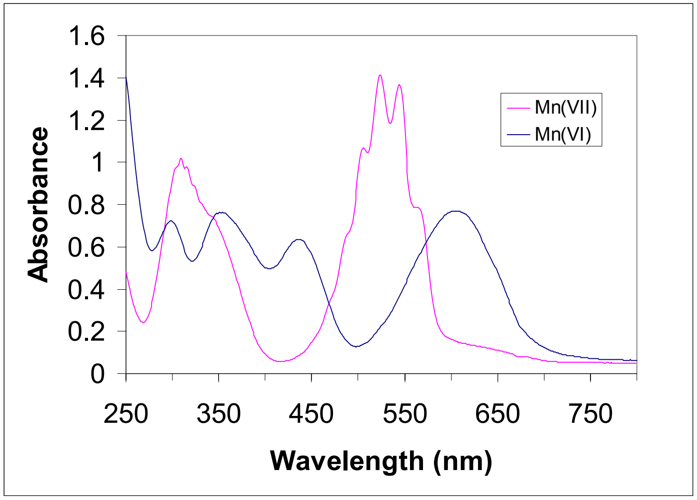

Figure 3.1. UV/Vis Spectra of $Mn^{VII}O_4^-$ and $Mn^{VI}O_4^{-2}$ in 0.1 *M* NaOH

(a) References to manganese dioxide and the formula MnO_2 are used in this report for simplicity. The actual precipitate from aqueous formate solutions was determined by analysis to be the deprotonated hydrated form containing Mn(IV), $NaMn(O)(OH)(O) \cdot x\ H_2O$. The composition from other reaction solutions may differ.

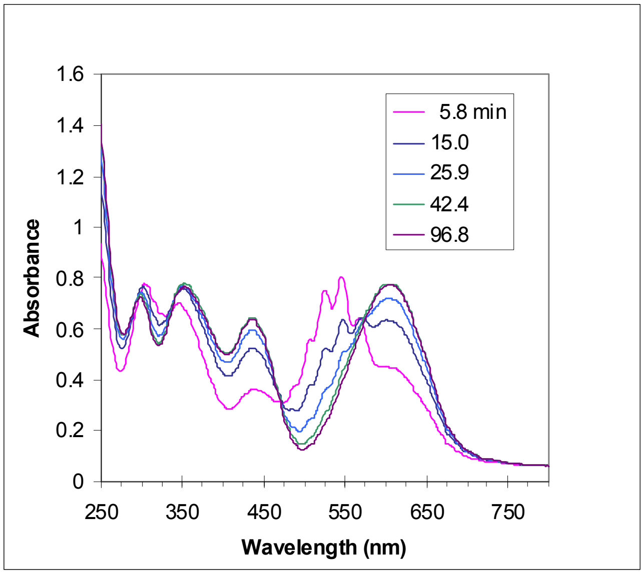

Figure 3.2. UV/Vis Spectra of MnO_4^- (0.0005 *M*) Oxidation of HCO_2^- (0.0005 *M*) in 0.1 *M* NaOH

Extinction coefficients can be used to calculate the concentrations of the Mn(VII) and Mn(VI) during the course of the reaction. Figure 3.3 plots the change in Mn species concentrations as a function of time. Under the reaction conditions, about half of the MnO_4^- has reacted within 10 min; higher formate concentrations, such as that found in the AN-102/C-104 waste blend, react much faster. A close examination of Figure 3.3 reveals that the MnO_4^- does not completely disappear over the time span

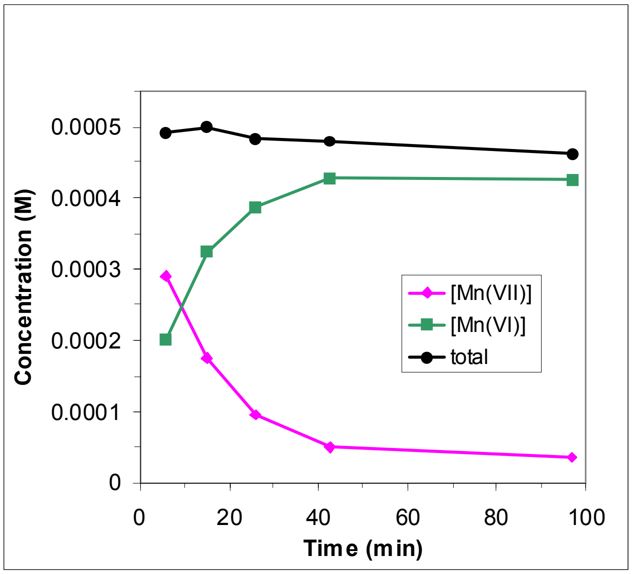

Figure 3.3. Change in Concentration of Mn Species in the MnO_4^- (0.0005 *M*) Oxidation of HCO_2^- (0.0005 *M*) in 0.1 *M* NaOH

shown, even though the reaction with formate is quite favorable and the formate is present in a twofold stoichiometric excess. The reason is that the disproportionation of Mn(VI) is an important reaction in 0.1 *M* NaOH (low base concentration) and one that occurs to a larger extent at higher Mn(VI) concentrations:

$$3\ \mathrm{Mn^{VI}O_4^{2-}} + 2\ \mathrm{H_2O} \rightleftharpoons 2\ \mathrm{MnO_4^-} + \mathrm{MnO_2} + 4\ \mathrm{OH^-}$$

The reduction of permanganate with MnO_2 is another method to prepare MnO_4^{2-}:

$$2\ \mathrm{MnO_4^-} + \mathrm{MnO_2} + 4\ \mathrm{OH^-} \rightleftharpoons 3\ \mathrm{MnO_4^{2-}} + 2\ \mathrm{H_2O}$$

This reaction is the reverse of the MnO_4^{2-} disproportionation reaction. The equilibrium is shifted toward Mn(VI) by conducting the reaction in strong base (2 *M*) [Cotton and Wilkinson 1972]. This reaction is not ideal for preparing a standard solution of Mn(VI), however, because MnO_2, present in excess, promotes the decomposition of Mn(VI). This reaction can be observed spectroscopically by monitoring Mn(VI) solutions with or without MnO_2 present (Figure 3.4). While the role of MnO_2 in this reaction is unknown, one possibility is that it results in the formation of small quantities of Mn(V), which rapidly hydrolyzes to MnO_2. The net reaction is the catalyzed hydrolysis of Mn(VI):

$$\begin{array}{ll} \mathrm{MnO_2} + \mathrm{MnO_4^{2-}} + 4\ \mathrm{OH^-} \rightleftharpoons 2\ \mathrm{MnO_4^{3-}} + 2\ \mathrm{H_2O} & K = 7.2 \times 10^{-11} \\ 2\ \mathrm{MnO_4^{3-}} + 3\ \mathrm{H_2O} \rightleftharpoons 2\ \mathrm{MnO_2} + 6\ \mathrm{OH^-} + \tfrac{1}{2}\ \mathrm{O_2} & K = 7.4 \times 10^{16} \\ \hline \mathrm{MnO_4^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{MnO_2} + 2\ \mathrm{OH^-} + \tfrac{1}{2}\ \mathrm{O_2} & K = 5.3 \times 10^{6} \end{array}$$

The oxidation of gluconate by permanganate occurs more rapidly and is more complicated than the oxidation of formate. Monitoring the course of the reaction by UV/Vis shows that a new species is formed, not previously observed in formate reductions, with an intense absorbance at 276 nm (Figure 3.5). In addition, instead of turning green and slowly precipitating brown MnO_2 as observed in

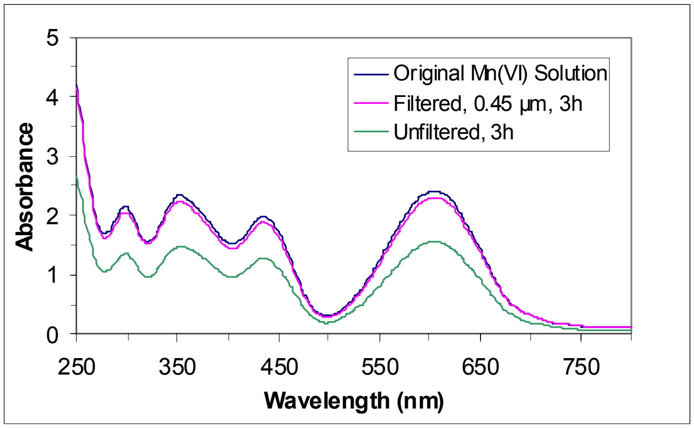

Figure 3.4. UV/Vis Spectra of the MnO_2-Promoted Decomposition of MnO_4^{2-} (2 *M* NaOH)

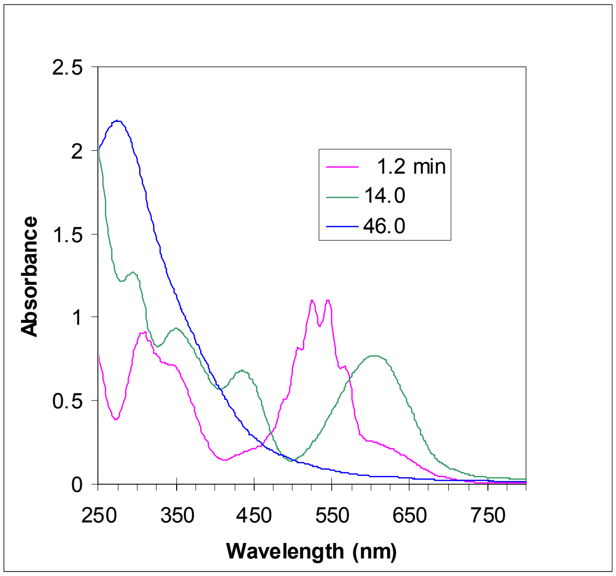

Figure 3.5. Selected UV/Vis Spectra in the Reaction of Sodium Gluconate (0.0005 *M*) and MnO_4^- (0.0005 *M*) in 0.1 *M* NaOH

the formate reactions, solutions turn green then yellow, usually with no visible precipitation. After 24h, the solutions retain the same yellow color, but filtration through a 0.2-µm filter produces a colorless or only lightly colored permeate.

The yellow product in this reaction is a dimeric Mn(IV) gluconate complex first reported by Bodini et al. (1976). This complex was formulated as $[Mn_2(glu)_4(O)_2(OH)_2]^{6-}$ and is thought to contain a four-membered oxo-bridged Mn_2O_2 core, similar to that found in Mn-Schiff base complexes active in photosynthesis. UV/Vis spectra of this dimer, which can be independently prepared either by air oxidation of the Mn(II) gluconate complex or by reaction of excess gluconate with MnO_2 in strong base, are identical with spectra obtained during permanganate oxidation. Gluconate complexation keeps the Mn(IV) in solution and slows precipitation of MnO_2. The MnO_2 forms slowly by hydrolysis, but remains suspended as very finely divided particles that cannot be seen. Relevant to waste processing, high base concentrations tend to favor dissolution of Mn (and other metal ions) as the gluconate complex. Low base concentrations favor hydrolysis and precipitation of the metal ion.

The intense peak at 276 nm is also observed during oxidation of other polyhydroxylic substrates, such as sorbitol, xylitol, arabitol, and, to a small extent, erithritol. The rate of disappearance of Mn(VI) with arabitol was different than with its stereoisomer, xylitol.

Plotting the concentrations of Mn species as a function of time during the oxidation of gluconate shows the stepwise formation of the various Mn oxidation states and compounds (Figure 3.6). Mn(VI) grows in as Mn(VII) disappears. The Mn(IV) gluconate complex then replaces the Mn(VI) as the oxidation continues. Eventually, the concentration of the gluconate complex decreases as it hydrolyzes and forms MnO_2. The total Mn concentration remains constant at 0.0005 *M* (the initial permanganate concentration) throughout the oxidation until MnO_2 precipitation begins.

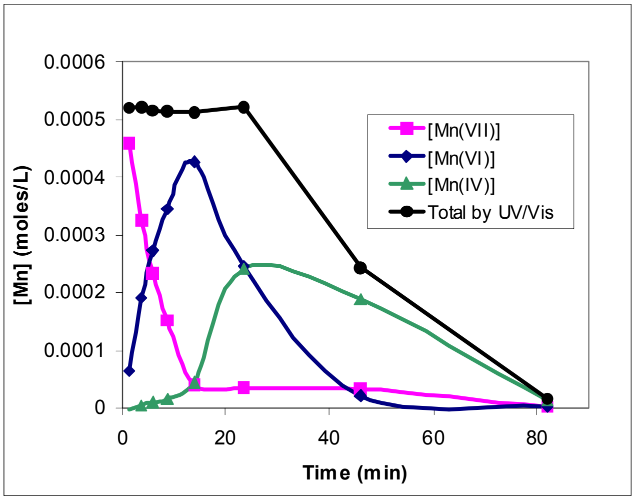

Figure 3.6. Change in Mn Species Concentrations in the Reaction of Sodium Gluconate (0.0005 *M*) and MnO_4^- (0.0005 *M*) in 0.1 *M* NaOH

The Mn(IV) gluconate dimer is photosensitive. Exposure of a yellow solution to visible light slowly bleaches the solution to a very light yellow color. Placing this bleached solution in the dark results in a reversal of the reaction and reformation of the starting dimer. The nature of this photochemical reaction is not known, and Bodini et al. did not comment on it. However, it is possible that light cleaves the Mn_2O_2 core, forming either separate monomeric complexes or an open-chain dimer.

The yellow solution and its photochemical bleaching were observed in samples taken during filtration testing with the treated waste simulant AN-102/C-104 (Geeting et al. 2002). Permeate samples taken from the CUF were initially yellow, having been protected from light in the CUF system. Upon exposure to light, however, the samples were observed to lighten significantly. ICP-AES analyses showed the Mn concentration of the samples was approximately 20 mg/L, which is higher than that in the starting simulant solution. It is very likely Mn that had dissolved in these samples was present as the Mn(IV) gluconate complex.

The observed Mn solubility in the CUF experiments was much higher than ever seen after permanganate treatment of actual waste samples. Also, while the Mn concentration increased from the initial value upon treatment of the simulant solution, actual wastes have always shown Mn removal as a result of permanganate addition. When a batch of the simulant had aged for 4 months and was treated before a second series of filtration tests, Mn was removed by approximately 50%, which is more representative of results from the treatment of actual waste samples.

It is believed that the initial concentration of complexants was higher in the simulant compared with actual waste and that air oxidation in the simulant likely occurred over the 4 months, reducing the concentration of complexants to a level more representative of actual waste samples. It has been reported that iron promotes the air (Traube et al. 1936) and photo oxidation (Neiger and Neuschul 1936) of gluconate via an iron gluconate complex. Other metal ions, such as Co, Ni, Cu, and Mn, are also believed to promote gluconate air oxidation.

These results suggest that using simulants to mimic TRU complexation and decontamination via permanganate addition needs to be carefully reviewed and compared with treatment of actual waste samples. The magnitude of post-filtration precipitation in tank supernatants based on the results of treated simulants is also likely overestimated because of the higher solubility of Mn in treated simulant solutions than in actual tank samples.

The addition of Nd, La, or Eu to the gluconate oxidation greatly sped the reaction, while the addition of Ce did not. The rate enhancement is illustrated for the case of Nd addition. The change in Mn species concentrations is shown in Figure 3.7 for reaction conditions identical to those for the reaction shown in Figure 3.6, except for the presence of Nd. When the first sample was taken, the Mn(VII) was nearly all consumed and the Mn(VI) concentration was already falling. The Mn(IV) concentration increased to a somewhat lower concentration than when Nd was absent, and the total Mn species concentration started dropping immediately. The nature of the rate acceleration is unknown, but it may be possible that an association of the lanthanide with the anionic Mn(VII) and Mn(VI) increases the oxidation power of these oxidants. It may be that Ce cannot participate in this type of association. Of these four ions, only Ce forms a complex with gluconate that is detectable by UV/Vis. Coordination sites around Ce would be occupied by gluconate and the complex would have a negative charge, making association with anionic Mn(VII) or Mn(VI) unfavorable.

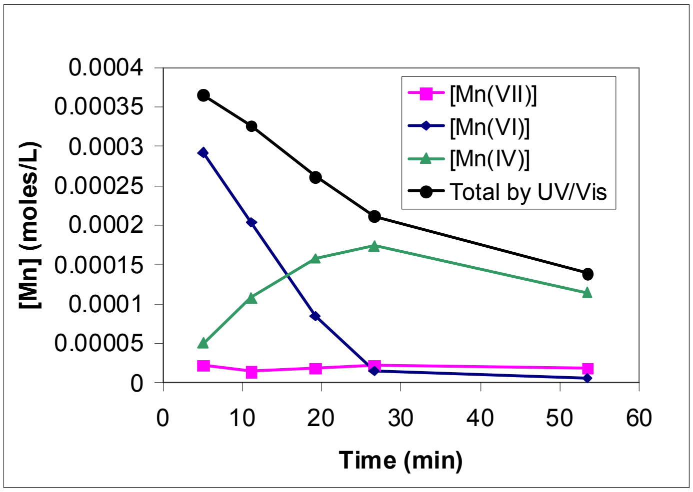

Figure 3.7. Change in Mn Species Concentrations in the Reaction of Sodium Gluconate (0.0005 *M*), $Nd(NO_3)_3$ (0.0005 *M*), and MnO_4^- (0.0005 *M*) in 0.1 *M* NaOH

3.2 Control and Duplicate Experiment Results for AN-102/C-104 Simulant

Control samples taken at 4h and 24h gave an estimate of the sampling and analytical error. For Test 1, the error in Ce, Eu, and Fe was 5 to 6% (Table 3.1). A slightly larger error of 10 to 13% was observed for La, Mn, and Nd. Most of the error arose from one sample (1-4h); the remaining three samples had

Table 3.1. Concentrations of Spike Elements in Test 1 Control Experiments After 4h and 24h

Analyte	Concentration in Control Sample, ppm (Test 1)				Average	Standard Deviation	% Standard Deviation
	1-4h	**2-4h**	**1-24h**	**2-24h**			
Ce	23.3	24.3	26.3	25.6	24.8	1.4	5.4
Eu	19.1	21.6	21.8	21.3	20.9	1.2	5.9
Fe	18.9	20.9	21.2	20.8	20.4	1.1	5.2
La	12.8	16.1	17.0	16.7	15.7	2.0	12.5
Mn	12.5	16.0	15.7	15.4	14.9	1.6	10.7
Nd	16.1	20.8	18.1	18.0	18.2	1.9	10.5

much less experimental error (1 to 4%, except Nd at 8%). In Test 2 controls (Table 3.2), the error for all of the elements was in the range of 4 to 6% except Fe, which was about 2%. Again, most of the error was in one sample (22-4h), without which the errors generally ran less than 2%.

Duplicate experiments were run in Test 2 with Mn(VII) (Experiments 23 and 28) and Mn(VI) (Experiments 24 and 32). The concentrations of the spike elements in these pairs of experiments are summarized in Tables 3.3 and 3.4, respectively. For the Mn(VII) experiments, greater variations in concentrations are observed in the 4h samples than in the 24h samples. This may arise if the solutions are not at equilibrium after 4h, but are closer to equilibrium after 24h. If so, the 4h samples would be more susceptible to minor differences in sampling times and solution work-up schedules. The deviations in the 24h samples are within those attributable to sampling and analytical error (Table 3.2).

Table 3.2. Concentrations of Spiked Elements in Test 2 Control Experiments After 4h and 24h

Analyte	Concentration in Control Sample, ppm (Test 2)				Average	Standard Deviation	% Standard Deviation
	22-4h	**34-4h**	**22-24h**	**34-24h**			
Ce	14.2	15.6	15.7	16.0	15.4	0.8	5.3
Eu	13.7	15.0	15.2	15.5	14.9	0.8	5.5
Fe	13.6	13.8	13.8	14.2	13.9	0.3	1.9
La	11.8	13.1	13.1	13.6	12.9	0.8	5.9
Mn	13.0	14.2	14.2	13.8	13.8	0.6	4.3
Nd	12.2	13.4	13.4	14.3	13.3	0.9	6.4

Table 3.3. Concentrations of Spike Elements in Test 2 Mn(VII) Experiments After 4h and 24h

Sample	Analyte	Concentration, ppm		Average	Standard Deviation	% Standard Deviation
		23-4h	**28-4h**			
4h	Ce	2.02	2.26	2.14	0.17	8.0
	Eu	2.36	2.51	2.44	0.10	4.1
	Fe	0.76	0.86	0.81	0.07	9.2
	La	2.63	2.56	2.60	0.05	2.0
	Mn	3.06	2.72	2.89	0.24	8.2
	Nd	1.98	2.02	2.00	0.03	1.4
		23-24h	**28-24h**			
24h	Ce	1.49	1.60	1.55	0.08	5.1
	Eu	1.74	1.79	1.76	0.03	1.9
	Fe	0.26	0.28	0.27	0.01	3.6
	La	1.95	2.04	1.99	0.07	3.3
	Mn	1.71	1.78	1.75	0.05	3.1
	Nd	1.49	1.54	1.51	0.03	2.3

Table 3.4. Concentrations of Spike Elements in Test 2 Mn(VI) Experiments After 4h and 24h

Sample	Analyte	Concentration, ppm		Average	Standard Deviation	% Standard Deviation
		24-4h	**32-4h**			
4h	Ce	2.03	2.06	2.04	0.02	0.9
	Eu	2.22	2.39	2.31	0.12	5.2
	Fe	0.90	1.00	0.95	0.07	7.6
	La	1.92	1.98	1.95	0.05	2.3
	Mn	3.84	3.74	3.79	0.07	2.0
	Nd	1.63	1.75	1.69	0.08	5.0
		24-24h	**32-24h**			
24h	Ce	1.52	1.65	1.58	0.09	6.0
	Eu	1.52	1.50	1.51	0.01	0.8
	Fe	0.42	0.97	0.70	0.39	55.5
	La	1.43	1.46	1.44	0.02	1.3
	Mn	2.41	2.02	2.21	0.28	12.6
	Nd	1.09	1.14	1.11	0.03	3.1

Deviations in the Mn(VI) experiments and deviations in the Mn(VII) experiments were similar in the 4h samples, but larger in the 24h samples. Spike element concentrations in the 4h samples were the same within the analytical error, except for Fe, which showed a slightly higher deviation. Some of the 24h results are not easily explained, however, such as the large deviations in Fe and Mn. Since the Eu, La, and Nd results for the same samples are within the analytical error, errors associated with sampling or dilution are not indicated. It may be that Fe and Mn nucleation rates were different in the two experiments.

3.3 TRU Removal Mechanism Testing Results

Experiments 3, 23, and 28 are considered the optimized treatment conditions, in which the treatment consisted of Sr addition (0.02 *M* target concentration), followed by MnO_4^- addition (0.02 *M* target concentration), with continuous stirring at ambient temperature. Other experiments are compared with these optimized conditions. This treatment was effective at reducing the spike element concentrations as shown in Figure 3.8; 60 to 90% of these elements were removed (Figure 3.9), corresponding to DFs of between about 3 and 17 (see Figure A.3, appendix, for DFs). In addition, spike element removal was comparable to Eu-154 and TRU decontamination obtained by treatment of actual AN-102/C-104 waste blend (Table 3.5). DFs for Eu agreed very well. While there was variation in individual ion DFs, the Am and Cm values were in about the same range as La and Nd in the inactive tests. Ce DFs were lower than for other spike elements in the inactive waste simulant or TRUs in the active waste.

The Sr/MnO_4^- treatment was much more effective than simply adding Sr alone, which removed less than 6% of the Ce, Eu, Fe or Mn (Figure 3.9). The Sr-only treatment removed about 30% of the Nd [in contrast to 80% for Sr/Mn(VII)], and as much as 50% of the La [in contrast to 70% for Sr/Mn(VII)].

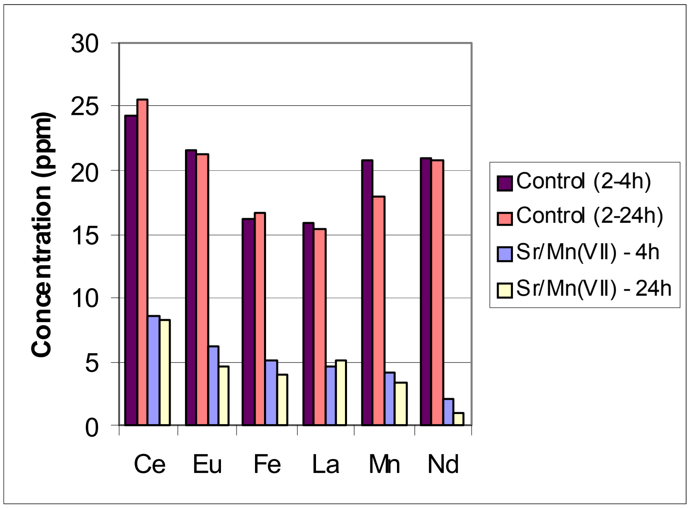

Figure 3.8. Concentrations in Treated and Untreated Simulant (Test 1)

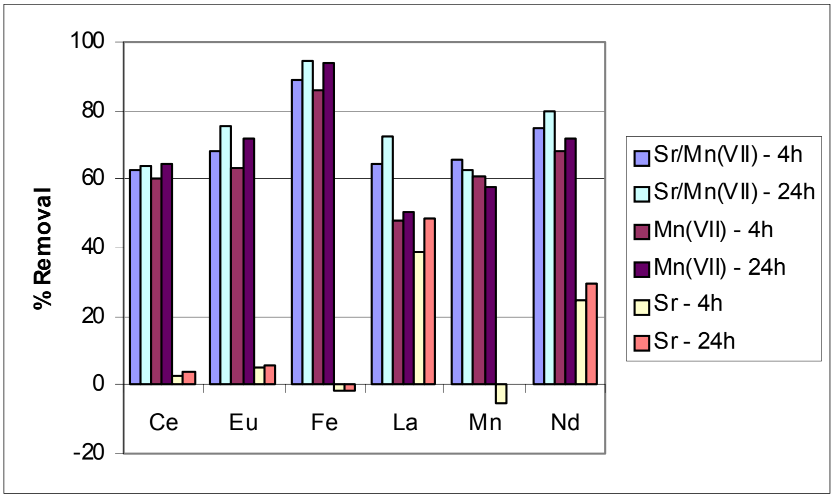

Figure 3.9. Sr/Mn(VII) vs. Mn(VII)-Only vs. Sr-Only (Test 1)

Table 3.5. Comparison of DFs for Actual (Hallen et al. 2002c) and Simulated (This Study) AN-102/C-104 Waste Blend

Hallen et al. (2002c)		**This Study - Test 1**	
Analyte	**DF**	**Analyte**	**DF**
Eu-154	3.7	Eu	4.1
Am-241	5.5	La	3.6
Cm	4.0	Nd	4.9
--	--	Ce	2.8

Results for the MnO_4^--only treatment (Figure 3.9) were generally comparable to the Sr/MnO_4^- treatment, suggesting that oxidation combined with sorption by MnO_2 was important for removal of the spike elements. The MnO_2 sorption results suggest the same conclusion (discussed below).

The order of Sr and MnO_4^- addition made little difference in these experiments (Figure 3.10). The results of the reverse addition experiment, in which MnO_4^- was added first followed by Sr addition, were about the same as with normal addition. Adding both reagents simultaneously gave similar results. Figure 3.10 (and other figures) clearly shows that removal was not complete after 4h. Another approximately 5% of the elements were removed by waiting 24h.

An additional 0.3 *M* hydroxide in the test solution had very little effect on spike element removal (Figure 3.11). The exception was Mn, which was only removed by about 40% in the higher base compared with about 65% in the as-received simulant. La and Nd may have been removed slightly more at higher base, but Ce, Eu, and Fe were nearly identical in the as-received and 0.3 *M* hydroxide solutions.

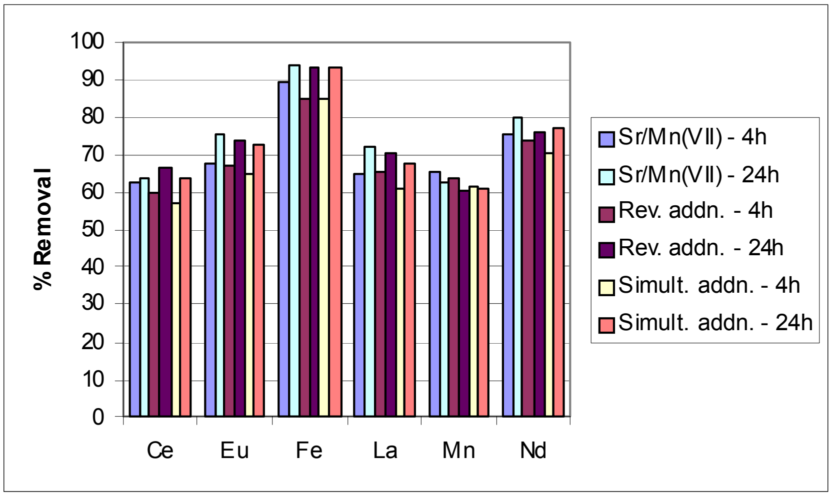

Figure 3.10. Mn(VII) vs. Reverse Addition vs. Simultaneous Addition (Test 1)

Not mixing the solution for 1h had little impact on removal (Figure 3.11). It was expected that in a static system the reaction of permanganate with organics would be minimized, thereby decreasing element removal. Permanganate oxidation of organics at the interface would form solid MnO_2, which would remain at the interface and tend to hinder further contact. MnO_2 would also promote the decomposition of permanganate and MnO_4^{2-} (presumably by hydrolysis), as discussed above.

However, mixing during the permanganate reaction stage did not appear to be important for spike element removal. In Test 1, the added Sr and MnO_4^- reagents appeared to mix with the top half of the simulant solution; more mixing occurred than was desired. In Test 2, the experiment was repeated with a narrower vial and very little mixing occurred before 1h. Nevertheless, no-mix experiments in both Test 1 and Test 2 gave about the same % removal as the identical, but mixed, experiments. The no-mix experiments still had better removal than experiments in which Sr and solid MnO_2 were added (discussed below).

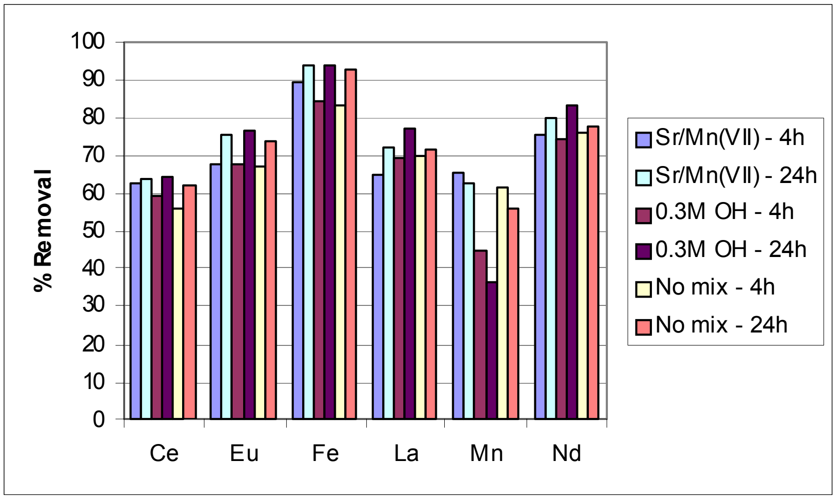

Figure 3.11. Mn(VII) As-Received vs. 0.3 *M* OH^- vs. No-Mix (Test 1)

Even though contact with the bulk solution was poor, organic oxidation and element removal may have occurred to a large extent right at the interface. Subsequent mixing after the reaction stage could give a net removal comparable to that in the continuously mixed experiments.

The effect of various Mn reagents on removal was investigated. The Mn(VII) and Mn(VI) treatments were superior to solid MnO_2 addition or addition of a Mn(II) solution (Figure 3.12). Oxidation enhanced the removal of the spike elements over sorption alone with MnO_2. Removal by MnO_4^- was up to about 25% more efficient than MnO_2. The Mn(VI) treatment performed about the same as Mn(VII). Also, Mn(II) gave essentially the same results as MnO_2 solids addition. Mn(II) in base precipitates as $Mn(OH)_2$, which air oxidizes to MnO_2.

The reaction of Mn(II) with air in base normally takes about 20 min in the presence of gluconate (Bodini et al. 1976), but in both the Test 1 and Test 2 experiments the oxidation was quite a bit slower. After 4h, relatively little MnO_2 had formed, judging by the light color of the solution. The appearance of the experiments after 24h was more like the other experiments with a larger amount of dark MnO_2 precipitate present. These observations are reflected in the Mn concentrations found in the solutions (Figure 3.13). In Test 2 after 4h, the Mn(II) solution contained 171 ppm Mn, while the Mn(VII) solution contained only 3 ppm and the Mn(IV) solution 22 ppm soluble Mn. After 24h, the concentration in the Mn(II) solution had dropped to 11 ppm, the same as in the MnO_2 24h sample. Similarly in Test 1, the 4h Mn(II) solution contained 268 ppm soluble Mn, while after 24h, the concentration was only 15 ppm.

The Mn(II) was apparently stabilized and held in solution by organics, such as EDTA, in the simulant solution. To test this possibility, a series of independent experiments were performed in which Mn(II) (0.0175 *M*) was mixed with EDTA (0.0175 *M*), either with or without Sr (0.0175 *M*) present, in 0.1 *M* NaOH solution. Samples were taken at 10 min, 4h, and 24h, and analyzed by ICP-AES. With no ligand present, Mn precipitated from solution and was not detected in any of the samples (Figure 3.14).

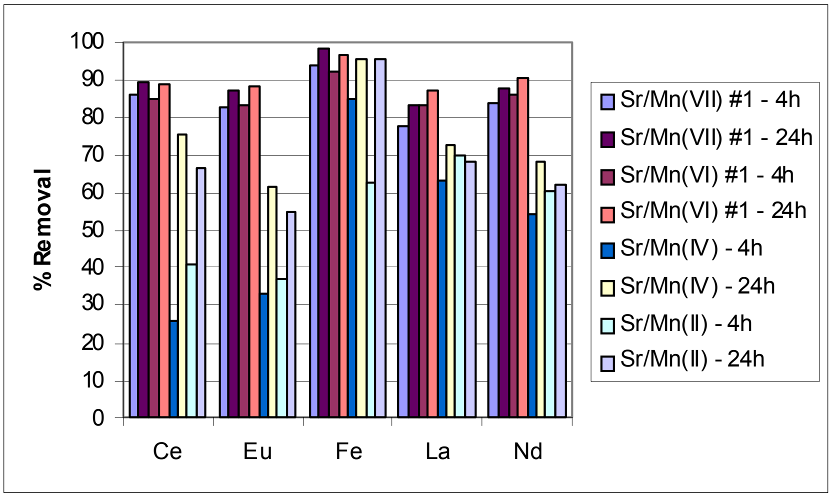

Figure 3.12. Mn(VII) vs. Mn(VI) vs. Mn(IV) vs. Mn(II) (Test 2)

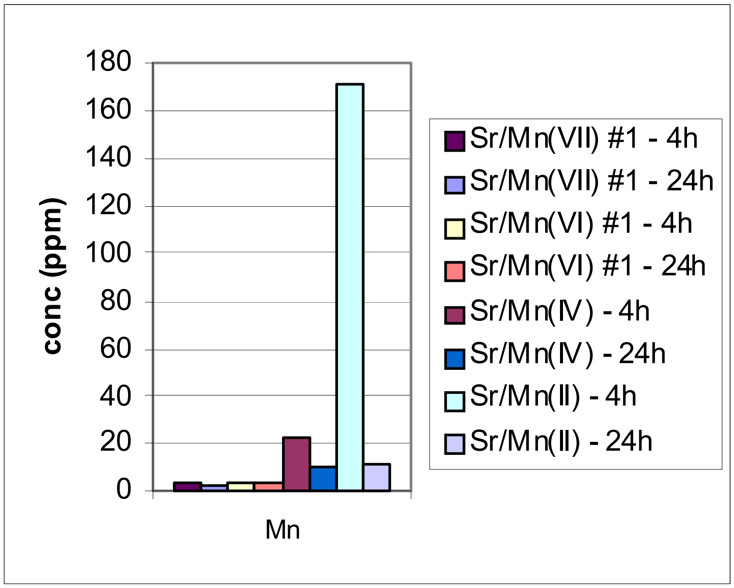

Figure 3.13. Mn(VII) vs. Mn(IV) vs. Mn(II) (Test 2)

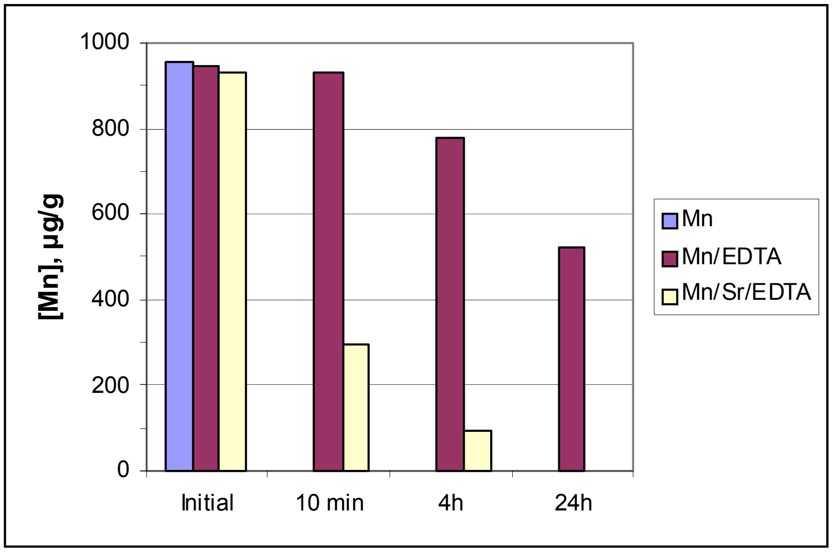

Figure 3.14. 0.1 *M* NaOH Containing Mn(II); Mn(II) with EDTA Added; and Mn(II), EDTA, and Sr. Initial concentrations are calculated.

EDTA, however, temporarily kept the Mn(II) in solution, not unlike the behavior seen in the test solutions. Presumably, the decrease in soluble Mn is caused by oxidation to the Mn(IV) EDTA complex, which hydrolyzes to precipitate MnO_2. The presence of Sr accelerated the precipitation of Mn, possibly by competition for EDTA and precipitation of $Mn(OH)_2$.

Ce(IV) was tested (with Sr addition) to investigate its performance compared with permanganate. Ce(IV) was added as either the solid $(NH_4)_2Ce(NO_3)_6$ (solution remains basic) or as acidic Ce(IV) in nitric acid solution followed by base to keep the final hydroxide concentration comparable to the other experiments. Ce(IV) is a much weaker oxidant in base ($E°_{red} = -0.7V$) than it is in acid ($E°_{red} = 1.76V$), so the two experiments are not necessarily equivalent. Ce(III) was also tested, since it should be formed if Ce(IV) is reduced by the organic complexants. The $(NH_4)_2Ce(NO_3)_6$ and Ce(III) treatments tended to be less effective than Mn(VII) (Figure 3.15). However, the Ce(IV)/OH^- treatment was just as effective as Mn(VII) in removing Eu, Fe, La, Mn, and probably Nd. [The Nd analysis is not accurate in the presence of high Ce concentrations because Ce interferes with the determination.] It is likely that the addition of the acidic Ce(IV) solution resulted in more oxidation than in the addition of the $(NH_4)_2Ce(NO_3)_6$, resulting in the somewhat better performance. The 4h and 24h Ce concentrations in the two Ce(IV) experiments were between 1000 and 1300 ppm; almost half of the added Ce remained in solution. Since unligated Ce(III) and Ce(IV) are not soluble in base, the organics must play a role in keeping the Ce soluble. This would be likely if the stability constant trend in basic solutions is the same as that for gluconate binding the bare metal ion: Ce(IV) > Ce(III) ~ Fe(III) > Nd(III) ~ La(III) > Sr(II).

The MnO_4^- added in these experiments acted both as an oxidant, oxidizing organics in the simulant solution, and as a precipitant when MnO_2 was formed. Experiments were performed in an attempt to separately evaluate these functions; reagents that oxidize or precipitate were examined. Periodate is a good oxidant for vicinal diols, such as gluconate, that do not precipitate on reduction. Periodate showed decreased effectiveness for spike element removal compared with permanganate (Figure 3.16).

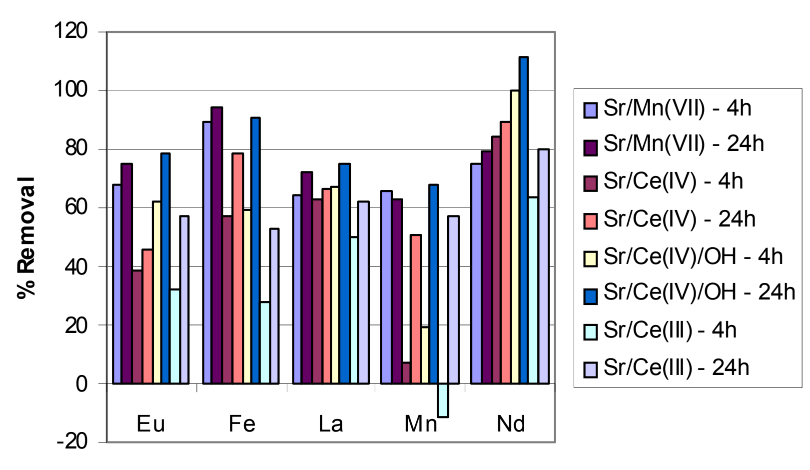

Figure 3.15. Mn(VII) vs. Ce(IV) vs. Ce(IV)/OH^- vs. Ce(III) (Test 1)

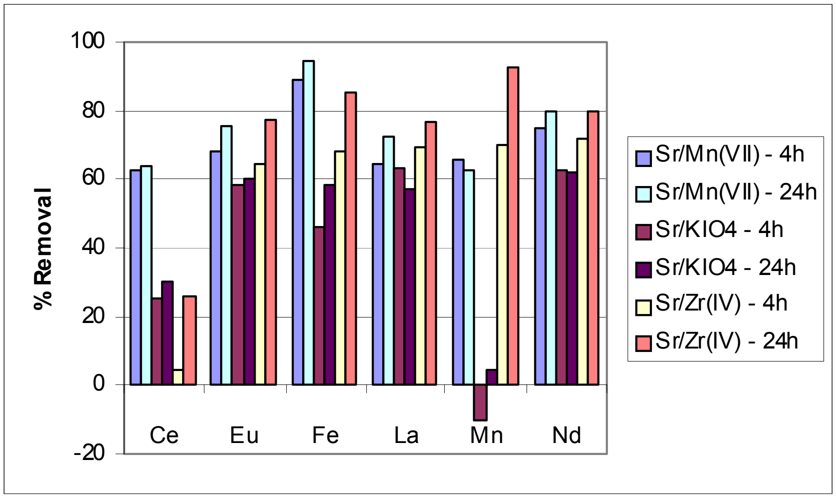

Figure 3.16. Mn(VII) vs. IO_4^- vs. Zr(IV)

Periodate was ineffective at removing Mn from the solution. Zr(IV) added as a non-oxidizing precipitant (Figure 3.16) was less effective than MnO_4^-, but about the same as MnO_2, for Ce and Fe removal. It was as good as or better than MnO_4^-, and much better than MnO_2, for Eu, La, Mn, and Nd removal. It is likely that Zr(IV) displaces other metal ions from organic ligands. Similar to Ce(IV), this would be likely if the stability constant trend in basic solutions is the same as that for EDTA binding the bare metal ion: Zr(IV) ~ Fe(III) > Nd(III) ~ La(III) ~ Eu(III) ~ Ce(III) ~ Mn(II) > Sr(II). In addition, the concentration of Zr in the 4h and 24h samples (100 ppm) was high and stable over the 24h period, indicating that Zr was bound to organic ligands.

$K_2Fe^{VI}O_4$ was investigated as a strong oxidant that also precipitates Fe(III) upon reduction. Ferrate is a stronger oxidant than permanganate, but it is also less stable in basic solutions. In 0.1 *M* NaOH, the half-life of the ferrate is about 10 min, decomposing by reaction with water. Although ferrate stability increases as the hydroxide concentration increases, decomposition occurs slowly, even in 10 *M* NaOH. In Test 2, ferrate showed less effectiveness at removing the spike elements than permanganate (Figure 3.17), even though the number of equivalents of ferrate in the experiment shown was 50% higher than the equivalents of permanganate. One explanation is that not all of the ferrate oxidizes organics in the solution and that some decomposes unproductively by reaction with water. The ferrate performed better than an equivalent amount of Fe(III), suggesting again that oxidation enhances removal.

Strontium concentrations in these experiments are not at equilibrium after 4h. In every experiment in which Sr was added, regardless of treatment, [Sr] continued to drop until the 24h sample, sometimes by over 50% after the 4h sample. Figures 3.18 and 3.19 show this trend for Test 1 and Test 2 experiments.

Strontium concentrations were on the order of those observed in earlier small-scale experiments in which the concentrations were about 170 µg/g (Hallen et al. 2002b). An interesting result is that when Ce(IV) is added, the Sr concentration is up to four times lower than when MnO_4^- is added (Figure 3.18). This may be another example of Ce(IV) displacement of metal ions from the organic ligands.

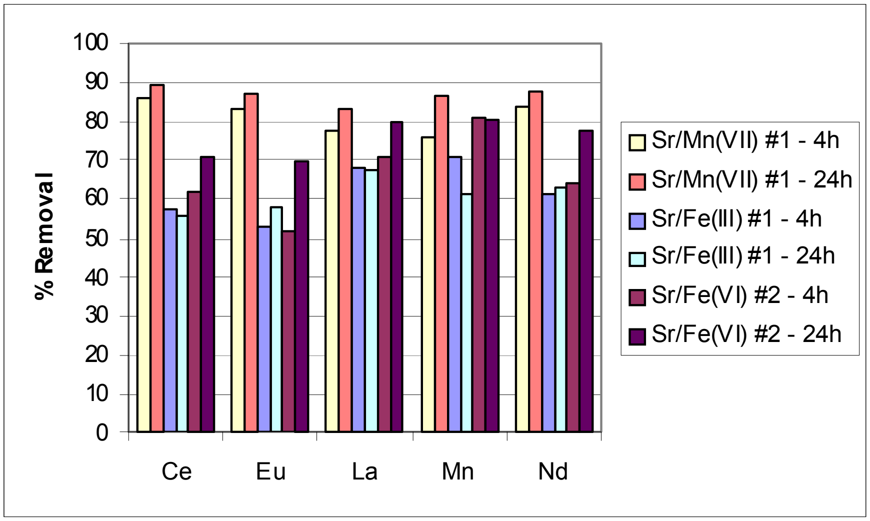

Figure 3.17. Mn(VII) vs. Fe(III) vs. Fe(VI) (Test 2)

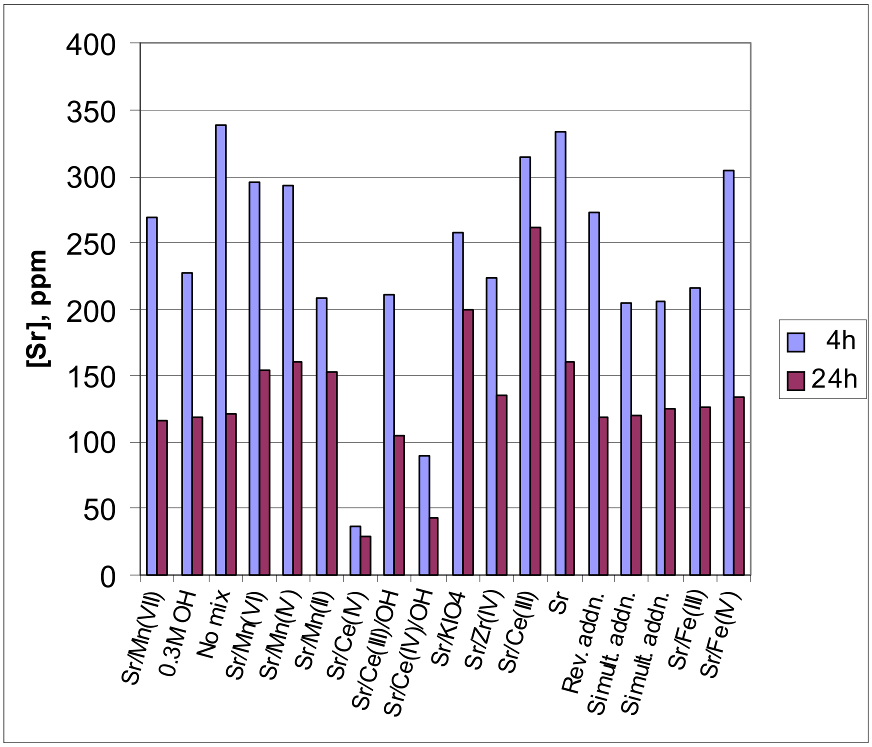

Figure 3.18. Sr Concentration After 4h and 24h (Test 1)

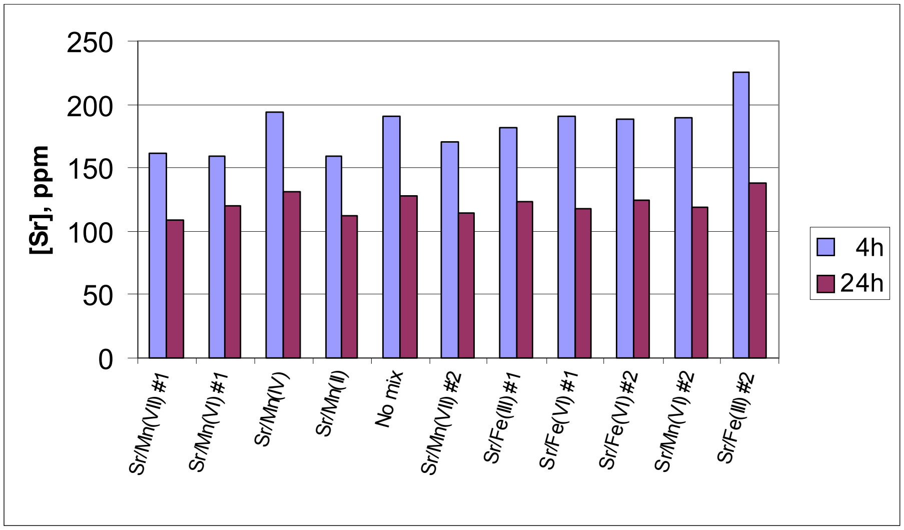

Figure 3.19. Sr Concentration After 4h and 24h (Test 2)

The drop in Sr concentration from 4h to 24h was investigated further. Samples of aged AN-102/C-104 waste blend simulant (the simulant is slightly different from that used above because of different aging times) were spiked to a target concentration of 0.02 *M* Sr and maintained at 20°C or 30°C for 7 days. Samples were taken, filtered, and analyzed for Sr by ICP-AES. Figure 3.20 clearly shows that the Sr concentration was falling relatively rapidly at 4h, but was closer to the final value by 24h and changing much less rapidly.

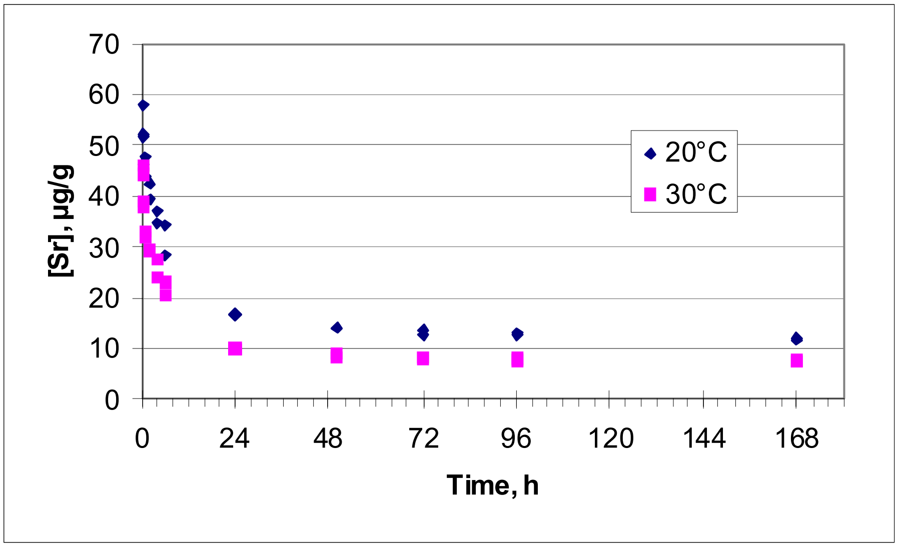

Figure 3.20. Decrease in Sr Concentration as a Function of Time

At 20°C the [Sr] dropped 54%, and at 30°C it dropped 62% from 4h to 24h (Table 3.6). The solubility is lower at 30°C because of the retrograde solubility of $SrCO_3$. Figure 3.21 shows similar data over a wider temperature range. At each temperature, the solution concentration at 24h is about half that at 4h.

Table 3.6. Strontium Concentrations at 20°C and 30°C at 4h and 24h

Temperature	ppm, 4h	ppm, 24h	Percent of Decrease
20°C	35.9	16.6	53.7
30°C	25.8	9.9	61.7

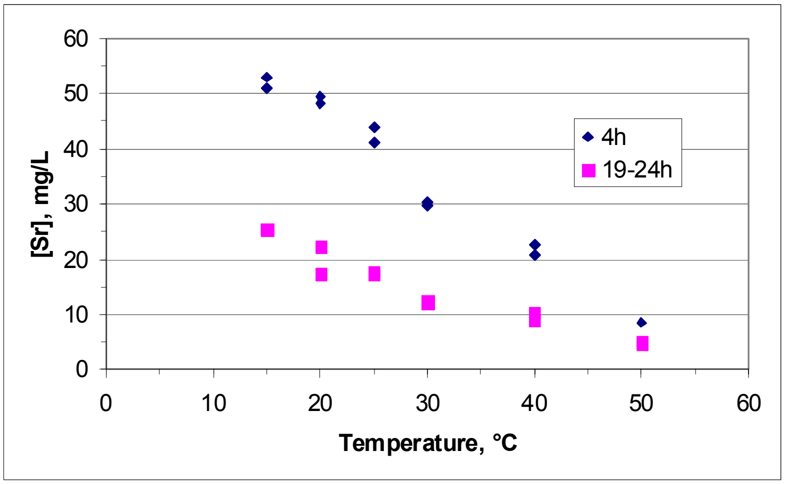

Figure 3.21. Sr Concentration as a Function of Time and Temperature

4.0 Conclusions and Recommendations

Experiments were conducted to investigate the reaction chemistry of Mn species relevant to the mechanism of TRU removal by permanganate treatment and to determine the importance of precipitation, absorption, ligand exchange, and oxidation on decontamination. These studies, conducted with an inactive simulated supernatant based on the "AN-102/C-104 waste blend," gave information about mechanisms of TRU decontamination and supported prior conclusions about Sr-90 removal in the treatment process. In addition, the results will guide planned experiments with actual tank waste samples from AN-102 and AN-107.

Mn(VII), added as permanganate ion, was demonstrated to undergo stepwise reduction to Mn(VI) and Mn(IV) species, reduced by organics and formate in the waste simulant. In the presence of gluconate, a Mn(IV) gluconate complex is formed that remains soluble in base. Stability of this complex increases with increasing base concentration, meaning that base added to the waste during processing could increase the concentration of soluble Mn (and possibly other metal ions). Evidence for the presence of the Mn(IV) gluconate complex was seen in earlier waste simulant filtration testing.

Several treatments employing various species of Mn, other oxidants, and precipitants were examined in testing of inactive AN-102/C-104 waste blend simulant spiked with nonradioactive metal ions. Strontium was added to all experiments except for one. The optimized treatment conditions—no added hydroxide, addition of Sr (0.02 *M* target concentration) followed by sodium permanganate (0.02 *M* target concentration) with mixing at ambient temperature—were used as a reference for comparison. The removal of the spiked elements was used as an indication of the extent/effectiveness of treatment. The performance of the optimized treatment conditions was very similar with simulated waste (this study) and actual waste (Hallen et al. 2002c). For example, DFs for Eu were quite close for both waste solutions, and DFs for Am and Cm for the actual waste treatment were in the same range as observed for La and Nd removal from the simulated waste. In general, the optimized conditions gave the best spike element removal of the treatments tested. Overall, the treatments involving oxidation performed the best, although addition of Zr(IV) also performed well for spike element removal. Ligand displacement, followed by precipitation of metal ions, appeared to be important for treatments with Ce(IV) and Zr(IV); spike elements were removed efficiently, but the Ce or Zr concentrations in solution remained high. Ce(III) concentrations remained high in treatments involving Ce, but treatment effectiveness was unaltered. It appears, then, that incorporating Ce-containing recycle streams from canister decontamination with Envelope C waste will not impair, and may actually improve, the efficiency of Sr/TRU removal.

The order of addition of Sr and permanganate and whether the solution was mixed during the reaction phase had little bearing on element removal. About the same performance was observed whether permanganate was added first, second, or simultaneously with the Sr. Two different no-mixing experiments (unstirred during the first hour of reaction) gave the same results as mixed experiments under otherwise identical conditions.

Strontium concentrations, and therefore decontamination levels, are time dependent. In all experiments in which Sr was added, the Sr concentrations decreased significantly between 4h and 24h. In some cases, the concentration was halved over this time; i.e., a doubling of the Sr-90 DF would be expected in actual waste processing. The precipitation of $SrCO_3$ is slow, and adequate time must be allowed for equilibrium to be approached. This behavior is the same as that observed with actual waste. In addition, the solution Sr concentrations in the actual waste and the simulated waste were about the same. Therefore, these results suggest that treated waste should be filtered longer than 4h after reagent addition.

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Appendix

Sample Data, Concentrations of Key Elements, and Calculated DFs for Spike Elements

Table A.1. Mass Dilution Factors Used in DF and Percent Removed Calculations for Test 1

Experiment Number	AN-102 Added		Sr Added (0.44 *M*)		Reagents Added			Mass Dilution Factor (MDF)
	Target mL	Actual Wt, g	Target mL	Actual Wt, g	Reagent	Target mL	Actual Wt, g	
1	10	12.5621	--	--	--	--	--	1
2	10	12.5230	--	--	--	--	--	1
3	20	25.3220	1	1.0816	Mn(VII)	1	1.0203	1.0830
4	20	25.3197	--	--	Mn(VII)	1	1.0365	1.0409
5	20	25.3118	1	1.0720	Mn(VII)/OH^-	1.66	1.9102	1.1178
6	20	25.2936	1	1.0445	Mn(VII)	1	1.0536	1.0829
7	20	25.3054	1	1.0726	Mn(VI)	2	2.2027	1.1294
8	20	25.3108	1	1.0756	Mn(IV)	Solid	0.0656	1.0451
9	20	25.3292	1	1.0885	Mn(II)	1	1.0447	1.0842
10	20	25.2967	1	1.0842	Ce(IV)	Solid	0.7117	1.0710
11	20	25.2740	1	1.0879	Ce(III)/OH^-	1.88	2.2623	1.1326
12	20	25.2832	1	1.0751	Ce(IV)/OH^-	1.88	2.2443	1.1313
13	20	25.3067	1	1.0711	IO_4^-	Solid	0.2989	1.0541
14	20	25.3176	1	1.0742	Zr(IV)	1	1.1197	1.0867
15	20	25.2975	1	1.0677	Ce(III)	1	1.1552	1.0879
16	20	25.3039	1	1.0857	--	--	--	1.0429
17	20	25.2989	1	1.0722	Mn(VII)	1	1.0398	1.0835
18	20	25.2936	1	(a)	Mn(VII)	1	2.0863(a)	1.0825
19	10	12.6609	--	--	--	--	--	1
20	10	12.6309	0.5	0.5360	Fe(III)	1	1.0255	1.1236
21	10	12.5779	0.5	0.5321	Fe(IV)	Solid	0.0625	1.0473

(a) Simultaneous addition; no individual weights.

Table A.2. Mass Dilution Factors Used in DF and Percent Removed Calculations for Test 2

Experiment Number	AN-102 Added		Sr Added (0.44 *M*)		Reagents Added			Mass Dilution Factor (MDF)
	Target mL	Actual Wt, g	Target mL	Actual Wt, g	Reagent	Target mL	Actual Wt, g	
22	10	12.3124	--	--	--	--	--	1
23	20	24.8213	1	1.1009	Mn(VII)	1	1.0215	1.0855
24	20	24.8848	1	1.0666	Mn(VI)	2	2.2304	1.1325
25	20	24.8604	1	1.0602	Mn(IV)	Solid	0.0665	1.0453
26	20	24.8402	1	1.0640	Mn(II)	1	1.0411	1.0847
27	20	24.8550	1	1.0434	Mn(VII)	1	1.0312	1.0835
28	20	24.8194	1	1.0664	Mn(VII)	1	1.0239	1.0842
29	20	24.8281	1	1.0617	Fe(III)	2	2.0904	1.1270
30	20	24.8419	1	1.0571	Fe(VI)	Solid	0.2126	1.0511
31	20	24.8143	1	1.0655	Fe(VI)	Solid	0.2597	1.0534
32	20	24.8194	1	1.0619	Mn(VI)	2	2.2407	1.1331
33	20	24.8250	1	1.0551	Fe(III)	1	1.0455	1.0846
34	10	12.3014	--	--	--	--	--	1

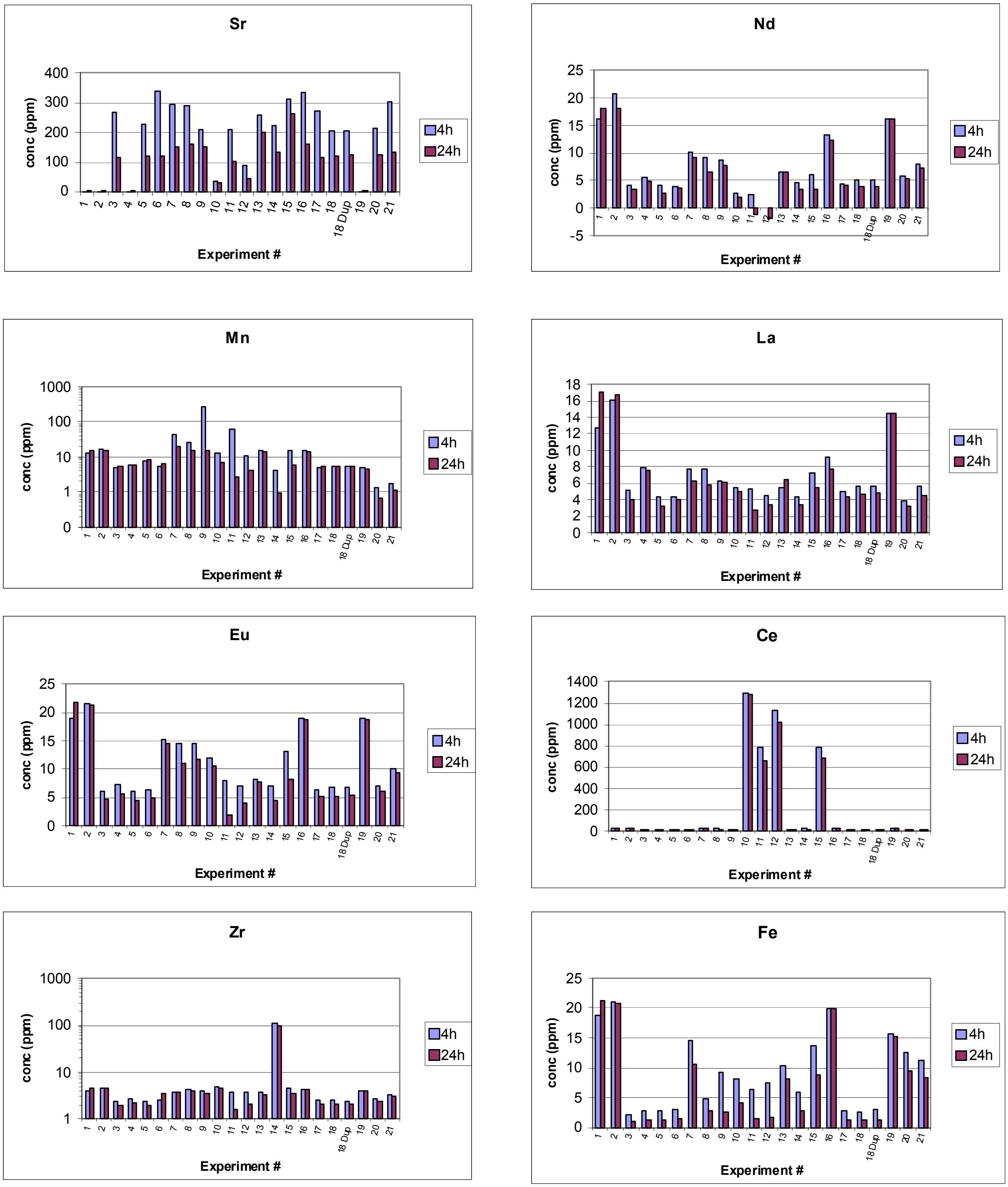


Figure A.1. Concentrations of Key Elements in Reaction Mechanism Test 1

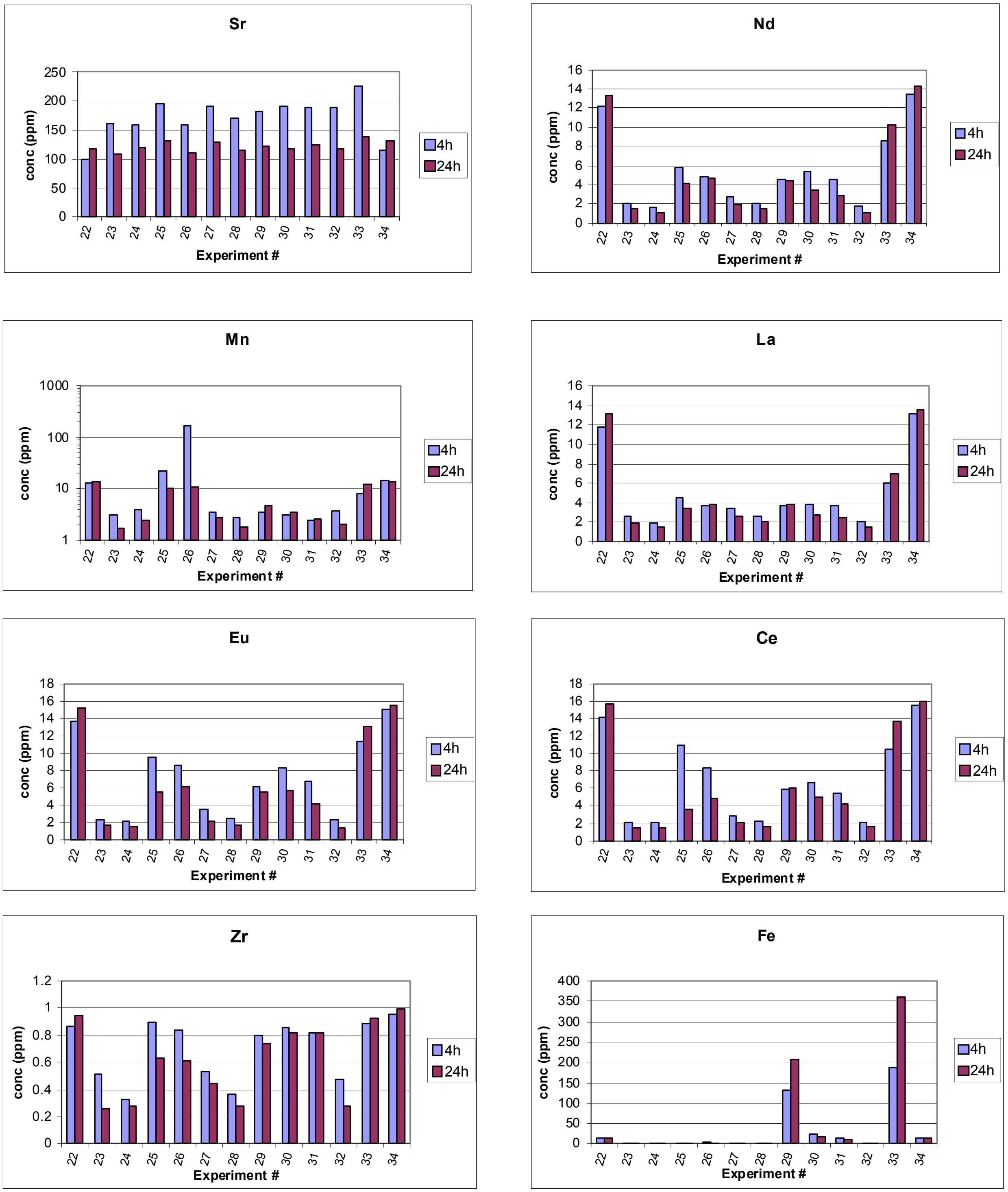
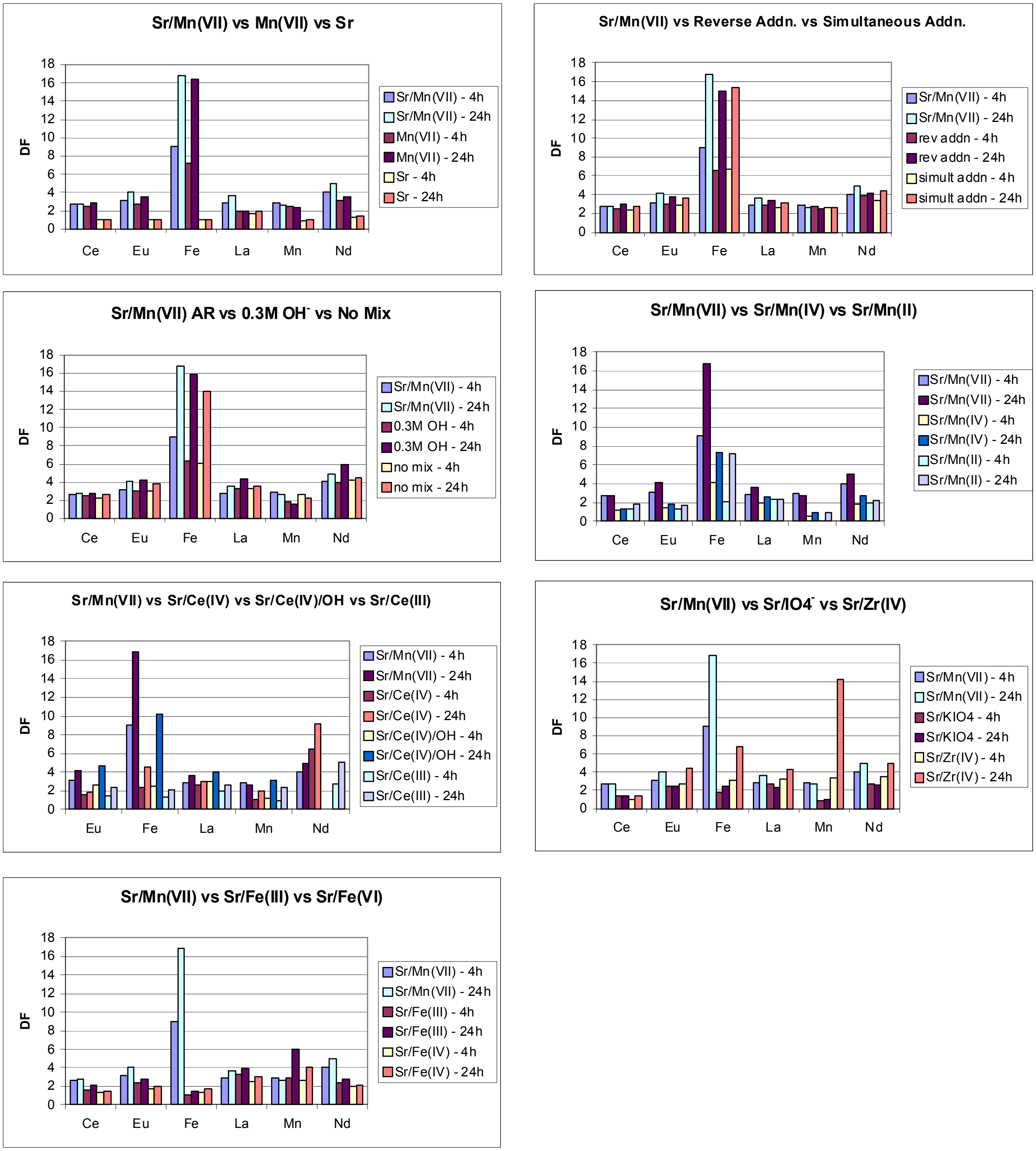


Figure A.2. Concentrations of Key Elements in Reaction Mechanism Test 2


Sr/Mn(VII) vs Mn(VII) vs Sr

Sr/Mn(VII) vs Reverse Addn. vs Simultaneous Addn.

Sr/Mn(VII) AR vs 0.3M OH^- vs No Mix

Sr/Mn(VII) vs Sr/Mn(IV) vs Sr/Mn(II)

Sr/Mn(VII) vs Sr/Ce(IV) vs Sr/Ce(IV)/OH vs Sr/Ce(III)

Sr/Mn(VII) vs Sr/IO_4^- vs Sr/Zr(IV)

Sr/Mn(VII) vs Sr/Fe(III) vs Sr/Fe(VI)

Figure A.3. DFs Calculated for AN-102/C-104 Spiked Simulant Test 1

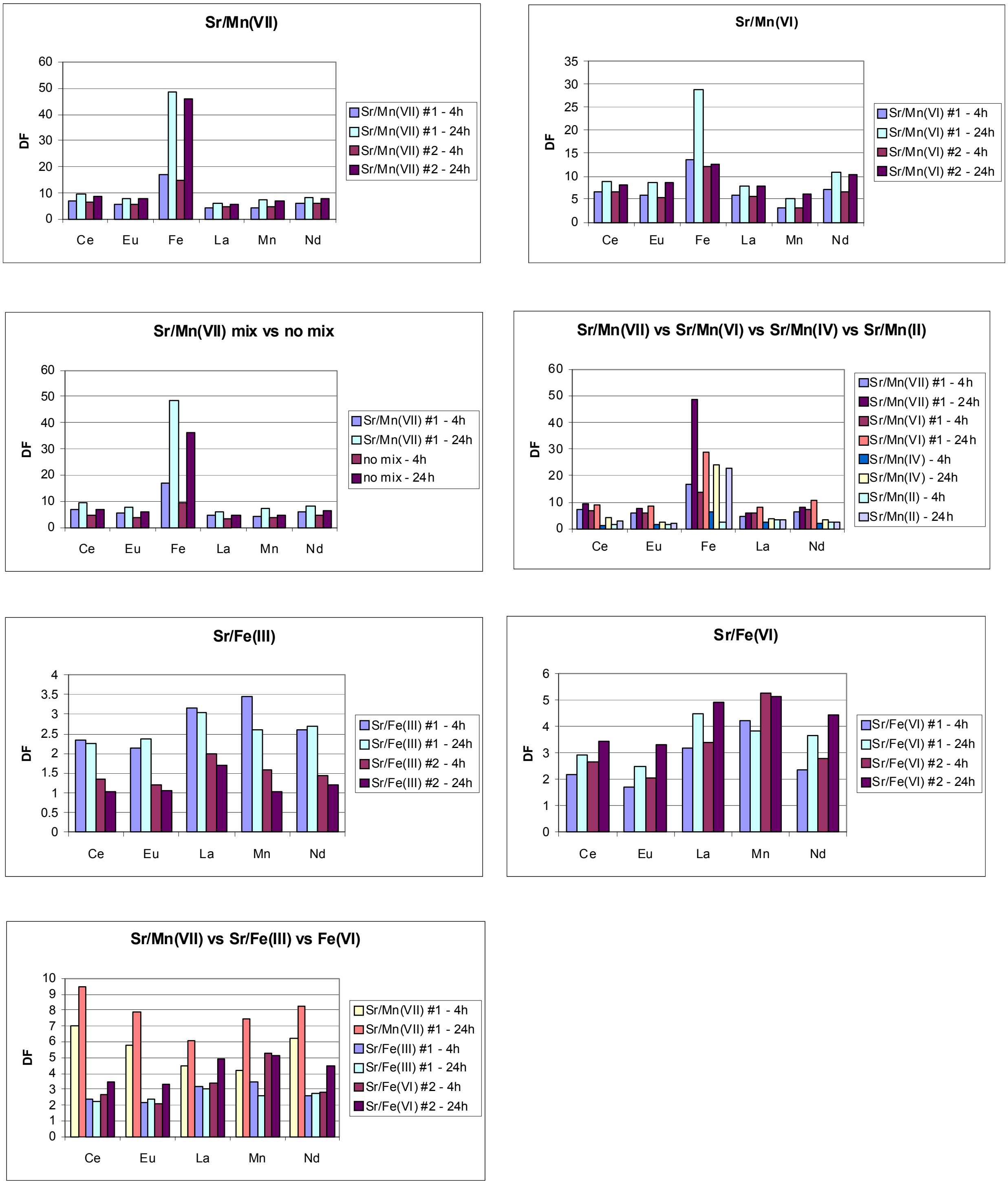


Figure A.4. DFs Calculated for AN-102/C-104 Spiked Simulant Test 2

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