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Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant - FY 1995 Test Results

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September 1995

**Prepared for Westinghouse Hanford Company and
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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Summary

Chelating organics and some of their degradation products in the Hanford tank waste, such as EDTA, HEDTA, and NTA act to solubilize strontium and transuranics (TRU) in the tank waste supernatant. Displacement of strontium and TRU will facilitate the removal of these radionuclides via precipitation/filtration, ion exchange, or solvent extraction so that low-level waste feed specifications can be met.

Pacific Northwest Laboratory has investigated two methods for releasing organic-complexed strontium and TRU components to allow for effective pretreatment of tank waste supernatant: metal cation addition (to promote displacement and flocculation) and chemical oxidant (permanganate) addition (to promote chelator destruction/defunctionalization and possibly flocculation). These methods, which can be conducted at near-ambient temperatures and pressures, could be deployed as in-tank processes.

The following metal cations were selected to cover the range of metals potentially applicable to tank supernatant: Fe(III), Fe(II), Cu(II), Ni(II), and Ca(II). These metal cations were chosen based on their expected affinities for the organic complexants being evaluated, their relative solubilities in the highly alkaline tank waste, and results from previous similar investigations.

Tests conducted with 101-SY simulant showed that strontium decontamination factors of 5 to 10 can be achieved via metal cation addition, but significant solids generation can occur. Of the metals tested, Ca(II) gave the most favorable results for strontium displacement with the least solids formation. Relatively high strontium removal rates (80% to 90%) were achieved at low addition rates (1 to 2 times the stoichiometric equivalent complexant concentration). However, because Ca(II) affinities for expected chelators are lower than those for TRU, it is not expected to displace significant TRU. Ni(II), which also showed promise for removing strontium, and has a higher affinity than Ca(II) for chelators such as EDTA, may be effective in removing TRU. Further testing of candidate metal cations such as Ni(II) is necessary to determine optimum addition rates for maximum removal of strontium and TRU with minimal solids generation. Additionally, the impacts of the solids generated on the HLW volume must be thoroughly assessed to determine the feasibility of metal cation addition.

The chemical oxidant addition testing involved potassium permanganate, which is frequently used for treatment of wastewater streams. Tests conducted with 101-SY simulant showed that strontium decontamination factors of 10 to 20 could be achieved via permanganate addition. It appeared that the permanganate was consumed preferentially by oxidation of insoluble Cr(III) to soluble Cr(VI), followed by reaction with organics, and finally via reaction with the nitrites in the waste simulant. The "efficiency" of permanganate addition for strontium removal/TOC destruction is relatively high because most of benefits related to strontium removal and TOC destruction are gained prior to consumption of permanganate via the oxidation of nitrite to nitrate.

The disadvantage of permanganate addition for TOC destruction and strontium removal was that a significant amount of solids were formed. Since smaller amounts of permanganate were required for the oxidation of Cr(III) to soluble Cr(VI), essentially no increase in solids was observed. Thus, permanganate addition could be an attractive treatment technique from a high-level waste (HLW) viewpoint for wastes that contain significant amounts of Cr(III) (e.g., Tank 101-SY).

In a permanganate addition test conducted with actual 101-SY waste, >99% of the ^{90}Sr and >90% of the plutonium was removed from the supernatant. Overall, it appeared that the actual waste was more susceptible to permanganate treatment than was the simulant, and that a lower permanganate dosage than used in the actual waste test (i.e., <0.15 M permanganate) would likely be sufficient to remove significant quantities of strontium and TRU while leading to a lower increase in solids.

A preliminary evaluation was performed using the experimental results (101-SY simulant and actual waste) obtained in this study to examine the impacts of metal cation and permanganate addition on HLW volume. The addition of metal cations, which appear to act primarily to displace strontium [e.g., Ca(II)] had no impact on the amount of HLW produced. The addition of metal cations, such as Fe(III) , which appear to remove strontium (and possibly TRU) primarily via flocculation, approximately doubles the number of HLW canisters (assuming Cr_2O_3 is not the limiting constituent in HLW). Permanganate addition can reduce the number of HLW canisters (if chromium is the limiting constituent in HLW) or can lead to a significant increase in the number of canisters (if chromium is not the limiting constituent in HLW).

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1.0 Introduction

The presence of chelating organics, such as EDTA (ethylenediaminetetraacetic acid), in Hanford tank waste supernatant can lead to inefficiencies in removing radioactive constituents, such as ^{90}Sr and transuranics (TRU). Recent studies at Pacific Northwest Laboratory (PNL)^(a) and Westinghouse Hanford Company (WHC) have shown that destruction or defunctionalization of the chelating organics via hydrothermal treatment (Schmidt et al. 1994; Orth et al. 1995) and metal cation displacement (Herting 1995) allow for the removal of ^{90}Sr and/or TRU via centrifugation, filtration or decantation. As a result of these studies, PNL investigated two methods for releasing organic-complexed-strontium and TRU components within the tank waste supernatant: 1) metal cation addition (i.e., displacement, flocculation) and 2) chemical oxidant (permanganate) addition (i.e., defunctionalization of chelator, flocculation). These methods could be applied as in-tank processes and conducted at near-ambient temperatures and pressures. However, the production of additional waste and potential incompatibility with the final high-level waste (HLW) form must be taken into account during process development.

Tests were conducted on selected metal cations, at different concentrations, to determine their effectiveness for displacing strontium from chelating organics. Displaced strontium will precipitate and can then be removed via filtration or decantation. A review of the literature (Dean 1985) indicated that many of the chelators present in Hanford tank waste have potentially higher affinities for numerous other metal cations beside strontium and TRU. Reported stability constants (Dean 1985), suggested that EDTA, HEDTA [N-(2-hydroxyethyl)-ethylenediaminetriacetic acid], and NTA (nitrilotriacetic acid) have a lower affinity for Sr(II) than for a variety of metal cations such as Fe(III) , Cu(II) , Ni(II) , Zn(II) , Ca(II) , the lanthanides, and others. In addition, based on complexation constants, metal cations such as Ni(II) and Fe(III) may also be effective in separating TRU from waste.

Herting (1995) showed that the addition of nonradioactive strontium (i.e., isotopic dilution) to actual waste from Tank AN-102 gives a ^{90}Sr decontamination factor (DF) of approximately 20, although the addition of nonradioactive strontium had little effect on TRU removal. Herting (1995) also examined the addition of Fe(III) . However, the strontium and TRU removal was not as good as might be expected based on complexation constants reported in the literature. This less-than-expected displacement may be attributed to the relatively low solubility of Fe(III) upon addition to the caustic tank waste solution.

From the literature review and test results from previous studies, five metal cations were chosen for evaluation based on their affinity for EDTA, HEDTA, and NTA and on their solubility in the highly alkaline simulant representing Tank 101-SY, which was used in the study. The results of tests on the five metal cations, Ca(II) , Cu(II) , Fe(III) , Fe(II) , and Ni(II) , are given in this report.

The tests on chemical oxidants centered on the use of permanganate addition and its effect on strontium removal from solution via filtration. The permanganate ion (MnO_4^-) is a powerful oxidizing agent that has found many uses in industrial and municipal wastewater treatment. The reactivity of permanganate in industrial and municipal wastewater to oxidize specific organics and metals is well

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established. Although permanganate oxidation is a fully developed technology for conventional applications, the Hanford radioactive waste slurries present a considerably more complex solution matrix than typical wastewater. A series of tests, using tank waste simulants, actual waste, and various permanganate concentrations, were conducted to determine the potential applicability of this technology to Hanford waste.

This report covers work conducted in FY 1995. The following activities are described: Metal Cation Addition Testing with Simulant (Section 3.0), Chemical Oxidant Testing with Simulant (Section 4.0), and Chemical Oxidant Testing with Actual Waste (Section 5.0). For each of these activities, the objectives, test approach and apparatus, results, and suggested direction of future investigations are discussed. The major conclusions and recommendations that evolved from this work are given in Section 2.0. In addition, the potential implications on HLW for these two treatment techniques are discussed in Section 6.0.

2.0 Conclusions and Recommendations

2.1 Conclusions

2.1.1 Metal Cation Addition Testing

The tests on metal cation addition showed that it is possible to achieve strontium DFs of approximately 5 to 10 with this method. However, in many cases, metal cation addition resulted in significant solids generation. Of the metal cations tested, Ca(II) gave the most favorable results. Relatively high strontium removal (i.e., 80% to 90%) was achieved at relatively low amounts of metal cation addition (1 to 2 times the stoichiometric equivalent complexant concentration). Furthermore, for a given addition, Ca(II) resulted in the formation of less solids than the other metal cations tested with the possible exception of Ni(II). Although not evaluated as extensively as Ca(II), the results from Ni(II) were very similar to those of Ca(II) addition.

The test results also suggest that Fe(III) facilitated strontium removal via a flocculation mechanism rather than through displacement. Use of Fe(III) resulted in a significant increase in solids as compared to no Fe(III) addition (i.e., increases of 80 wt% to 500 wt%, depending upon the amount added).

In general, removal increased with increased amount of metal cation added; however, the rate of increase dropped off significantly at the higher metal cation additions (diminishing returns). For most of the metal cations tested, moderate increases in strontium removal were observed as time increased. Temperature and ammonia addition had little or no effect, and hydroxide addition resulted in a decrease in strontium removal for all of the metal cations tested. Higher DFs were achieved when HEDTA was used as the complexant as compared to EDTA. NTA did not appear to complex strontium as well as did HEDTA or EDTA, and lower decontamination factors were achieved.

2.1.2 Chemical Oxidant Testing

Potassium permanganate was found to be a very effective oxidizer in the tank waste environment, capable of achieving strontium DFs in excess of 10 to 20. These treatment DFs corresponded to a strontium concentration (after treatment) of approximately 10 $\mu\text{g/L}$, which may be approaching the solubility limit of unchelated strontium. Treatment to lower strontium concentrations may require the use of other techniques such as ion exchange.

The major disadvantage associated with the use of permanganate addition is that it results in the formation of a significant amount of solids.

Testing with actual 101-SY waste showed that permanganate addition removed greater than 99% of the ^{90}Sr and more than 90% of the Pu from the supernatant. In this test, the quantity of solids increased by 24 wt%. This increase in solids is very close to what would be expected if all of the potassium permanganate that was added precipitated from solution as manganese dioxide (MnO_2) or manganese hydroxide (Mn(OH)_2) after being reduced by reaction with components such as Cr(III), organics, and nitrite that are present in the waste.

The order in which key species present in the tank waste are oxidized by permanganate is chromium first, followed by EDTA, and nitrite last. It appears that nearly all insoluble chromium is oxidized to soluble chromate before significant degradation of EDTA occurs.

While it is not the prime focus of this testing, the observation that relatively small amounts of permanganate are required to solubilize chromium may have beneficial impacts on HLW disposal. It might prove quite useful in pretreatment (e.g., permanganate addition) to remove chromium from the filterable HLW in cases where chromium is a limiting factor (e.g., Tank 101-SY) in the HLW vitrification process, thus leading to a decrease in the amount of high-level vitrified waste that is produced.

The kinetics of permanganate oxidation are rapid. Reactions are essentially complete within the first hour following the addition.

To achieve significant strontium removal from the tank waste simulant supernatant (i.e., 67%), the addition of permanganate (0.067 M) was required. Addition of 0.11 M permanganate resulted in >80% strontium removal from the supernatant.

For the range investigated (30°C to 65°), temperature was found to have little effect on organic and nitrite destruction, strontium removal, and chromium solubilization.

In simulant tests, HEDTA and NTA were used as organic complexants in addition to EDTA. It was easier to defunctionalize HEDTA and remove strontium from supernatant as compared to EDTA. NTA did not complex strontium as well as HEDTA or EDTA, and low DFs were obtained. However, the absolute supernatant strontium concentration after treatment was comparable to treatment of simulant containing HEDTA or EDTA.

Within its effective range (i.e., 0.067 M to 1.1 M permanganate addition) permanganate resulted in an 80 wt% to 200 wt% increase in solids. Higher permanganate addition increased strontium removal marginally while increasing solids by up to 1000 wt%.

2.2 Recommendations

2.2.1 Metal Cation Addition Testing

The metal cation addition work conducted in this investigation focused on strontium removal. The assumption was made that the results would also be applicable to complexed TRU removal from tank waste supernatant. This assumption should be further validated by additional testing with actual tank waste.

A detailed tank-by-tank evaluation of limiting constituents (with respect to high-level glass) should be performed for those tanks which contain chelating organics and may require strontium and TRU removal. This limiting constituent evaluation along with the results from this effort would be used to drive the selection of the final round of candidate metal cations. Actual tank waste would be tested with the various candidate metal cations to generate sufficient data to determine the impacts (i.e., generation of addition glass logs) of the metal cation addition method.

Testing conducted within this investigation constituted a screening examination with one simulant/actual waste type (i.e., 101-SY). Further testing with this and other simulants and actual wastes should be done to optimize metal cation addition to provide maximize strontium and TRU removal while minimizing solids formation.

Ca(II) was found to be effective in removing strontium; however, based on the complexation constants, it is doubtful whether Ca(II) would be effective in removing TRUs. Thus, the use of metal cations with high complexations constants, such as Ni(II), which also showed promise for removing strontium, should be pursued further in actual waste testing. Future testing should include testing with actual wastes from various waste tanks.

2.2.2 Chemical Oxidant Testing

Although permanganate addition has been shown both to diminish organic carbon and to decrease the concentration of soluble strontium in treated waste supernatant, the testing did not necessarily show that organic destruction is solely responsible for the strontium removal. Organic destruction and metal scavenging precipitation by the manganese dioxide (MnO_2) product are independent mechanisms, and the separate effects of each should be established. Tests with manganese dioxide sorbent (commercially available) would help establish the actual mechanisms. Since permanganate shows promise for treating at least some difficult wastes, study of its reactions should be extended in a broader context than the qualitative screening tests.

Possible effects of oxidation on the behavior of other species (notably plutonium, technetium, and chromium) should be more thoroughly examined. For example, oxidation of plutonium to the hexavalent state may increase its solubility, particularly if carbonate is present. Although one test with actual waste showed that permanganate resulted in a decrease in soluble plutonium (> 90% decrease), a more thorough investigation of the possible oxidation effects is warranted.

Further evaluation of the impacts of manganese oxide on both low-level waste (LLW) and HLW glass is warranted. The evaluation should examine the increase in the number of glass logs generated, taking into account the removal of chromium from the sludge and the increase in sludge mass due to manganese oxide precipitation.

Additional testing should be done to optimize the permanganate addition rate. An upper limit of 0.11 M permanganate addition to 3:1 diluted actual 101-SY waste was established in this testing. Efforts should focus on obtaining lower permanganate addition levels that are still effective in removing strontium and TRU. It is likely that such optimization testing will be required for each tank waste matrix requiring strontium and/or TRU removal.

Due to the relatively fast kinetics, (i.e., ≤ 1 hr) it may be possible to perform permanganate oxidation of tank waste in a transfer line (i.e., metering pump followed by static mixers). Continuous bench-scale testing should be initiated to investigate and develop this potential deployment option.

3.0 Metal Cation Addition Testing with Tank Waste Simulant

3.1 Objectives

The objective of these tests was to evaluate selected metal cations, covering a wide range of solubilities and affinities for the complexing organics, to determine their effectiveness for use in strontium removal. The metal cations evaluated were selected based on 1) affinity for the organic complexants being evaluated, and 2) solubility in the highly alkaline 101-SY simulant that was used in the testing.

Before the metal cations were selected, the review of the literature (Dean 1985) showed that at least 24 metal cations had a greater affinity than strontium for EDTA (i.e., based on complexation constants). Fewer metal cations had greater affinity than TRU components (i.e., americium and plutonium) for EDTA. Similar trends for HEDTA, DTPA, and NTA were reported. In general, as the complexation increased (i.e., w/EDTA), the solubility constant decreased. Based on the data found in the literature, Ca(II), Cu(II), and Fe(III) selected first for evaluation. As the testing proceeded, a limited number of tests using Ni(II) and Fe(II) were also conducted. The complexation constants (w/EDTA) and solubility constants (w/OH⁻) for the metal cations are given in Table 3.1, along with those for Sr(II) and for some TRU elements for comparison. It should be noted that the complexation constants and solubility constants reported above were for infinitely dilute solutions at standard conditions, whereas the tank waste matrices are extremely complex. Thus, the literature values were only used for guidance in selecting the metal cations for the testing, based on the relative complexation/solubility constants.

Table 3.1. Complexation and Solubility Constants for Sr(II), TRU, and Other Metal Cations

Metal Cation	$\log K_{\text{complexation, EDTA}}^{(a)}$	$\log K_{\text{solubility, OH}}^{(b)}$
Fe(III)	24.2	-34.4
Cu(II)	18.7	-19.0
Ni(II)	18.6	-15.2
Am(III)	18.2	---
Pu(III, IV, VI)	18.1, 17.7, 17.7	---
Fe(II)	14.3	-15.1
Ca(II)	11.0	-5.2
Sr(II)	8.8	---
<p>(a) Taken from Dean (1985). (b) Taken from Smith and Martell (1976).</p>		

Fe(III) was evaluated because it had one of the highest complexation constants but a very low solubility [and had shown promise for removing both TRU and strontium in work by Herting (1995)]. Cu(II) and Ni(II) both had mid-range complexation affinity and mid-range solubility and, based on the complexation constants, could potentially remove both strontium and TRU. Ca(II) had a complexation constant that was slightly higher than Sr(II) and a relatively high solubility. Limited testing was conducted using Fe(II) because it is more soluble than Fe(III), although it has a lower affinity for complexing agents such as EDTA.

Scope and time constraints limited the testing to only those metal cations cited above. The goal was to find the most effective metal for testing on actual wastes and include others that may behave similarly, as indicated in the literature. For example, if, from a high-level/low-level waste standpoint, the addition of another metal cation with similar complexation/solubility characteristics is a more attractive option, it will be considered for future actual waste testing.

3.2 Test Approach

All testing discussed in this section was conducted using nonradioactive 101-SY simulant. The simulant composition and recipe are documented in Hohl (1993). Most of the testing was conducted by diluting 1 volume of the 101-SY simulant with 3 volumes of water (i.e., 3:1 diluted 101-SY simulant). The formulation of the 3:1 diluted 101-SY simulant (denoted as SYI-SIM-93A), using Na₄EDTA as the organic source, is given in Table 3.2. In some tests, other organics (i.e., HEDTA and NTA) were added to the simulant instead of EDTA. In these cases, the organic species was added such that the total moles added were equivalent to the EDTA that is typically added in the standard formulation (see Table 3.2).

At the beginning of a test, approximately 220 g simulant were added to a 250-mL polyethylene flask, weighed, capped, and placed in an incubator to allow the simulant to come to the target test temperature. A temperature of 65°C was used as the baseline temperature, because this is fairly typical of the tank waste as it exists. The system used for the experiments had the capacity for conducting 18 different tests (e.g., 18 flasks) during a run. The solutions were agitated at all times during the testing. Once the simulant reached the target temperature, 20 mL of a designated metal cation solution (added as a nitrate salt solution) were added to the simulant in each flask, and the test continued. At designated sampling times approximately 5-mL samples were taken from each flask, and filtered through 0.45- μ m filters. This filter size was used because prior filtering tests of untreated and hydrothermally treated 101-SY simulant solutions showed that filtration using 0.45- μ m filters was as effective as 0.04- μ m filters at removing "insoluble" strontium (Schmidt et al. 1995). The filtrates were submitted for strontium analyses to determine the effectiveness of the metal cation added to facilitate strontium displacement and removal from solution.

At the completion of a test, approximately 20-mL samples of the remaining test solutions were weighed and filtered through 0.45- μ m (pre-weighed) filters. The solids that were retained on the filters were dried at approximately 100°C for 24 hr so that the effect of metal cation addition on the presence of solids in the simulants could be determined.

The parameters considered during this testing included the type of metal cation added, testing time, metal cation addition concentration, temperature, ammonia and hydroxide addition, chelating organic source, and simulant dilution and prefiltration. Typical analyses included solution phase strontium

Table 3.2. Hanford Tank 101-SY Simulant Formulation (3:1 diluted) - (SYI-SIM-93A, Hohl 1993)

Component	Weight Percent	Molarity
Na ₄ EDTA	1.67	5.1x10 ⁻²
Na ₃ PO ₄ - 12H ₂ O	0.88	2.7x10 ⁻³
NaNO ₂	5.42	0.91
NaNO ₃	4.49	0.61
Na ₂ CO ₃	1.91	0.21
Na ₂ SO ₄	0.20	1.6x10 ⁻²
NaCl	0.45	8.9x10 ⁻²
NaF	2.4x10 ⁻²	6.6x10 ⁻³
Ca(NO ₃) ₂ - 4H ₂ O	4.8x10 ⁻²	2.4x10 ⁻³
KNO ₃	0.29	3.3x10 ⁻²
ZnCl ₂	1.4x10 ⁻³	1.2x10 ⁻⁴
CsNO ₃	7.2x10 ⁻⁴	4.3x10 ⁻⁵
Sr(NO ₃) ₂ ^(a)	4.1x10 ⁻⁵	2.3x10 ⁻⁶
NaOH	2.02	0.59
Cr(NO ₃) ₃ - 9H ₂ O	1.09	3.2x10 ⁻²
Fe(NO ₃) ₃ - 9H ₂ O	6.9x10 ⁻²	2.0x10 ⁻³
Ni(NO ₃) ₂ - 6H ₂ O	2.4x10 ⁻²	9.6x10 ⁻⁴
NaAlO ₂ - 0.21NaOH - 1.33H ₂ O	4.72	0.48
H ₂ O	76.69	
Total	100.00	

(a) In some cases significant amounts of Sr were introduced into the simulant as an impurity in the Ca(NO₃)₂ - 4H₂O. Sr(NO₃)₂ represents the minimum amount of Sr present in the simulant, according to the recipe.

via inductively coupled plasma-mass spectroscopy (ICP-MS, detection limit = 5 to 20 µg/L), and dry solids measurements. In addition, in some limited cases, other metal concentrations in solution were measured via ICP-MS. Samples were taken after 70 hr of testing and analyzed for effect on strontium removal (after 1, 4, 20, and 70 hr for concentration and time effects) and solids formation (after 20 and 70 hr for concentration and time effects).

For the metal cation concentration and time effect testing, 3:1 diluted 101-SY simulant (i.e., 1 volume simulant diluted with 3 volumes of water), containing EDTA as the organic source, was used as the feed material. The tests were conducted at 65°C. The effects of three different metal cation concentrations (0.04 M, 0.11M, and 0.21M) were evaluated.

The effect of temperature was evaluated by conducting tests at 30°C and 65°C. The 3:1 diluted 101-SY simulant containing EDTA as the organic source was used as the feed material. Three different metal cation addition concentrations were evaluated: 0.04 M, 0.11 M, and 0.21 M.

Ammonia addition tests were conducted with and without metal cation addition to 3:1 diluted 101-SY simulant containing EDTA as the organic source. The tests were conducted at 65°C.

This testing was conducted to determine whether the metal cations added would become more soluble (i.e., as metal cation-amine type complexes) in the presence of ammonia, which would make the metal cations more accessible to the chelating organic and allow for more effective removal of strontium from the chelated organic.

For the ammonia addition testing, 10 mL of ammonium nitrate stock solution (i.e., 150 mg/L or 15,000 mg/L) were added to the simulant solution after the simulant solution had come to the desired temperature (65°C). After the ammonia addition, 20 mL of the metal cation-nitrate stock solution were added to simulant/ammonia solution. In all cases, 0.11 M final metal cation concentration was added. In addition, three final solution ammonia concentrations were evaluated (no addition, 7 mg/L, and 700 mg/L).

Hydroxide addition was evaluated because of evidence (Herting 1995) that suggested hydroxide addition alone might be effective in removing strontium from solution. This prior testing had been conducted using actual waste from a hydroxide deficient tank (Tank AN-107). The hydroxide addition tests were conducted at 65°C with and without metal cation addition to 3:1 diluted 101-SY simulant containing EDTA. First, 10 mL of sodium hydroxide stock solution (i.e., 0.25 M or 10 M) were added to the simulant solution after the simulant solution had come to the desired testing temperature (65°C). Next, 20 mL of the metal cation-nitrate stock solution were added to the simulant/hydroxide solution. In all cases, 0.11 M final metal cation concentration was added. In addition, three hydroxide concentrations were evaluated (no addition, 0.01 M, and 0.5 M).

The effectiveness of metal cation addition was evaluated for removing strontium from different chelators (EDTA, HEDTA, and NTA) known to exist in Hanford tank waste (Campbell 1994). Tests were conducted with 3:1 diluted 101-SY simulant at 65°C. In all cases, the chelating organic concentration was approximately 0.05 M. In this testing, 0.11 M (final metal cation concentration) was evaluated.

The effects of simulant dilution and prefiltration were evaluated by conducting tests, at 65°C, with 101-SY simulant containing EDTA. The dilution tests were conducted by adding metal cation stock solution to undiluted, 1:1 diluted (1 volume water to 1 volume simulant), and 3:1 diluted simulant. The prefiltration tests were conducted using 3:1 diluted simulant that was pre-filtered through a 0.45- μ m filter prior to metal cation addition. In all cases, the amount of metal cation added to 220 g of the simulant solutions was equivalent to 0.11 M addition to 3:1 diluted 101-SY simulant (i.e., the same total amount of metal cation was added to each simulant solution).

3.3 Test Apparatus

The metal cation addition testing was conducted using a New Brunswick Scientific Controlled Environment Incubator Shaker located in the Process Development Laboratory East at PNL. The incubator shaker was selected instead of the six-station stirrer in an oil immersion bath (originally planned) because it could process 18 tests simultaneously and eliminated the chance for TOC contamination from an oil bath. The sample flasks were agitated by placing them in metal claws affixed to an orbital platform shaker in the incubator. The temperature inside the incubator was maintained via circulating air controlled by an internal thermostat controllable in the range of 25°C to 75°C.

3.4 Results and Discussion

3.4.1 Concentration and Time Effects

The effects of metal cation concentration and treatment time are given in Table 3.3 for the metal cations evaluated in this testing. In some cases, multiple tests were conducted at given conditions.

A comparison of the Ca(II), Cu(II), and Fe(III) metal cation addition results given in Table 3.3 showed a significant increase in strontium removal when going from 0.04 M to 0.11 M metal cation addition. An increase in metal cation addition from 0.11 to 0.21 M did not appear to significantly enhance strontium removal when Ca(II) and Fe(III) were the metal cations added; however, a slight increase in strontium removal is apparent when increasing the Cu(II) level from 0.11 to 0.21 M. Fe(III) appeared to be affected most consistently by time. For all three Fe(III) concentrations, the 20- and 70-hr samples always resulted in significantly more strontium removal. At the highest Fe(III) addition, it appeared that NO_x was formed, as a brownish off-gas was produced.

Limited testing was also conducted by adding Ni(II) and Fe(II) to solution. This testing was only conducted at the medium metal cation addition concentrations to compare with the effectiveness of the other metal cations. Significant strontium removal was achieved in both cases. Time appeared to have a slight impact on the Ni(II) addition effectiveness in removal of strontium.

From the results presented in Table 3.3, Ca(II) addition appears slightly more effective than the other metal cations tested for removing strontium from solution. Upon comparison of the 1-hr data and metal cation addition = 0.11 M simulant, >80% strontium removal was achieved by addition of Ca(II). If more Cu(II) was added, or Fe(III) was allowed to "react" for longer periods of time, the effectiveness of these two metal cations for removal of strontium approached that of Ca(II) addition.

From a stoichiometric viewpoint, based on the approximate EDTA concentration (0.05 M) present in the 3:1 diluted simulant, and based on the assumption that 1 mole metal cation complexes 1 mole EDTA, it would be expected that a final metal cation concentration of 0.05 M would be the most effective in displacing strontium. This also assumes that all of the metal cation added to solution is complexed by the chelating organic. At lower metal cation additions (e.g., 0.04 M), not all of the strontium would be displaced; and at higher additions, metals may precipitate from solution, which would lead to an increase in solids. The increased removal of strontium when going from 0.04 M metal cation addition to 0.11 M metal cation addition, and no apparent increase in strontium removal when going from 0.11 M to 0.21 M for Ca(II) (see Table 3.3), is consistent with what would be expected, based on this stoichiometry. The solids increase and final metal cation concentrations in solution (i.e., filtered through a 0.45- μm filter) were measured during these tests to provide a better understanding of what occurred upon metal cation addition.

The solids increase is given in Table 3.4. The weight percent solids were determined after completion of the metal cation addition tests. In all cases, the addition of Fe(III) led to a dramatic increase in solids. For Cu(II) and Ca(II), the addition of 0.04 M led to essentially no increase in solids;

Table 3.3. Strontium Removal Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Concentration and Time Effects)^(a)

Metal Cation Added/ Sample Time	% Strontium Removal From Filtered Supernatant		
	0.04 <u>M</u> Metal Cation Addition	0.11 <u>M</u> Metal Cation Addition	0.21 <u>M</u> Metal Cation Addition
Cu(II)/ 1 hour	39 ^(b) , 12 ^(b) , 6 ^(c)	54 ^(b) , 18 ^(b) , 15 ^(c) , 73 ^(c)	69 ^(b) , 70 ^(b) , 49 ^(c)
Cu(II)/ 4 hours	35 ^(b) , 0 ^(b)	47 ^(b) , 1 ^(b)	66 ^(b) , 49 ^(b)
Cu(II)/ 20 hours	33 ^(b) , 41 ^(b)	51 ^(b) , 43 ^(b)	62 ^(b) , 59 ^(b)
Cu(II)/ 70 hours	18 ^(b) , 28 ^(b) , 0 ^(c) , 46 ^(c)	49 ^(b) , 28 ^(b) , 10 ^(c) , 54 ^(d)	71 ^(b) , 40 ^(b) , 20 ^(c) , 70 ^(d)
Ca(II)/ 1 hour	0 ^(b) , 0 ^(c)	82 ^(b) , 83 ^(c) , 86 ^(c)	72 ^(b) , 80 ^(c)
Ca(II)/ 4 hours	3 ^(b)	80 ^(b)	70 ^(b)
Ca(II)/ 20 hours	37 ^(b)	87 ^(b)	81 ^(b)
Ca(II)/ 70 hours	42 ^(b) , 32 ^(c)	83 ^(b) , 80 ^(c) , 80 ^(c) , 79 ^(d)	78 ^(b) , 76 ^(c)
Fe(III)/ 1 hour	32 ^(b) , 37 ^(c)	43 ^(b) , 49 ^(c) , 52 ^(c)	44 ^(b) , 32 ^(c)
Fe(III)/ 4 hours	31 ^(b)	44 ^(b)	55 ^(b)
Fe(III)/ 20 hours	50 ^(b)	65 ^(b)	74 ^(b)
Fe(III)/ 70 hours	53 ^(b) , 51 ^(c)	74 ^(b) , 76 ^(c) , 75 ^(c) , 72 ^(d)	79 ^(b) , 77 ^(c)
Fe(II)/ 1 hour	---	72 ^(c) , 52 ^(c)	---
Fe(II)/ 70 hours	---	57 ^(c) , 56 ^(c)	---
Ni(II)/ 1 hour	---	56 ^(c) , 32 ^(c)	---
Ni(II)/ 70 hours	---	75 ^(c) , 78 ^(c) , 79 ^(c)	---
<p>(a) Tests conducted at 65°C, using 3:1 diluted 101-SY simulant containing EDTA as the organic source. Reported values are based on 101-SY simulant weight/volume prior to metal cation solution addition (i.e., dilution due to metal cation solution taken into account). In all cases filtered supernatant = filtrate resulting from filtering simulant through a 0.45-μm filter. Metal cations added as nitrate salts in solution, unless noted otherwise.</p> <p>(b) Filtered control sample (no metal cation addition): 0.31 mg/L strontium.</p> <p>(c) Filtered control sample (no metal cation addition): 0.39 mg/L strontium.</p> <p>(d) Filtered control sample (no metal cation addition): 0.10 mg/L strontium.</p> <p>(e) Fe(II) added as sulfate salt in solution.</p>			

however, at the two higher metal cation additions, increases in solids were observed. From Table 3.3, it was observed that addition of 0.11 and 0.21 M Ca(II) led to comparable reductions in strontium levels; however, addition of 0.11 M Ca(II) led to a greater reduction of strontium than addition of 0.04 M Ca(II). This information, together with the approximate EDTA concentration of 0.05M, indicates that it may be possible to add between 0.04 and 0.11 M Ca(II), and achieve a strontium removal efficiency comparable to that obtained at 0.11 M Ca(II). Furthermore, Table 3.4 indicates that addition of between 0.04 and 0.11 M Ca(II) may lead to a dramatic decrease in solids formation as compared to 0.11 M Ca(II) addition. These observations would be more fully evaluated in future work.

Table 3.4. Increase in Solids Content Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Concentration Effects)

Metal Cation Added	Wt% Increase in Solids ^(a)		
	0.04 M Metal Cation Addition	0.11 M Metal Cation Addition	0.21 M Metal Cation Addition
Cu(II)	3 ^(b) , -18 ^(b) , -29 ^(c) , 19 ^(d)	67 ^(b) , -30 ^(b) , -6 ^(c) , 100 ^(b)	220 ^(b) , 46 ^(b) , 90 ^(c) , 280 ^(d)
Ca(II)	1 ^(b) , -9 ^(c)	53 ^(b) , 89 ^(c) , 87 ^(c) , 137 ^(d)	180 ^(b) , 200 ^(c)
Fe(III)	84 ^(b) , 80 ^(b)	250 ^(b) , 200 ^(c) , 190 ^(c) , 280 ^(d)	510 ^(b) , 360 ^(c)
Fe(II) ^(e)	---	140 ^(c) , 120 ^(c)	---
Ni(II)	---	77 ^(c) , 76 ^(c) , 200 ^(d)	---

(a) Reported values are $100 \times [\text{wt\% solids (metal cation added)} - \text{wt\% solids (control)}] / \text{wt\% solids (control)}$. Weight percent solids (metal cation added) were based on solution weight prior to metal cation addition. Weight percent solids were determined at the completion of the test (i.e., > 70 hr into the test). Metal cations added as nitrate salts, unless noted otherwise.

(b) Control sample (no metal cations added): 0.7 wt% solids.

(c) Control sample (no metal cations added): 1.1 wt% solids.

(d) Control sample (no metal cations added): 0.9 wt% solids.

(e) Fe(II) added as sulfate salt in solution.

A significant increase in solids upon Ni(II) and Fe(II) addition (0.11 M final metal cation concentration) was observed.

The approximate 0.05 M EDTA concentration in the simulant indicates that 0.05 M Cu(II), 0.05 M Ca(II), and 0.05 M Fe(III) would be required to complex all of the EDTA as $\text{Cu} \cdot \text{EDTA}^{2-}$, $\text{Ca} \cdot \text{EDTA}^{2-}$, and FeEDTA^- , respectively. It was observed that upon addition of 0.04 M Ca(II) or Cu(II), approximately 0.032 ± 0.001 M calcium and 0.036 ± 0.01 M copper remained in solution. Upon addition of 0.11 M and 0.21 M Ca(II) or Cu(II), the amounts that remained in solution were comparable to the amounts remaining in solution upon 0.04 M addition: 0.037 ± 0.007 M calcium and 0.035 ± 0.005 M copper. The iron concentration in the filtrate was below its detection limit of 9×10^{-6} M for 0.04, 0.11, and 0.21 M Fe(III) addition. These results suggest that Ca(II) and Cu(II) additions are acting primarily by displacing strontium from the EDTA by forming metal cation-EDTA complexes. The Fe(III) results indicate that Fe(III) is acting primarily as a floccing agent to carry the strontium out of solution.

3.4.2 Temperature Effects

The effects of operating temperature on strontium removal via metal cation addition are given in Table 3.5. No consistent trend is apparent for the metal cations as a whole. For Ca(II), Fe(III), and Fe(II) addition, a minimal to slight increase in strontium removal was observed with an increase in temperature. For Ni(II) and Cu(II) addition, on the other hand, minimal to slight decreases in

Table 3.5. Strontium Removal Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (at 30°C and 65°C)^(a)

Metal Cation Added/Temperature	% Strontium Removal From Filtered Supernatant		
	0.04 M Metal Cation Addition	0.11 M Metal Cation Addition	0.21 M Metal Cation Addition
Cu(II)/ 30°C	43 ^(b)	61 ^(b)	67 ^(b)
Cu(II)/ 65°C	18 ^(c) , 28 ^(c) , 0 ^(d) , 46 ^(d)	49 ^(c) , 28 ^(c) , 10 ^(d) , 54 ^(e)	71 ^(c) , 40 ^(c) , 20 ^(d) , 70 ^(e)
Ca(II)/ 30°C	17 ^(b)	64 ^(b)	76 ^(b)
Ca(II)/ 65°C	42 ^(c) , 32 ^(d)	83 ^(c) , 80 ^(d) , 80 ^(d) , 79 ^(e)	78 ^(c) , 76 ^(d)
Fe(III)/ 30°C	22 ^(b)	51 ^(b)	58 ^(b)
Fe(III)/ 65°C	53 ^(c) , 51 ^(d)	74 ^(c) , 76 ^(d) , 75 ^(d) , 72 ^(e)	79 ^(c) , 77 ^(d)
Fe(II)/ 30°C ^(f)	26	49 ^(b)	---
Fe(II)/ 65°C ^(f)	---	57 ^(d) , 56 ^(d)	---
Ni(II)/ 30°C	34	93 ^(b)	---
Ni(II)/ 65°C	---	75 ^(c) , 78 ^(c) , 79 ^(c)	---
<p>(a) Tests conducted using 3:1 diluted 101-SY simulant containing EDTA as the organic source. Reported values are based on 101-SY simulant weight/volume prior to metal cation solution addition (i.e., dilution due to metal cation solution taken into account). In all cases filtered supernatant = filtrate resulting from filtering simulant through a 0.45-μm filter. Measurements taken on samples taken after 70 hr into the test. Metal cations added as nitrate salts in solution, unless noted otherwise.</p> <p>(b) Filtered control sample (no metal cation addition): 0.37 mg/L strontium.</p> <p>(c) Filtered control sample (no metal cation addition): 0.31 mg/L strontium.</p> <p>(d) Filtered control sample (no metal cation addition): 0.39 mg/L strontium.</p> <p>(e) Filtered control sample (no metal cation addition): 0.10 mg/L strontium.</p> <p>(f) Fe(II) added as sulfate salt in solution.</p>			

strontium removal were observed. Overall, it can be concluded that for the temperature range tested, temperature had minimal effect on strontium removal.

The percent increase in solids concentration upon metal cation addition is given in Table 3.6. No consistent trend relating temperature to solids increase was observed.

3.4.3 Ammonia Addition Effects

The strontium removal results from the ammonia addition testing are given in Table 3.7. In the absence of metal cation addition, ammonia addition resulted in no removal of strontium from solution. Either the ammonia did not act as expected to solubilize some of the precipitated metals that already

Table 3.6. Increase in Solids Content Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (at 30°C and 65°C)

Metal Cation Added/ Temperature	% Solids Increase ^(a)		
	0.04 M Metal Cation Addition	0.11 M Metal Cation Addition	0.21 M Metal Cation Addition
Cu(II)/ 30°C	-29 ^(a)	5 ^(a)	113 ^(a)
Cu(II)/ 65°C	3 ^(c) , -18 ^(c) , -29 ^(d) , 19 ^(e)	67 ^(c) , -30 ^(c) , -6 ^(d) , 100 ^(e)	220 ^(c) , 46 ^(c) , 90 ^(d) , 280 ^(e)
Ca(II)/ 30°C	-30 ^(a)	40 ^(a)	130 ^(a)
Ca(II)/ 65°C	1 ^(c) , -9 ^(d)	53 ^(c) , 89 ^(d) , 87 ^(d) , 140 ^(e)	180 ^(c) , 200 ^(d)
Fe(III)/ 30°C	68 ^(a)	150 ^(a)	310 ^(a)
Fe(III)/ 65°C	84 ^(c) , 80 ^(c)	250 ^(c) , 200 ^(d) , 190 ^(d) , 280 ^(e)	510 ^(c) , 360 ^(d)
Fe(II)/ 30°C ^(f)	-5 ^(a)	120 ^(a)	---
Fe(II)/ 65°C ^(f)	---	140 ^(d) , 120 ^(d)	---
Ni(II)/ 30°C	6 ^(b)	46 ^(a)	---
Ni(II)/ 65°C	---	77 ^(d) , 76 ^(d) , 200 ^(e)	---

(a) Reported values are $100 \times [\text{wt\% solids (metal cation added)} - \text{wt\% solids (control)}] / \text{wt\% solids (control)}$. Weight percent solids (metal cation added) were based on solution weight prior to metal cation addition. Weight percent solids were determined at the completion of the test (i.e., >70 hr into the test). Metal cations added as nitrate salts, unless noted otherwise.

(b) Control sample (no metal cations added): 1.5 wt% solids.

(c) Control sample (no metal cations added): 0.7 wt% solids.

(d) Control sample (no metal cations added): 1.1 wt% solids.

(e) Control sample (no metal cations added): 0.9 wt% solids.

(f) Fe(II) added as sulfate salt in solution.

existed in the simulant, or the precipitated metals concentration initially present in the simulant was so low that solubilization and subsequent chelation by EDTA had no effect on strontium removal. Furthermore, ammonia addition, along with Ca(II), Fe(III), and Ni(II) addition, had minimal, if any, effect on the removal of strontium from solution. Ammonia addition, along with Cu(II) addition, may be detrimental in removing strontium from solution. For all of the metal cations tested, it can be concluded that ammonia addition did not enhance the removal of strontium from solution.

The percent solids increase due to ammonia and metal cation addition is given in Table 3.8. The most obvious impact of ammonia addition on solids formation is for the Fe(III) tests. The percent solids decreased dramatically upon 7 mg/L ammonia addition, and showed additional decrease upon 700 mg/L ammonia addition in the presence of Fe(III) addition. These data suggest that the ammonia is acting to keep the Fe(III) in solution; however, the strontium removal effectiveness was not enhanced (see Table 3.7). One possible explanation is that the EDTA may be complexing Fe(III); however, this action is merely comparable to the floccing action that Fe(III) appears to exhibit in the absence of

Table 3.7. Strontium Removal Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Ammonia Effects)^(a)

Metal Cation Added	% Strontium Removal From Filtered Supernatant		
	No Ammonia Addition	7 mg/L Ammonia Addition	700 mg/L Ammonia Addition
None	---	0 ^(b)	0 ^(b)
Cu(II)	49 ^(c) , 28 ^(c) , 10 ^(d) , 54 ^(e)	5 ^(b)	0 ^(b)
Ca(II)	83 ^(c) , 80 ^(d) , 80 ^(d) , 79 ^(e)	72 ^(b)	72 ^(b)
Fe(III)	74 ^(c) , 76 ^(d) , 75 ^(d) , 72 ^(e)	58 ^(b)	55 ^(b)
Ni(II)	75 ^(c) , 78 ^(c) , 79 ^(c)	70 ^(b)	70 ^(b)

(a) Tests conducted at 65°C, using 3:1 diluted 101-SY simulant containing EDTA as the organic source. Reported values are based on 101-SY simulant weight/volume prior to metal cation solution addition (i.e., dilution due to metal cation solution taken into account).
In all cases filtered supernatant = filtrate resulting from filtering simulant through a 0.45- μ m filter. Measurements taken on samples taken after 70 hr into the test.
Metal cations added as nitrate salts in solution, unless noted otherwise.
In all cases, metal cations added = 0.11 M (final concentration in simulant).

(b) Filtered control sample (no metal cation addition): 0.37 mg/L strontium.
(c) Filtered control sample (no metal cation addition): 0.31 mg/L strontium.
(d) Filtered control sample (no metal cation addition): 0.39 mg/L strontium.
(e) Filtered control sample (no metal cation addition): 0.10 mg/L strontium.

Table 3.8. Increase in Solids Content Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Ammonia Effects)

Metal Cation Added	% Solids Increase ^(a)		
	No Ammonia Addition	7 mg/L Ammonia Addition	700 mg/L Ammonia Addition
None	---	---	-47 ^(b)
Cu(II)	67 ^(c) , -30 ^(c) , -6 ^(d) , 100 ^(e)	25 ^(b)	6 ^(b)
Ca(II)	53 ^(c) , 89 ^(d) , 87 ^(d) , 140 ^(e)	47 ^(b)	33 ^(b)
Fe(III)	250 ^(c) , 200 ^(d) , 190 ^(d) , 280 ^(e)	68 ^(b)	35 ^(b)
Ni(II)	77 ^(d) , 76 ^(d) , 200 ^(e)	140 ^(b)	170 ^(b)

(a) Reported values are 100x[wt% solids (metal cation added) - wt% solids (control)]/wt% solids (control). Weight percent solids (metal cation added) were based on solution weight prior to metal cation addition. Weight percent solids were determined at the completion of the test (i.e., > 70 hr into the test). Metal cations added as nitrate salts, unless noted otherwise.

(b) Control sample (no metal cation added): 1.5 wt% solids.
(c) Control sample (no metal cation added): 0.7 wt% solids.
(d) Control sample (no metal cation added): 1.1 wt% solids.
(e) Control sample (no metal cation added): 0.9 wt% solids.

ammonia. Ammonia addition may have a slight beneficial impact on reducing the amount of solids formed upon Ca(II) addition, but appeared to have no beneficial impact in reducing the amount of solids formed upon Ni(II) or Cu(II) addition.

Based on the information provided above, it can be concluded that ammonia addition has minimal or no beneficial impact when Ni(II) or Ca(II) is added to displace strontium. If Cu(II) is added, the presence of ammonia appears to be detrimental in the removal of strontium. In the case of Fe(III) addition, the removal of strontium is comparable in the presence and absence of ammonia, and dramatically fewer solids are produced upon ammonia addition along with Fe(III) addition. Improved results might be obtained if the metal cations are first added to an ammonia solution so that the complexes can form prior to addition to the caustic solution.

3.4.4 Hydroxide Addition Effects

The strontium removal results from the hydroxide addition testing is given in Table 3.9. Note that the simulant itself contains substantial amounts of hydroxide; the values given in Table 3.9 represent the final OH⁻ concentration in the simulant, based only on the amount added.

In the absence of metal cation addition, hydroxide addition resulted in no removal of strontium from solution. In the presence of metal cation addition, hydroxide addition either had a detrimental effect on strontium removal or little or no effect for the metal cations evaluated.

The percent solids increase due to hydroxide and metal cation addition is given in Table 3.10. As was the case with ammonia addition, the most significant impact of hydroxide addition on solids formation is for the Fe(III) addition tests. The percent solids decreased significantly upon 0.01 M OH⁻ addition, and showed further decrease upon 0.5 M OH⁻ addition in the presence of Fe(III) addition. One explanation might be that, upon addition of hydroxide, insoluble iron hydroxide may become soluble as metal-hydroxy-anions [e.g., Fe(OH)₄⁻]. Hydroxide addition with no metal cation addition appeared to decrease the percent solids somewhat.

3.4.5 Chelating Organics Effects

The strontium removal results for the tests on chelating organics effects are given in Table 3.11. Note that the control sample (no metal cation addition) for the simulant containing HEDTA as the organic source contained 370 mg/L "soluble" strontium. When NTA was added as the organic source, only 60 mg/L "soluble" strontium was present in the untreated control solution, indicating that NTA does not complex strontium as readily as either EDTA or HEDTA.

The addition of any of the metal cations evaluated to the simulant containing HEDTA as the organic source was very effective in removing strontium from solution. The addition of Cu(II), Fe(III), and Ni(II) to the HEDTA-containing simulant resulted in significantly greater removal of strontium over the EDTA-containing simulant, while the strontium removals upon Ca(II) addition were comparable. Moderate removals of strontium were achieved from simulant containing NTA when Ca(II) or Fe(III) was added. No measurable decrease in strontium concentration was achieved from simulant containing NTA when Cu(II) or Ni(II) was added.

Table 3.9. Strontium Removal Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Hydroxide Effects)^(a)

Metal Cation Added	% Strontium Removal From Filtered Supernatant		
	No NaOH Addition	0.01M ^(b) NaOH Addition	0.5M ^(b) NaOH Addition
None	---	0 ^(c)	0 ^(c)
Cu(II)	49 ^(d) , 28 ^(d) , 10 ^(e) , 54 ^(f)	7 ^(c)	0 ^(c)
Ca(II)	83 ^(d) , 80 ^(e) , 80 ^(e) , 79 ^(f)	71 ^(c)	61 ^(c)
Fe(III)	74 ^(d) , 76 ^(e) , 75 ^(e) , 72 ^(f)	56 ^(c)	66 ^(c)
Ni(II)	75 ^(d) , 78 ^(d) , 79 ^(d)	71 ^(c)	35 ^(c)

(a) Tests conducted at 65°C, using 3:1 diluted 101-SY simulant containing EDTA as the organic source. Reported values are based on 101-SY simulant weight/volume prior to metal cation solution addition (i.e., dilution due to metal cation solution taken into account).
In all cases filtered supernatant = filtrate resulting from filtering simulant through a 0.45- μ m filter. Measurements taken on samples taken after 70 hr into the test.
Metal cations added as nitrate salts in solution, unless noted otherwise.
In all cases, metal cations added = 0.11 M (final concentration in simulant).

(b) The simulant contains substantial amounts of hydroxide to begin with, these values represent the final OH⁻ concentration in the simulant, based only on the additional amount added. The total amount of OH⁻ present after addition = amount given here (as added) + initial OH⁻ in simulant.

(c) Filtered control sample (no metal cation addition): 0.37 mg/L strontium.

(d) Filtered control sample (no metal cation addition): 0.31 mg/L strontium.

(e) Filtered control sample (no metal cation addition): 0.39 mg/L strontium.

(f) Filtered control sample (no metal cation addition): 0.10 mg/L strontium.

The solids increase due to metal cation addition is given in Table 3.12 for this testing. The percent increase in solids formed when HEDTA was present as the organic source was comparable to the amount of solids formed when EDTA was present as the organic source. When NTA was added as the organic source, a notable increase in solids for Ca(II) and possibly Ni(II) was observed.

3.4.6 Dilution and Prefiltration Effects

The strontium removal results for dilution and prefiltration effects testing are given in Table 3.13. In these tests, the highest overall strontium removal results were achieved for 3:1 diluted 101-SY (unfiltered), which might be expected compared with the undiluted and 1:1-diluted cases. In these cases, the total metal cation added was the same as for the 3:1 diluted case; however, the EDTA-Sr concentration in these two cases is higher than for the 3:1 diluted case. Thus, to achieve equivalent strontium removal from the undiluted and 1:1 diluted simulants as compared to the 3:1 diluted case, it would be expected that more metal cation would need to be added. This would be expected, whether the metal cation being added is acting to displace the strontium from the EDTA as appears to be the case, for example, with Ca(II), or whether the metal cation is acting as a floccing agent to remove the strontium from solution as appears to be the case with Fe(III).

Table 3.10. Increase in Solids Content Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Hydroxide Effects)

Metal Cation Added	% Solids Increase ^(a)		
	No NaOH Addition	0.01M NaOH Addition	0.5M NaOH Addition
None	---	-28 ^(b)	-51 ^(b)
Cu(II)	67 ^(c) , -30 ^(c) , -6 ^(d) , 100 ^(e)	2 ^(b)	16 ^(b)
Ca(II)	53 ^(c) , 89 ^(d) , 87 ^(d) , 140 ^(e)	59 ^(b)	40 ^(b)
Fe(III)	250 ^(c) , 200 ^(d) , 190 ^(d) , 280 ^(e)	70 ^(b)	16 ^(b)
Ni(II)	77 ^(d) , 76 ^(d) , 190 ^(e)	140 ^(b)	150 ^(b)

(a) Reported values are 100x[wt% solids (metal cation added) - wt% solids (control)]/wt% solids (control). Weight percent solids (metal cation added) were based on solution weight prior to metal cation addition. Weight percent solids were determined at the completion of the test (i.e., > 70 hr into the test). Metal cation added as nitrate salts, unless noted otherwise.

(b) Control sample (no metal cation added): 1.5 wt% solids.

(c) Control sample (no metal cation added): 0.7 wt% solids.

(d) Control sample (no metal cation added): 1.1 wt% solids.

(e) Control sample (no metal cation added): 0.9 wt% solids.

Table 3.11. Strontium Removal Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Chelating Organics Effects)^(a)

Metal Cation Added	% Strontium Removal From Filtered Supernatant		
	EDTA	HEDTA	NTA
Cu(II)	49 ^(b) , 28 ^(b) , 10 ^(c) , 54 ^(d)	> 94 ^(e)	0 ^(f)
Ca(II)	83 ^(b) , 80 ^(c) , 80 ^(c) , 79 ^(d)	88 ^(e)	34 ^(f)
Fe(III)	74 ^(b) , 76 ^(c) , 75 ^(c) , 72 ^(d)	> 94 ^(e)	35 ^(f)
Ni(II)	75 ^(b) , 78 ^(b) , 79 ^(b)	> 94 ^(e)	0 ^(f)

(a) Tests conducted at 65°C, using 3:1 diluted 101-SY simulant. Reported values are based on 101-SY simulant weight/volume prior to metal cation solution addition (i.e., dilution due to metal cation solution taken into account). In all cases filtered supernatant = filtrate resulting from filtering simulant through a 0.45- μ m filter. Measurements taken on samples taken after 70 hr into the test. Metal cations added as nitrate salts in solution, unless noted otherwise. In all cases, metal cations added = 0.11 M (final concentration in simulant).

(b) Filtered control sample (no metal cation addition): 0.31 mg/L strontium.

(c) Filtered control sample (no metal cation addition): 0.39 mg/L strontium.

(d) Filtered control sample (no metal cation addition): 0.10 mg/L strontium.

(e) Filtered control sample (no metal cation addition): 0.37 mg/L strontium.

(f) Filtered control sample (no metal cation addition): 0.06 mg/L strontium.

Table 3.12. Increase in Solids Content Upon Metal Cation Addition to 3:1 Diluted 101-SY Simulant (Chelating Organics Effects)

Metal Cation Added	% Solids Increase ^(a)		
	EDTA	HEDTA	NTA
Cu(II)	67 ^(b) , -30 ^(b) , -6 ^(c) , 100 ^(d)	51 ^(e)	61 ^(f)
Ca(II)	53 ^(b) , 89 ^(c) , 87 ^(c) , 140 ^(d)	89 ^(e)	200 ^(f)
Fe(III)	250 ^(b) , 200 ^(c) , 190 ^(c) , 280 ^(d)	170 ^(e)	260 ^(f)
Ni(II)	77 ^(c) , 76 ^(c) , 190 ^(d)	97 ^(e)	250 ^(f)
<p>(a) Reported values are $100 \times [\text{wt\% solids (metal cation added)} - \text{wt\% solids (control)}] / \text{wt\% solids (control)}$. Weight percent solids (metal cation added) were based on solution weight prior to metal cation addition. Weight percent solids were determined at the completion of the test (i.e., >70 hr into the test). Metal cations added as nitrate salts, unless noted otherwise.</p> <p>(b) Control sample (no metal cation added): 0.7 wt% solids.</p> <p>(c) Control sample (no metal cation added): 1.1 wt% solids.</p> <p>(d) Control sample (no metal cation added): 0.9 wt% solids.</p> <p>(e) Control sample (no metal cation added): 1.2 wt% solids.</p> <p>(f) Control sample (no metal cation added): 1.0 wt% solids.</p>			

When comparing the 3:1 diluted unfiltered and prefiltered cases, the unfiltered case again appears to give superior removal of strontium, although no definite explanation has yet been determined. If the metal cations are acting primarily to displace the strontium, no significant effect would be expected. If the metal cations are acting as a flocking agent, the presence of solids might be expected to enhance the removal of strontium somewhat. One possible explanation is that the solids in the 101-SY simulant act as flocking agents to draw strontium out of solution once it is released from the EDTA.

The percent solids increase upon metal cation addition is given in Table 3.14. The solids increase for the undiluted, 1:1 diluted, and 3:1 diluted (unfiltered) cases are based on these solutions without metal cation addition. The solids increase for the 3:1 diluted (prefiltered) case is based on the 3:1 diluted (unfiltered) without metal cation addition. Only one value is reported for the undiluted simulant because filtering (to obtain weight percent solids) was extremely difficult to perform on these solutions.

Upon comparison of the solids increase for the 3:1 diluted (unfiltered) case with the 3:1 diluted (prefiltered) case, it can be seen that, overall, the prefiltered 3:1 diluted simulant resulted in a slightly higher increase in solids. This is somewhat surprising but is consistent with what was observed, based on strontium removal results. These values can be directly compared because the 3:1 diluted (unfiltered) case with no metal cation addition is used as the basis.

Table 3.13. Strontium Removal Upon Metal Cation Addition to 101-SY Simulant (Dilution and Prefiltration Effects)

Metal Cation Added	% Strontium Removal From Filtered Supernatant ^(a)			
	Undiluted 101-SY Simulant	1:1 Diluted 101-SY Simulant	3:1 Diluted 101-SY Simulant	3:1 Diluted 101-SY Simulant (Prefiltered)
Cu(II)	0 ^(b) , 46 ^(c)	0 ^(d) , 43 ^(e)	49 ^(f) , 28 ^(f) , 10 ^(g) , 54 ^(h)	0 ⁽ⁱ⁾
Ca(II)	0 ^(b) , 53 ^(c)	60 ^(d) , 79 ^(e)	83 ^(f) , 80 ^(g) , 80 ^(g) , 79 ^(h)	47 ⁽ⁱ⁾
Fe(III)	53 ^(c)	35 ^(e)	74 ^(f) , 76 ^(g) , 75 ^(g) , 72 ^(h)	53 ⁽ⁱ⁾
Ni(II)	0 ^(b) , 47 ^(c)	5 ^(d) , 49 ^(e)	75 ^(f) , 78 ^(f) , 79 ^(f)	54 ⁽ⁱ⁾

(a) Tests conducted at 65°C, using 101-SY simulant containing EDTA as the organic source. Reported values are based on 101-SY simulant weight/volume prior to metal cation solution addition (i.e., dilution due to metal cation solution taken into account).
In all cases filtered supernatant = filtrate resulting from filtering simulant through a 0.45-μm filter. Measurements taken on samples taken after 70 hr into the test.
Metal cations added as nitrate salts in solution, unless noted otherwise.
In all cases, 20 mL of 1.1 M stock solution added to 220g simulant (i.e., equivalent to 0.11 M (final concentration in 3:1 diluted simulant)).

(b) Filtered control sample (no metal cation addition): 0.3 mg/L strontium.
(c) Filtered control sample (no metal cation addition): 1.4 mg/L strontium.
(d) Filtered control sample (no metal cation addition): 0.30 mg/L strontium.
(e) Filtered control sample (no metal cation addition): 0.62 mg/L strontium.
(f) Filtered control sample (no metal cation addition): 0.31 mg/L strontium.
(g) Filtered control sample (no metal cation addition): 0.39 mg/L strontium.
(h) Filtered control sample (no metal cation addition): 0.10 mg/L strontium.
(i) Filtered control sample (no metal cation addition): 0.16 mg/L strontium.

3.5 Direction of Future Work

Although future testing should concentrate on using actual waste, a limited amount of simulant testing should be conducted. The results given above suggest that metal cation [e.g., Ca(II), Ni(II)] addition at/or near the stoichiometric amounts is sufficient for removal of significant amounts of strontium, with a reduction of solids produced. Testing with different tank waste simulants should also be conducted. A detailed evaluation of the impact of metal cation addition on HLW and LLW should be undertaken to determine whether this treatment technique should be pursued.

Ammonia addition did not appear to be beneficial in the tests conducted here, where ammonia was first added to the simulant, and metal cation-nitrate solutions then added. Improved results might be obtained if tests were conducted where the metal cations are added to an ammonia solution prior to addition to the simulant.

Table 3.14. Increase in Solids Content Upon Metal Cation Addition to 101-SY Simulant (Dilution and Prefiltration Effects)

Metal Cation Added	% Increase in Solids Content ^(a)			
	Undiluted 101-SY Simulant	1:1 Diluted 101-SY Simulant	3:1 Diluted 101-SY Simulant	3:1 Diluted 101-SY Simulant (Prefiltered)
Cu(II)	---	14 ^(b)	67 ^(c) , -30 ^(c) , -6 ^(d) , 100 ^(e)	110 ^(f)
Ca(II)	---	31 ^(b)	53 ^(c) , 89 ^(d) , 87 ^(d) , 140 ^(e)	160 ^(f)
Fe(III)	280 ^(g)	370 ^(h)	250 ^(c) , 200 ^(d) , 190 ^(d) , 280 ^(e)	430 ^(f)
Ni(II)	---	69 ^(b)	77 ^(d) , 76 ^(d) , 190 ^(e)	290 ^(f)
<p>(a) Reported values are 100x[wt% solids (metal cation added) - wt% solids (control)]/wt% solids (control). Weight percent solids (metal cation added) were based on solution weight prior to metal cation addition. Weight percent solids were determined at the completion of the test (i.e., > 70 hr into the test). Metal cations added as nitrate salts, unless noted otherwise.</p> <p>(b) Control sample (no metal cation added): 2.2 wt% solids.</p> <p>(c) Control sample (no metal cation added): 0.7 wt% solids.</p> <p>(d) Control sample (no metal cation added): 1.1 wt% solids.</p> <p>(e) Control sample (no metal cation added): 0.9 wt% solids.</p> <p>(f) Control sample (no metal cation added, prior to prefiltration): 0.9 wt% solids.</p> <p>(g) Control sample (no metal cation added): 2.2 wt% solids.</p> <p>(h) Control sample (no metal cation added): 1.1 wt% solids.</p>				

The simulant tests indicate that Fe(III) addition, while effective in removing strontium, produces much more solids than the other metal cations evaluated. It is also evident from the simulant testing that Ca(II) is effective in removing strontium; however, based on the complexation constants, it is doubtful whether Ca(II) would be effective in removing TRUs. Thus, the use of metal cations with high complexations constants, such as Ni(II), which also showed promise for removing strontium, should be pursued further in actual waste testing, which should also include testing with wastes from various tanks.

4.0 Chemical Oxidant Addition Testing with Tank Waste Simulant

4.1 Objectives

In initial screening tests for chemical oxidants, potassium permanganate and hydrogen peroxide were examined. Both are used frequently for organic destruction in wastewater streams and elsewhere. For the tests with hydrogen peroxide, the standard EDTA-based 3:1 diluted 101-SY simulant was treated with a 5% relative volume of 30 wt% H_2O_2 . When hydrogen peroxide was added severe foaming occurred, and the resultant stable foam was three to four times the original volume of the simulant sample. The foam was transferred to another container and appeared to be fairly stable overnight with no agitation. When added to the simulant, the hydrogen peroxide simply decomposed into oxygen and water without oxidizing the organics present. This behavior is typical of hydrogen peroxide when exposed to high pH. Consequently, the use of hydrogen peroxide was eliminated from further consideration.

Preliminary testing with potassium permanganate (KMnO_4), in contrast, yielded no unexpected events. Thus, the use of potassium permanganate to facilitate strontium removal from tank waste was pursued further in this testing.

The various manganese oxidation states that might be encountered with this chemical are bright and distinct colors that can each be used to qualitatively determine the extent of the manganese reduction. In the expected high pH range for tank waste, the expected oxidation half reaction for permanganate is:

The resultant solid, manganese dioxide, is brown and quite insoluble. At very high pH, the permanganate ion is only reduced to manganate in:

However, the green manganate ion was only seen during chemical oxidant testing in the first few hours of "high" (15.8 g dose/200 mL) potassium permanganate. Apparently it is an intermediate in the reduction of permanganate to manganese dioxide and is visible when there is an excess of oxidant added to the simulant.

The last manganese reduction reaction occurs primarily under acidic conditions but may play a role in simulant oxidation at temperatures tested around 65°C . Under acidic conditions, the permanganate ion forms the colorless manganous ion in the reaction:

Additionally, under the basic conditions in the tank waste simulant and at higher temperatures ($\sim 65^\circ\text{C}$), the manganese dioxide precipitate may undergo further reduction to form this manganous ion in the form of manganous hydroxide in:

As the permanganate oxidation reaction is electrochemically driven, it is expected that there are other competing reactions besides the oxidation of the organics involved during the reduction of the permanganate. The more common electrochemically possible reactions for this simulant matrix, along with their standard oxidation potentials (E_o), include:

Presently, it is not known exactly what steps and half reactions make up the electrochemical oxidation of EDTA (or other organics known to exist in Hanford tank waste such as HEDTA and NTA); however, the various breakdown steps do not necessarily have similar oxidation potentials. The overall (global) half reaction, assuming the EDTA goes completely to CO_2 , may be represented as:

4.2 Test Approach

All permanganate addition testing discussed here was conducted using nonradioactive 101-SY simulant (mostly 3:1 diluted). The tests were conducted in the same way as the metal cation addition tests, except a predetermined amount of permanganate (solid or as a stock solution) was added to the simulant in each flask at the target temperature. In some tests, other organics (HEDTA or NTA) were added to the simulant instead of EDTA. In these cases, the total moles of organic species added were equivalent to the EDTA that is typically added in the standard formulation (see Table 3.2).

Parameters considered during this testing included the addition of dry permanganate versus permanganate solution addition (i.e., wet addition), reaction time, permanganate concentration, reaction temperature, chelating organic source, simulant dilution and prefiltration, and stagewise addition. Typical analyses included solution phase strontium via ICP-MS, and dry solids measurement. In addition, in some limited cases, TOC analyses via a Zertex-Dohrmann Model DC-80 carbon analyzer, nitrate/nitrite analyses via IC, and chromium analyses via ICP-MS were conducted. All tests were performed at 65°C , except for temperature effects, which were performed at 30°C and 65°C .

Initially, potassium permanganate addition was to be performed similarly to the metal cation addition testing, in which the substrate was predissolved into a stock solution prior to addition to the tank waste. However, upon comparing the desired testing concentrations of potassium permanganate to its relative solubility, it was decided that the increased volume of the tank waste achieved through this addition would cause unnecessary burden on further waste pretreatment unit operations and should be avoided if possible. Thus, cursory testing was performed to compare the use of chemical oxidant solutions (wet addition) with the dry addition.

In both wet and dry addition cases, the total amount of permanganate addition was the same (3.2 g), and was added to 3:1 diluted 101-SY simulant containing EDTA. In the dry addition test, 3.2 g of potassium permanganate were added directly to 220 g (200 mL) of the simulant. For wet

addition, 3.2 g of potassium permanganate were dissolved in 50 mL of distilled water and added to 220 g (200 mL) of the simulant. Samples were taken at 1 and 20 hr and filtered and analyzed.

For the concentration and time testing, dry potassium permanganate was added to 3:1 diluted 101-SY simulant containing EDTA. The effects of six different permanganate concentrations (0.017 M, 0.033 M, 0.067 M, 0.11 M, 0.32 M, and 0.53 M) were evaluated. Samples were taken, filtered, and analyzed at three different times in the tests (1, 20, and 70 hr). These samples were analyzed for TOC and nitrite as soon as possible (i.e., within 1 hr of taking the sample in many cases) to get as close to "real time" measurements as possible. Since the samples were filtered at the time they were taken, immediate analyses for strontium and chromium was not necessary to obtain "real-time" measurements of these components.

Temperature effects were evaluated by conducting tests at 30°C and 65°C, using 3:1 diluted 101-SY simulant containing EDTA. Dry potassium permanganate was added to the simulant, and six different permanganate concentrations were evaluated: 0.017 M, 0.033 M, 0.067 M, 0.11 M, 0.32 M, and 0.53 M. For these tests, and the following tests, 70-hr samples were taken, filtered, and analyzed.

Permanganate addition for defunctionalizing different chelators known to exist in Hanford tank waste (Campbell 1994) was evaluated by conducting tests with 3:1 diluted 101-SY simulant. The chelating organics evaluated in this testing were EDTA, HEDTA, and NTA. In all cases, the chelating organic concentration was approximately 0.05 M. Four different permanganate concentrations were evaluated in this testing: 0.033 M, 0.11 M, 0.32 M, and 0.53 M.

The effects of simulant dilution and prefiltration were evaluated by conducting tests with 101-SY simulant containing EDTA as the organic source. The dilution tests were conducted by adding dry potassium permanganate to undiluted, 1:1 diluted (1 volume water to 1 volume simulant), and 3:1 diluted simulant. The prefiltration tests were conducted using 3:1 diluted simulant, which was prefiltered through a 0.45- μ m filter prior to permanganate addition. In all cases, 9.5 g of dry potassium permanganate were added to 220 g of the simulant.

The effects of gradual addition of permanganate in a stagewise manner were evaluated because it was believed that some of the permanganate might be precipitating out before it could react with the complexing organics. If that were the case, then slow, stagewise addition of the permanganate may enhance the efficiency of the reaction of permanganate with the organics in the waste simulant. For the tests, 1.9 g permanganate was initially added to 200 mL (220 g) of 3:1 diluted simulant. Over the first 40 min of the test, 1.9 g more permanganate was added to the simulant, resulting in a total permanganate addition of 9.5 g (0.33 M). The effects of this treatment on simulant containing EDTA, HEDTA, and NTA were then evaluated.

4.3 Test Apparatus

The New Brunswick Scientific Controlled Environment Incubator Shaker that was used for the metal cation addition tests was also used in this testing.

4.4 Results and Discussion

4.4.1 Dry Versus Wet Permanganate Addition

As shown in Table 4.1, the TOC destruction, strontium removal, chromium solubilization, and nitrite destruction results obtained from wet and dry permanganate addition were nearly equivalent. [All results have been normalized to account for the dilution effects of adding the liquid potassium permanganate stock solution.] Following this determination, subsequent tests used only dry addition.

It is interesting to note from the results given in Table 4.1 that, while only minimal TOC destruction occurred, significant reductions in strontium removal were achieved. The minimal TOC reduction is most likely due to the breakdown of most of the EDTA to nonchelating organics. The precipitation of manganese hydroxide or manganese dioxide may also be playing a role by acting as flocculants to enhance strontium removal from solution. Furthermore, for the permanganate additions tested here, it appeared that significant quantities of the initially insoluble chromium was solubilized. Prior to permanganate treatment, the soluble chromium concentration was approximately 38 mg/L (i.e., approximately 2.3% of the total chromium was soluble), as compared with post-permanganate-

Table 4.1. Dry Versus Wet Permanganate Addition Test Results^(a) (Organic/Nitrite Destruction, Strontium Removal, Chromium Solubility)

Permanganate Concentration/ Sample Time	TOC Destruction ^(b) (%)	Strontium Removal ^(b) (%)	Chromium in Supernatant ^(c) (%)	Nitrite Destruction ^(b) (%)
Wet Permanganate Addition Tests^(d)				
0.08 M/ 1 hour	---	79	81	---
0.08 M/ 20 hours	2 ^(f)	62	80	0 ^(f)
Dry Permanganate Addition Tests^(e)				
0.1 M/ 1 hour	---	81	74	---
0.1 M/ 20 hours	2 ^(f)	68	88	1 ^(f)
<p>(a) Tests conducted at 65°C, using 3:1 diluted 101-SY simulant containing EDTA as the organic source. In all cases analyses conducted on supernatant resulting from filtration through a 0.45-μm filter. Filtered control sample (no permanganate addition): strontium = 0.39 mg/L strontium; TOC = 6200 mg/L; chromium = 38 mg/L; nitrite = 42700 mg/L.</p> <p>(b) TOC destruction, strontium removal, nitrite destruction = (control supernatant concentration - "permanganate addition" supernatant concentration)/(control supernatant concentration)x100.</p> <p>(c) Initial total chromium concentration = 1680 mg/L in 3:1 diluted 101-SY simulant, based on simulant recipe. Chromium in supernatant = ("permanganate addition" supernatant concentration/total chromium concentration)x100.</p> <p>(d) 3.2 g KMnO₄ dissolved in 50 mL water then added to 220 g (190 mL) simulant. Reported values are based on 101-SY simulant volume prior to permanganate solution addition (i.e., dilution due to permanganate solution taken into account).</p> <p>(e) 3.2 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(f) Analyses performed at completion of test (i.e. > 20 hr into test).</p>				

treated samples where the soluble chromium concentration approached 1500 mg/L (i.e., 88% of the total chromium was soluble). In all of the tests, minimal nitrite destruction was noted. It also appeared that time had little effect on the test results. The data presented in Table 4.1 suggest that 1 hr is sufficient to allow for the removal of strontium; also see Section 4.4.2.

The increase in solids from wet and dry addition of permanganate is given in Table 4.2. As can be seen, the results given here are consistent with those given in Table 4.1; the solids increase is comparable for both cases.

4.4.2 Concentration and Time Effects

The TOC, strontium, chromium, and nitrite results from the permanganate concentration and reaction time testing are given in Table 4.3. At the lowest permanganate concentrations, 0.017 M and 0.033 M, minimal, if any, organic or nitrate destruction was detected. In addition, no strontium was removed from solution via treatment at these low permanganate concentrations. However, in both cases, the majority of the chromium was solubilized. In both cases, the soluble chromium prior to treatment was approximately 54 mg/L, and after treatment was approximately 1500 mg/L. It is interesting to note that upon treatment, the solution color changed from a clear, greenish color to a yellow color, suggesting perhaps that the insoluble $\text{Cr}(\text{OH})_3$ was being oxidized to soluble CrO_4^{2-} (which yields a yellow color), according to the following half reaction:

It is also interesting to note that the lowest permanganate concentration tested yielded nearly complete solubilization of chromium, even though the permanganate concentration is only half of what is stoichiometrically required to completely oxidize the $\text{Cr}(\text{OH})_3$ to soluble CrO_4^{2-} , assuming the following half reaction for permanganate reduction to manganese dioxide:

Table 4.2. Dry Versus Wet Permanganate Addition Test Results^(a) (Increase in Solids Content)

Permanganate Concentration	Wt% Increase in Solids ^(a)
Wet Permanganate Addition Test^(b)	
0.08 <u>M</u>	160
Dry Permanganate Addition Test^(c)	
0.1 <u>M</u>	200
<p>(a) Control sample, in which no permanganate addition was made contained 1.1% dry solids. Reported values are $100 \times [\text{wt\% solids (permanganate addition)} - \text{wt\% solids (control)}] / \text{wt\% solids (control)}$. Weight percent solids (permanganate added) were based on solution weight prior to permanganate addition. Weight percent solids were determined at the completion of the test (i.e., >20 hr into the test). Control sample (no permanganate added): 1.1 wt% solids.</p> <p>(b) 3.2 g KMnO_4 dissolved in 50 mL water added to 220 g (190 mL) simulant.</p> <p>(c) 3.2 g dry KMnO_4 added to 220 g (190 mL) simulant.</p>	

This indicates that, under these conditions, the manganese dioxide may be at least partially further reduced to manganese hydroxide, according to the following half reaction:

While the high pH of the 101-SY simulant matrix may tend to limit or slow this reaction, the possibility remains that it may be the source of the additional oxidizing power required to fully oxidize the chromium to a soluble species. While it is not the prime focus of this testing, the observation that relatively small amounts of permanganate are required to solubilize chromium may have beneficial impacts on HLW disposal. It might prove quite useful in pretreatment to remove chromium from the filterable HLW in cases where chromium is a limiting factor (e.g., Tank 101-SY) in the HLW vitrification process, which would decrease the amount of high-level vitrified waste that is produced. This potential viability of chromium solubilization using potassium permanganate has also been reported by Lumetta and Swanson (1993).

At the intermediate permanganate concentrations, 0.067 M and 0.11 M, again very little, if any, organic and nitrate destruction was apparent; however, significant amounts of strontium were removed from solution via permanganate addition. It is unclear at this point, whether destruction or "defunctionalization" of EDTA to nonchelating fragments by reaction with permanganate is solely responsible for the removal of strontium, or whether manganese dioxide and/or manganese hydroxide are also playing a role by acting as flocking agents to enhance the removal of strontium from solution. As was the case for the two lowest permanganate concentrations, the solution turned yellow, and the majority of the chromium was solubilized.

Upon addition of permanganate to yield a 0.32 M concentration in the simulant, significant TOC destruction was observed, along with the removal >90% of the strontium from solution. Again, insignificant nitrite destruction was observed, and >90% of the chromium was soluble.

At the highest permanganate concentration tested, 0.53 M, increased organic destruction was observed, along with >90% strontium removal from solution and >90% chromium in the soluble form. In addition, a significant decrease in nitrite concentration was observed. The decrease in nitrite concentration was accompanied by an increase in nitrate concentration from 34,100 mg/L in the untreated sample to 43,700 mg/L in the treated sample. In all of the other, lower permanganate addition tests, little or no increase in nitrate concentration was observed. The observed increase in nitrate is in fair agreement with what would be expected according to the observed decrease in nitrite concentration and the following half reaction:

Based on the observed decrease in nitrite concentration, and the above half reaction, the nitrate concentration after treatment would be expected to increase by 11,460 mg/L, yielding a final nitrate concentration of 45,560 mg/L. Thus, the observed final nitrate concentration was approximately 4% lower than would be expected, based on the initial and final nitrite concentrations and the half reaction given above.

The observations noted above indicate that, under the conditions evaluated, the permanganate is preferentially consumed by reaction with Cr(III) to yield soluble chromium, followed by reaction with the EDTA and other organic intermediates. Then, while still reacting with the more refractory organic

fragments, the permanganate is consumed by reaction with nitrite to form nitrate. The "efficiency" of permanganate addition for strontium removal/TOC destruction is relatively high because most of benefits relating to strontium removal and TOC destruction are gained prior to consumption of permanganate via the oxidation of nitrite to nitrate.

The effects of operating time were evaluated by analyzing samples taken at 1, 20, and 70 hr during the higher permanganate addition tests (i.e., 0.11 M, 0.32 M and 0.53 M permanganate concentrations). The results given in Table 4.3 indicate that time had little, if any, effect on TOC destruction or strontium removal for the conditions and time intervals tested. The data suggest that a treatment time of approximately 1 hr (or shorter) is sufficient for defunctionalizing the organic and removing strontium. Again, it should be emphasized that although it appears strontium is being removed primarily by defunctionalization of the organic, as was the case with previous hydrothermal testing (Schmidt et al. 1994; Orth et al. 1995), the flocking action of the manganese dioxide (or hydroxide) may also be contributing. Additional testing using manganese dioxide (or hydroxide) is required to separate the two effects.

The percent increase in solids content upon permanganate addition is given in Table 4.4 for the permanganate concentrations tested here. At 0.017 M permanganate addition, no increase in solids was observed, and at 0.033 M permanganate addition, only minimal solids generation was observed. From Table 4.3, it was observed that chromium was being solubilized at these conditions; thus, the chromium solubilization appears to offset any significant increase in solids by any manganese precipitation that might occur under these conditions. As was discussed previously, the use of permanganate to remove chromium from radioactive solids may be beneficial from a HLW vitrification viewpoint. Furthermore, the data given in Table 4.4 suggest that chromium removal may be accomplished via permanganate addition with a negligible increase in solids.

At 0.067 M permanganate addition and higher, a significant increase in solids was observed upon treatment with permanganate. As the permanganate dosage was increased from 0.067 M to 0.53 M, the amount of solids formed increased steadily. Thus, to achieve significant strontium removal, it appears that a significant increase in solids will be realized. In cases where chromium is a limiting constituent for the vitrification process, this increase in solids content may be offset by the removal of chromium.

4.4.3 Temperature Effects

The results from the testing conducted at 30°C and 65°C to evaluate the effects of temperature are given in Table 4.5. At the lowest permanganate concentration (0.017 M) and at the lower temperature (30°), only 55% of the chromium is soluble as compared with 88% soluble chromium at 65°C. Solubilization of 55% of the chromium is approximately what would be expected based on this permanganate concentration and on permanganate conversion to manganese dioxide (discussed in Section 4.4.2). These results suggest that in the 101-SY simulant matrix, at the lower temperature, permanganate is reduced to manganese dioxide, and a higher temperature (e.g., 65°C) is required to further reduce the manganese dioxide to manganese hydroxide.

Table 4.3. Concentration/Time Effects: Permanganate Addition Test Results^(a) (Organic/Nitrite Destruction, Strontium Removal, Chromium Solubility)

Permanganate Concentration/ Sample Time	TOC Destruction ^(b) (%)	Strontium Removal ^(b) (%)	Chromium in Supernatant ^(c) (%)	Nitrite Destruction ^(b) (%)
0.017 <u>M</u> / 1 hour ^(d)	4 ^(e)	---	---	1 ^(e)
0.017 <u>M</u> / 20 hours ^(d)	6 ^(e)	---	---	0 ^(e)
0.017 <u>M</u> / 70 hours ^(d)	1 ^(e)	0 ^(e)	86 ^(e)	1 ^(e)
0.033 <u>M</u> / 1 hour ^(f)	4 ^(e)	---	---	3 ^(e)
0.033 <u>M</u> / 20 hours ^(f)	3 ^(e)	---	---	0 ^(e)
0.033 <u>M</u> / 70 hours ^(f)	4 ^(e)	0 ^(e)	85 ^(e)	1 ^(e)
0.067 <u>M</u> / 1 hour ^(g)	3 ^(e)	---	---	1 ^(e)
0.067 <u>M</u> / 20 hours ^(g)	3 ^(e)	---	---	---
0.067 <u>M</u> / 70 hours ^(g)	9 ^(e)	67 ^(e)	91 ^(e)	2 ^(e)
0.11 <u>M</u> / 1 hour ^(h)	1 ^(e)	81 ^(e)	---	2 ^(e)
0.11 <u>M</u> / 20 hours ^(h)	4 ^(e) , 0 ⁽ⁱ⁾	68 ⁽ⁱ⁾	---	0 ^(e) , 1 ⁽ⁱ⁾
0.11 <u>M</u> / 70 hours ^(h)	12 ^(e)	> 81 ^(e)	87 ^(e)	5 ^(e)
0.32 <u>M</u> / 1 hour ⁽ⁱ⁾	37 ^(e)	94 ⁽ⁱ⁾	---	4 ^(e)
0.32 <u>M</u> / 20 hours ⁽ⁱ⁾	56 ^(e) , 38 ⁽ⁱ⁾	92 ⁽ⁱ⁾	---	0 ^(e) , 5 ⁽ⁱ⁾
0.32 <u>M</u> / 70 hours ⁽ⁱ⁾	58 ^(e)	> 81 ^(e)	90 ^(e)	5 ^(e)
0.53 <u>M</u> / 1 hour ^(k)	51 ^(e)	94 ⁽ⁱ⁾	---	22 ^(e)
0.53 <u>M</u> / 20 hours ^(k)	59 ^(e) , 77 ⁽ⁱ⁾	95 ⁽ⁱ⁾	---	19 ^(e) , 11 ⁽ⁱ⁾
0.53 <u>M</u> / 70 hours ^(k)	66 ^(e)	> 81 ^(e)	92 ^(e)	24 ^(e)

- (a) Tests conducted at 65°C, using 3:1 diluted 101-SY simulant containing EDTA as the organic source.
In all cases analyses conducted on supernatant resulting from filtration through a 0.45- μ m filter.
- (b) TOC destruction, strontium removal, nitrite destruction = (control supernatant concentration - "permanganate addition" supernatant concentration)/(control supernatant concentration)x100.
- (c) Initial total chromium concentration = 1680 mg/L in 3:1 diluted 101-SY simulant, based on simulant recipe.
Chromium in supernatant = ("permanganate addition" supernatant concentration/total chromium concentration)x100.
- (d) 0.5 g KMnO₄ added to 220 g (190 mL) simulant.
- (e) Filtered control sample (no permanganate addition): strontium = 0.10 mg/L; TOC = 5200 mg/L; chromium = 54 mg/L; nitrite = 35000 mg/L.
- (f) 1.0 g dry KMnO₄ added to 220 g (190 mL) simulant.
- (g) 2.0 g KMnO₄ added to 220 g (190 mL) simulant.
- (h) 3.2 g dry KMnO₄ added to 220 g (190 mL) simulant.
- (i) Filtered control sample (no permanganate addition): strontium = 0.39 mg/L; TOC = 6200 mg/L; chromium = 38 mg/L; nitrite = 43000 mg/L.
- (j) 9.5 g KMnO₄ added to 220 g (190 mL) simulant.
- (k) 15.8 g dry KMnO₄ added to 220 g (190 mL) simulant.

Table 4.4. Concentration/Time Effects: Permanganate Addition Test Results (Increase in Solids Content)

Permanganate Concentration/Sample Time	Wt% Increase in Solids ^(a)
0.017 <u>M</u> /70 hours ^(b)	-2 ^(c)
0.033 <u>M</u> /70 hours ^(d)	18 ^(c)
0.067 <u>M</u> /70 hours ^(e)	82 ^(c)
0.11 <u>M</u> /70 hours ^(f)	200 ^(c)
0.11 <u>M</u> /20 hours ^(f)	200 ^(g)
0.32 <u>M</u> /70 hours ^(h)	780 ^(c)
0.32 <u>M</u> /20 hours ^(h)	480 ^(g)
0.53 <u>M</u> /70 hours ⁽ⁱ⁾	1000 ^(c)
0.53 <u>M</u> /20 hours ⁽ⁱ⁾	850 ^(g)
<p>(a) Reported values are 100x[wt% solids (permanganate addition) - wt% solids (control)]/wt% solids (control). Weight percent solids (permanganate added) were based on solution weight prior to permanganate addition. Weight percent solids were determined at the completion of the test (i.e., >70 hr into the test).</p> <p>(b) 0.5 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(c) Control sample (no permanganate added): 0.9 wt% solids.</p> <p>(d) 1.0 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(e) 2.0 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(f) 3.2 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(g) Control sample (no permanganate added): 1.1 wt% solids.</p> <p>(h) 9.5 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(i) 15.8 g dry KMnO₄ added to 220 g (190 mL) simulant.</p>	

At the higher permanganate concentrations (0.033 M and higher), the 30°C data and 65°C data were in good agreement. These observations indicate for this temperature range and these permanganate concentrations, temperature has little effect on organic and nitrate destruction, strontium removal, and chromium solubilization in the 101-SY simulant matrix.

The percent increase in solids content upon permanganate addition is given in Table 4.6 for the two different temperatures evaluated here. For the temperature range investigated, no effect of temperature on solids formation is evident from the data presented in Table 4.6. At the two lower permanganate concentrations tested (0.017 M and 0.033 M), a minimal, if any, increase in solids was observed at either temperature. At 0.067 M permanganate addition and higher, a significant increase in solids was observed upon treatment with permanganate for both temperatures. Furthermore, the amounts of solids formed at both temperatures were comparable for a given permanganate dosage.

4.4.4 Chelating Organics Effects

The results from the tests to evaluate the effectiveness of permanganate addition on defunctionalizing HEDTA, NTA, as well as EDTA, are given in Table 4.7. In all cases, the soluble chromium concentration was less than 140 mg/L (i.e., less than 9% of the total chromium in the

Table 4.5. Temperature Effects: Permanganate Addition Test Results^(a) (Organic/Nitrite Destruction, Strontium Removal, Chromium Solubility)

Operating Temperature	TOC Destruction ^(b) (%)	Strontium Removal ^(b) (%)	Chromium in Supernatant ^(c) (%)	Nitrite Destruction ^(b) (%)
0.017 M Permanganate Addition, 70 hour data^(d)				
30°C	5	2	55	0
65°C	1	0	86	1
0.033 M Permanganate Addition, 70 hour data^(e)				
30°C	6	11	78	0
65°C	4	0	85	1
0.067 M Permanganate Addition, 70 hour data^(f)				
30°C	5	> 81	91	0
65°C	9	67	91	2
0.11 M Permanganate Addition, 70 hour data^(g)				
30°C	0	> 81, 72 ^(h)	89, 100 ^(h)	0
65°C	12	> 81	87	5
0.32 M Permanganate Addition, 70 hour data⁽ⁱ⁾				
30°C	62	> 81, 97 ^(h)	89, 100 ^(h)	0
65°C	58	> 81	90	5
0.53 M Permanganate Addition, 70 hour data^(j)				
30°C	71	> 81, 97 ^(h)	90, 100 ^(h)	18
65°C	66	> 81	92	24
<p>(a) Tests conducted using 3:1 diluted 101-SY simulant containing EDTA as the organic source. In all cases analyses conducted on supernatant resulting from filtration through a 0.45-μm filter. Unless noted otherwise, filtered control sample (no permanganate addition): strontium = 0.10 mg/L; TOC = 5200 mg/L; chromium = 54 mg/L; nitrite = 35000 mg/L.</p> <p>(b) TOC destruction, strontium removal, nitrite destruction = (control supernatant concentration - "permanganate addition" supernatant concentration)/(control supernatant concentration)x100.</p> <p>(c) Initial total chromium concentration = 1680 mg/L in 3:1 diluted 101-SY simulant, based on simulant recipe. Chromium in supernatant = ("permanganate addition" supernatant concentration/total chromium concentration)x100.</p> <p>(d) 0.5 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(e) 1.0 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(f) 2.0 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(g) 3.2 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(h) Filtered control sample (no permanganate addition): strontium = 0.37 mg/L; chromium = 95 mg/L.</p> <p>(i) 9.5 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(j) 15.8 g dry KMnO₄ added to 220 g (190 mL) simulant.</p>				

Table 4.6. Temperature Effects: Permanganate Addition Test Results (Increase in Solids Content)

Operating Temperature	Wt% Increase in Solids ^(a)
0.017 M Permanganate Addition, 70 hour data^(b)	
30°C	-19 ^(c)
65°C	-2 ^(d)
0.033 M Permanganate Addition, 70 hour data^(e)	
30°C	-5 ^(c)
65°C	18 ^(d)
0.067 M Permanganate Addition, 70 hour data^(f)	
30°C	54 ^(c)
65°C	82 ^(d)
0.11 M Permanganate Addition, 70 hour data^(g)	
30°C	140 ^(c) , 41 ^(h)
65°C	200 ^(d)
0.32 M Permanganate Addition, 70 hour data⁽ⁱ⁾	
30°C	580 ^(c) , 320 ^(h)
65°C	780 ^(d)
0.53 M Permanganate Addition, 70 hour data^(j)	
30°C	920 ^(c) , 620 ^(h)
65°C	1000 ^(d)
<p>(a) Reported values are 100x[wt% solids (permanganate addition) - wt% solids (control)]/wt% solids (control). Weight percent solids (permanganate added) were based on solution weight prior to permanganate addition. Weight percent solids were determined at the completion of the test (i.e., > 70 hr into the test).</p> <p>(b) 0.5 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(c) Control sample (no permanganate added): 1.0 wt% solids.</p> <p>(d) Control sample (no permanganate added): 1.1 wt% solids.</p> <p>(e) 1.0 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(f) 2.0 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(g) 3.2 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(h) Control sample (no permanganate added): 1.5 wt% solids.</p> <p>(i) 9.5 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(j) 15.8 g dry KMnO₄ added to 220 g (190 mL) simulant.</p>	

Table 4.7. Organic Source Effects: Permanganate Addition Test Results^(a) (Organic/Nitrite Destruction, Strontium Removal, Chromium Solubility)

Organic Source	TOC Destruction ^(b) (%)	Strontium Removal ^(b) (%)	Chromium in Supernatant ^(c) (%)	Nitrite Destruction ^(b) (%)
0.033 M Permanganate Addition, 70 hour data^(d)				
EDTA	4 ^(e)	0 ^(e)	85 ^(e)	1 ^(e)
HEDTA	4 ^(f)	28 ^(f)	96 ^(f)	0 ^(f)
NTA	1 ^(g)	0 ^(g)	100 ^(g)	0 ^(g)
0.11 M Permanganate Addition, 70 hour data^(h)				
EDTA	12 ^(e)	> 81 ^(e)	87 ^(e)	5 ^(e)
HEDTA	5 ^(f)	92 ^(f)	100 ^(f)	0 ^(f)
NTA	12 ^(g)	39 ^(g)	100 ^(g)	3 ^(g)
0.32 M Permanganate Addition, 70 hour data⁽ⁱ⁾				
EDTA	58 ^(e)	> 81 ^(e)	90 ^(e)	5 ^(e)
HEDTA	36 ^(f)	90 ^(f)	100 ^(f)	0 ^(f)
NTA	69 ^(g)	50 ^(g)	93 ^(g)	1 ^(g)
0.53 M Permanganate Addition, 70 hour data^(j)				
EDTA	66 ^(e)	> 81 ^(e)	92 ^(e)	24 ^(e)
HEDTA	72 ^(f)	91 ^(f)	100 ^(f)	0 ^(f)
NTA	83 ^(g)	48 ^(g)	99 ^(g)	22 ^(g)
<p>(a) Tests conducted AT 65°C, using 3:1 diluted 101-SY simulant. In all cases analyses conducted on supernatant resulting from filtration through a 0.45-µm filter.</p> <p>(b) TOC destruction, strontium removal, nitrite destruction = (control supernatant concentration - "permanganate addition" supernatant concentration)/(control supernatant concentration)x100.</p> <p>(c) Initial total chromium concentration = 1680 mg/L in 3:1 diluted 101-SY simulant, based on simulant recipe. Chromium in supernatant = ("permanganate addition" supernatant concentration/total chromium concentration)x100.</p> <p>(d) 1.0 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(e) Filtered control sample (no permanganate addition): strontium = 0.10 mg/L; TOC = 5200 mg/L; chromium = 54 mg/L; nitrite = 35000 mg/L.</p> <p>(f) Filtered control sample (no permanganate addition): strontium = 0.37 mg/L; TOC = 6200 mg/L; chromium = 98 mg/L; nitrite = 45000 mg/L.</p> <p>(g) Filtered control sample (no permanganate addition): strontium = 0.06 mg/L; TOC = 6300 mg/L; chromium = 134 mg/L; nitrite = 40000 mg/L.</p> <p>(h) 3.2 g dry KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(i) 9.5 g KMnO₄ added to 220 g (190 mL) simulant.</p> <p>(j) 15.8 g dry KMnO₄ added to 220 g (190 mL) simulant.</p>				

simulant was soluble). Upon treatment with the lowest permanganate addition tested, nearly all of the chromium was solubilized regardless of the organic source. For EDTA and NTA, essentially no reduction in TOC, strontium, or nitrite was observed. However, when HEDTA was present as the organic source, a small, but measurable, removal of strontium was observed.

At 0.11 M permanganate addition, a significant amount of strontium was removed in the presence of all of the organics evaluated. The percent strontium removal in the presence of NTA was significantly lower than either EDTA or HEDTA; however, the initial solution phase strontium concentration in the untreated NTA-containing simulant was significantly lower than either the EDTA or HEDTA case. No nitrite removal was noted for this permanganate concentration, and minimal organic carbon destruction was noted for all of the organics tested.

The strontium removal at 0.32 M and 0.53 M permanganate addition was comparable to that observed at 0.11 M permanganate addition for all of the organics tested. This is an indication that optimal strontium removal from the 3:1 diluted 101-SY simulant might be achievable in all cases at a permanganate concentration of 0.11 M or possibly lower. Significant and comparable organic carbon destruction efficiencies were observed for all three organics at 0.32 M and 0.53 M permanganate concentration. As the permanganate concentration was increased from 0.32 M to 0.53 M, the organic destruction increased for the three organics evaluated. In the 0.53 M permanganate addition case, measurable and comparable decreases in nitrite concentration were observed when EDTA and NTA were the organic sources, but no measurable nitrite reduction was observed when HEDTA was the organic source.

Note that for the three organics tested, the absolute amounts of strontium remaining after treatment with 0.11 M, 0.32 M, and 0.53 M were comparable, which could be an indication that the remaining strontium detected is "soluble" (unchelated) strontium. If this is the case, then other techniques such as ion exchange would be required to reduce the supernatant strontium level further.

The increase in solids upon permanganate addition is given in Table 4.8 for the simulants containing the three different chelating organics. At all permanganate concentrations, the increase in solids for the three different organics evaluated were fairly comparable.

4.4.5 Dilution and Prefiltration Effects

The effects of simulant dilution and prefiltration are given in Table 4.9. Simulant dilution had little effect on chromium solubilization. In all cases, essentially all of the chromium present in the simulants was solubilized upon treatment. The three samples also behaved similarly for strontium removal, although the strontium removal from the undiluted sample was slightly lower than for the other two. From the test results given in Table 4.3, it was observed that 0.11 M (3.2 g, 0.02 mole potassium permanganate addition to 190 mL simulant) was about as effective in removing strontium from solution as 0.32 M (9.5 g, 0.06 mole potassium permanganate addition to 190 mL simulant). The EDTA concentration in the 3:1 diluted simulant was approximately 0.05 M. These data indicated that on the order of 2 moles potassium permanganate/mole EDTA were required to achieve significant strontium removal. The EDTA content in 220 g (the amount of simulant used in all of these tests) is approximately 0.017 mole and 0.029 mole in 1:1 diluted and undiluted 101-SY simulant, respectively. Thus, the results obtained here for the undiluted and 1:1 diluted simulant samples are comparable with what would be expected based on the 3:1 diluted testing.

Table 4.8. Organic Source Effects: Permanganate Addition Test Results^(a) (Increase in Solids Content)

Organic Source	Wt% Increase in Solids ^(a)
0.033 M Permanganate Addition, 70 hour data^(b)	
EDTA	-18 ^(c)
HEDTA	3 ^(d)
NTA	26 ^(e)
0.11 M Permanganate Addition, 70 hour data^(f)	
EDTA	200 ^(c)
HEDTA	110 ^(d)
NTA	130 ^(e)
0.32 M Permanganate Addition, 70 hour data^(g)	
EDTA	780 ^(c)
HEDTA	550 ^(d)
NTA	710 ^(e)
0.53 M Permanganate Addition, 70 hour data^(h)	
EDTA	1000 ^(c)
HEDTA	820 ^(d)
NTA	1000 ^(e)
<p>(a) Reported values are $100 \times [\text{wt\% solids (permanganate addition)} - \text{wt\% solids (control)}] / \text{wt\% solids (control)}$. Weight percent solids (permanganate added) were based on solution weight prior to permanganate addition. Weight percent solids were determined at the completion of the test (i.e., > 70 hr into the test).</p> <p>(b) 1.0 g KMnO_4 added to 220 g (190 mL) simulant.</p> <p>(c) Control sample (no permanganate added): 1.1 wt% solids.</p> <p>(d) Control sample (no permanganate added): 1.2 wt% solids.</p> <p>(e) Control sample (no permanganate added): 1.0 wt% solids.</p> <p>(f) 3.2 g dry KMnO_4 added to 220 g (190 mL) simulant.</p> <p>(g) 9.5 g dry KMnO_4 added to 220 g (190 mL) simulant.</p> <p>(h) 15.8 g dry KMnO_4 added to 220 g (190 mL) simulant.</p>	

Results for the prefiltered 101-SY simulant (Table 4.9) indicate there is no significant effect of prefiltration on TOC destruction, strontium removal, or nitrite oxidation. The soluble chromium concentration remained low after treatment (comparable to the control samples) because the insoluble Cr(III) was removed via filtration prior to potassium permanganate addition.

The percent solids increase upon permanganate addition is given in Table 4.10 for undiluted, 1:1 diluted, and 3:1 diluted (prefiltered, and non-prefiltered) simulant. The solids increase for the 3:1 diluted (prefiltered) case is based on the 3:1 diluted (unfiltered) without permanganate addition. The

Table 4.9. Dilution and Prefiltration Effects: Permanganate Addition Test Results^(a) (Organic/Nitrite Destruction, Strontium Removal, Chromium Solubility)

Organic Source	TOC Destruction ^(b) (%)	Strontium Removal ^(b) (%)	Chromium in Supernatant ^(c) (%)	Nitrite Destruction ^(b) (%)
Dilution Effects, 70 hour data				
3:1 Diluted Simulant	58 ^(d)	> 81 ^(d)	90 ^(d)	5 ^(d)
1:1 Diluted Simulant	27 ^(e)	88 ^(e)	98 ^(e)	0 ^(e)
Undiluted Simulant	22 ^(f)	72 ^(f)	94 ^(f)	1 ^(f)
Prefiltration Effects, 70 hour data				
3:1 Diluted Simulant	58 ^(d)	> 81 ^(d)	90 ^(d)	5 ^(d)
Prefiltered 3:1 Diluted Simulant ^(g)	69 ^(h)	81 ^(h)	5 ^(h)	7 ^(h)
<p>(a) Tests conducted at 65°C, using 101-SY simulant containing EDTA as the organic source. In all cases 9.5 g dry KMnO₄ added to 220 g simulant (i.e., equivalent to 0.32 M KMnO₄ in 3:1 diluted 101-SY). In all cases analyses conducted on supernatant resulting from filtration through a 0.45-μm filter.</p> <p>(b) TOC destruction, strontium removal, nitrite destruction = (control supernatant concentration - "permanganate addition" supernatant concentration)/(control supernatant concentration)x100.</p> <p>(c) Initial total chromium concentration = 1680 mg/L in 3:1 diluted 101-SY simulant, 3360 mg/L in 1:1 diluted 101-SY simulant, 6720 mg/L in undiluted simulant, based on simulant recipe. Chromium in supernatant = ("permanganate addition" supernatant concentration/total chromium concentration)x100.</p> <p>(d) Filtered control sample (no permanganate addition): strontium = 0.10 mg/L; TOC = 5200 mg/L; chromium = 54 mg/L; nitrite = 35000 mg/L.</p> <p>(e) Filtered control sample (no permanganate addition): strontium = 0.62 mg/L; TOC = 8900 mg/L; chromium = 134 mg/L; nitrite = 78000 mg/L.</p> <p>(f) Filtered control sample (no permanganate addition): strontium = 1.36 mg/L; TOC = 20200 mg/L; chromium = 664 mg/L; nitrite = 161000 mg/L.</p> <p>(g) Prior to conducting the test (i.e., prior to permanganate addition), the simulant was passed through a 0.45-μm filter to remove solids initially present in the simulant.</p> <p>(h) Filtered control sample (no permanganate addition): strontium = 0.16 mg/L; TOC = 5000 mg/L; chromium = 54 mg/L; nitrite = 38000 mg/L.</p>				

percent solids increase is comparable for the 1:1 diluted and 3:1 diluted (unfiltered case), whereas the percent solids increase for the undiluted case is considerably larger. A larger amount of solids is initially present in the undiluted and 1:1 diluted cases; therefore, if the same amount of total solids were precipitated upon permanganate addition, lower percent solids increase would be expected for these two cases as compared with the 3:1 diluted case. Thus, it appears that the permanganate addition is causing the precipitation of considerably more solids (other than just manganese dioxide or manganese hydroxide) in the 1:1 and undiluted simulant than for the 3:1 diluted case.

Upon comparison of the solids increase for the 3:1 diluted (unfiltered case) with the 3:1 diluted (prefiltered case), the percent increase in solids is significantly lower for the prefiltered case. These values can be directly compared since the 3:1 diluted (unfiltered) case with no permanganate addition is used as the basis.

Table 4.10. Dilution and Prefiltration Effects: Permanganate Addition Test Results^(a) (Increase in Solids Content)

Organic Source	Wt% Increase in Solids ^(a,b)
Dilution Effects, 70 hour data	
3:1 Diluted Simulant	780 ^(c)
1:1 Diluted Simulant	940 ^(d)
Undiluted Simulant	1300 ^(e)
Prefiltration Effects, 70 hour data	
3:1 Diluted Simulant	780 ^(c)
Prefiltered 3:1 Diluted Simulant ^(f)	470 ^(g)
<p>(a) Reported values are $100 \times [\text{wt\% solids (permanganate addition)} - \text{wt\% solids (control)}] / \text{wt\% solids (control)}$. Weight percent solids (permanganate added) were based on solution weight prior to permanganate addition. In all cases 9.5 g dry KMnO_4 added to 220 g simulant (i.e., equivalent to 0.33 M KMnO_4 in 3:1 diluted 101-SY).</p> <p>(c) Control sample (no permanganate added): 1.1 wt% solids.</p> <p>(d) Control sample (no permanganate added): 1.1 wt% solids.</p> <p>(e) Control sample (no permanganate added): 2.2 wt% solids.</p> <p>(f) Prior to conducting the test (i.e., prior to permanganate addition), the simulant was passed through a 0.45-μm filter to remove solids initially present in the simulant.</p> <p>(g) Weight percent increase in solids based on 3:1 diluted, unfiltered control (no permanganate added) = 1.1 wt% solids.</p>	

4.4.6 Stagewise Addition Effects

The strontium removal results for this testing are given in Table 4.11. Comparison of all of the stagewise addition data with corresponding one-time addition data indicates that, for the conditions tested, the stagewise addition of permanganate has no beneficial effect on strontium removal. This observation is consistent, regardless of which organic component was added to solution.

The increase in solids due to stagewise and one-time permanganate addition is given in Table 4.12. These data indicate that no benefit is realized by stagewise permanganate addition. In all cases, the solids increase was on the order of 600% to 800%.

4.4.7 Qualitative Observations Upon Permanganate Addition

Several observations were made regarding the use of chemical oxidation in a sealed test vessel. These observations, while primarily qualitative in nature, will be useful in predicting the behavior and for designing a larger-scale system.

At the higher potassium permanganate concentrations tested, following heatup to 65°C and the addition of the oxidant, the vessels developed a slight positive pressure, observed from a slight pressure release upon opening the vessels for the 1-hr sampling. However, at the 4-hr sampling, the flask with the highest dose of potassium permanganate was observed to have been under a vacuum, shown by the

Table 4.11. Stagewise Addition Effects: Permanganate Addition Test Results^(a) (Organic/Nitrite Destruction, Strontium Removal, Chromium Solubility)

Organic Source	TOC Destruction ^(b) (%)	Strontium Removal ^(b) (%)	Chromium in Supernatant ^(c) (%)	Nitrite Destruction ^(b) (%)
EDTA As Organic Source, 70 hour data				
0.3 M Permanganate Addition ^(d)	58 ^(e)	> 81 ^(e)	90 ^(e)	5 ^(e)
0.3 M Permanganate Addition (Stagewise) ^(f)	48 ^(e)	69 ^(e)	79 ^(e)	0 ^(e)
HEDTA As Organic Source, 70 hour data				
0.3 M Permanganate Addition ^(d)	36 ^(g)	90 ^(g)	100 ^(g)	0 ^(g)
0.3 M Permanganate Addition (Stagewise) ^(f)	24 ^(g)	91 ^(g)	100 ^(g)	0 ^(g)
NTA As Organic Source, 70 hour data				
0.3 M Permanganate Addition ^(d)	69 ^(h)	50 ^(h)	93 ^(h)	1 ^(h)
0.3 M Permanganate Addition (Stagewise) ^(f)	62 ^(h)	48 ^(h)	82 ^(h)	2 ^(h)
<p>(a) Tests conducted at 65°C, using 3:1 diluted 101-SY simulant. In all cases analyses conducted on supernatant resulting from filtration through a 0.45-µm filter.</p> <p>(b) TOC destruction, strontium removal, nitrite destruction = (control supernatant concentration - "permanganate addition" supernatant concentration)/(control supernatant concentration)x100.</p> <p>(c) Initial total chromium concentration = 1680 mg/L in 3:1 diluted 101-SY simulant, based on simulant recipe. Chromium in supernatant = ("permanganate addition" supernatant concentration/total chromium concentration)x100.</p> <p>(d) 9.5 g dry KMnO₄ added to 220 g (200 mL) simulant.</p> <p>(e) Filtered control sample (no permanganate addition): strontium = 0.10 mg/L; TOC = 5200 mg/L; chromium = 54 mg/L; nitrite = 35000 mg/L.</p> <p>(f) 1.9 g dry permanganate was added initially to 220 g (200 mL) 3:1 diluted simulant, initially. Over the first 40 minutes of the test, 1.9 g of additional permanganate was added to the simulant, resulting in a total permanganate addition of 9.5 g (0.32 M).</p> <p>(g) Filtered control sample (no permanganate addition): strontium = 0.37 mg/L; TOC = 6200 mg/L; chromium = 98 mg/L; nitrite = 45000 mg/L.</p> <p>(h) Filtered control sample (no permanganate addition): strontium = 0.06 mg/L; TOC = 6300 mg/L; chromium = 134 mg/L; nitrite = 40000 mg/L.</p>				

Table 4.12. Stagewise Addition Effects: Permanganate Addition Test Results^(a) (Increase in Solids Content)

Organic Source	Wt% Increase in Solids ^(a)
EDTA As Organic Source, 70 hour data	
0.32 <u>M</u> Permanganate Addition ^(b)	780 ^(c)
0.32 <u>M</u> Permanganate Addition (Stagewise) ^(d)	660 ^(c)
EDTA As Organic Source, 70 hour data	
0.32 <u>M</u> Permanganate Addition ^(b)	550 ^(e)
0.32 <u>M</u> Permanganate Addition (Stagewise) ^(d)	770 ^(e)
EDTA As Organic Source, 70 hour data	
0.32 <u>M</u> Permanganate Addition ^(b)	710 ^(f)
0.32 <u>M</u> Permanganate Addition (Stagewise) ^(d)	740 ^(f)
<p>(a) Reported values are $100 \times [\text{wt\% solids (permanganate addition)} - \text{wt\% solids (control)}] / \text{wt\% solids (control)}$. Weight percent solids (permanganate added) were based on solution weight prior to permanganate addition. Weight percent solids were determined at the completion of the test (i.e., > 70 hr into the test).</p> <p>(b) 9.5 g dry KMnO_4 added to 220 g (200 mL) simulant.</p> <p>(c) Control sample (no permanganate added): 1.1 wt% solids.</p> <p>(d) 1.9 g dry permanganate was added initially to 220 g (200 mL) 3:1 diluted simulant, initially. Over the first 40 minutes of the test, 1.9 g of additional permanganate was added to the simulant, resulting in a total permanganate addition of 9.5 g (0.32 <u>M</u>).</p> <p>(e) Control sample (no permanganate added): 1.2 wt% solids.</p> <p>(f) Control sample (no permanganate added): 1.0 wt% solids.</p>	

deformation of the vessel. For the screening tests, the vessels used were constructed of soft, low-density polyethylene, which tended to deform easily and display that the contents were under vacuum. When the atmosphere was re-equilibrated inside the flasks, the solution again drew a slight vacuum on the flask after about 1 hr. However, after this time period, no further indication of a negative pressure within the flask was observed. Finally, the simulant was observed to yield an ammonia-like scent at sample times after 20 hr, which could be either ammonia gas or possibly ethylene diamine released in the decomposition of EDTA.

Two tests were conducted in which the composition of off-gas generated due to permanganate addition was measured. In the tests, 9.5 g potassium permanganate and 15.8 g potassium permanganate were added to 200 g (190 mL) 3:1 diluted 101-SY simulant. In both cases EDTA was the organic source, and the tests were conducted at 65°C. The flasks containing the simulant/permanganate solution were sealed, and air was used as the cover gas. For the lower potassium

permanganate dosage, no off-gases were detected upon treatment; however, for the higher potassium permanganate dosage, nitrous oxide was detected as an off-gas produced from the permanganate treatment.

When higher doses of dry potassium permanganate were added to the 101-SY simulant, increases in solution temperature were observed. In the EDTA-based simulant it was seen to a small extent, with temperature increases of approximately 15°C upon the addition of the "high" dose (15.8 g) of potassium permanganate and approximately 10°C by the 1-hr sample. By the 4-hr sample, the solution returned to the incubator temperature. In the NTA-based simulant, the "high" dose of potassium permanganate resulted in an increase from 63°C to 91°C upon addition and was still around 4°C above the temperature of the incubator at the 1-hr sampling event. The HEDTA-based simulant slowly built up pressure within the reaction flask and was vented to release pressure several-times in the first minute of testing. The reaction was very exothermic and heated the simulant up from 63°C to over 100°C and was visibly boiling in the flask. For both the NTA- and HEDTA-based simulants, the solution temperature returned to incubator temperature by the 4-hr sampling.

Unexpected and undesirable gas generation and heat output may result if proper controls are not established for the methods used to add the potassium permanganate to the actual waste. Considering the variability among the tanks scheduled for treatment, it is recommended that the final design for a system for pretreating actual waste should contain enough flexibility to handle a wide variety of tank waste responses to chemical oxidant addition.

4.5 Direction of Future Work

Future testing should involve a limited amount of simulant testing focused on reduction of solids formed via permanganate addition while removing the maximum amount of strontium possible. Testing here suggests that approximately 0.11 M permanganate addition was optimum for providing strontium removal and minimizing solids production for the EDTA concentration present in this simulant (i.e., approximately 0.05 M EDTA). In addition to conducting permanganate testing in this range, slow, continuous permanganate addition should be evaluated to determine whether the amount of solids produced is affected. Testing with simulants other than 101-SY should be conducted.

Simulant testing should be conducted at different (higher) temperatures to determine whether the oxidizing power of permanganate is indeed increased upon increase in temperature (i.e., converted to manganese hydroxide rather than manganese dioxide). Testing should also include adding manganese dioxide and/or manganese hydroxide to solution. This testing would be helpful in separating out the flocking effects and the oxidation effects on strontium removal. Addition of manganese dioxide at different temperatures may be useful in determining whether manganese dioxide is further reduced to manganese hydroxide at higher temperatures.

5.0 Chemical Oxidant Addition Testing with Actual Tank Waste

5.1 Objectives

The objective of the work described in this section was to test permanganate addition on actual 101-SY waste (obtained from Window C sampling). The results obtained from the simulant testing were used to determine the most promising conditions to use in the actual waste test. The target permanganate concentration was 0.11 M because in the simulant testing this concentration led to significant (and measurable) strontium removal while minimizing the solids formed.

5.2 Test Approach

The approach for this testing was to duplicate, as close as possible, a previous simulant test using actual tank waste to compare results of TOC destruction, strontium precipitation, chromium dissolution, and solids generation. Additionally, solution analyses of the actual waste samples provided results on TRU removal from solution.

A 20.11-g (approximately 17.3 mL) waste sample was taken from the 3:1 diluted 101-SY stock solution. The sample was placed in a flask on a stirring plate. Agitation was low, just enough to mix solids in the waste. Potassium permanganate was added to the flask as a dry solid (0.41 g), resulting in a final potassium permanganate concentration of approximately 0.15 M. The test was conducted at ambient hot cell temperature ($\sim 29^{\circ}\text{C}$), and allowed to proceed for approximately 1 hr, during which time the temperature of the sample increased to about 39°C then decreased to about 34°C by the end of the hour. After 1 hr of stirring, the sample was centrifuged for 30 min, and the supernatant liquid was decanted and filtered through a $0.45\text{-}\mu\text{m}$ filter. The filtrate was submitted for chemical analyses. The solids were dried and weighed to determine the increase in solids from reaction with the permanganate.

5.3 Test Apparatus

Testing was performed in the hot cell facility at PNL. The testing was conducted in a flask, at room temperature. No external heating or cooling source was used. A magnetic stirrer was used to mix the solution during the test.

5.4 Results and Discussion

The results from the untreated and potassium permanganate-treated actual waste filtrate are given in Table 5.1. The TOC content in the treated actual waste filtrate decreased by approximately 56%, and $>99.4\%$ of the ^{90}Sr that had been present in the untreated actual waste filtrate had been removed from solution via the permanganate addition. The strontium removal results are consistent with those obtained in the simulant testing when EDTA or HEDTA were used as the organic sources (see Table 4.7). However, the TOC destruction is greater than observed in the simulant testing for this permanganate dosage (i.e., comparable to 0.32 M addition results in Table 4.7), which indicates that the organics present in the actual tank waste are more susceptible to permanganate treatment, and is also an indication that less than 0.15 M potassium permanganate may be required to remove significant amounts of strontium from the actual tank waste supernatant.

Table 5.1. Permanganate Additions Results (Testing with Actual 101-SY Waste)

Component	Untreated Filtrate $\mu\text{g/mL}$	Treated Filtrate $\mu\text{g/mL}$	% Removed From Filtrate Upon Treatment
Total Organic Carbon	4060	1800	55.7
Cr	20, 201 ^(a)	1072	-5260, -433
⁹⁰ Sr	1.37	$< 9 \times 10^{-3}$	> 99.3
²³⁸ Pu	2.70×10^{-3}	1.82×10^{-5}	99.3
^{239/40} Pu	1.63×10^{-3}	1.34×10^{-4}	91.8
(a) Two chromium analyses conducted.			

As can be seen, the plutonium concentration in the filtrate decreased upon potassium permanganate addition, suggesting that the plutonium was initially complexed, and once the complexing agent was defunctionalized, the plutonium precipitated from solution. The initial ²⁴¹Am concentration is below detection limits; therefore the effect of potassium permanganate addition on the fate of ²⁴¹Am could not be evaluated in this test. Also, the actual waste filtrate chromium concentration increased by at least a factor of 5X upon permanganate addition, indicating that significant amounts of insoluble Cr(III) had been oxidized to soluble Cr(VI). All of these results are consistent with results from the simulant testing.

The amount of solids in untreated and potassium permanganate-treated 101-SY actual waste is given in Table 5.2. The amount of solids that would be predicted, based on all of the potassium permanganate being converted to insoluble manganese dioxide or manganese hydroxide (i.e., essentially equivalent molecular weights), is also given in Table 5.2. Upon potassium permanganate treatment the weight percent solids increased by 21%. This compares well with what would be predicted, assuming all of the potassium permanganate is being converted to manganese dioxide or manganese hydroxide.

The percent increase in solids in the actual waste testing cannot be directly compared with that observed in the simulant testing (see Section 4.0), primarily because the solids content of the actual waste control sample was much higher. However, based on 1 wt% solids, which was typical of the simulant testing, addition of 0.11 M potassium permanganate would be expected to result in roughly an 80% increase in solids, if the solids were due solely to manganese hydroxide or manganese dioxide. The simulant testing showed that the percent solids increase was between 100% and 200% at 0.11 M permanganate addition, depending on what chelating organic was present (see Table 4.8). Thus, it appears that the treatment of the actual waste results in slightly lower solids production, which can be predicted based on the permanganate dosage.

Table 5.2. Actual 101-SY Waste Testing: Permanganate Addition Test Results^(a) (Increase in Solids Content)

Sample	Initial Waste Weight (g)	KMnO ₄ Addition (g)	Dry Solids (g)	Dry Solids (wt%)	Dry Solids Increase upon Treatment with KMnO ₄ (wt%)
Control (Untreated), 3:1 Diluted 101-SY	16.93	---	0.98	5.8	---
Treated 3:1 Diluted 101-SY (test results)	20.11	0.41	1.44	7.2 ^(a)	24
Treated 3:1 Diluted 101-SY (predicted) ^(c)	20.11	0.41	1.39	6.9 ^(a)	19

(a) Reported wt% solids are based on the initial waste weight, prior to KMnO₄ addition.

(b) The "control (untreated)" and "treated" samples were two different samples taken from the 101-SY actual waste stock solution.

(c) "Predicted" is the amount of solids formed upon KMnO₄ addition, assuming that all KMnO₄ is converted to MnO₂ (MW=87 g/mol) or Mn(OH)₂ (MW=89 g/mol) solids. Based on the amount of solids in the untreated solids, and the beginning weight of treated sample, and the amount of KMnO₄ added during that test.

Overall, it can be concluded that potassium permanganate addition was effective in removing strontium and TRU (plutonium) from the actual waste. In addition, it appeared that the actual waste was more susceptible than the simulant to permanganate treatment, and that permanganate dosages of less than 0.15 M may be sufficient to remove significant quantities of strontium and TRU from actual 3:1 diluted 101-SY waste, while reducing solids formation.

5.5 Direction of Future Work

Future testing on actual waste should continue to concentrate on decreasing the amount of solids formed while removing the maximum amount of strontium and TRU. The actual waste test results obtained here (when compared with simulant test results) suggest that for actual 101-SY waste, less than 0.15 M permanganate would be adequate for removal of the maximum amount of strontium and TRU. In addition, if future simulant testing, implementing slow, continuous permanganate addition, is successful in reducing solids formation while maintaining strontium and TRU removal, this method should be evaluated using actual waste. Testing with actual wastes from different waste tanks should also be pursued. A detailed evaluation of the impact of permanganate addition on HLW and LLW should be undertaken to further determine the applicability of this treatment technique.

6.0 Implications of Metal Cation and Chemical Oxidant Addition on High-Level Waste

This section provides a preliminary or "order of magnitude" analysis of the potential impact of metal cation addition and permanganate addition on HLW. The impact of these treatment methods on tank waste contained in 101-SY is given here as an example. Tank 101-SY is being used primarily because it is a complexant concentrate waste, and all of the data obtained in this report was related to this tank waste. It is recognized that other waste contained, for example, in Tanks 102-AN and 107-AN might be more applicable because of the higher TOC, strontium and TRU levels; however, direct application of the data obtained here for 101-SY may be inappropriate for these other tanks (e.g., the metal cation and permanganate dosages might be quite different). Although the analyses conducted here can be used as a preliminary extrapolation to these other tank wastes, a more detailed analysis, using data obtained from these simulants or actual wastes, should be conducted.

It should be noted that current HLW oxide and specific constituent limits are subject to change. Changes in these limits will affect the feasibility of using metal cation and permanganate addition as treatment techniques.

As a basis for conducting the analysis discussed here, the following assumptions were made.

- The water washed solids from 101-SY (oxide basis) going to HLW prior to metal cation or permanganate addition were taken from Geeting and Kurath (1993), and are given in Table 6.1.
- The number of glass canisters for 101-SY waste prior to metal cation or permanganate addition was taken from Geeting and Kurath (1993):

4277 canisters (based on Cr_2O_3 as the limiting constituent in HLW; maximum allowable Cr_2O_3 limit is 0.5 wt% in HLW, based on 25 wt% waste oxides in HLW).

427 canisters (assuming Cr_2O_3 is removed, 25 wt% waste oxides in HLW is limiting constituent). It did not appear that the Al_2O_3 HLW limit was considered in obtaining this volume, and thus was not used in this evaluation.

- HLW canister = 1650 kg (Geeting and Kurath 1993).
- The current waste volume of tank 101-SY is 4.22×10^6 L (Colton et al. 1994). This corresponds to 16.9×10^6 L of 3:1 diluted 101-SY tank waste.

For 101-SY tank waste, chromium (solids) is the primary limiting constituent in HLW. However, for other complexant concentrate wastes (e.g., 102-AN and 107-AN), chromium is not the limiting constituent. Thus, in an attempt to make a preliminary extrapolation of 101-SY results to tank wastes that do and do not contain chromium, both HLW canister baselines given above were used (i.e., HLW canisters based on chromium limitation and HLW canisters based on 25% waste oxide loading) in the HLW.

Table 6.1. Sludge Washed 101-SY Solids to HLW^(a)

Component (Oxide Basis)	Oxide To HLW After Sludge Washing (g)
Al ₂ O ₃	1.11x10 ⁸
CaO	7.99x10 ⁶
Cr ₂ O ₃	3.53x10 ⁷
Fe ₂ O ₃	3.66x10 ⁶
MoO ₃	8.42x10 ⁵
Na ₂ O	5.50x10 ⁷
NiO	2.62x10 ⁶
P ₂ O ₅	2.85x10 ⁶
SO ₃	1.28x10 ⁶
Other	1.51x10 ⁷
Total Oxides	2.35x10 ⁸
(a) Taken from Geeting and Kurath (1993).	

6.1 Impacts of Metal Cation Addition on HLW

The metal cation addition results presented in this report indicate that, depending on the metal cation being added, minimal to considerable solids generation can take place to achieve strontium removal. Ca(II) addition appears to be acting to displace strontium and, as a result, minimal solids generation is observed. In fact, the results indicate that it might be possible to remove maximum amounts of strontium while generating essentially no solids [see Tables 3.3 and 3.4, 0.04 M and 0.11 M Ca(II) addition]. In contrast, Fe(III) addition appears to be removing strontium primarily via flocculation and bulk precipitation. Thus, although it was observed in the simulant tests that Fe(III) is fairly effective in removing strontium, a considerable amount of solids were formed. The results indicated that approximately 0.11 M Fe(III) addition was required to achieve "maximum" strontium removal while minimizing solids production. From Tables 3.3 and 3.4, it was observed that addition of 0.21 M Fe(III) provided no additional strontium removal, while the solids increased significantly. Thus, in the HLW impact analyses, 0.11 M Fe(III) addition was used as the baseline.

The solids formed upon Fe(III) addition were bracketed by using two values: those observed experimentally (e.g., Table 3.4) and those predicted if the increase in solids was only due to the precipitation of all of the Fe(III) added as Fe(OH)₃. Based on 1 wt% solids initially present in 3:1 diluted 101-SY simulant, a solids increase of 110% would be predicted if it were solely due to the precipitation of Fe(III) as Fe(OH)₃. The basis for this value and the calculations are given in the appendix.

Based on the experimental results given in Table 3.4 [average of 0.11 M Fe(III) data], the solids formed upon Fe(III) addition resulted in an approximately 230% increase in solids. The experimental results suggested that all of the Fe(III) precipitated out (e.g., analyses of the supernatant showed no detectable iron in solution) in addition to the precipitation of approximately an equal quantity of other solids.

Thus, the following three metal addition cases (along with additional assumptions) were compared with the two HLW canister baselines, given previously:

1. No increase in HLW solids. This is the most optimistic case, and assumes that strontium (and TRU) are removed via displacement [e.g., Ca(II) addition].
2. The solids increase is solely due to the precipitation of the metal cation that is added.
 - Addition of 0.11 M Fe(III) (final concentration, based on 3:1 diluted 101-SY waste) is assumed.
 - Precipitation of all of the Fe(III) as Fe(OH)₃ is assumed.
 - A maximum Fe₂O₃ loading of 15 wt% in HLW (25% waste oxide basis) is assumed (Geeting and Kurath 1993).
3. Solids increase was due to precipitation of the metal cation added, in addition to the precipitation of an equal amount of "other" undetermined solids.
 - Addition of 0.11 M Fe(III) (final concentration, based on 3:1 diluted 101-SY waste) is assumed.
 - Precipitation of all of the Fe(III) as Fe(OH)₃ is assumed. The "other" undetermined precipitated solids were assumed to be on an oxide basis [equivalent weight to Fe(OH)₃ precipitate] and were included in the "other" component category given in Table 6.1.
 - A maximum Fe₂O₃ loading of 15 wt% in HLW (25% waste oxide basis) was assumed (Geeting and Kurath 1993).

The results of this analysis are given in Table 6.2. When all three metal cation addition cases are compared against the Cr₂O₃-limiting baseline, no increase in HLW is observed. This is because, in all cases, Cr₂O₃ remains the limiting constituent in the HLW.

Comparison of the three metal addition cases with the 25% total oxide waste loading baseline gives quite different results. No increase in HLW is observed for Case 1, since it is assumed that no increase in solids occurs [e.g., Ca(II) addition]. However, for Cases 2 and 3 [e.g., Fe(III) addition], a significant increase in HLW is observed: between 79% and 153%. Thus, if Fe(III) is used to remove strontium and TRU, a significant increase in HLW solids should be expected.

Table 6.2. Impact of Metal Cation Addition on HLW (101-SY Waste Used as Baseline).

	Total Number of HLW Canisters	Increase in HLW Canisters Above Baseline (%) ^(a)	Limiting Constituent in HLW
Cr ₂ O ₃ Limiting Baseline	4277	---	Cr ₂ O ₃
Metal Cation Addition Case 1	4277	0	Cr ₂ O ₃
Metal Cation Addition Case 2	4277	0	Cr ₂ O ₃
Metals Cation Addition Case 3	4277	0	Cr ₂ O ₃
25% Total Oxide Waste Loading Baseline	475	---	Total Oxide Waste
Metal Cation Addition Case 1	475	0	Total Oxide Waste
Metal Cation Addition Case 2	850	79	Total Oxide Waste
Metals Cation Addition Case 3	1200	153	Total Oxide Waste
(a) % increase in HLW canisters = [(number HLW canisters for treatment case) - (number of HWL canisters for baseline)/(number of HLW canisters for baseline)]*100			

6.2 Impacts of Potassium Permanganate Addition on HLW

The simulant and actual waste permanganate addition test results presented in this report indicate that permanganate addition is effective in removing strontium and TRU (plutonium). In addition, permanganate is effective in solubilizing essentially all of the insoluble chromium that is present.

The testing with simulant indicated the addition of 0.11 M potassium permanganate was effective in removing significant amounts of strontium from the supernatant. Actual waste test results verified this, indicating that 0.15 M potassium permanganate addition was more than sufficient (i.e., even lower additions are likely to be as effective) to remove strontium and TRU from solution. Furthermore, the actual waste test results indicated that the solids increase could be attributed to the reduction of potassium permanganate to form manganese dioxide or manganese hydroxide precipitates.

Thus, the following treatment case (along with additional assumptions) was compared with the two HLW canister baselines given above:

- Potassium permanganate addition results in 0.11 M potassium permanganate final concentration in 3:1 diluted 101-SY waste.
- Solids increase was due to potassium permanganate reaction to form manganese dioxide solids.

- 100% of the Cr(III) solids present (i.e., chromium limiting base) are converted to soluble Cr(VI).
- A maximum MnO₂ loading of 5 wt% in HLW (25% waste oxide basis) was assumed (Geeting and Kurath 1993).

The results of this analysis are given in Table 6.3. When permanganate addition is compared with the Cr₂O₃-limiting baseline, the beneficial impact of the ability of permanganate to oxidize and solubilize Cr(III) is readily apparent. When the MnO₂ HLW limit of 5 wt% is applied, the number of canisters is decreased upon permanganate addition by 54% (i.e., decreased by 2317 canisters for 101-SY). If the MnO₂ HLW limit is ignored (i.e., if it is found that more MnO₂ can be incorporated in HLW), and total oxide waste becomes the limiting factor, the total number of canisters is decreased by 80%.

Comparison of HLW resulting from permanganate addition with the 25% total oxide wasteloading baseline shows a significant increase in HLW. This general trend might be also be extrapolated to wastes that contain little or no chromium. The HLW canisters increase by 85% to 313%, depending on whether or not the MnO₂ limitation is applied. Although the permanganate dosage used in this evaluation is a worst case scenario, removal of strontium and TRU from wastes containing little or no Cr(III) will result in a significant increase in HLW solids. Additional actual waste testing (with 101-SY and other wastes) is required to determine the minimum amount of permanganate dosage required for removal of strontium and TRU.

Table 6.3. Potential Impact of Potassium Permanganate Addition on HLW (101-SY Waste Used as Baseline).

	Total Number of HLW Canisters	Increase in HLW Canisters Above Baseline (%) ^(a)	Limiting Constituent in HLW
Cr ₂ O ₃ Limiting Baseline	4277	---	Cr ₂ O ₃
Permanganate Addition	1960 (878) ^(b)	-54 (-80) ^(b)	MnO ₂ (Total Oxide Waste) ^(b)
25% Total Oxide Waste Loading Baseline	475	---	Total Oxide Waste
Permanganate Addition	1960 (878) ^(b)	313 (85) ^(b)	MnO ₂ (Total Oxide Waste) ^(b)
<p>(a) % increase in HLW canisters = [(number HLW canisters for potassium permanganate treatment) - (number of HLW canisters for baseline)]/(number of HLW canisters for baseline)]*100</p> <p>(b) Assumes the MnO₂ limit of 5 wt% does not apply, and HLW is limited by total oxide waste.</p>			

6.3 Direction of Future Work

A more detailed evaluation of the impact on metal cation addition and permanganate addition should be conducted for 101-SY and other potentially applicable wastes. This evaluation requires additional testing with simulants and actual wastes from tanks other than 101-SY. Testing with 101-SY actual waste is also required to determine the minimum amounts of permanganate and metal cation [e.g., Cu(II), Ni(II), and Fe(III)] addition required to achieve strontium and TRU removal.

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Appendix

Solids Production Calculations Used to Estimate Implications of Metal Cation Addition on HLW

Appendix

Solids Production Calculations Used to Estimate Implications of Metal Cation Addition on HLW

Estimation of Increase in Solids Assuming All Fe(III) precipitates as Fe(OH)₃.

Basis: 3:1 diluted 101-SY simulant
1 wt% solids initially in the simulant
simulant density = 1.16 g/mL
20 mL of 1.1 M Fe(III) added to 220 g simulant
Fe(III) precipitates as Fe(OH)₃ (MW = 107 g/mol)

Calculation #1: Amount of Fe(III) precipitated as Fe(OH)₃

$$(1.1 \text{ moles Fe(III)/L}) * (0.02 \text{ L}) \\ * (1 \text{ mol Fe(OH)}_3 / 1 \text{ mol Fe(III)}) * (107 \text{ g Fe(OH)}_3 / \text{mol Fe(OH)}_3) = \underline{2.4 \text{ g Fe(OH)}_3}$$

Calculation #2: Amount of solids initially present in 3:1 diluted 101-SY simulant

$$(0.01 \text{ g solids/g simulant}) * (220 \text{ g simulant}) = \underline{2.2 \text{ g solids}}$$

Calculation #3: Percent increase in solids based on Fe(III) precipitating as Fe(OH)₃:

$$[(2.4 \text{ g Fe(OH)}_3 + 2.2 \text{ g solids}) - 2.2 \text{ g solids}] / (2.2 \text{ g solids}) * 100 = \underline{110\% \text{ increase in solids}}$$

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