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Recommended Decontamination Factors for Use in Flowsheet Modeling of the Permanganate Treatment Process for Strontium and Actinide Removal

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Acronyms and Abbreviations

DF	decontamination factor
DFs	decontamination factors
DWPF	Defense Waste Processing Facility
M	molar (mole/L)
Mn	manganese
MnO_2	manganese dioxide
MnO_4^-	permanganate
MST	monosodium titanate
$NaMnO_4$	sodium permanganate
Np	neptunium
Pu	plutonium
Sr	strontium

SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
U	uranium

Summary

Based on a review of available testing data, I recommend engineering flowsheet modeling calculations for the permanganate treatment process use the decontamination factors (DFs) shown in Table I below. For a combined treatment process in which both sodium permanganate and strontium nitrate are added to the waste solution, I recommend substituting a strontium DF of 30 in Table I below for both the average and bounding ^{90}Sr cases. Note that the recommended DF values are based on available laboratory measurements as of the issue date of this report. The Savannah River Technology Center (SRTC) plans to conduct further tests on the permanganate treatment process to provide a more complete understanding of the factors that control and optimize the process efficiency. I expect the additional testing will result in an optimized permanganate treatment process with different values for the recommended DFs.

Table I. Recommended Decontamination Factors upon Treatment with 0.005 to 0.05 Molar (M) $NaMnO_4$

	Decontamination Factor						
[NaMnO4]	Initial [Sr] 191 nCi/g	Initial [Sr] 1130 nCi/g	Initial [Pu] 200 µg/L	Initial [Pu] 1100 µg/L	Initial [U] 10000 µg/L	Initial [U] 59000 µg/L	Initial [Np] 1900 µg/L
0.005	1.61	1.069	1.26	1.038	1.022	1.0037	1.002
0.01	4.18	1.147	1.69	1.08	1.045	1.0074	1.004
0.02	>100	1.345	5.37	1.17	1.094	1.0148	1.008
0.03	>100	1.625	>100	1.29	1.148	1.0224	1.012
0.04	>100	2.053	>100	1.42	1.208	1.0301	1.015
0.05	>100	2.786	>100	1.59	1.275	1.0379	1.019

Introduction

Strontium and actinide removal from alkaline waste solutions occurs upon the reduction of permanganate (MnO_4^-) and the precipitation of manganese oxide. Presumably the strontium and actinides either coprecipitate or adsorb onto the freshly precipitated manganese oxide. The mass fraction of strontium and actinides removed by this method depends on a number of parameters including the concentrations of permanganate, reductant, strontium and the actinides. Permanganate concentrations tested to date for Savannah River Site (SRS) waste range from 0.005 molar (M) to 0.05 molar. Reductants tested to date include sodium formate and hydrogen

peroxide. Generally the process requires addition of an excess of reductant to produce complete precipitation of the manganese oxide. Testing completed to date featured both simulated waste solutions and actual tank materials including entrained undissolved solids over a narrow range of strontium and actinide concentrations.

Evaluation of the freshly precipitated manganese oxide process for pretreatment of SRS waste solutions includes the completion of flowsheet calculations to assess the quantities of waste streams sent forward to the Defense Waste Processing Facility (DWPF) and Saltstone facility, a water balance for the Tank Farm and flowrates within the proposed Salt Waste Processing Facility (SWPF) and Actinide Removal facility. This report provides the basis for DFs for strontium and the actinides [plutonium (Pu), neptunium (Np) and uranium (U)] in the manganese oxide treatment process. The DFs derive from testing completed at SRTC with both actual tank waste and simulated waste solutions.

Results and Discussion

Recent testing with radioactive wastes (M. J. Barnes, D. T. Hobbs, M. C. Duff and S. D. Fink, "Strontium and Actinides Removal from Savannah River Site Actual Waste Samples by Freshly Precipitated Manganese Oxide," WSRC-TR-2002-00048, Rev. 2, August 12, 2002.) and simulated wastes (M. C. Duff, D. T. Hobbs and S. D. Fink, "Permanganate Treatment Optimization Studies for Strontium and Actinide Removal from High Level Waste Simulants, "WSRC-TR-2002-00027, Rev. 0, January 14, 2002.) indicates that the quantities of the actinides removed by manganese oxide increase with the quantity of manganese oxide solids. At concentrations of about 1 μ molar or higher, the loading of the actinides (μ mole) on the manganese oxide (grams of MnO_2) reaches a constant value consistent with an apparent maximum loading in single contact batch testing. I determined an average loading for strontium and the actinides from a subset (Second-Generation tests) of the tank waste testing results. (M. J. Barnes, D. T. Hobbs, M. C. Duff and S. D. Fink, "Strontium and Actinides Removal from Savannah River Site Actual Waste Samples by Freshly Precipitated Manganese Oxide," WSRC-TR-2002-00048, Rev. 2, August 12, 2002.) This dataset featured tests using filtered tank waste with both hydrogen peroxide and sodium formate as reductants and with varying reaction times (<24 h). The earlier tests (First-Generation tests) featured unfiltered tank waste and exhibited a higher variability for actinide loadings. Researchers attributed the variability to undissolved actinides in the entrained solids. Thus, the Second-Generation test results appear to represent a more accurate dataset for determining actinide loadings from waste solutions onto the manganese oxide solids.

I also excluded results from tests using simulants. In general, loadings with simulated waste solutions are higher than those measured with tank waste. Thus, the loadings obtained from tests with tank waste samples represent lower and more conservative values. Table II provides the calculated average loading, standard deviation and percent relative standard deviation for ^{90}Sr, uranium, neptunium and plutonium. Total strontium loading proved indeterminate due to dilution of samples below the detection limit by the analytical measurement technique.

Table II. ^{90}Sr and Actinide Loadings with Freshly Precipitated Manganese Oxide

Sorbate	Average Loading	Standard Deviation	% RSD

^{90}Sr	1.51E+05 nCi/g	6.00E+02	0.28
U	2.08E+00 µ mol/g	7.33E-01	35.2
Np	3.50E-02 µ mol/g	1.24E-02	35.5
Pu	3.92E-01 µ mol/g	6.79E-02	17.3

A frequent term used in characterizing the efficiency of radiochemical separation processes is the DF. By definition this term is the value obtained by dividing the initial radionuclide concentration by the final radionuclide concentration. Personnel use this term to calculate mass balances across each process step for decontamination of the waste. Rigorously, the DF should be specified at particular mass concentrations or ranges of mass concentrations since the removal of the component depends on the mass concentrations. This detail is of particular importance when the waste contains more than one isotope of an element. Since the stable isotopes also load onto the solid, a variation in the isotopic distribution directly influences the resulting DF for the radioisotope. For SRS wastes, the isotopic distribution for strontium and plutonium may vary appreciably for waste from different tanks.

In the case of strontium, ^{90}Sr is the radioisotope requiring separation, but significant stable strontium exists from uranium fission as well as that introduced as impurities in processing chemicals (e.g., sodium hydroxide). From fission yield the mass fraction of ^{90}Sr is about 0.38. However, the actual mass fraction will prove lower than this due to the addition of stable strontium. For example, an analysis of a sludge sample (N. E. Bibler, W. F. Kinard, W. T. Boyce and C. J. Coleman, "Determination of Long-lived Fission Products and Actinides in Savannah River Site HLW Sludge and Glass for Waste Acceptance," *J. Radioanal. and Nucl. Chem*., **234** (1998), 159-163.) determined a mass fraction of ^{90}Sr at 0.053, which is well below the fission yield value indicating the presence of a relatively large amount of stable strontium.

Two principal sources exist for the plutonium in SRS high-level waste: weapon grade plutonium composed primarily of ^{239}Pu with smaller amounts of ^{240}Pu and heat source plutonium composed primarily of ^{238}Pu. Weapons grade plutonium originated primarily in F-Area waste tanks and heat source plutonium originated in H-Area tanks. However, mixing of the supernates from both areas occurred over the years of storage and, therefore, waste solutions will contain a mixture of both plutonium sources. Furthermore, assembly of salt solution batches for pretreatment in Salt Waste Processing and Actinide Removal facilities will result in further mixing so that the plutonium activity may vary considerably.(F. A. Washburn, S. G. Subosits, J. A. Pike and S. G. Campbell, "Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives," WSRC-RP-99-00006, Rev. 3, May 2001.)

The specific activities of neptunium and uranium do not present a concern for determining mass balances across radionuclide separation processes. ^{237}Np is the only neptunium isotope in significant quantities in SRS high-level waste. The uranium isotopics can vary significantly. For example, H-Area Separations processed uranium having a wide range of ^{235}U enrichments, whereas F-Area processed primarily depleted uranium. However, the specific

activities of the principal uranium isotopes in SRS wastes are very small. Consequently, uranium does not contribute significantly to the radioactivity of the waste. Uranium is important, however, in determining the efficiency of the separation chemistry, as it can compete with strontium, plutonium, and neptunium reducing the removal efficiencies for these radionuclides.

Flowsheet calculations specify the addition of sodium permanganate to provide a sodium permanganate ($NaMnO_4$) concentration of between 0.005 and 0.05 M. Assuming that all of the permanganate reduces to produce manganese dioxide, MnO_2, the process produces between 0.435 and 4.35 g/L of MnO_2. With this range of MnO_2 solids, we calculated the quantities of strontium and actinides removed on a volume basis using the loadings reported in Table I. I then calculated the treated solution concentration and DFs for each radioactive component and performed the DF calculation over a range of initial component concentrations.

Figures 1 – 3 show plots of the calculated DFs versus initial concentrations for each actinide. The shape of the curve is similar for the three actinides. The DFs are highest when the initial actinide concentration is just greater than the quantity removed at a given permanganate concentration. As the initial actinide concentration increases, the DF decreases rapidly with a smaller fraction of the component removed from solution. At high sorbate concentrations the DFs approach a value of 1 indicating no removal.

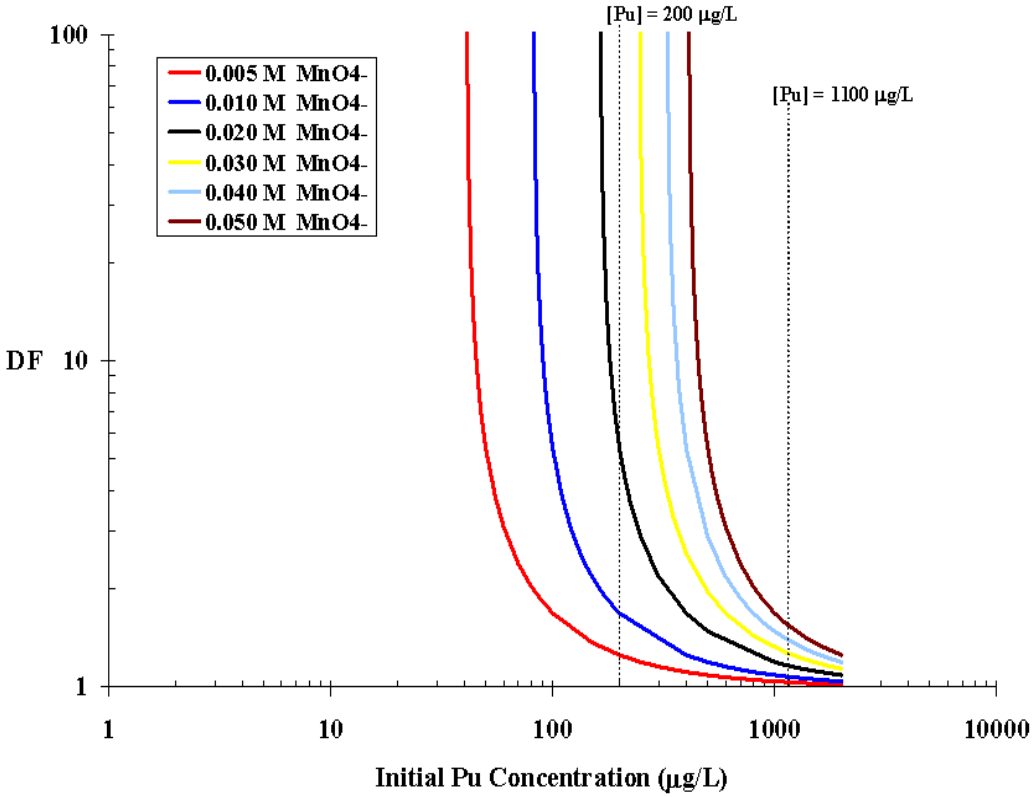

Figure 1. Graph of Calculated DF versus Initial Plutonium Concentration upon Treatment of Waste Solution with $NaMnO_4$

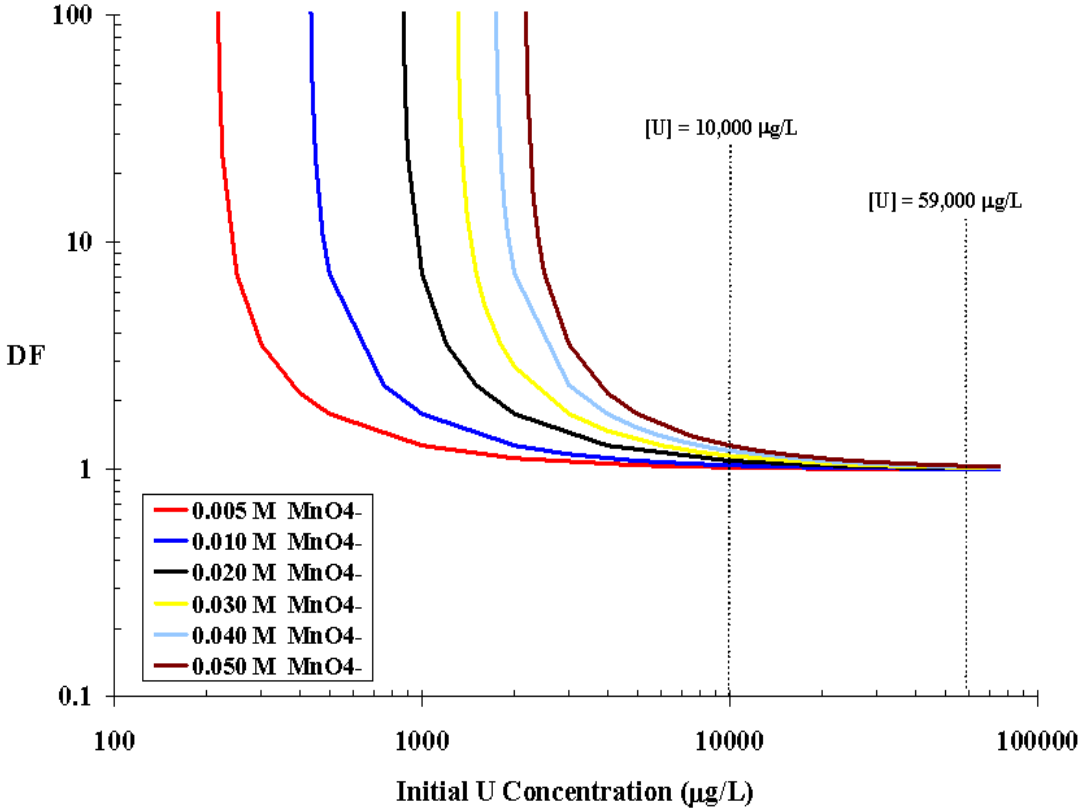

Figure 2. Graph of Calculated DF versus Initial Uranium Concentration upon Treatment of Waste Solution with $NaMnO_4$

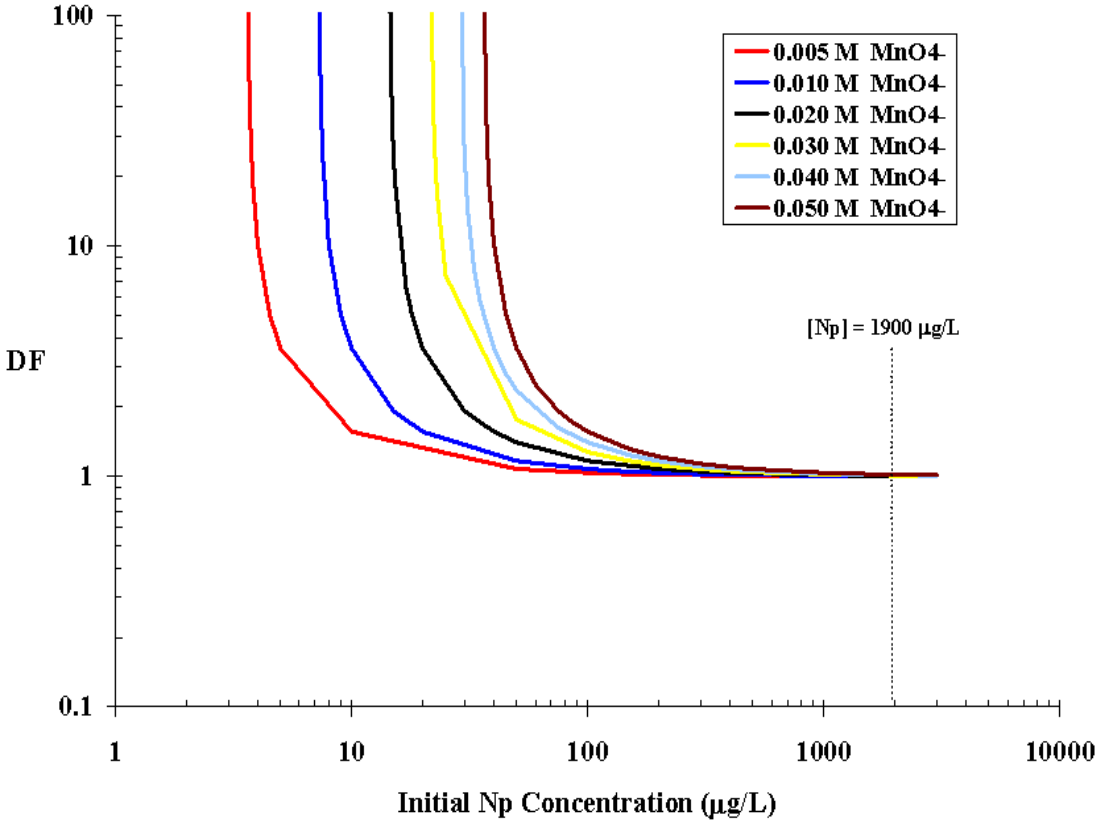

Figure 3. Graph of Calculated DF versus Initial Neptunium Concentration upon Treatment of Waste Solution with $NaMnO_4$

Table III provides the calculated DFs and percentage removal for uranium and the other components of interest. Uranium is typically present in SRS supernates at a concentration between about 1000 and 20000 µ g/L. At the 0.005 to 0.05 M permanganate treatment conditions, the MnO_2 will remove between 216 and 2160 µ g/L uranium. We report DF values for uranium at two cases, 59,000 µ g/L and 10,000 µ g/L. The larger value is the current value calculated by the Speedup Flowsheet model. .(F. A. Washburn, S. G. Subosits, J. A. Pike and S. G. Campbell, "Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives," WSRC-RP-99-00006, Rev. 3, May 2001.) The smaller concentration is more typical of measured uranium concentrations in tank supernate samples. For a uranium concentration of 59,000 µ g/L, the calculated DF ranges from 1.0037 to 1.0379, which represents the removal of between 0.37 to 3.65 wt % of the uranium. At 10,000 µ g/L of uranium, the DF ranges from 1.022 to 1.275 or 2.15 to 21.6 wt % uranium removal.

I determined the neptunium DF value at an initial neptunium concentration of 1900 μ g/L. The current Speedup flowsheet model does not include a term for neptunium. This concentration of neptunium is the bounding neptunium concentration in SRS waste. .(F. A. Washburn, S. G. Subosits, J. A. Pike and S. G. Campbell, "Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives," WSRC-RP-99-00006, Rev. 3, May 2001.) The calculated DFs at this initial concentration ranges from 1.002 to 1.019 at sodium permanganate concentrations ranging from 0.005 to 0.05 M. This represents between 0.20 and 1.86 wt % removal of neptunium. Note that this range of sodium permanganate concentrations fails to provide sufficient removal of neptunium to meet the waste acceptance criterion for Saltstone.

Table III. Recommended Decontamination Factors upon Treatment with 0.005 to 0.05 M $NaMnO_4$

Decontamination Factor

[NaMnO4]	Initial [Sr] 191 nCi/g	Initial [Sr] 1130 nCi/g	Initial [Pu] 200 μg/L	Initial [Pu] 1100 μg/L	Initial [U] 10000 μg/L	Initial [U] 59000 μg/L	Initial [Np] 1900 μg/L
0.005	1.61	1.069	1.26	1.038	1.022	1.0037	1.002
0.01	4.18	1.147	1.69	1.08	1.045	1.0074	1.004
0.02	>100	1.345	5.37	1.17	1.094	1.0148	1.008
0.03	>100	1.625	>100	1.29	1.148	1.0224	1.012
0.04	>100	2.053	>100	1.42	1.208	1.0301	1.015
0.05	>100	2.786	>100	1.59	1.275	1.0379	1.019

Weight Percent Removed

[NaMnO4]	Initial [Sr] 191 nCi/g	Initial [Sr] 1130 nCi/g	Initial [Pu] 200 μg/L	Initial [Pu] 1100 μg/L	Initial [U] 10000 μg/L	Initial [U] 59000 μg/L	Initial [Np] 1900 μg/L
0.005	38.0	6.4	20.6	3.66	2.15	0.37	0.20
0.01	76.1	12.8	40.8	7.41	4.31	0.73	0.40
0.02	>99	25.6	81.4	14.5	8.59	1.46	0.79
0.03	>99	38.5	>99	22.5	12.9	2.19	1.19
0.04	>99	51.3	>99	29.6	17.2	2.92	1.48
0.05	>99	64.1	>99	37.1	21.6	3.65	1.86

I calculated that between 40.8 and 408 μ g/L of plutonium will be removed at a permanganate treatment level of between 0.005 and 0.05 molar. At sodium permanganate additions of 0.03 molar or higher, the quantity of plutonium removed is well above the average waste concentration of 200 μ g/L plutonium resulting in a DF of greater than 100. At lower sodium permanganate treatment levels, the quantity of plutonium removed is below 200 μ g/L resulting in lower DFs. Low DFs are calculated over the entire range of sodium permanganate concentrations at the bounding plutonium concentration of 1100 μ g/L.

Of all the actinides, plutonium removal performance is perhaps the most difficult to predict because of the two different waste sources and possible range of alpha activities and mass concentrations. Weapons grade plutonium represents most of the mass concentration. Heat source plutonium contributes more activity, because of a higher

specific activity. The most challenging condition involves a waste solution containing high concentrations of both weapons grade and heat source plutonium. We evaluated the allowable plutonium activity in the waste solution given initial mass concentrations of 200 and 1100 μ g/L plutonium that when treated with between 0.005 and 0.05 M sodium permanganate would meet the Saltstone waste acceptance criterion of 18 nCi/g. Table IV provides a listing of the allowable plutonium activities. The results indicate that solutions that have appreciable levels of alpha activity will require large amounts of sodium permanganate to meet the Saltstone waste acceptance criterion.

Table IV. Calculated Plutonium Activity in Waste Solutions which when Treated with Sodium Permanganate will Meet the Saltstone Waste Acceptance Criterion

[NaMnO4] (M)	Initial Pu Activity (nCi/g) for Solution having Total [Pu] of 200 μg/L	Initial Pu Activity (nCi/g) for Solution having Total [Pu] of 1100 μg/L
0.005	22.7	18.7
0.01	30.4	19.4
0.02	96.7	21.1
0.03	>1800	23.2
0.04	>1800	25.6
0.05	>1800	28.6

In the actual waste samples treated with permanganate, the non-radioactive strontium concentration fell below the detection limits after the needed dilution to allow for chemical analysis. Hence, that study could not determine the total strontium DFs. However, Barnes, et.al. reported an average ^{90}Sr loading upon addition of sodium permanganate at 1.51E+05 nCi/g (see Table II). (M. J. Barnes, D. T. Hobbs, M. C. Duff and S. D. Fink, "Strontium and Actinides Removal from Savannah River Site Actual Waste Samples by Freshly Precipitated Manganese Oxide," WSRC-TR-2002-00048, Rev. 2, August 12, 2002.) Current estimates for the average and bounding ^{90}Sr activities in SRS waste solutions are 191 and 1130 nCi/g, respectively, at 6.44 M sodium concentration. (F. A. Washburn, S. G. Subosits, J. A. Pike and S. G. Campbell, "Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives," WSRC-RP-99-00006, Rev. 3, May 2001.) Using these activities as the initial concentrations, we calculated DFs for ^{90}Sr over the range sodium permanganate additions (see Table III). Note that these DFs are based only upon the addition of sodium permanganate. Addition of non-radioactive (stable) strontium such as strontium nitrate, $Sr(NO_3)_2$, will produce higher ^{90}Sr removal by precipitation of the strontium primarily as strontium carbonate. The addition of 0.01 molar stable strontium (876,000 μ g/L) would be sufficient to raise the concentration of strontium well above its solubility limit and precipitate the bulk of the strontium. The exact solubility of strontium will depend on the solution composition, of particular importance is the carbonate concentration. For a combined treatment process employing both 0.01 M strontium addition and sodium permanganate addition (0.005 to 0.05 M), we recommend using a DF of 30 for flowsheet modeling calculations.