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Permanganate Treatment of Savannah River Site Simulant Wastes for Strontium and Actinide Removal

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ACRONYMS AND ABBREVIATIONS

HLW	High Level Waste
HS	Heat Source (i.e., mostly ^{238}Pu)
H_2O_2	Hydrogen Peroxide
ICP-MS	Inductively-Coupled Plasma Mass Spectrometry
M	Moles per Liter
Mn	Manganese
MnO_4^-	Permanganate Ion
MST	Monosodium Titanate
Na	Sodium
$Na_4Mn_{14}O_{27}\bullet 9H_2O_{(s)}$	Sodium Birnessite
Np	Neptunium
Pu	Plutonium
Sr	Strontium
$SrCO_{3(s)}$	Strontium carbonate
SRS	Savannah River Site
SRTC	Savannah River Technology Center
WAC	Waste Acceptance Criterion
WG	Weapons Grade (i.e., mostly ^{239}Pu)
WPTS	Waste Processing Technology Section
WSRC	Westinghouse Savannah River Company
ARP	Alpha Removal Program
SWPF	Salt Waste Processing Facility
TTA	ThenoylTrifluoroAcetone
DFs	Decontamination Factors
TRU	TransUranicWaste

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ABSTRACT

This study examined the use of sodium permanganate and strontium nitrate to remove the actinides and radio-strontium from Savannah River Site (SRS) waste supernate. We examined the quantities of chemical feed reagents along with increased mixing and the excess of organic reductant. Additionally, we examined two processing schemes including that applicable to either the Salt Waste Processing Facility or the Alpha Removal Process (ARP) (5.6 M sodium ion concentration) conditions and the conditions for an In-Tank application (7.5 M sodium ion concentration). Our results support the following conclusions:

- The process met minimum required decontamination factors (DFs) within the tested parameter sets for strontium and plutonium in both the ARP and In-Tank application. The strontium DFs far exceeded the required values within the tested parameter sets.
- Within the ARP application, the use of peroxide as the reductant for permanganate produced higher plutonium DFs than the use of sodium formate.
- Reductant concentration and degree of mixing strongly influenced radionuclide decontamination. In the formate application under the ARP process, increasing the reductant concentration and mixing energy resulted in higher Sr and Pu decontamination.

INTRODUCTION

Project personnel identified the slow kinetics of actinide removal by treatment of Savannah River high-level waste using monosodium titanate as a technology risk for implementation in the Salt Waste Processing Facility.[1] Table 1 provides processing requirements for the removal of radiostrontium and the transuranic (TRU) elements that emit alpha activity. Since spike simulants are being used in this testing, decontamination factors (DF) of 5 and 12 are required for strontium and the transuranic actinides, respectively, at initial concentrations of 100 μg/L Sr, 200 μg/L ^{239}Pu, 10 mg/L U and 400 μg/L ^{2379}Np.[2] Studies in support of strontium and transuranic (Sr/TRU) removal for the Hanford wastes showed that an isotopic dilution with natural strontium and permanganate reduction proved effective at removing the Sr/TRU constituents and could potentially produce the required decontamination in SRS wastes.[3]

Table 1. Radionuclide Removal Requirements

Radionuclide	Requirement
^{90}Sr	< 40 nCi/g
Total alpha	< 18 nCi/g
Np	< 0.03 nCi/g

Work performed by Barnes,[4] et al., and Duff,[5] et al., with Savannah River actual waste samples and simulants showed the permanganate treatment removed the strontium and transuranic constituents but decontamination was not as efficient in actual waste testing. Also, tests did not give highly reproducible results. Results showed that formate or peroxide effectively reduced the permanganate. Reaction of the formate occurred slowly at low concentration (0.01 M), requiring as long as 24 hours to complete. Studies by Krot et al. (1998) indicate that the reduction of permanganate by peroxide to Mn(IV) oxide is nearly instantaneous whereas the reduction of permanganate by formate is slower due because the Mn(VII) is slowly converted by formate to Mn(IV) via single electron reduction steps.[6] We believe we may overcome this slow oxidation of formate by either increasing the formate concentration or elevating the temperature. Hence personnel developed an alternate recipe using higher reagent concentrations.[7] and successfully demonstrated the process with actual waste.[8]

While conducting similar experiments in support of the development of a Sr/TRU decontamination process for the Hanford Waste Treatment Plant, SRS researchers observed rapid kinetics with minimal reagent additions.[3,8] Therefore, personnel completed a series of tests to further explore the permanganate reduction process for Sr/TRU decontamination of SRS wastes. The primary parameters of that work included strontium and permanganate levels, concentration of organic reductant, and degree of mixing. The tests used organic concentrations levels based on a stoichiometric amount (1X) being equivalent to 1.5 times the permanganate concentration in molar units. The testing showed that good mixing is vital to promote a rapid interaction between the organic reductant and the permanganate ion. Secondly, a high reductant concentration provides for rapid permanganate reduction facilitating actinide removal.

EXPERIMENTAL DETAILS

The research program aims at identifying conditions where the reduction of permanganate is relatively quick with the minimal amount of reductant used while minimizing the amount of manganese sent for vitrification. Testing examined two deployment strategies. The first used the permanganate flowsheet at conditions applicable to the Salt Waste Processing Facility or the Actinide Removal Process in 512-S facility. This deployment adds the reductant and the permanganate to waste containing ~ 5.6 M sodium ion. The second deployment, applicable for an in-tank strategy, assumes a sodium ion concentration in excess of 7 M. Deploying a permanganate treatment in the large source tanks for waste containing relatively low soluble actinides and strontium could allow for the direct disposal of waste through the Saltstone Production Facility. This would avoid the need to process the material through the Actinide

Removal Process in Building 512-S. Similarly, such a first treatment on waste containing high concentrations of actinides could reduce the processing burden for monosodium titanate in either the Salt Waste Processing Facility or the Actinide Removal Process. Presumably, deployment in the large tanks would use either existing slurry pumps or Flygt mixers to mix the chemical feeds that will be added directly into the tank. Also, we omitted peroxide as a reagent for this deployment because of perceived safety- and corrosion-based concerns about the direct addition of a high volume of peroxide to carbon steel tanks.

For these tests, we prepared an SRS simulant using the recipe from prior studies.[5] Technicians added radioactive tracer of ^{85}Sr, ^{238}U, ^{237}Np and ^{239}Pu to the simulant. Appendix 1 contains the concentration of the reagents for making the stimulant. Personnel analyzed the solution to determine the concentration of analytes in the spiked simulant solutions. Initial analyses include only Pu and ^{85}Sr until we judged the solution reached equilibrium. Personnel then added peroxide after permanganate and strontium nitrate were well mixed in the solution. For the formate test, personnel added permanganate after sodium formate was well mixed in the solution.

Table 2 lists the tests scheduled for the 5.6 M solution. Table 3 lists the tests for the In-Tank deployment with sodium ion concentrations of 7.5 M. For the In-Tank deployment tests, we used a syringe pump to deliver the permanganate solution at a scaled rate to the liquid surface containing the formate as the reductant. When using peroxide as the reductant, we added the permanganate solution to the waste simulant prior to the addition of the reductant. We added formate to the waste prior to treating with permanganate.

Table 2. Test Matrix for ARP-related Sr/TRU Removal

5.6 M Sodium ARP Support Tests(Reductant Level 1X=stoichiometric and 3x= 3 times stochiometric)

Test No.	Mn (M)	Reductant Choice	Reductant Level	Sr (M)	Mixing	Temp (°C)
1	0.01	Peroxide	1x	0	Stir bar	25
2	0.01	Peroxide	1x	0.005	Stir bar	25
3	0.01	Peroxide	1x	0.01	Stir bar	25
4	0.01	Peroxide	3x	0	Stir bar	25
5	0.01	Peroxide	3x	0.005	Stir bar	25
6	0.01	Peroxide	3x	0.01	Stir bar	25
7	0.03	Peroxide	1x	0	Stir bar	25
8	0.03	Peroxide	1x	0.005	Stir bar	25
9	0.03	Peroxide	1x	0.01	Stir bar	25
10	0.03	Peroxide	3x	0	Stir bar	25
11	0.03	Peroxide	3x	0.005	Stir bar	25
12	0.03	Peroxide	3x	0.01	Stir bar	25
13	0.03	Formate	1x	0	Stir bar	25
14	0.03	Formate	1x	0	orbital	25
15	0.03	Formate	1x	0.01	Stir bar	25
16	0.03	Formate	3x	0	Stir bar	25
17	0.03	Formate	3x	0	orbital	25
18	0.01	Formate	3x	0.01	Stir bar	25
19	0.01	Formate	3x	0.01	orbital	25
20	0.03	Formate	1x	0	Stir bar	45
21	0.03	Formate	1x	0.01	Stir bar	45
22	0.03	Formate	3x	0	Stir bar	45
23	0.01	Formate	3x	0.01	Stir bar	45

Tests used ~ 50 mL of simulant. Personnel collected samples after 4 hours and submitted for gamma analysis and plutonium- triphenyltrifluoroacetone (Pu-TTA) analysis. In performing the plutonium analyses, personnel performed a TTA separation. They spiked an aliquot of the sample with a ^{238}Pu tracer. All of the plutonium in the sample was reduced; an anion complexing agent (aluminum nitrate) was then added. The plutonium in the sample was then oxidized to a +4 oxidation state. The plutonium(IV) was then extracted from the matrix using a TTA solution. The TTA layer was mounted in a counting dish and analyzed by alpha spectroscopy. A blank sample was run with the batch of samples.

For the elevated temperature tests, we heated the salt solution to the designed temperature and added the appropriate reagents. After mixing at temperature for 4 hours, we cooled the mixtures to ambient laboratory temperature and filtered through 0.45 μm nylon membrane filter.

We used the calculated decontamination factors (DFs) along with the variable parameter values from the tests in the JMP Statistical software package[9] (version 4.0.4) for model regression. We selected models using a centered polynomial function to ensure proper identification of statistically significant variables. After identifying these variables, we obtained coefficient estimates using a linear model. Because many tests included a large excess of organic reductant, we corrected the measured DF for the volume dilution.

Table 3. In-Tank Deployment Test Matrix

Test No.	Mn (M)	Reductant Level	Sr (M)	Temp (°C)
1	0.01	3X	0	35
2	0.01	3X	0	45
3	0.03	5X	0.005	35
4	0.03	5X	0.005	45
5	0.01	5X	0.01	45
6	0.01	5X	0	45
7	0.03	3X	0.01	35
8	0.03	3X	0.005	45
9	0.03	1X	0.01	35
10	0.03	1X	0.01	45
11	0.01	1X	0.005	35

Reductant Level: 1X=Stochiometric and 3X= 3 times stoichiometric

RESULTS AND DISCUSSION

Salt Waste Processing Facility and Actinide Removal Process: Peroxide Reductant

The Salt Waste Processing Facility and the Actinide Removal Project assume a baseline of 5.6 M sodium ion concentration and use monosodium titanate as the Sr/TRU sorbent. This testing employed an addition of strontium nitrate followed by the reduction of sodium permanganate with one of two organic reducing agents: hydrogen peroxide or sodium formate. In the experiments with peroxide, we added the permanganate to the waste simulant prior to peroxide addition. This step minimized foaming during peroxide addition. Conversely, in the experiments with formate, we added the formate prior to the permanganate. This step made the stimulant resemble Hanford complexant waste.

Figure 1 shows the plutonium model developed from the data (Table 2) from the tests (5.6 M sodium ion concentration) using peroxide as the reductant. Appendix 1 contains the data measured during all of our experiments. The model has a correlation coefficient (R^2) of 0.68 and the data scatters randomly through the model range. Plutonium decontamination factors (Pu DFs) ranged from 1 (or no decontamination) to 95 after a 4 hour reaction time. The lowest value of Pu DF occurred with the addition of 0.01 M permanganate and 1X organic reductant. Conversely, the highest DF of 95 occurred with 0.03 M permanganate and 3X organic reductant.

Table 4 contains the statistical analysis of the modeling effort. The statistically meaningful model takes the following form:.

$$DF_{Pu} = 79.8 - 3680 * [Mn] - 27.1 * \text{Red Level} + 1980 * [Mn] * \text{Red Level}$$

Two variables proved statistically significant at 95% confidence (i.e., a probability of the value exceeding the t-test, Prob.>$|t|$, less than 0.05): the amount of sodium permanganate added to the system and a cross term of the molar level of sodium permanganate added and the reductant level. The model shows the strong positive effect of a coupled permanganate-reductant interaction. This cross term supports the theory that the decontamination needs a large excess of reductant to accelerate the reduction of permanganate.

Note that the plutonium removal does not (statistically) depend on the addition of strontium nitrate. Hence, the precipitation of strontium solids carries notable less plutonium – either by sorption or by coprecipitation – than the precipitating manganese solids. Inspection of the data revealed that the presence of Sr and not in excess amount is required for Pu DF. This onset effect of Sr on Pu DF is not statistically detected since the effect is not dependent on Sr concentration.

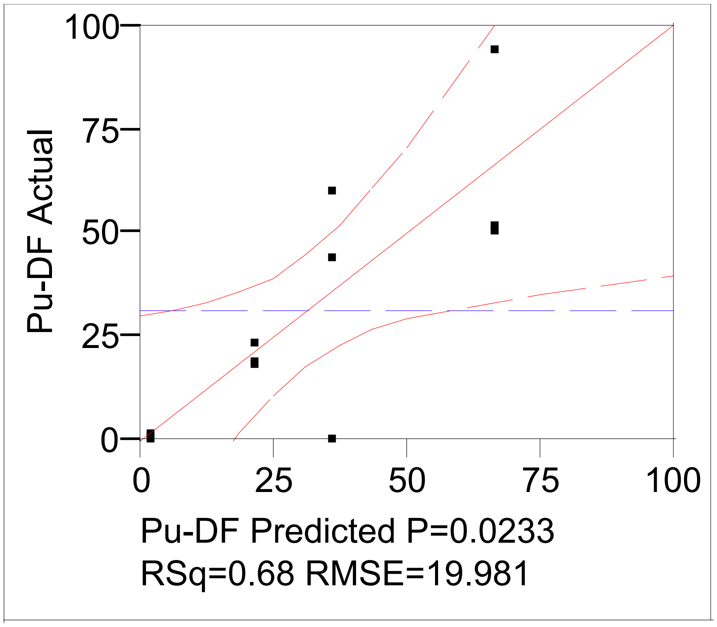

Figure 1. Plutonium Model for Peroxide Reduction using Simulated 5.6 M Sodium Waste

Table 4. Plutonium Model for Peroxide Reduction using Simulated 5.6 M Sodium Waste Parameter Estimates.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	79.8	28.8	2.77	0.0244
$NaMnO_4$	-3680	1290	-2.85	0.0214
Red Level	-27.1	12.9	-2.10	0.0685
$NaMnO_4$*Red Level	1980	580	3.43	0.0089

Figure 2. Effect of Strontium on the Reduction of Permanganate

The level of strontium added to the system was not statistically significant since the effect is due to the presence of Sr and it is not proportional to the amount of Sr in solution. Polynomials can not fit step changes in Pu DF behavior with Sr. However, experimental observations indicate that the presence of strontium precipitate was important as shown in Figure 2. These flasks contain solution from experiments numbered 1 and 2. These tests included the addition of 0.01 M sodium permanganate to a 5.6 M sodium salt solution followed by the addition of a 1X addition of peroxide as the reductant. In the test labeled number 1, we omitted the strontium nitrate and decontamination for plutonium did not occur (Pu DF = 1). However, in the test labeled number 2 (in Figure 2), we added 0.05 M strontium nitrate prior to the addition of permanganate and peroxide obtaining a Pu DF of 61. It is clear from Figure 2 that in test number 1 the permanganate did undergo completely reduction as is evidenced by the blue color of Mn(V). We did not determine the length of time the solution retained its blue color.

Figure 3 shows the model for permanganate-peroxide decontamination of strontium using 5.6 M sodium waste. The model more closely replicates the data and exhibits a correlation coefficient (R^2) of 0.89. Under all conditions tested with sodium permanganate and peroxide in the 5.6 M salt solution, strontium decontamination occurred rapidly and with high efficiency. The Sr DFs ranged from 39 to ~ 4000. Table 5 includes parameter estimates for the model.

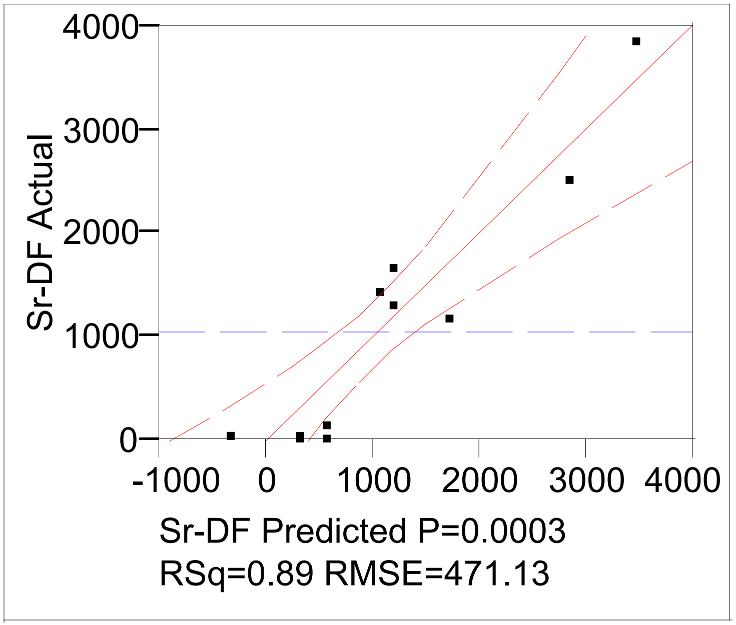

Figure 3. Sr Model for Peroxide Reduction using Simulated 5.6 M Sodium Waste

Table 5. Sr Model for Peroxide Reduction using Simulated 5.6 M Sodium Waste

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2920	360	8.11	<.0001
$Sr(NO_3)_2$	-1.84E5	2.89E4	-6.37	0.0002
Red Level	-323	136	-2.38	0.0447
$(Sr(NO_3)_2-0.007)*(NaMnO_4-0.02)$	1.32E7	2.89E6	4.58	0.0018

Several factors in Table 5 are statistically significant including: the strontium nitrate concentration, the organic reductant concentration, and a cross term between the strontium and permanganate concentrations. The model's equation is shown below:

$$DF_{Sr} = 2920 - 1.84E5 * [Sr(NO_3)_2] - 323 * \text{Red Level} + 1.32E7 * ([Sr(NO_3)_2] - 0.007) * ([NaMnO_4] - 0.02)$$

Due to the large value of the intercept in this model, the strontium nitrate term and the reductant level have negative estimates. The cross term involving the strontium and permanganate does, however, strongly indicate that manganese is involved in the strontium decontamination. Wilmarth, et al.,[3] found a similar behavior for manganese in the strontium removal from Hanford's complexant concentrate waste. Hence, strontium removal appears to occur by two mechanisms: through isotopic dilution and precipitation effected by added strontium nitrate as well as by sorption or precipitation effected by reduction of the permanganate.

Salt Waste Processing Facility and Alpha Removal Process: Formate Reductant

Duff, et al.,[5] previously examined the use of sodium formate as the reductant and formate offers a reaction basis similar to the Hanford process since the organic reductant is dissolved in solution prior to addition of sodium permanganate solution. Therefore, we performed a series of experiments to examine the effects of reductant level, permanganate level, and temperature on decontamination of the feed (5.6 M sodium). We allowed the heated solutions to cool to room temperature before sampling. The cooling effect may have dissolved $SrCO_3$ particles and released sorbed actinides. We can not quantify the impact of cooling on the resulting data. Thus, models which contain temperature terms are confounded with the effects resulting from allowing the test mixture to cool before sampling.

Note that 4 of the 11 experiments occurred at an elevated temperature (i.e., 45 °C) outside the current conceptual design for either the Actinide Removal Process or the Salt Waste Processing Facility. The reader may view these as intending to examine the ability to expand the capacity of the facilities without additional capital investment. Also, the reader is cautioned that the modeling effort is fundamentally shifted from the work on peroxide. By not including Temperature as a variable in the peroxide study, we implicitly assumed that the peroxide induced reduction of permanganate would occur extremely rapidly, would serve as the dominant mechanism for decontamination, and that heating would offer little value to speed the reaction. The modeling work for peroxide confirm these assumptions relative to plutonium but suggest that improved strontium performance may result had higher temperature been used (since strontium carbonate, a presumed precipitate from addition of strontium, shows retrograde solubility with temperature).

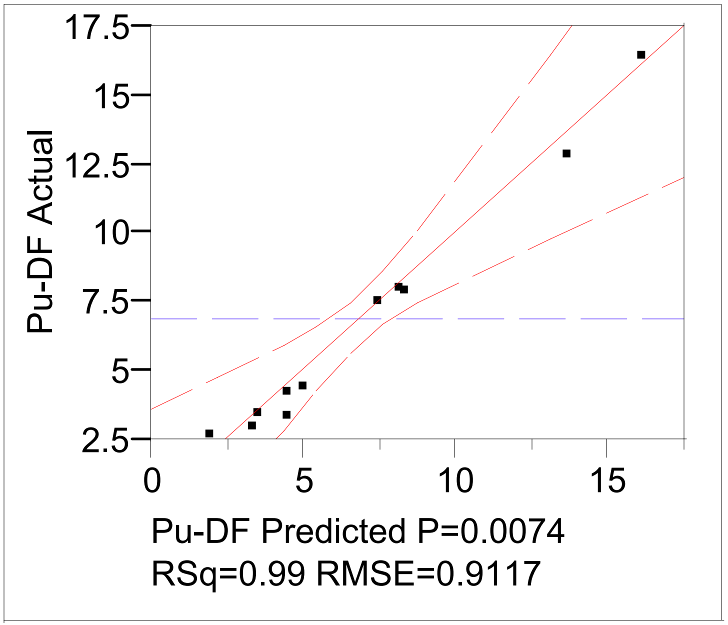

Figure 4. Pu Model for Formate Reduction using Simulated 5.6 M Sodium Waste

Figure 4 shows the plutonium model for the formate reduction of permanganate using simulated waste containing 5.6 M sodium. The plutonium decontamination factors ranged from 2.5 to above 16. These decontamination factors are significantly lower than those resulting from the peroxide reduction. However, observations indicated that reduction of the permanganate completed in the 4 hour reaction period (i.e., all filtrates after 4 hours appeared clear). The model generated from this data set had a correlation coefficient (R^2) of 0.99.

Table 6 includes the model parameter estimates for the formate reduction tests. Four primary effects prove statistically significant including: the strontium concentration, the reductant concentration, mixing level, and temperature. Two other cross terms proved significant at the 95% level: the term involving Sr and mixing as well as the term involving Sr and temperature. The primary variable of permanganate concentration is not significant for this data set, in strong contrast to the findings for peroxide. This indicates that at the levels tested (0.01 M and 0.03 M) insufficient variation in the response variable (Pu DF) exists. Hence, in these tests the strontium chemistry dominated the removal of plutonium, likely through a co-precipitation mechanism. Formate reduction proves much less effective in rapidly reducing permanaganate in a manner the effects plutonium removal.[6] The statistically significant variables are included in the model equation as shown below:

$$\begin{aligned}
&DF_{Pu} = 18.1 - 117.2 \times [Sr] + 0.49 \times [\text{Reductant Level}] - 0.41 \times [\text{Temperature}] \\
&- 117.5 \times [\text{Sr - 0.005}] \times [\text{Reductant Level - 2}] \\
&+ [\text{Sr - 0.005}] \times [\text{273.5 if no mixing or - 273 if there is mixing}] \\
&+ 34.2 \times [\text{Sr - 0.005}] \times [\text{Temp - 33}] + [\text{-3.2 if no mixing or 3.2 if} \\
&\text{there is mixing}]
\end{aligned}$$

Table 6. Pu Model for Formate Reduction using Simulated 5.6 M Sodium Waste

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	22.6	1.61	14.05	0.0008
$Sr(NO_3)_2$	-1005	245	-4.10	0.0263
Red Level	1.23	0.372	3.31	0.0453
$Sr(NO_3)_2$*Red Level	-133	58.8	-2.27	0.1083
Mixing[0]	-4.33	0.456	-9.49	0.0025
$Sr(NO_3)_2$*Mixing[0]	250	75.6	3.31	0.0455
Temp	-0.58	0.0456	-12.78	0.0010
$Sr(NO_3)_2$*Temp	34.3	6.45	5.31	0.0130

Figure 5 shows the model for strontium decontamination using sodium formate as a reductant for sodium permanganate. The model shows a very strong bias to a single point with a very high measured decontamination factor. For this reason, we generated a second model without this point with Table 7 containing these parameter estimates. The equation for this model is shown below:

$$DF_{Sr} = 8690 - 8.41E5 * [Sr(NO_3)_2] + 2.73E4 * (Temp\text{-}33\ °C) * ([NaMnO_4] - 0.024) + 310 * (Temp\text{-}33\ °C) * (Red\ Level - 2)$$

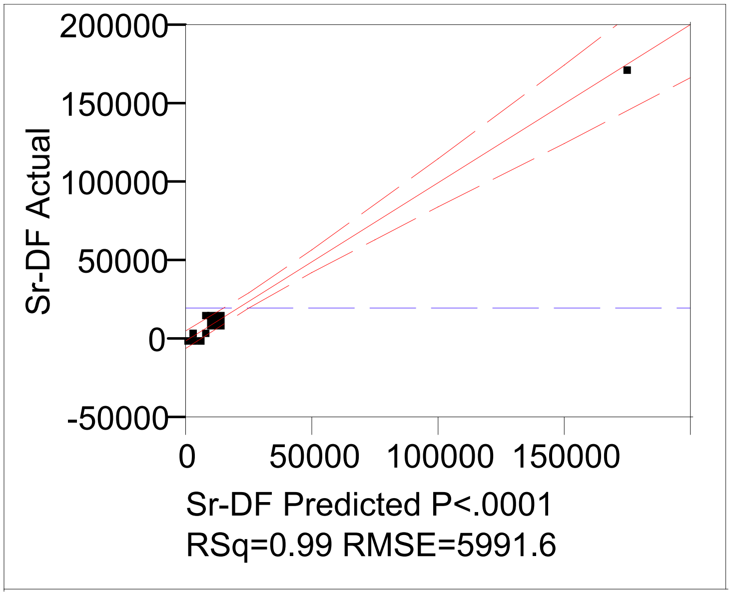

Figure 5. Sr Model for Formate Reduction using Simulated 5.6 M Sodium Waste

The new model of the decontamination of strontium from the 5.6 M sodium feed using an addition of strontium nitrate and sodium formate to reduce sodium permanganate includes terms in the model. The first term is the amount of strontium nitrate. The strontium decontamination model for the formate reduction is very similar to the peroxide in that the magnitude of the Sr term is large and negative. This indicates that low levels of strontium are advantageous and that higher levels do not significantly assist in further decontamination. Two temperature cross terms appear in the model. The first involving the permanganate concentration and the second involving the reductant level. These two terms influence the amount of strontium removed via the manganese solids sorption or co-precipitation along with the temperature effect on the solubility of strontium carbonate. In general, both strontium models agree in the 5.6 M sodium feed and indicate two mechanisms are occurring: isotopic dilution and manganese sorption/co-precipitation.

Table 7. Sr Model for Formate Reduction using Simulated 5.6 M Sodium Waste

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	8690	1075	8.08	0.0002
$Sr(NO_3)_2$	-8.41E5	1.52E5	-5.52	0.0015
(Temp-33)*($NaMnO_4$-0.024)	2.73E4	1.10E4	2.47	0.0482
(Temp-33)*(Redu-Level-2)	310	100	3.08	0.0217

In-Tank Application Permanganate Treatment Process

To examine the effectiveness at high sodium ion concentrations, we performed tests using a 7.5 M sodium salt solution, followed by the addition of sodium formate as a reductant, and finally sodium permanganate. We sampled the reaction system after four hours and analyzed for soluble strontium and plutonium. Table 3 contains the experimental design for these tests.

Figure 6 shows the plutonium model from the formate reduction of permanganate under In-Tank conditions (7.5 M sodium). The model replicates the data well over the response space and possesses a high correlation coefficient. The Pu DFs ranged from 1 to 9.2 at the 7.5 M sodium level. Table 8 contains the parameter estimates. The plutonium decontamination model takes the form of the following:

$$\begin{aligned} DF_{Pu} = {} & 6.98 + 224 * [NaMnO_4] - 0.242 * \text{Red Level} - 0.19 * \text{Temp} \\ & - 25.4 * ([NaMnO_4] - 0.021)*(\text{Temp} - 40.5) \\ & + 0.104 * (\text{Red Level} - 3.2)*(\text{Temp} - 40.5) \end{aligned}$$

Several terms influence the plutonium decontamination including the primary variables of permanganate, reductant level and temperature. The effect of permanganate addition is as expected with the higher level of addition leading to a higher decontamination. The amount of reductant does not appear to have much of effect differing from the experimental results at 5.6 M sodium ion concentration. Temperature, also, is not a strong influence on the removal of plutonium. The other terms included in the model and are a cross term of permanganate and temperature and a cross term involving the reductant level and temperature. It appears that the higher ionic strength (starting less than 5.6 M) reduces the dependency on reductant and temperature to effect a rapid reduction of the permanganate ion. Possibly the stability of the permanganate is lower at 7.5 M sodium compared to 5.6 M sodium ion.

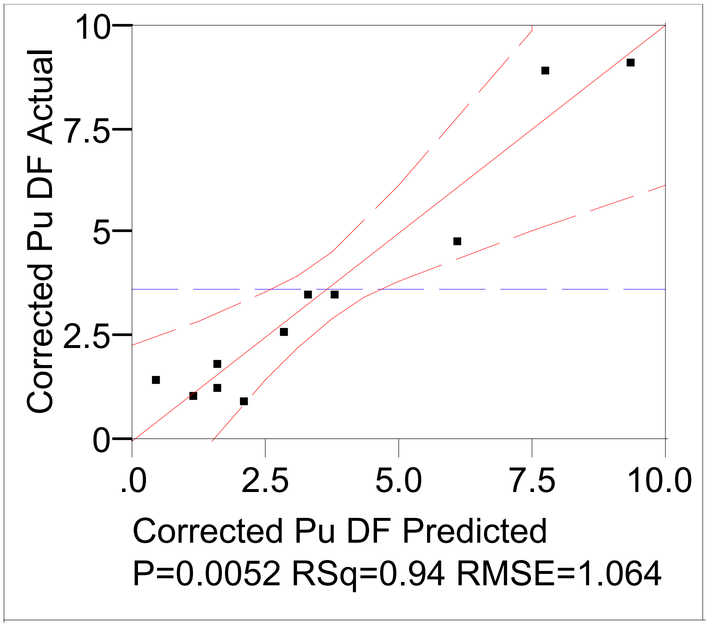

Figure 6. Pu Model for In-Tank Permanganate Treatment (7.5 M Sodium Waste)

Table 8. Pu Model for In-Tank Permanganate Treatment (7.5 M Sodium Waste)

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	6.98	2.88	2.42	0.0599
$NaMnO_4$(M)	224	35.3	6.35	0.0014
Reductant Level	-0.242	0.23	-1.03	0.3492
Temp(C)	-0.190	0.070	-2.73	0.0413
($NaMnO_4$(M)-0.021)*(Temp(C)-40.5)	-25.4	7.07	-3.60	0.0156
(Reductant Level-3.2)*(Temp(C)-40.5)	0.104	0.047	2.22	0.0768

Figure 7 and Table 9 show the performance of the strontium model and estimated parameters. The model is somewhat limited since the data is weighted by a data point with a Sr DF ~9000. Note, however the model exhibits a high correlation coefficient. Three primary terms are statistically significant and are cross terms involving the four tested variables. The model's equation is shown below:

$$
\begin{aligned}
DF_{Sr} = 507 &+ 7.15E7 * ([NaMnO_4] - 0.012)*([Sr(NO_3)_2] - 0.0055) \\
&+ 2.02E5 * (\text{Red Level} - 3.18)*([Sr(NO_3)_2] - 0.0055) \\
&+ 7.82E4 * ([Sr(NO_3)_2] - 0.0055)*(\text{Temp} - 40.5)
\end{aligned}
$$

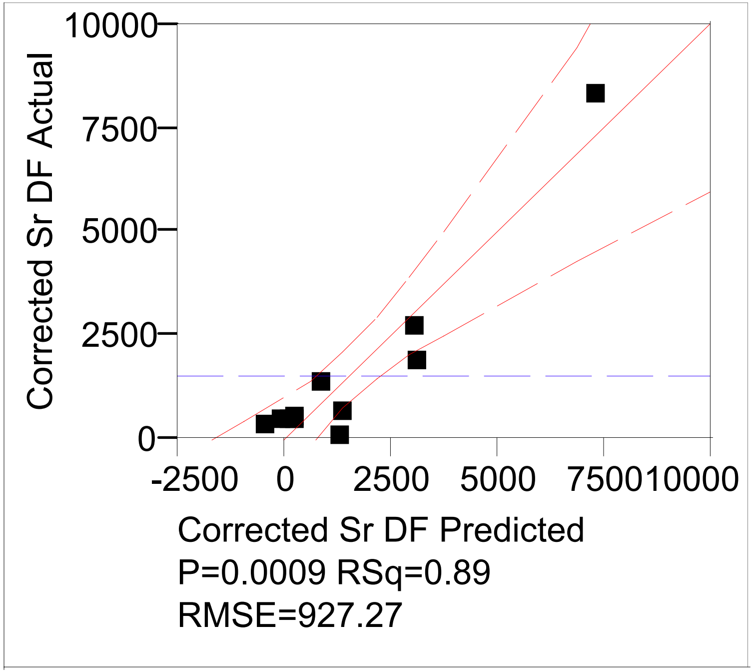

Figure 7. Sr Model for In-Tank Permanganate Treatment (7.5 M Sodium Waste)

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	507	336	1.51	0.1754
($NaMnO_4$(M)-0.021)*($Sr(NO_3)_2$(M)-0.0055)	7.15E7	1.06E7	6.74	0.0003
(Red Level-3.18)*($Sr(NO_3)_2$(M)-0.0055)	2.02E5	6.59E4	3.07	0.0180
($Sr(NO_3)_2$(M)-0.0055)*(Temp(C)-40.5)	7.82E4	1.58E4	4.93	0.0017

Table 9. Sr Model for In-Tank Permanganate Treatment (7.5 M Sodium Waste)

The strontium decontamination model clearly indicates that removal is accomplished via two mechanisms. The first involves a simple isotopic dilution and strontium solubility and the second involves co-precipitation/sorption onto manganese oxide surfaces.

CONCLUSIONS

The models developed for the removal of strontium and plutonium from simulated waste solutions show that several of the tested variables influence radionuclide removal. The same level of each of the tested variables may not support simultaneous removal of strontium and plutonium. Likewise, due to the differences in ionic strength and chemical activity, the tested variables may influence the decontamination differently at higher sodium concentrations.

Therefore, Table 10 shows a compilation of the variables that influence strontium and plutonium removal for both the ARP, the SWPF, and In-Tank applications of the SRS Sr/TRU permanganate flowsheet. It is recognized that the models present in this report are generated from only a very few number of tests and that larger, more complete experimental designs could improve the model's predictive capability. However, the data presented in Table 10 does provide general insights the process chemistry. The optimal process and reagent levels were generated from maximizing models.

Table 10. Decontamination Comparisons for ARP and In-Tank Applications

Permanganate Treatment using Simulated 5.6 M Sodium Waste

Peroxide Reduction

	Sr Level	Mn Level	Reductant
Sr DF	Low	Low	Low
Pu DF		High	High

Formate Reduction

	Sr Level	Mn Level	Reductant	Mixing	Temp
Sr DF	Low	High	High		High
Pu DF	Low		High	High	Low

In-Tank Permanganate Treatment (7 M Sodium Waste)

	Sr Level	Mn Level	Reductant	Temp
Sr DF	Low	Low		Low
Pu DF		High	Low	Low

In the peroxide testing, three variables were examined (Strontium, Permanganate and Reductant levels). To maximize strontium decontamination, the models indicates one would keep each of the variables to their lowest levels tested. Conversely, to maximize plutonium decontamination, the opposite extremes of the levels of the tested variables are required with the exception of strontium addition. This dichotomy may help explain previous test results. Since reaching the required decontamination factor for strontium has not proven difficult in the peroxide tests report herein and the plutonium decontamination factors surpassed requirements, these data suggest that reagents levels of 0.005 M strontium nitrate, 0.02 M sodium permanganate, and 2X reductant (peroxide) concentration would accomplish the required radionuclide decontamination.

The data from the tests employing sodium formate as the reduction examined the same variables as the peroxide tests but also included mixing and temperature. Counter to the peroxide reduction results, the formate results mostly show agreement between the process parameter influence and the response (Sr or Pu DF) except for temperature. For maximum decontamination, the strontium level should be low, reductant level should be high and the permanganate level high for Sr DF (not statistically significant for Pu DF). The two decontamination models, however, differ with respect to temperature. Since the range includes relatively low plutonium DF, a lower process temperature would aid in obtaining Pu DF and not adversely affect Sr DF. Therefore, process conditions would be 0.005 M Sr, 0.03 M MnO_4^-, 25 °C, reductant level at 3 times the permanganate level, and high level of mixing.

For an In-Tank application of the sodium formate reduction process (see results in Table 10), the testing indicates that strontium nitrate addition influences only the Sr DF but permanganate addition affects Sr and Pu DF. Additionally, the maximum radionuclide decontamination occurs under opposite levels for Sr DF (Mn level low) and Pu DF (Mn level high). Under the high ionic strength of these test matrices, the dependence on reductant levels (concentration) is reduced. Lastly, for both radionuclides, the precipitation temperature should be maintained at the lower value (25 °C). The optima process and reagent level would be 0.005 M Sr, 0.03 M Mn, reductant level at 1 times the permanganate level, and 25 °C.

In conclusion, the test results show several factors influence the degree to which the radionuclides are removed. However, with regards to the two premises that are proposed in this work (mixing and degree of excess of organic reductant), both conditions appear to be statistically significant. The higher the degree of mixing and the higher the excess of organic reductant studied in these tests, in general, the higher the decontamination factors.

QUALITY ASSURANCE

The following documents govern the work reported in this document.

- D. T. Hobbs, T. B. Peters, M. J. Barnes, M. C. Duff and K. M. Marshall, "Task Technical and Quality Assurance Plan for FY01 Strontium and Actinide Removal Testing," WSRC-RP-2001-00188, Rev. 1, July 31, 2001.

- Savannah River Site Salt Processing Project: FY 2002 Research and Development Program Plan, PNNL-13707, Rev. 1, December 2001.
- Data is kept in notebook # "WSRC-NB-2002-00141" titled "SRS Sr TRu".

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Appendix 1. Simulated Waste Solution 5.6 M Na.

Component	Solution Concentration (M)
Free NaOH	1.33
Total $NaNO_3$	2.6
$NaAL(OH)_4$	0.429
$NaNO_2$	0.134
Na_2SO_4	0.521
Na_2CO_3	0.026
U^{238}	4.2E-5
Pu^{239}	9.5E-7
Np^{237}	2.1E-6
Sr^{85}	Tracer Amounts

Simulated Waste Solution 7.5 M Na

Component	Solution Concentration (M)
Free NaOH	2.33
Total $NaNO_3$	3.05
$NaAL(OH)_4$	0.429
$NaNO_2$	0.584
Na_2SO_4	0.521
Na_2CO_3	0.026
U^{238}	4.2E-5
Pu^{239}	9.5E-7
Np^{237}	2.1E-6
Sr^{85}	Tracer Amounts

Table 11. Data for 5.6 M Sodium Waste

Test No.	Sr	Mn	Red Choice	Red Level	Mixing	Temp	Pu-239 (dpm/mL)	Corrected Pu DF	Sr-85 (dpm/mL)	Corrected Sr DF
1	0	0.01	Peroxide	1x	Stir bar	25	3.04E+04	1.1	3.20E+01	4.E+03
2	0.005	0.01	Peroxide	1x	Stir bar	25	5.26E+02	61.1	3.19E+03	39
3	0.01	0.01	Peroxide	1x	Stir bar	25	7.17E+02	44.8	1.93E+03	64
4	0	0.01	Peroxide	3x	Stir bar	25	1.32E+03	24.4	4.90E+01	2.54E+03
5	0.005	0.01	Peroxide	3x	Stir bar	25	1.70E+03	18.9	1.80E+03	69
6	0.01	0.01	Peroxide	3x	Stir bar	25	1.63E+03	19.7	2.38E+03	52
7	0	0.03	Peroxide	1x	Stir bar	25	1.36E+04	2.3	1.02E+02	1.20E+03
8	0.005	0.03	Peroxide	1x	Stir bar	25	1.99E+04	1.6	9.24E+01	1.32E+03
9	0.01	0.03	Peroxide	1x	Stir bar	25	2.72E+04	1.2	7.17E+01	1.70E+03
10	0	0.03	Peroxide	3x	Stir bar	25	6.03E+02	52.4	8.39E+01	1.45E+03
11	0.005	0.03	Peroxide	3x	Stir bar	25	6.16E+02	51.2	6.98E+02	175
12	0.01	0.03	Peroxide	3x	Stir bar	25	3.31E+02	95.1	2.69E+03	45
13	0	0.03	Formate	1x	Stir bar	25	2.42E+03	13.0	20.5	5.95E+03
14	0	0.03	Formate	1x	orbital	25	6.97E+03	4.6	105	1.11E+04
15	0.01	0.03	Formate	1x	Stir bar	25	3.90E+03	8.1	3.12E+03	39
16	0	0.03	Formate	3x	Stir bar	25	1.90E+03	16.6	19	6.40E+03
17	0	0.03	Formate	3x	orbital	25	4.16E+03	7.7	6.685	1.74E+05
18	0.01	0.01	Formate	3x	Stir bar	25	3.87E+03	8.2	8.14E+02	150
19	0.01	0.01	Formate	3x	orbital	25	7.45E+03	4.4	6.38E+04	19
20	0	0.03	Formate	1x	Stir bar	45	1.11E+04	2.8	2.12E+01	5756.66
21	0.01	0.03	Formate	1x	Stir bar	45	8.72E+03	3.6	2.43E+02	501
22	0	0.03	Formate	3x	Stir bar	45	9.05E+03	3.5	69.8	1.67E+04
23	0.01	0.01	Formate	3x	Stir bar	45	1.05E+04	3.1	2.97E+03	398

Table 12. Data for 7.5 M Sodium Waste (Formate as Reductant)

Test No.	Mn (M)	Reductant Level	Sr (M)	Temp (oC)	Pu-239 (dpm/mL)	Corrected Pu DF	Sr-85 (dpm/mL)	Corrected Sr DF
1	0.01	3X	0	35	2.20E+04	1.5	18.6	8286
2	0.01	3X	0	45	2.98E+04	1.1	5.80E+01	2659
3	0.0299	5X	0.005	35	6.73E+03	4.9	3.17E+02	476
4	0.03	5X	0.005	45	9.16E+03	3.6	1.65E+02	391
5	0.01	5X	0.01	45	1.75E+04	1.9	1.53E+02	429
6	0.01	5X	0	45	2.62E+04	1.3	49.04	1345
7	0.03	3X	0.01	35	3.65E+03	9.0	108	597
8	0.03	3X	0.005	45	9.07E+03	3.6	1.58E+02	409
9	0.03	1X	0.01	35	3.54E+03	9.2	2.24E+02	288
10	0.03	1X	0.01	45	1.22E+04	2.7	80.8	1864
11	0.01	1X	0.005	35	3.33E+04	1.0	6.75E+03	23

References

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[1] D. T. Hobbs, "Evaluation of Alternative Materials and Methods for Strontium and Alpha Removal from Savannah River Site High-Level Waste Solutions," WSRC-TR-2000-00229, August 2000.

[2] R. A. Dimenna, et al., "Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives," WSRC-RP-99-00006, Rev. 3.

[3] W. R. Wilmarth, S. W. Rosencrance, C. A. Nash, D. P. DiPrete and C. C. DiPrete, "Transuranium removal from Hanford High Level Waste simulants using sodium permanganate and calcium," *J. Radioanal. Nucl. Chem*., **247**, 2001, p. 501.

[4] M. J. Barnes, D. T. Hobbs, M. C. Duff and S. D. Fink, "Strontium and Actinide Removal from Savannah River Site Actual Waste Samples by Freshly Precipitated Manganese Oxide," WSRC-TR-2002-00048, Rev. 1, May 22, 2002.

[5] 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.

[6] N. N., Krot, A. A. Bessonov, A. V. Gelis, V. P. Shilov, V. P., Perminov. and L. N. Astafurova,. Coprecipitation of transuranium elements from alkaline solution by the method of appearing agents. I. Coprecipitation of Pu(VI, V) with manganese dioxide. *Radiochem.* **40**, 1998, 347-352.

[7] D. T. Hobbs, "Recommended Decontamination Factors for Use in Flowsheet Modeling of the Manganese Oxide Treatment Process for Strontium and Actinide Removal," WSRC-TR-2002-00379, August 20, 2002.

[8] D. T. Herman, M. R. Poirier, D. T. Hobbs and S. D. Fink, "Testing of a Rotary Microfilter using SRS Actual Waste," WSRC-MS-2003-00030, February 2003.

[9] Statistical Consulting Section, "Software Verification and Validation for Commercial Statistical Packages Utilized by the Statistical Consulting Section of SRTC," WSRC-RP-99-00422, Rev. 0, May 21, 1999.