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Strontium and Actinide Removal Testing with Monosodium Titanate and Other Sorbents

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1.0 Summary

SRTC researchers examined the affects of solution phase composition, the oxidation state of plutonium and neptunium and different production batches on the performance of monosodium titanate (MST) to remove strontium and actinides from alkaline salt solutions. Testing also evaluated the performance of alternate sorbents including sodium nonatitanate (ST), crystalline silicotitanate and pharamacosiderite materials. Results indicated the following.

- The solution composition does affect the performance of MST to remove strontium and the actinides.
- In general, the decontamination factor (DF) increased with increasing sodium nitrate concentration.
- Evidence suggests that the relationship between MST performance and solute concentration does not fit a linear model.
- Preliminary evidence suggests that Pu(VI) is stable in alkaline solutions for several weeks and exhibits a higher solubility than Pu(IV).
- Test results suggest that the rates of Pu(IV) and Pu(VI) removal are similar.
- Test results yielded inconclusive evidence for the stability of Np(IV) in an alkaline salt solution.
- Test results indicated no significant changes in neptunium removal upon contact of solutions prepared with Np(V) or Np(IV).
- Measurable differences in strontium removal, but not in actinide removal, occurred with different MST production batches.
- Measurable changes in the performance of MST Lot #33180 occurred during the course of testing which we attribute to errors associated with delivering the same quantity of MST, sampling and analytical measurements.
- Samples of ST and pharamacosiderites exhibited strontium and actinide removal performance as good or better than that observed for MST.

Based on these finding we recommend the following.

- Conduct additional tests to more completely understand and model the performance of MST as a function of solution composition.
- Conduct additional tests to determine the stability of Pu(VI), Pu(V), Np(IV) and Np(VI) oxidation states in alkaline salt solutions.
- Increase database on MST batch variability by sampling and measuring strontium and actinide removal for archived MST presently stored at SRS.
- Continue evaluation of sorbent materials as alternates to MST including examinations of performance over a range of solution compositions.

2.0 Introduction

The baseline process for the removal of ⁹⁰Sr and alpha-emitting radionuclides from high-level liquid waste solution at the Savannah River Site uses an inorganic material, monosodium titanate (MST).¹ Previous testing indicated that plutonium removal kinetics and neptunium capacity of the MST material impacts the size of equipment and waste blending plans for the proposed Salt Processing Project facility. Consequently, the

Salt Processing Project requested that SRTC conduct tests evaluating the effects of solution composition, plutonium and neptunium oxidation states and MST synthesis batch variability on removal performance as well as evaluate alternate sorbent materials and removal methods.² Additional testing features characterization of the interaction between the sorbate and the MST using fine structure X-ray absorption fine structure spectroscopy (XAFS) techniques. This information will provide a more complete understanding of the removal mechanism of the MST for each sorbate. Separate reports will summarize the findings of the measurements to date.

Previous testing with simulants used a single solution composition.^{3,4,5} Changes in solution composition could affect the nature of the sorbate species present in solution and thus the rate and extent of removal with MST. For example, increasing hydroxide concentration may change the predominant sorbate species to a more highly hydroxide substituted complex (e.g., Sr^{2+} vs. $\text{Sr}(\text{OH})^+$ and $\text{UO}_2(\text{NO}_3)_4^{2-}$ vs. $\text{UO}_2(\text{OH})_4^{2-}$ or $\text{UO}_2(\text{OH})_5^{3-}$). The more highly hydroxide substituted complex may sorb differently than the uncomplexed or nitrate substituted complex. Thus, we conducted a series of tests with simulants having a range of solution compositions to determine if solution composition significantly influences sorbate removal with MST.

Literature data indicate plutonium and neptunium exhibit multiple oxidation states in alkaline aqueous solutions.^{6,7,8} No previous studies exist that definitively identify plutonium and neptunium oxidation states in the range of solution compositions that will exist during supernatant processing. Multiple oxidation states and species in solution could affect the extent and rate of removal with the MST. For example, Phase IV test results exhibited a change in the plutonium removal rate after about 10 hours.^{9,10} Thus, tests used solutions containing different plutonium and neptunium oxidation states to determine if the oxidation state of the plutonium and neptunium significantly influences sorption.

Previous testing for the Salt Processing Project featured a single batch of MST (Optima Lot #33180) originally produced for use in the In-Tank Precipitation (ITP) process. During qualification of vendors for the production of MST, testing indicated considerable variance among various samples in strontium removal performance. The large variance prevented successful correlation of the strontium removal performance with a physical property (e.g., particle size distribution or surface area) and, therefore, qualification of each MST batch included the determination of the strontium decontamination factor.¹¹ Actinide removal variability was not tested during this time, but we expect it to vary to some degree as observed with strontium.

Initial evaluation of alternate materials featured sodium titanate materials available from commercial vendors.⁴ In general, strontium removal with the alternate materials was similar to that with MST. Actinide removal proved poorer with the alternate materials compared to the MST. We attributed the poorer actinide removal to the large particle size of these alternate materials. SRTC contracted with Professor Abraham Clearfield of Texas A&M University during FY2001 to prepare a range of new titanate-based sorbent materials for evaluation. Professor Clearfield has over 40 years of experience in the

synthesis and characterization of inorganic sorbents and ion-exchange materials. This report includes strontium and actinide removal characteristics of several samples prepared at TAMU and submitted to SRTC for evaluation. In addition to the TAMU samples, we also evaluated one new sample from a commercial vendor.

3.0 Experimental

3.1 Preparation of Salt Solutions

Personnel prepared all solutions using reagent grade chemicals and deionized distilled water. Except as noted personnel treated the alkaline salt solutions with MST to remove tramp strontium. After filtering the salt solution to remove MST solids, personnel added the targeted amount of ^{85}Sr radiotracer (NEN Cat. #NEZ082, Lot #00M51M7) and the actinides. Actinide sources included uranyl nitrate hexahydrate (Mallinckrodt Lot # 8640KDAL) and nitric acid solutions of plutonium(IV) (19.328 g/L) and neptunium(V) (67.1 g/L) supplied by the Actinide Technology Section of SRTC. After addition of the ^{85}Sr and actinides, we allowed the solutions to mix for one week at ambient room temperature. After one week, we filtered the solutions through 0.45-micron pore size nylon membrane filters to remove any residual solids. Table 3.1 lists the initial sorbate and radiotracer concentrations.

Table 3.1. Measured Initial and Predicted Sorbate Concentrations for Salt Solutions

Trial No.	Meas. [Sr] ($\mu\text{g/L}$)	Meas.[Pu] ($\mu\text{g/L}$)	Pred. [Pu] ($\mu\text{g/L}$)	Meas. [U] ($\mu\text{g/L}$)	Pred. [U] ($\mu\text{g/L}$)	Meas. [Np] ($\mu\text{g/L}$)
1	621	231	404	7050	12,300	241
2	656	102	404	8080	7420	244
3	302	42.8	83.8	5960	10600	242
4	541	140	151	7120	8360	249
5	537	121	76.8	4490	1550	249
6	828	119	404	5490	22100	190
7	617	208	226	6620	8480	218
8	649	203	226	6980	8400	220
9	742	242	217	10400	8440	307
10	628	203	226	6950	8480	225
11	568	65.7	112	4320	3360	215
Std. Dev.*	16.3	2.95		200		3.54
Targeted Conc.	100	200		10000		400

Predicted values are those assuming the predictive equations from uranium and plutonium solubility studies.^{12,13}

* Single standard deviation of triplicate analyses for centroid salt solution in Trials 7, 8, and 10.

Plutonium and neptunium oxidation state testing required the preparation of simulant salt solution (see Table 3.2 for composition) containing single isotopes of Pu (IV), Pu (VI), Np (IV), or Np (V). Researchers used the nitric acid stock solutions of Pu (IV) and Np (V) described above. They oxidized Pu (IV) to Pu (VI) by treating 4.021 mL of 0.965 mg/mL acidic Pu (IV) with a stoichiometric amount (15.9 mL) of 0.001 M KMNO₄ (in 1 M HNO₃ acid).¹⁴ The color of the solution provided an indicator of complete oxidation. The initial solution was colorless. Upon first addition of the purple-colored KMNO₄, the Pu solution turned purple but soon thereafter turned colorless again. After addition of all required KMnO₄, the solution remained colored indicating complete oxidation.

Personnel reduced Np (V) to Np (IV) by treating 1.448 mL of 2.68 mg/mL acidic Np (V) with a stoichiometric quantity (1.28 mL) of 0.0128 M H₂O₂.¹⁵ Again, the color of the solutions provided an indicator of reduction. The starting Np (V) solution was pale yellow and turned colorless upon addition of the H₂O₂. The difficulty and requirements associated with handling the materials prevented spectroscopic or electrochemical analysis to verify their oxidation states.

Table 3.2. Salt Solution Composition Used in Adsorption Testing

Component	Concentration (M)
NaNO ₃	2.60
NaOH	1.33
Na ₂ SO ₄	0.521
NaAl(OH) ₄	0.429
NaNO ₂	0.134
Na ₂ CO ₃	0.0260
Total Na ⁺	5.6

We prepared a 2000 µg/L Pu (VI)-spiked, salt solution by adding the acidic Pu(VI) solution prepared above to a portion of the 5.6 M Na⁺ simulated salt solution. We prepared similar solutions using the Np (IV) solution, as well as the starting Pu(IV) and Np(V) solutions. All four solutions contained 2000 µg/L of their respective isotope. After stirring the solutions overnight, we sampled each bottle and continued stirring. After 3 or 4 days of stirring, we filtered each solution and stored the filtered solutions in clean polyethylene (PE) bottles. Personnel sampled each bottle and analyzed for plutonium and neptunium content.

Table 3.3 presents the analytical data for each test solution. The data indicate that both plutonium solutions appeared unstable as evidenced by decreasing plutonium concentrations. Furthermore, the Pu(VI)-spiked solution had a higher solubility under the preparation conditions compared to the Pu(IV)-spiked solutions. Both Np solutions appeared stable with time with similar concentrations.

Table 3.3. ICP-MS and PuTTA Analyses of the Starting Salt Solutions

Time (h)	Pu (IV) ($\mu\text{g/L}$)^a	Pu (VI) ($\mu\text{g/L}$)^a	Np (IV) ($\mu\text{g/L}$)^a	Np (V) ($\mu\text{g/L}$)^a
25	NA ^b	1193	1150	NA ^b
47	107	NA ^b	NA ^b	1375
126	NA ^b	715	1160	NA ^b
148	37.3	NA ^b	NA ^b	1260

^aPu values determined by PuTTA. Np values determined by ICP-MS.

^bNA indicates no analysis performed.

Testing for MST batch affects and alternate sorbent materials salt solution comprised of the same solution composition provided in Table 3.2. We treated the salt solution with MST to remove tramp strontium and then spiked as previously described with ⁸⁵Sr radiotracer (NEN Cat. #NEZ082, Lot #00M51M7) and nitric acid solutions of uranyl nitrate hexahydrate (Mallinckrodt Lot # 8640KDAL), plutonium(IV) (19.328 g/L) and neptunium(V) (67.1 g/L) supplied by the Actinide Technology Section of SRTC. After filtering to remove undissolved solids, we stored the filtered solutions in clean PE bottles.

3.2 Adsorption Tests

Researchers added between 115 and 200 mL of the appropriate salt solution into labeled PE bottles and then randomly placed the bottles in a Lab Line shaking waterbath (Cole-Parmer Catalog #E-01290-20) set to maintain a temperature of 25 °C. Personnel kept the level of the water at or above the liquid level in the sample bottles. Temperature measurements occurred via a thermistor thermometer (Omega[®] Model # 5831) with probes (Omega[®] Model #OL-703). After incubating for one day, testing began with an initial sampling of each bottle, and the addition of the appropriate quantity of MST to provide a MST concentration of 0.4 g/L. For sorbents other than MST, researchers placed a weighed quantity of the sorbent, which provided the same quantity of titanium equivalent to 0.4 g/L MST. Sampling of each bottle occurred in random order at the desired sampling interval after the addition of MST.

The sampling method consisted of removing the test bottle from the waterbath, briskly shaking for about 30 seconds to provide a homogeneous suspension, and pulling approximately 5-6 mL of the suspension into a disposable plastic syringe. The researcher then inserted a 0.45 μm disk filter (nylon membrane) onto the syringe, collected about 5 mL of filtrate into a clean PE sample bottle and pipetted 4 mL of the resulting filtrate into a glass vial containing 4 mL of 5M nitric acid. A white precipitate formed immediately upon mixing of the sample and the nitric acid. Personnel then capped the glass sample vial, gently agitated it and then allowed it to stand at ambient laboratory temperature until all solids dissolved. Personnel recapped the test bottle and returned it to the waterbath. The total time outside of the waterbath for sampling did not exceed three minutes.

The Analytical Development Section of SRTC performed all radiostrontium and actinide analyses.¹⁶ The ⁸⁵Sr activity measurement occurred by gamma pulse height

spectroscopy.¹⁷ Personnel determined concentrations of ²³⁷Np, ²³⁸U, ²³⁹Pu and ²⁴⁰Pu by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis.¹⁸ The ^{239/240}Pu and ²³⁸Pu activity determination relied on alpha spectroscopy after chemically separating the plutonium from neptunium.¹⁹

4.0 Results and Discussion

4.1 Affects of Solution Composition

Solution composition testing featured a statistically designed test matrix consisting of 11 experimental trials, as listed in Table 4.1.1.²⁰ The purpose of the first six trials examined whether a linear relationship exists between MST adsorption ability and the concentrations of NaNO₃, free NaOH, NaNO₂, NaAl(OH)₄, Na₂CO₃, and Na₂SO₄. We selected the range of molar concentrations for each salt to fall within expected value and so that the change in concentrations would likely produce a measurable affect, but these values do not represent a bounding range of concentrations that may occur during facility operations. Table 4.1.2 provides a list of the lower and upper range of molar concentrations tested.

Table 4.1.1. Statistically Designed Trials

Trial	Description	Component Concentration (M)					
		NaNO ₃	Free NaOH	NaNO ₂	NaAl(OH) ₄	Na ₂ CO ₃	Na ₂ SO ₄
1	Statistical Trial	1.000	3.000	0.500	0.100	0.020	0.490
2	Statistical Trial	1.000	3.000	0.100	0.100	0.200	0.443
3	Statistical Trial	3.000	1.070	0.100	0.100	0.020	0.600
4	Statistical Trial	3.000	1.630	0.500	0.100	0.200	0.100
5	Statistical Trial	1.730	1.000	0.500	0.500	0.200	0.600
6	Statistical Trial	2.170	3.000	0.100	0.500	0.020	0.100
7	Centroid	1.959	2.122	0.292	0.299	0.106	0.379
8	Centroid	1.959	2.122	0.292	0.299	0.106	0.379
9 [‡]	Centroid with secondary salts	1.907	2.066	0.284	0.291	0.104	0.369
10	Centroid with no MST	1.959	2.122	0.292	0.299	0.106	0.379
11	Phase V salt solution	2.600	1.330	0.134	0.429	0.026	0.521

[‡]Trial 9 also spiked with salts listed in Table 4.1.3.

Additional input to the development of these trials included two constraints. First, we required that the ionic strength would remain constant for each trial solution at 6.13 M (i.e., ionic strength for 5.6 M Na⁺ simulated waste solution of composition provided in Table 3.2). The second constraint required that the concentration of NaNO₃ in the salt solutions equaled at least three times that of the NaAl(OH)₄ concentration. The solution preparation generates NaAl(OH)₄ from the reaction of Al(NO₃)₃ and four equivalents of NaOH releasing three equivalents of nitrate per equivalent of aluminum and thus necessitating this constraint.

Table 4.1.2. Range of Molar Concentrations for Salts of Interest

Lower Limit		Salt		Upper Limit
1.0	≤	NaNO ₃	≤	3.0
1.0	≤	Free NaOH	≤	3.0
0.1	≤	NaNO ₂	≤	0.5
0.1	≤	NaAl(OH) ₄	≤	0.5
0.020	≤	Na ₂ CO ₃	≤	0.2
0.1	≤	Na ₂ SO ₄	≤	0.6

The relative ionic strengths of the six primary salt solution components subject to the ranges provided in Table 4.1.2 and the two constraints of the previous paragraph define the region of interest for this mixture study. Cornell provides a detail discussion of the statistical methods for the design and analysis of such mixture experiments.²¹ We used these methods to determine a minimal (only 6 trials) experimental design²⁰ that supported the evaluation of a six-term linear model relating each decontamination factor (DF) response of interest to the six primary salt solution components. These six trials were optimally selected from the set of extreme vertices bounding the region defined by the ranges of Table 4.1.2 and the two associated constraints.

Trials 7–10 in the statistical matrix specified a centroid concentration determined by averaging the extreme compositional vertices of the defined area for the six salt components. The constraints as previously defined also applied to this composition. Trials 7 and 8 used the centroid as is, while Trial 10 utilized the centroid as a control by omitting the addition of MST. Trial 9 used the centroid spiked with trace amounts of secondary salts as listed in Table 4.1.3 to determine the gross effect on MST performance of having these secondary salts present.

Table 4.1.3. Secondary Salts Added to Trial Nine

Component	Concentration (M)
Na ₂ C ₂ O ₄	0.0080
Na ₃ PO ₄	0.0100
NaF	0.0320
NaCl	0.0250
Na ₂ SiO ₃	0.0040
Na ₂ MoO ₄	0.0002
KNO ₃	0.0150
CsNO ₃	0.00014

The last trial of the experimental series, Trial 11, specified the use of salt solution previously used in strontium and actinide removal testing (referred to as Phase V salt

solution).³ This trial provides a quantitative measure of the reproducibility of this data set with that in previous testing.

Researchers intended to use a constant set of initial sorbate concentrations across the 11 trials. The actual concentrations differed significantly from the targets and across the different solution compositions. Table 3.1 provides the initial concentrations for each sorbate. The strontium values exceeded the targeted because personnel did not remove tramp strontium from the reagent chemicals prior to solution preparation. A second contributing factor to the variations may have been that the solutions sat unmixed after spiking with the radionuclides for 9 days prior to being placed on stir plates and mixed due to an expected laboratory outage.

A third probable cause of the variations in sorbate levels involves the effect of solution composition on the solubility of each sorbate. Prior to design of the experiment, SRTC researchers expected different sorbate concentrations for the trials due to wide range of solution compositions and previous studies that showed significant changes in uranium and plutonium solubilities as a function of the solution composition.^{12,13,22} Table 3.1 presents the measured and predicted concentrations for uranium and plutonium in each of the test solutions. The predicted concentration assumes that there is sufficient uranium present to achieve the predicted solubility. Researchers targeted uranium and plutonium concentrations at 10,000 µg/L and 200 µg/L, respectively. Thus, for those solutions that have predicted concentrations equal to or greater than the target concentrations, the measured concentrations will not achieve the predicted concentrations.

Solutions for Trials #3, 4, 5 and 11 all have predicted solubilities below 200 µg/L. Measured plutonium concentrations followed the predicted concentration for all of the solutions with the exception of solution in Trial #5. For Trial #5, the measured concentration was below the target, but higher than the predicted concentration. At the 95% confidence limit, the measured concentration is within the higher prediction value (169 µg/L). Only the Trial #9 solution had a measured concentration that exceeded the target concentration.

Uranium concentrations for all of the solutions measured at or below the target concentration of 10,000 µg/L. Replicate measurements of the solutions for Trials #7, #8 and #10 exhibited a single standard deviation of ± 200 µg/L. This result indicates a small error for the determination of the uranium concentrations. Three solutions, Trials #2, #5 and #9 exhibited uranium concentrations above the predicted concentration. The uranium concentrations for Trial #2 and Trial #9 solutions are within the range of values predicted at the 95% confidence interval. The uranium concentration for the Trial #5 solution is about a factor of 3 higher than the predicted value and well outside the 95% confidence interval.

Trial 6 solution represented one of the extreme vertices of the salt compositional region investigated. A relatively hard-to-dissolve white precipitate formed in Trial 6 samples taken directly after addition of strontium and actinides. Although most of the trial samples exhibited the precipitates upon addition of 5M nitric acid, the Trial 6 sample

required a second addition of the 5.0 M nitric acid to completely dissolve the solids. The additional acid was needed to neutralize all of the alkalinity in the Trial 6 composition, which had the highest combination of NaAl(OH)_4 (0.5M) and free NaOH (3.0 M).

The investigation included one test bottle, Trial 10, containing no MST to serve as a control. Trial 10 solution represented the centroid or center of the compositional region tested in Trials 1 - 6. This trial served as a means to correct for removal of sorbates by sorption onto the bottle walls, the filter or by precipitation. The results indicated no significant removal of sorbates in the control sample (See Table 4.1.4) within the duration of the experiments. For this reason, the results for tests with MST did not require correction for sorption by mechanisms other than that with MST.

Table 4.1.4. Control Sample Results

Sample Time	Sorbate Concentration ($\mu\text{g/L}$)			
	Total Sr	Total Pu	Total U	Np-237
Time 0	628	203	6952	225
Time 24 hours	578	200	8208	286
Time 168 hours	541	205	6893	239
Average	582	203	7351	250
Std. Dev.	43.9	2.55	742	31.9
% RSD	7.5%	1.3%	10.1%	12.7%

Trials 7 and 8 of the experimental series served as duplicates of the centroid composition. Initial sorbate concentrations in each were in close agreement (See Table 3.1.1). Table 4.1.5 presents the DFs calculated from the 24-hour and 168-hour sample results. All values showed good agreement except for the 24-hour strontium result. The difference in the strontium sample analyses results at 24 hours may reflect error associated with the handling of the sample prior to or during analysis. Reanalysis of the 24-hour samples using the residues from the gamma and alpha counting aliquots confirmed the relatively high strontium concentration in Trial 8, which results in a low strontium DF value. Since good agreement resulted for the 7-day strontium values and all of the actinide values in both trials, we conclude that the 24-h result for Trial #8 cannot be discarded. Consequently, statistical analysis includes the 24-hour result for Trial #8.

Trial 11 of the experimental series used the same salt solution composition previously used in strontium and actinide removal testing for the program.^{3,4,5} Table 4.1.6 contains a summary of the data from Trial 11 and values previously reported. We averaged the four individual results and compared the average to the values obtained in Trial 11. The measured DFs in Trial 11 agreed well with the averages determined in the previous tests as evident by the small percent difference values calculated for each sorbate at 24-hours and 7-days. Poorer agreement occurred for the uranium 7-day and neptunium 24-hour values. However, even in these cases, the Trial 11 values fall within the range spanned by the average and (plus or minus) two standard deviations.

Table 4.1.5. Duplicate Sample Results

	Decontamination Factor							
	Sr	Sr	Pu	Pu	U	U	Np	Np
	24 h	7d	24 h	7d	24 h	7d	24 h	7d
Trial 7: EV Centroid	100	126	5.70	13.8	1.15	1.66	1.24	2.17
Trial 8: EV Centroid	18.8	141	4.64	13.9	1.15	1.74	1.41	2.64
Average	59.6	133	5.17	13.9	1.15	1.70	1.33	2.41
Std Dev	57.7	11.0	0.75	0.09	0.01	0.06	0.12	0.34
RSD	96.7%	8.2%	14.6%	0.7%	0.4%	3.3%	8.9%	14.1%

Table 4.1.6. Comparison of Trial 11 and Previous Test Results

Trial	Decontamination Factor							
	Sr	Sr	Pu	Pu	U	U	Np	Np
	24 h	7d	24 h	7d	24 h	7d	24 h	7d
Trial 11	1.37E+02	1.81E+02	1.24E+01	3.76E+01	1.42E+00	2.27E+00	2.25E+00	8.27E+00
Test #1 reference 3	1.38E+02	1.43E+02	1.23E+01	3.68E+01	9.50E-01	1.47E+00	2.91E+00	8.17E+00
Test #2 reference 3	1.21E+02	1.38E+02	1.36E+01	3.65E+01	1.63E+00	1.52E+00	5.13E+00	6.80E+00
Test #3 reference 5	1.50E+02	3.05E+02	1.13E+01	3.23E+01	1.14E+00	1.36E+00	3.47E+00	8.08E+00
Test #4 reference 5	1.58E+02	1.90E+02	1.03E+01	2.96E+01	2.08E+00	1.36E+00	5.56E+00	1.34E+01
Average Tests #1-4	1.42E+02	1.94E+02	1.19E+01	3.38E+01	1.45E+00	1.43E+00	4.27E+00	9.11E+00
Standard Deviation Tests #1-4	1.61E+01	7.76E+01	1.41E+00	3.47E+00	5.08E-01	8.06E-02	1.28E+00	2.93E+00
Relative Std Dev Tests #1-4	11.4%	40.0%	11.9%	10.3%	35.1%	5.6%	29.9%	32.1%
% Difference (Trial 11 - Average)/Average	-3.19%	-6.57%	4.75%	11.22%	-2.37%	59.32%	-47.17%	-9.24%

This agreement in DF values confirms the assumption that the initial sorbate concentration does not significantly affect the measured DF. As seen in Table 4.1.7, the initial sorbate concentrations differ among the three test sets from about a factor of 2 for neptunium to as high as about a factor of 6 for strontium. The differences in DFs between Trial 11 and the two previous data sets prove much smaller. The greatest difference (uranium – 7days) equaled 59.3% which is consistent with the initial lower uranium concentration in Trial 11 compared to the previous test sets.

Table 4.1.7. Initial Sorbate Concentrations

Sorbate	Concentration ($\mu\text{g/L}$)		
	Trial 11	Set #1 ^a	Set #2 ^b
Sr	568	86.7	92.4
Pu	65.7	190	222
U	4316	9040	11500
Np	215	416	489

^a reference 3

^b reference 5

Table 4.1.8 provides the measured decontamination factors for each trial in the statistical design. Exhibits 3 through 10 in the Appendix provide Box Plots of the DFs for each species of interest. These plots group the extreme vertices (Trials 1 through 6) and the duplicate centroids. The plots display the other trials individually. The DF for Trail 10, the control, ranged from 0.79 to 1.16, versus an anticipated value of 1.0.

Table 4.1.8. Decontamination Factors for Solution Composition Trials

Trial	Sr 24 h	Sr 7d	Pu 24 h	Pu 7d	U 24 h	U 7d	Np 24 h	Np 7d
Trial 1	123	155	4.13	9.10	1.36	1.62	1.53	2.02
Trial 2	10.8	112	3.40	8.42	1.27	1.58	1.59	2.72
Trial 3	78.5	246	16.5	43.3	1.56	2.30	2.50	9.82
Trial 4	174	190	7.91	20.9	1.43	2.08	1.90	3.55
Trial 5	102	140	10.6	24.2	1.48	2.35	2.21	4.28
Trial 6	50.5	137	4.14	8.06	1.26	1.74	1.94	3.56
Trial 7: EV Centroid	100	126	5.70	13.8	1.15	1.66	1.24	2.17
Trial 8: EV Centroid	18.8	141	4.64	13.9	1.15	1.74	1.41	2.64
Trial 9: EV Centroid w/ Trace Salts	90.7	127	3.85	9.31	1.16	1.56	1.00	1.43
Trial 10: EV Centroid, No MST, Control	1.09	1.16	1.01	0.99	0.85	1.01	0.79	0.94
Trial 11: Phase V Solution	137	181	12.4	37.6	1.42	2.27	2.25	8.27

Exhibit 11 provides correlations among the DFs for these 11 trials as well as the corresponding scatter plots. Strong linear correlations exist for the following pairs of these data: Pu DF-24h and Pu DF-7d (0.9853), and U DF-24h and U DF-7d (0.9127), Np DF-7d and Pu DF-24h (0.9326), Np DF-7d and Pu DF-7d (0.9466), Np DF-24h and U DF-24h (0.9142), and Np DF-24h and U DF-7d (0.9156).

Exhibit 12 provides a series of plots of the DFs versus the normalized ionic strength (N_{is}) fractions of the six primary salt solution components. The plots offer an opportunity to investigate trends and other patterns in the DF values relative to each of the six primary salt solution components in turn.

Exhibits 13 through 20 of the Appendix provide a formal statistical analysis using the JMP statistical analysis software for each set of DFs.²³ Each of these exhibits contains the JMP output from fitting a linear (mixture) model (in normalized ionic strength fractions) relating the six primary salt solution components to a set of DF values. We only used Trials 1 through 8 to conduct these analyses. However, the corresponding “Actual by Predicted” plots presented as part of the exhibits provide results for Trials 9 and 11. These exhibits also include estimated effects, plots of “Residual by Predicted,” and tests for “lack of fit” for the linear models. A value, for **Prob>|t|** (for an estimated linear effect) or **Prob>F** (for a “lack of fit” test) less than 0.05, indicates a statistically significant effect or lack of fit, respectively, at a 5% significance level. The following sections discuss the results from each model fit.

Sr 24-hour DFs

The results presented in Exhibit 13 indicate no significant linear effects for these data. In addition, there is no indication of a lack of fit for the model. However, these conclusions are tempered by the poor repeatability demonstrated for Trials 7 and 8 discussed earlier.

Sr 7-day DFs

The results of Exhibit 14 indicate a significant linear effect for NaNO_3 at the 5% significance level. There is no indication of a lack of fit for the model at the 5% level. However, the residual plot indicates that the centroids of the factor space (Trials 7 and 8) are (relatively) poorly predicted by the linear model suggesting that a more complex model might be worth investigating.

Pu 24-hour DFs

The results in Exhibit 15 indicate a significant linear effect for NaNO_3 at the 5% significance level. There is no indication of a lack of fit for the model at the 5% level. However, the residual plot indicates that the centroids of the factor space (Trials 7 and 8) are (relatively) poorly predicted by the linear model suggesting that a more complex model might be worth investigating.

Pu 7-day DFs

The results presented in Exhibit 16 indicate significant linear effects for NaNO_3 and Na_2SO_4 at the 5% significance level. There is no indication of a lack of fit for the model at the 5% level. However, at a 10% significance level an indication of a lack of fit does occur, and the residual plot indicates that the centroids of the factor space (Trials 7 and 8) are (relatively) poorly predicted by the linear model suggesting that a more complex model might be worth investigating.

U 24-hour DFs

The results in Exhibit 17 indicate no significant linear effects at the 5% significance level. At a 10% level of significance, only the effect for NaNO_3 would be considered statistically significant for these data. In addition, there is no indication of a lack of fit for the model at the 5% level. However, at a 10% significance level there would be an indication of a lack of fit, and the residual plot indicates that the centroids of the factor space (Trials 7 and 8) are (relatively) poorly predicted by the linear model suggesting that a more complex model might be worth investigating.

U 7-day DFs

The results in Exhibit 18 indicate a significant linear effect for NaNO_3 at the 5% significance level and an indication of a lack of fit for the model at the 5% level. The residual plot indicates that the centroids of the factor space (Trials 7 and 9) are poorly predicted by the linear model suggesting that a more complex model might be worth investigating.

Np 24-hour DFs

The results in Exhibit 19 indicate no significant linear effects at the 5% significance level. In addition, there is no indication of a lack of fit for the model at the 5% level. However, at a 10% significance level there would be an indication of a lack of fit, and the residual plot indicates that the centroids of the factor space (Trials 7 and 8) are (relatively) poorly predicted by the linear model suggesting that a more complex model might be worth investigating.

Np 7-day DFs

The results in Exhibit 20 indicate no significant linear effects at the 5% significance level. In addition, there is no indication of a lack of fit for the model at the 5% level. However, at a 10% significance level, the effect for NaNO₃ is significant and there would be an indication of a lack of fit. The residual plot indicates that the centroids of the factor space (Trials 7 and 8) are (relatively) poorly predicted by the linear model suggesting that a more complex model might be worth investigating.

Modeling

Exhibits 21 through 28 provide plots of the actual DFs versus predictions from the fitted models. For each fitted model, the plots show actual DFs as individual points, and depicts the model predictions (Pred Formula ...) as a straight, dark line. The exhibits also provide a 95% confidence interval (Lower 95% Mean ... and Upper 95% Mean ...) for the expected fitted line as the pair of lines closest to the straight, dark line, and a 95% prediction interval (Lower 95% Indiv ... and Upper 95% Indiv ...) for an individual DF value shown as the other pair of lines.

Equations 1 – 8 provide the predictive equations for calculating the sorbate DF derived from the statistical analysis with solution component expressed in units of mole per liter (M).

$$DF_{24h}^{Sr} = 25.4*[NO_3^-] + 0.513*[OH^-] + 238*[NO_2^-] - 56.4*[Al(OH)_4^-] - 106*[CO_3^{2-}] - 39.8*[SO_4^{2-}] \quad (1)$$

$$DF_{7d}^{Sr} = 53.7*[NO_3^-] + 13.3*[OH^-] + 42.3*[NO_2^-] - 54.0*[Al(OH)_4^-] - 135*[CO_3^{2-}] + 89.5*[SO_4^{2-}] \quad (2)$$

$$DF_{24h}^{Pu} = 3.50*[NO_3^-] - 1.63*[OH^-] - 1.55*[NO_2^-] - 0.457*[Al(OH)_4^-] - 3.39*[CO_3^{2-}] + 11.9*[SO_4^{2-}] \quad (3)$$

$$DF_{7d}^{Pu} = 9.76*[NO_3^-] - 4.29*[OH^-] - 5.85*[NO_2^-] - 7.28*[Al(OH)_4^-] - 6.47*[CO_3^{2-}] + 30.5*[SO_4^{2-}] \quad (4)$$

$$DF_{24h}^U = 0.272*[NO_3^-] + 0.169*[OH^-] + 0.330*[NO_2^-] + 0.149*[Al(OH)_4^-] + 0.544*[CO_3^{2-}] + 0.817*[SO_4^{2-}] \quad (5)$$

$$DF_{7d}^U = 0.446*[NO_3^-] + 0.100*[OH^-] + 0.420*[NO_2^-] + 0.732*[Al(OH)_4^-] + 1.14*[CO_3^{2-}] + 1.19*[SO_4^{2-}] \quad (6)$$

$$DF_{24h}^{Np} = 0.484*[NO_3^-] + 0.128*[OH^-] - 0.0629*[NO_2^-] + 0.737*[Al(OH)_4^-] + 0.280*[CO_3^{2-}] + 1.40*[SO_4^{2-}] \quad (7)$$

$$DF_{7d}^{Np} = 2.28*[NO_3^-] - 0.444*[OH^-] - 4.73*[NO_2^-] - 0.885*[Al(OH)_4^-] - 4.68*[CO_3^{2-}] + 7.14*[SO_4^{2-}] \quad (8)$$

Looking at equations 1 – 8, the predicted DF increases with increased nitrate concentration for all sorbates. In general, the hydroxide concentration decreases, or has limited affect (i.e., small factor coefficient) on, the predicted DF. This trend for the two main solution components may indicate the role of complexation on strontium and

actinide removal. At high hydroxide concentration, the predominant solution phase sorbate species may be a hydroxide complex such as $\text{Sr}(\text{OH})^+$, $\text{Pu}(\text{OH})_6^{2-}$, $\text{NpO}_2(\text{OH})_4^{3-}$, $\text{UO}_2(\text{OH})_4^{2-}$ or $\text{UO}_2(\text{OH})_5^{3-}$. With decreasing hydroxide and increasing nitrate concentrations, the predominant sorbate species may shift to a mixed nitrate/hydroxide complex or the corresponding nitrate complex. Nitrate typically forms weaker complexes than hydroxide and thus the strontium and actinide species in high nitrate media may exhibit increased tendency to sorb onto the MST due to more favorable reaction thermodynamics.

Alternatively, solution components could be interacting directly with the MST surface (e.g., binding the hydroxide, nitrate or other component to the MST), which alters the interaction between the sorbate and the MST. Nitrate and hydroxide are the two predominant anions and, therefore, would be expected to produce the more pronounced, if any, affect on the MST surface. Interaction of oxyanions and titanate surfaces would be expected to be minor since the titanate framework is negatively charged. A literature search failed to identify any reports of strong surface interactions between inorganic oxyanions and titanates and titanium oxides. Bourikas, Hiemstra and Van Riemsdijk reported recently that interactions of anions are weaker than cations for titanium oxides.²⁴ Thus, we conclude that direct interaction between oxyanions and the MST surface plays a minor role, if any, on the observed variances in sorbate DFs.

4.2 Affects of Plutonium and Neptunium Oxidation States

These tests examined whether the oxidation state of either Pu or Np significantly affected the extent and rate of their removal using MST as the removal agent. The tests targeted Pu (IV) and Pu (VI) for comparison and, similarly, Np (IV) and Np (V). These oxidation states represent the two most probable (i.e., stable) oxidation states for each element in alkaline radioactive waste. We tested each species in triplicate. The Appendix contains concentration vs. time data from the twelve individual tests. Data discussed below represents the average of each set of three tests. We compare the data with Pu (IV) and Np (V) data from previous tests performed under similar conditions (5.6 M Na^+ and 0.4 g/L MST).^{3,4,5} However, the previous testing used multiple sorbate solutions while the current tests used single sorbate solutions.

4.2.1 Plutonium Removal

Figure 4.2.1.1 compares the average plutonium concentration as a function of time for the two plutonium oxidation state tests along with previous data. Initial observation shows the starting soluble plutonium concentration in the Pu(VI) tests at 712 $\mu\text{g/L}$. Correspondingly, the starting plutonium concentration in the Pu(IV) tests measured 37 $\mu\text{g/L}$, nearly twenty times less than that of Pu(VI). In the previous testing,³ the initial soluble Pu concentration measured 190 $\mu\text{g/L}$. The equilibrium soluble plutonium concentration for the Pu(IV), Pu(VI) and the previous Pu(IV) tests measured 2.68, 25.27, and 5.19 $\mu\text{g/L}$, respectively.

No data exists to establish stability and lifetime of Pu(VI) in alkaline waste solutions. A potential exists that Pu(VI) reduces to Pu(IV) over time due to radiolytic or chemical reactions (e.g., reduction with nitrite). However, the persistent high concentration of

plutonium in the experiments that added Pu(VI) suggest that reduction did not likely complete during the duration of the experiment (i.e., 2 weeks). Furthermore, recent data from the Extended X-ray Absorption Fine Spectroscopy (EXAFS) analysis of MST loaded with plutonium indicates that Pu(VI) persisted on the solids with about 20% of the plutonium present as Pu(VI) based on the observation of plutonyl axial oxygen atoms.²⁵

Table 4.2.1.1 contains decontamination factors (DFs) and equilibrium distribution constants (K_d), and removal rate constants from the average plutonium concentration data. The listed DFs and K_d s derive from samples collected after about 1 day (29.7 hours in these tests and 24.1 hours in the earlier testing³) and 7 days of contact. DF and K_d data for the three data sets (Pu(IV), Pu(VI) and previous Pu(IV)) are within a factor of approximately two of each other. Inspection of Figure 4.2.1.1 indicates similar changes in the solution plutonium concentration with time for each test suggesting similar removal kinetics for both Pu(IV) and Pu(VI).

Removal rates for sorption or ion-exchange of sorbates and porous sorbents depend on three consecutive mass transport steps; (1) bulk transport of the sorbate in the solution phase, (2) transport of the sorbate through a hydrodynamic boundary layer or film and (3) transport of the sorbate within the pore volume of the sorbent to the active sorption or ion exchange site.²⁶ The latter step also includes the steps involved in sorption or exchange at the sorbent site (e.g., dehydration, exchange, etc.). Generally, the latter two steps are the major factors controlling rates of removal. Since these steps act in series, the slower of the two steps will be rate limiting. In the system under investigation, the removal kinetics are further complicated by the fact that at least four different sorbates (Sr, Pu, Np and U) interacting with the MST. Each could have a different rate limiting step or influence the transport of other sorbates during any of the above steps.

During the early stages of contact between the MST and alkaline solutions containing the sorbates removal kinetics may exhibit a first or second order dependence on the sorbate concentration. Inspection of graphs plotting the plutonium concentration versus time indicate that overall, the removal kinetics do not fit first or second order expressions in plutonium concentration. However, between 1 and 4 hours, plutonium removal fits first order kinetics with respect to the concentration of plutonium (see Figure 4.2.1.2).

We calculated removal rate constants from the linear fit of the average concentrations for the time interval of 1 to 4 hours using equation 1. The rate constants are reported in Table 4.2.1.1. Reaction rate constants are known to vary with oxidation state²⁷ and, thus, determination of the rate constants for the Pu(IV) and Pu(VI) spiked solutions may provide additional information concerning the stability and reactivity of Pu(IV) and Pu(VI) in alkaline solutions. The average rate constants for the tests using the Pu(IV) spiked solutions ranged from 1.29 to 1.42 times greater than that for the solution spiked with Pu(VI). This suggests a slight increase in the removal rate for Pu(IV) compared to Pu(VI). However, given the experimental variance in rate constants calculated for each individual test, the ranges in rate constants defined by $\pm 2\sigma$ overlap all three test cases. Thus, with this limited data set, we cannot conclusively establish that Pu(IV) removal is faster than Pu(VI) between 1 and 4 hours of contact with MST.

$$\text{Rate Constant (k) [mole/L-h]} = - \text{slope}/2.303 \quad (1)$$

Figure 4.2.1.1. Plutonium Concentration as a Function of Elapsed Time

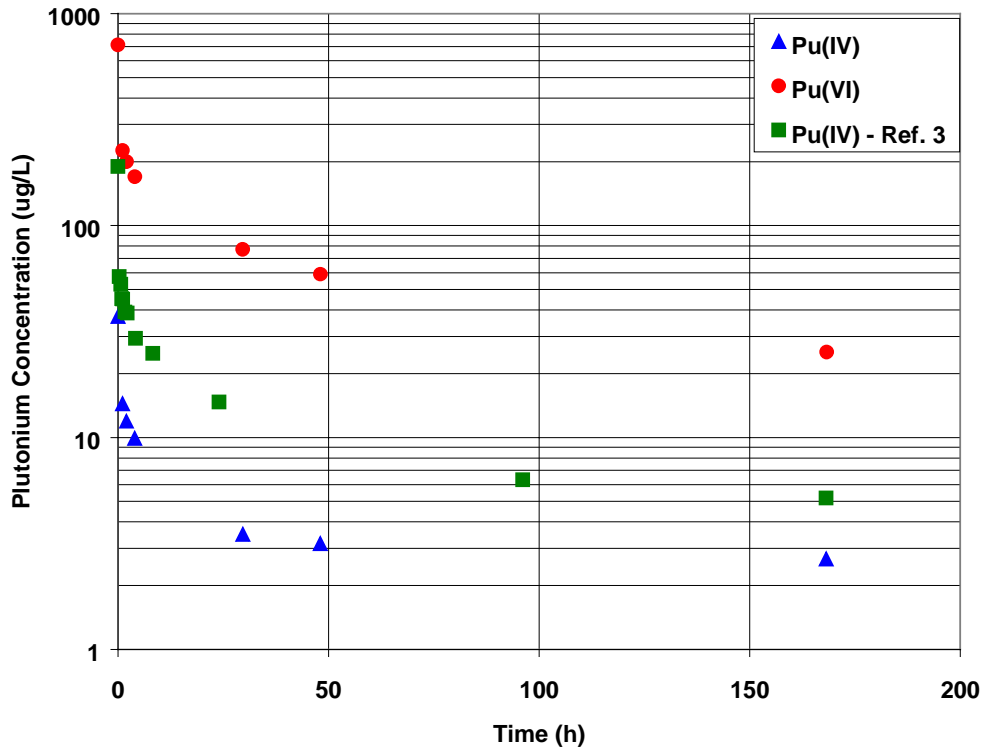
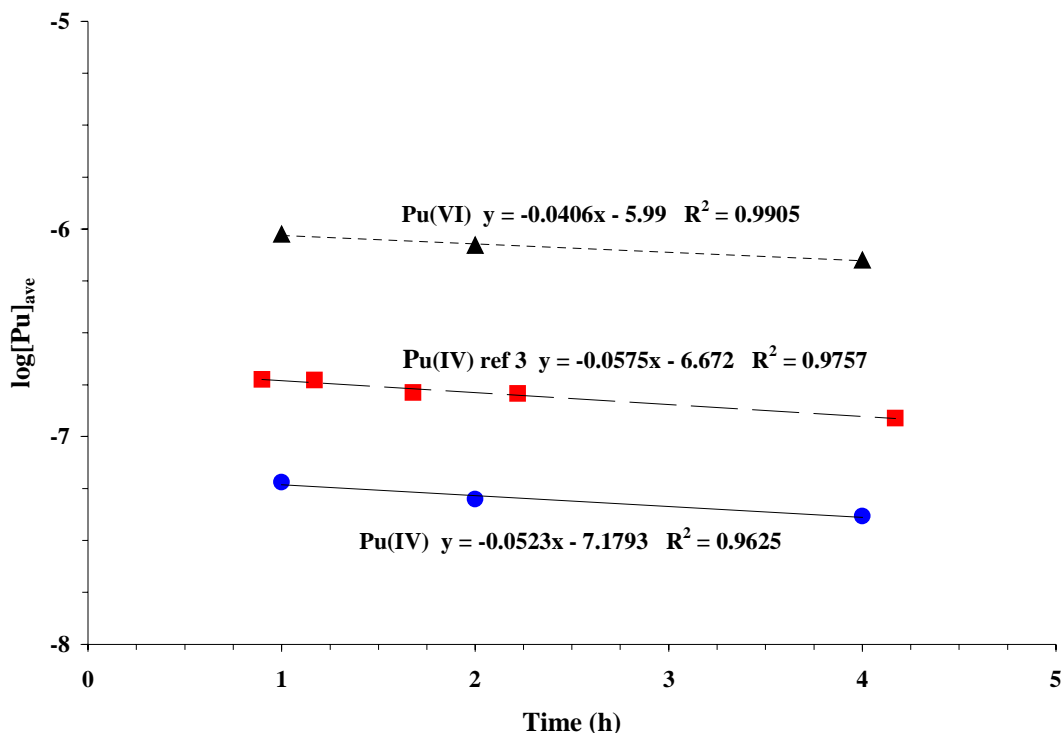


Table 4.2.1.1. Plutonium Decontamination Factors, Equilibrium Distribution Constants, and Sorption Rates

Species	DF		$K_d \times 10^{-4}$ (mL/g)		Rate Constant* (h ⁻¹)
	1 Day	7 Day	1 Day	7 Day	
Pu(IV)	14.8	18.5	3.46	4.36	0.0227
Pu(VI)	9.2	28.2	2.05	6.77	0.0176
Pu(IV) – Ref. 3	12.9	36.6	2.99	8.92	0.0250

* Determined by linear fit of concentration data between approximately 1 and 4 hours of contact with the MST (see Figure 4.2.1.2.)

Figure 4.1.1.2. Plutonium Removal as a Function of Time Between 1 and 4 Hours of Contact with MST



4.2.2 Neptunium Removal

Figure 4.2.2 compares the average neptunium concentration as a function of time for the two neptunium oxidation state tests along with previous testing data.³ The starting soluble neptunium concentrations in the Np(IV) and Np(V) tests were nearly the same (1159 $\mu\text{g/L}$ and 1259 $\mu\text{g/L}$, respectively). The soluble neptunium concentration in the earlier testing³ measured 415 $\mu\text{g/L}$. The lower value in the earlier testing does not represent the solubility limit but rather a lower target concentration. The equilibrium soluble neptunium concentrations measured 40.6, 122, and 55.8 $\mu\text{g/L}$ for Np(IV), Np(V) and the earlier Np(V) testing, respectively. Only the test with the Np(IV) spiked solution met the Z-Area limit for neptunium activity (53 $\mu\text{g/L}$ Np). The lack of difference in concentration data provides no evidence to support or refute the presumption that the testing featured two different neptunium oxidation states. Unlike that observed for the plutonium experiments, EXAFS analysis identified only one oxidation state of neptunium on the MST solids.²⁸ Note that the EXAFS analysis could not conclude which oxidation state existed.

Table 4.2.2.1 contains decontamination factors (DFs), equilibrium distribution constants (K_d s) and the removal rate constants calculated from the average neptunium concentration data. We calculated the neptunium removal rate constants based upon the average concentration changes between 4 and 48 hours on contact with the MST. The 1-day DF and K_d values for all 3 data sets show good agreement. One would expect this finding if all the solutions contained neptunium with the same oxidation state. The 7-day Np(IV) DF and K_d values proved significantly larger than those of the other two. The

higher Np(IV) values may reflect precipitation of the Np(IV) from solution in addition to sorption onto the MST. The chemical literature reports a lower solubility of Np(IV) compared to Np(V).

Figure 4.2.3.2 provides a plot of the log of the neptunium concentration versus time for the contact interval from 4 to 48 hours. During this interval, the graphs indicate a fairly linear relationship suggesting first order dependence on neptunium concentration during this time period. As discussed previously for plutonium, we determined the first order rate constants based on the average concentrations (see Table 4.2.2.1). The rate constants for the Np(V) and Np(IV) spiked solutions prepared in this test set proved very similar. The rate constant obtained from previous testing proved about 50% higher. However, given the experimental variance in rate constants calculated for each individual test, the ranges in rate constants defined by $\pm 2\sigma$ overlap all three test cases. Thus the reaction kinetics do not provide information confirming the presence of Np(IV) and whether the removal rate of Np(IV) is different from that of Np(V).

Figure 4.2.3.1. Neptunium Concentration as a Function of Elapsed Time

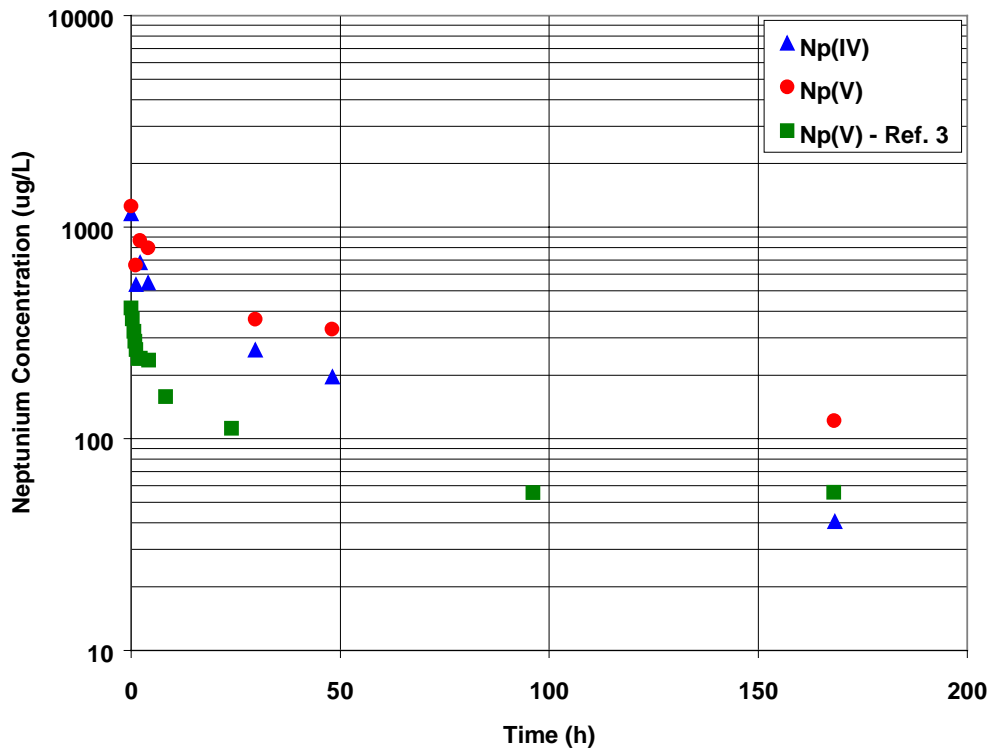
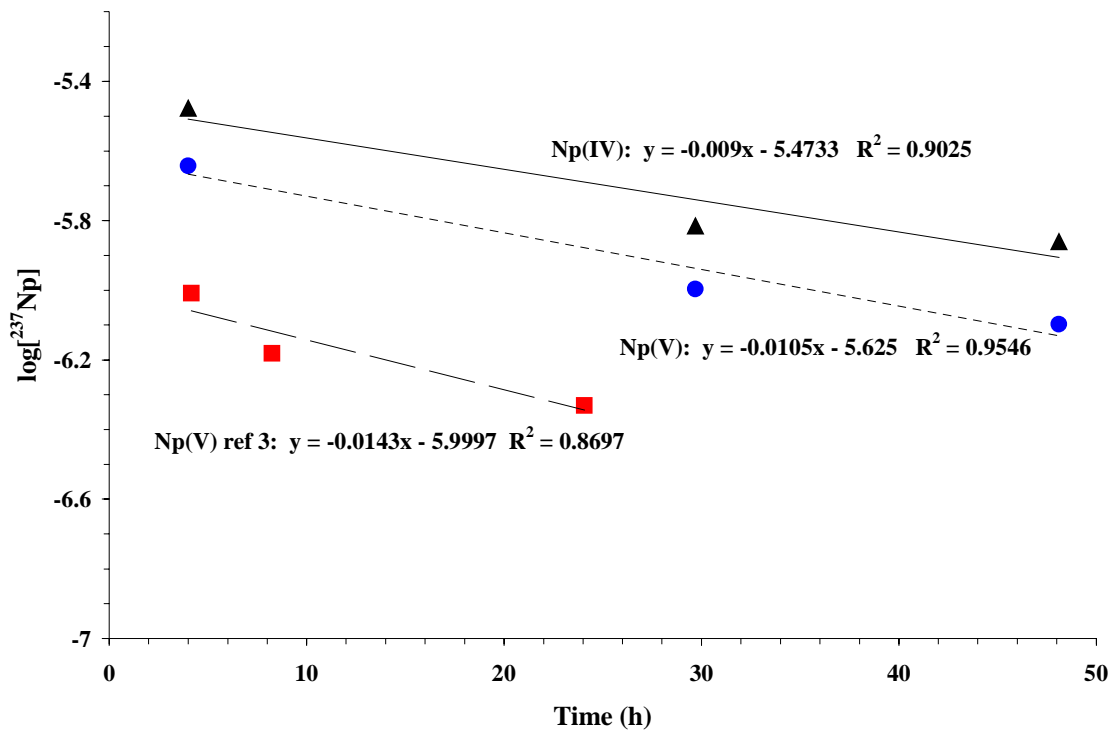


Table 4.2.2.1. Neptunium Decontamination Factors, Equilibrium Distribution Constants and Removal Rate Constants

Species	DF		$K_d \times 10^{-3}$ (mL/g)		Rate Constant* (h ⁻¹)
	1 Day	7 Day	1 Day	7 Day	
Np(IV)	4.43	29.8	8.56	71.9	0.00391
Np(V)	3.45	12.4	6.07	28.2	0.00456
Np(V) – Ref. 3	3.7	7.4	6.78	16.1	0.00621

* Determined by linear fit of concentration data between approximately 4 and 48 hours of contact with the MST (see Figure 4.2.3.2.)

Figure 4.2.3.2. Neptunium Removal as a Function of Time Between 4 and 48 Hours of Contact with MST



4.2.3 Plutonium and Neptunium Oxidation State Testing Conclusions

Single component oxidation state tests yielded the following observations and conclusions.

- Preliminary evidence suggests that Pu(VI) remains stable in alkaline solutions for periods as long as 2 weeks and exhibits a higher solubility than Pu(IV).
- Test results suggest that the rates of Pu(IV) and Pu(VI) removal are similar.
- Test results yielded inconclusive evidence for the stability of Np(IV) in an alkaline salt solution.
- Test results indicated no significant changes in neptunium removal upon contact of solutions prepared with Np(V) or Np(IV).

4.3 Evaluation of Different MST Samples

Testing featured three different samples of MST (see Table 4.3.1) prepared by Optima Chemical Company. All three samples were prepared several years ago for use in the In-Tank Precipitation process. Samples identified as #33180 and #33407 represent archived process samples produced by Optima Chemical Company and sent to SRTC during vendor qualification testing. The MST #TNX sample was obtained from a drum of MST slurry stored at SRS which had been produced by Optima Chemical Company for use in pilot-scale testing at SRTC. The much lower titanium content in the #33180 sample occurred upon the deliberate addition of water to the sample after delivery and storage at SRTC for several years. The original titanium concentration of the #33180 sample was very similar to those for the other two samples.

Table 4.3.1 Identification and Weight Percent Titanium Content of MST Samples

<u>Sample ID</u>	<u>wt % Ti</u>
33180	9.25
33407	23.4
TNX	21.1

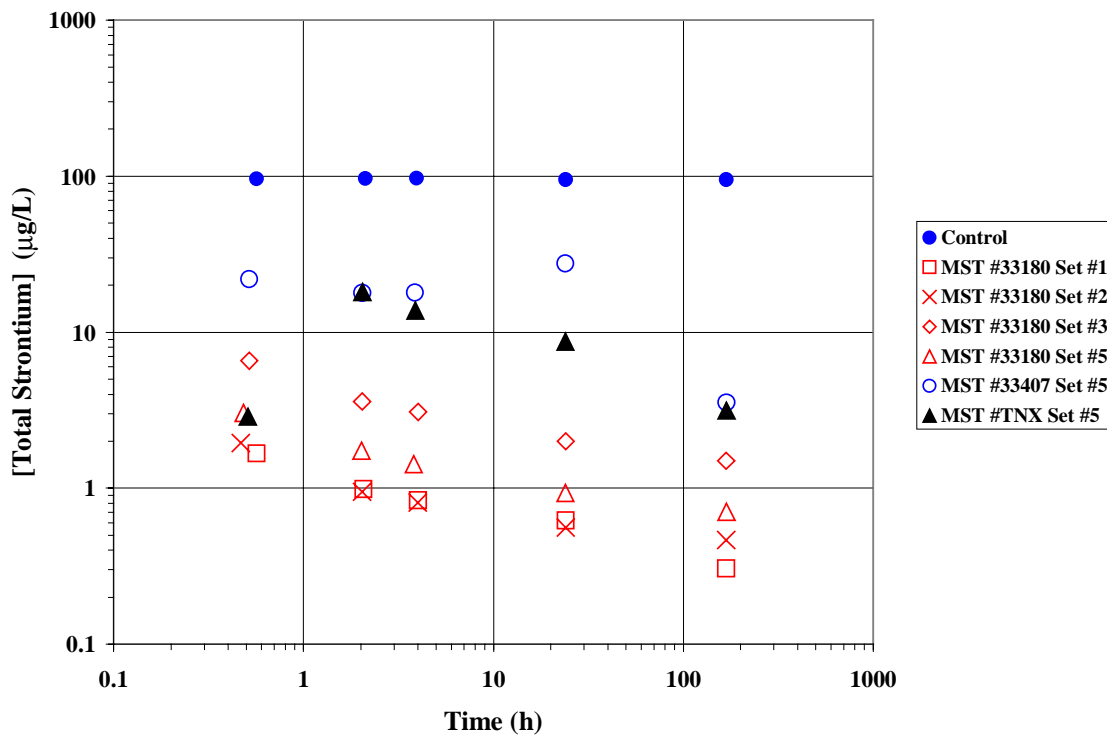
Evaluation of the MST samples used the 5.6M Na⁺ salt solution previously used in testing of MST performance. Each test had a MST concentration of 0.4 g/L. Figures 4.3.1 through 4.3.4 provide graphs of each sorbate concentration (Sr, Pu, U and Np, respectively) versus time for each MST sample. Each figure also includes the results for sample #33180 for each set of tests conducted during FY2000 and FY2001 (labeled as Sets # 1, 2 and 3).

MST samples #33407 and #TNX exhibited a lower capacity for strontium compared to #33180. At each sampling period, the DF and K_d values for both of these samples averaged about an order of magnitude lower than that of #33180 (see Table 4.3.2). Note however, that the rate of removal appeared similar for all three materials as evidence by similar slopes in the graphs. We attribute the different strontium removal performance of the three MST samples to an unidentified characteristic (e.g., degree of crystallinity, population of active sites) of the samples that does not affect removal kinetics. Removal

kinetics may be limited by transport of the sorbate to the reaction site, whereas removal capacity reflects the total number of site available to a particular sorbate.

The average strontium DF for samples #33407 determined after 24 hours of contact falls below the values required for the bounding (DF = 5.1) waste case.¹ For sample #TNX, the 24-hour DF measured 11.4, which is more than twice the value needed for the bounding case. Thus, the sample identified as #TNX would provide satisfactory performance for all planned waste processing operations. In contrast, sample #33407 may not provide satisfactory performance for all planned waste processing operations.

Figure 4.3.1 Strontium Concentration versus Time for Different MST Samples



Note that a measurable difference exists in the performance of the same MST sample (#33180) over the multiple test sets conducted during FY00 and FY01. Table 4.3.2 presents the strontium DF and K_d values for all MST samples. With the exception of Set #2 (64.5 µg/L), the initial total strontium concentration for each data set averaged 93.9 ± 5.67 µg/L (including that reported in the Phase V testing but not shown in Figure 4.3.1). The low DF measured for the sample in set #2 may in part result from the lower initial strontium concentration. Note however, based on the results investigating the affects of solution composition (section 4.1), we concluded that the initial sorbate concentration does not significantly affect strontium removal. As shown in Table 4.3.2, the variance between test sets decreases if we omit the results for Set #2. We attribute the majority of the variance to errors associated with weighing out and delivering the same

quantity of MST to each test and analytical measurement errors. Analytical measurement errors include those resulting from sampling, preparation of samples for measurement and actual radiochemical measurements.

Table 4.3.2 Strontium Decontamination Factors and Distribution Constants for MST Samples

<u>MST ID</u>	<u>Data Set</u>	<u>DF</u>		<u>K_d (mL/g)</u>	
		<u>24 hour</u>	<u>7 day</u>	<u>24 hour</u>	<u>7 day</u>
33180	Phase V ^a	130	140	3.23E+05	3.48E+05
33180	1	151	305	3.75E+05	7.61E+05
33180	2	32.3	43.1	7.83E+04	1.05E+05
33180	3	158	190	3.92E+05	4.72E+05
33180	5	107	141	2.65E+05	3.51E+05
	Average	115	164	2.86E+05	4.07E+05
	Standard Deviation	50.6	95.2	1.26E+05	2.38E+05
	Relative Standard Deviation ([Pu] _o ~ 200 µg/L)	43.8%	58.1%	44.1%	58.5%
	Average w/o Set 2	136	194	3.388E+05	4.84E+05
	Standard Deviation	22.9	77.5	5.72E+04	1.94E+05
	Relative Standard Deviation ([Pu] _o ~ 100 µg/L)	16.8%	40.0%	16.9%	40.3%
33407	5	3.62	28.1	6.57E+03	6.80E+04
TNX	5	11.4	31.7	2.59E+04	7.63E+04

^a data reported in WSRC-TR-2000-00142 (reference 3).

Figure 4.3.2 and Table 4.3.3 present a summary of the plutonium removal performance for the three MST samples. All three samples exhibited similar plutonium removal kinetics. Plutonium removal performance for sample #33180 measured about a factor of two higher than the other two samples (#33407 and #TNX). Over all data sets, the average plutonium DF and K_d for sample #33180 exhibited a relative standard deviation of approximately 33%. As expected, the relative standard deviation proved smaller (i.e., ca. 9% - see Table 4.3.3) for the tests conducted with a higher initial plutonium concentration (ca. 200 µg/L). For the tests conducted with solutions containing approximately 100 µg/L plutonium, the relative standard deviation proved slightly greater (ca. 35%) than that for all of the data sets combined.

The average plutonium DFs for samples #33407 and #TNX determined after 24 hours of contact fell below the values required for the average (DF = 12) and bounding (DF = 49) waste cases. Thus, these materials may not satisfactorily remove plutonium in all planned operations. Comparison of the average DFs for plutonium in tests with MST sample #33180 indicated that the average DF decreased with a decrease in the initial plutonium concentration, as expected. Note however, that the DFs for the two data sets are not statistically different at the 95% confidence interval ($\pm 2\sigma$)

Figure 4.3.2 Plutonium Concentration versus Time for Different MST Samples

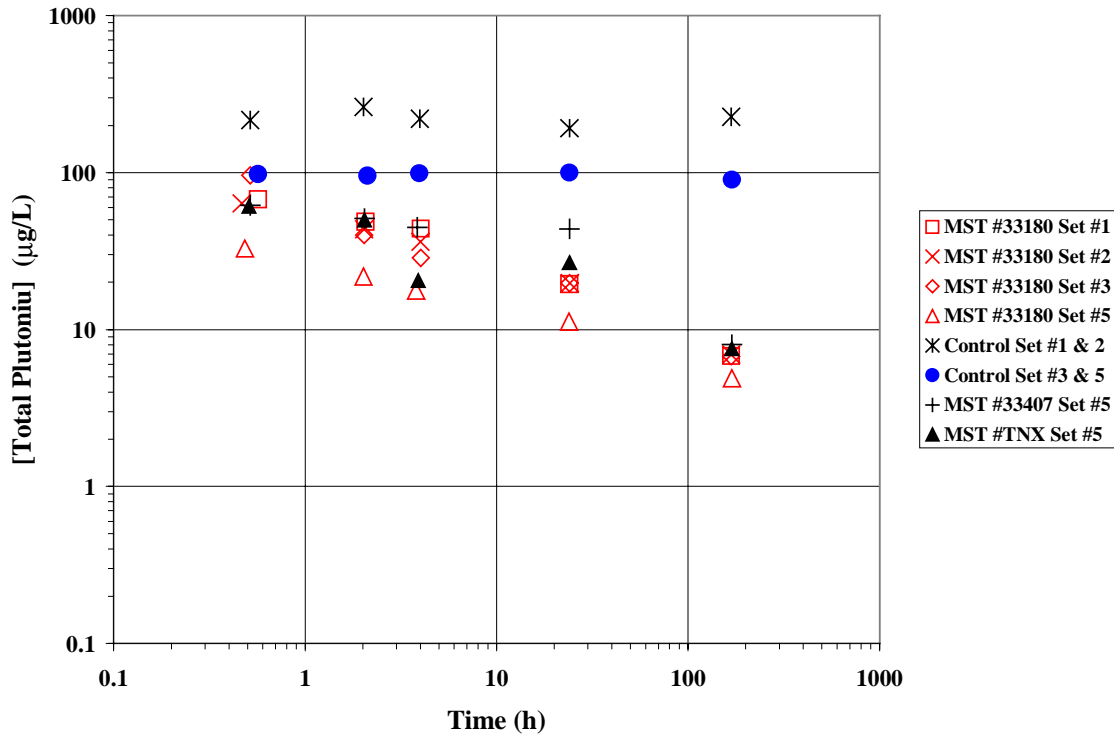


Table 4.3.3 Plutonium Decontamination Factors and Distribution Constants for MST Samples

<u>MST ID</u>	<u>Data Set</u>	<u>DF</u>		<u>K_d (mL/g)</u>	
		<u>24 hour</u>	<u>7 day</u>	<u>24 hour</u>	<u>7 day</u>
33180	Phase V ^a	12.9	36.6	2.98E+04	8.90E+04
33180	1	11.3	32.3	2.58E+04	7.85E+04
33180	2	4.93	14.4	9.85E+03	3.36E+04
33180	3	10.3	29.6	2.33E+04	7.14E+04
33180	5	9.21	21.1	2.06E+04	5.04E+04
	Average	9.73	26.8	2.19E+04	6.46E+04
	Standard Deviation	3.01	8.94	7.52E+03	2.23E+04
	Relative Standard Deviation	30.9%	33.4%	34.4%	34.6%
	Average Phase V & Set 1	12.1	34.5	2.78E+04	8.37E+04
	Standard Deviation	1.12	3.02	2.76E+03	7.43E+03
	Relative Standard Deviation	9.3%	8.8%	9.9%	8.9%
	Average Sets 2, 4 & 5	8.15	21.7	1.79E+04	5.18E+04
	Standard Deviation	2.85	7.95	7.11E+03	1.89E+04
	Relative Standard Deviation	34.9%	35.0%	39.7%	36.6%
33407	5	2.36	12.9	3.41E+03	2.98E+04
TNX	5	3.87	13.7	7.14E+03	3.16E+04

^a data reported in WSRC-TR-2000-00142 (reference 3).

Figure 4.3.3 and Table 4.3.4 present a summary of the uranium removal performance for the three MST samples. All three samples exhibited similar uranium removal kinetics and capacity. On average the addition of 0.4 g/L MST removed about 30% of the uranium in solution. Although the fraction of uranium removed proved low, uranium represents the greatest sorbate removed on a mass basis. The high mass removal reflects the much higher uranium concentration (ca. 11,000 µg/L) compared to the other sorbates (100 – 500 µg/L). Statistically, there appeared to be no significant difference in the quantity of uranium removed after 24 hours compared to that after 7 days.

Figure 4.3.3 Uranium Concentration versus Time for Different MST Samples

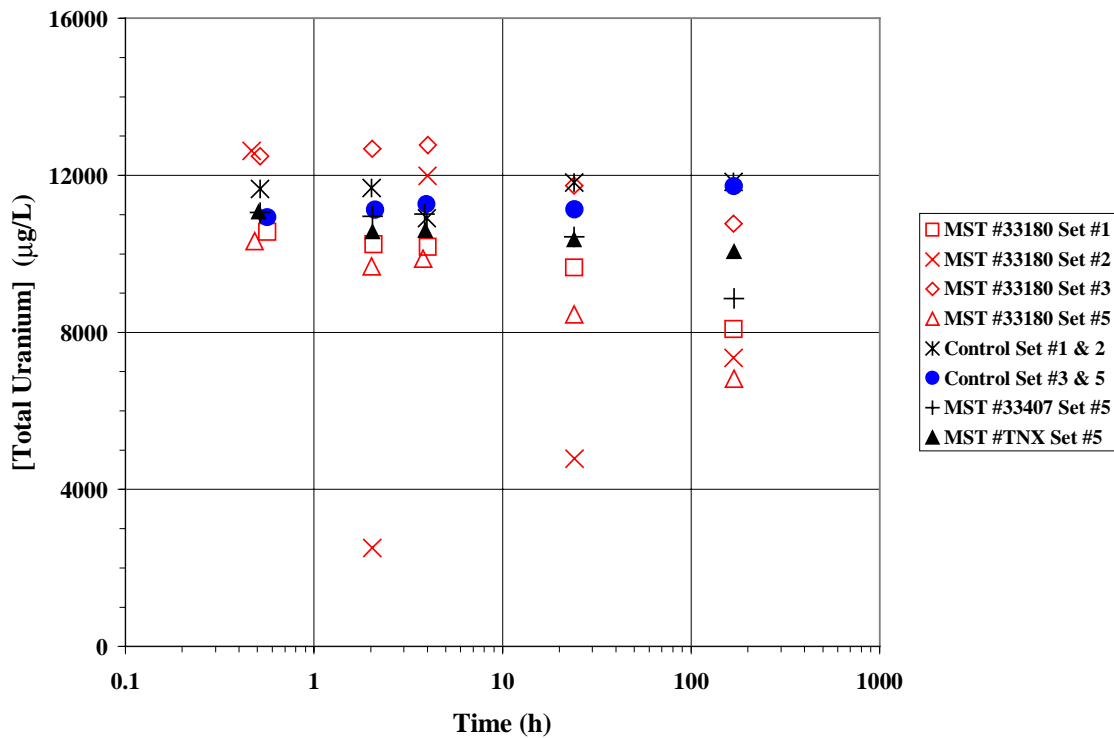


Table 4.3.4 Uranium Decontamination Factors for MST Samples

<u>MST ID</u>	<u>Data Set</u>	<u>DF</u>		<u>K_d</u>	
		<u>24 hour</u>	<u>7 day</u>	<u>24 hour</u>	<u>7 day</u>
33180	Phase V ^a	1.20	1.50	500	1250
33180	1	1.14	1.36	358	906
33180	2	1.12	1.22	308	562
33180	3	2.08	1.36	2710	888
33180	5	1.4	1.74	1010	1860
	Average	1.39	1.44	975	1090
	Standard Deviation	0.40	0.20	1010	492
	Relative Standard Deviation	29.0%	13.7%	103%	45.0%
33407	5	1.14	1.31	347	852
TNX	5	1.15	1.18	364	451

^a data reported in WSRC-TR-2000-00142 (reference 3).

Figure 4.3.4 and Table 4.3.5 present a summary of the neptunium removal performance for the three MST samples. All three samples exhibited similar neptunium removal kinetics. Over the five test sets, MST sample #33180 exhibited an average neptunium removal of 70% after 24 hours and 87% after 7 days. The relative standard deviation for neptunium removal proved rather large (44 – 52 %). The average DF for the other two MST samples (#33407 and #TNX) remained lower than that measured for #33180. This trend agrees with the results for other sorbates (e.g., strontium and plutonium). These results suggest that these two samples exhibit an inherently lower affinity for strontium and the actinides than does sample #33180. Based on the DFs measured after 24 hours of contact, only the MST sample #33180 exhibited neptunium removal that would meet the requirements at the bounding case (DF = 2).¹

Figure 4.3.4 Neptunium Concentration versus Time for Different MST Samples

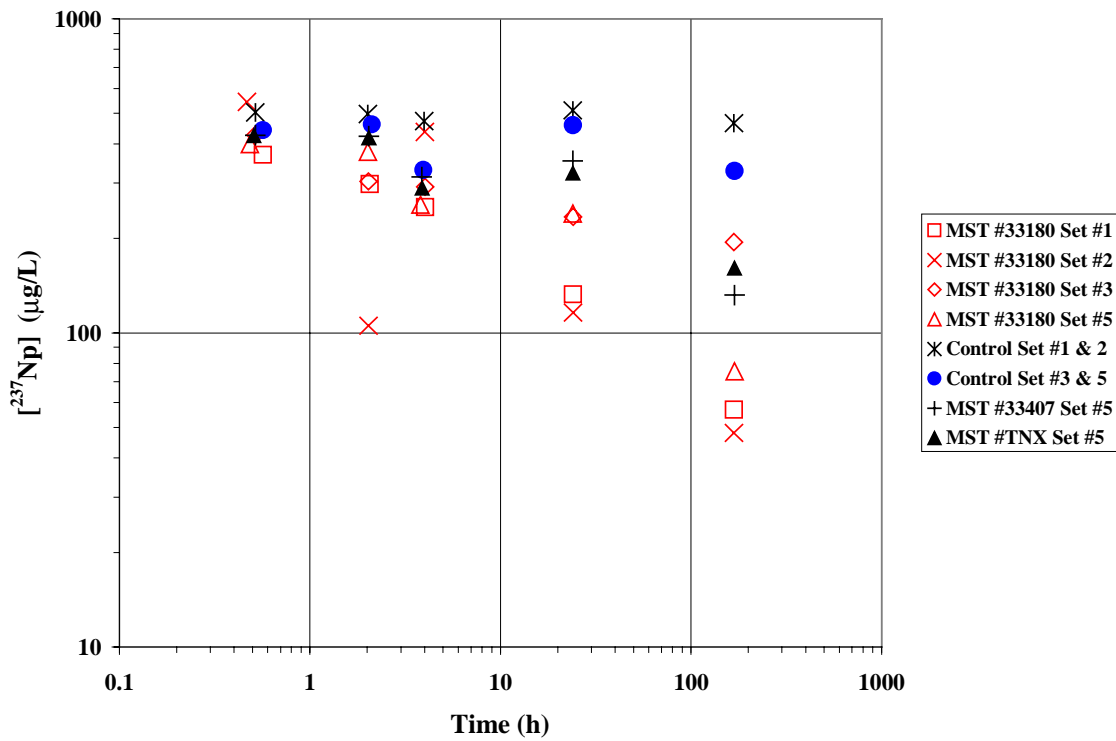


Table 4.3.5 Neptunium Decontamination Factors for MST Samples

<u>MST ID</u>	<u>Data Set</u>	<u>DF</u>		<u>K_d</u>	
		<u>24 hour</u>	<u>7 day</u>	<u>24 hour</u>	<u>7 day</u>
33180	Phase V ^a	3.70	7.44	6750	16100
33180	1	3.47	8.08	6180	17700
33180	2	1.98	2.47	2450	3690
33180	3	5.56	13.4	11400	31100
33180	5	2.02	6.42	2560	13600
	Average	3.35	7.57	5870	16400
	Standard Deviation	1.47	3.93	3670	9830
	Relative Standard Deviation	44.0%	52.0%	62.6%	59.8%
33407	5	1.37	3.68	938	6710
TNX	5	1.50	3.02	1250	5010

^a data reported in WSRC-TR-2000-00142 (reference 3).

4.4 Evaluation of Alternate Sorbent Materials

Previously, SRTC evaluated samples of sodium nonatitanate (ST), crystalline silicotitanate (CST) and SrTreat[®] for the removal of strontium and actinides from alkaline salt solution.^{29,30} Testing results indicated that some of these samples exhibited removal capacities and kinetics for strontium and actinides as good as or better than MST. Consequently, we recommended further testing of these materials.

Additional testing completed during FY01 featured one SrTreat[®] sample, one sample of CST and 2 pharmacosiderites samples. Table 4.4.1 provides a listing of all tested materials to date with the most recently tested materials highlighted in boldface. Since all samples are titanium based, we selected the quantity of sorbent to add in each test to provide the same quantity of titanium added by the addition of 0.4 g/L MST. Note, however, that the calculated distribution constants, K_d, are based on the total sorbent weight and not on a titanium basis alone.

Table 4.4.1 Alternate Sorbent Materials

<u>Sorbent ID</u>	<u>Source</u>	<u>Description</u>
ST-0073A	Honeywell	ST – pilot scale production
ST-0073B	Honeywell	ST – pilot scale production
ST-01520	Honeywell	ST – pilot scale production
ST-RC-4-23B	TAMU	ST – moderate crystallinity
ST-RC-4-64B	TAMU	ST – poor crystallinity
ST-39287-5A	Honeywell	ST – lab scale production
ST-39287 – 5B	Honeywell	ST – lab scale production
SrTreat [®] #48	Fortum	ST – commercial batch
SrTreat [®] #49	Fortum	ST – commercial batch
SrTreat[®] #8	Fortum	ST – commercial batch with smaller particle size distribution
CST IE-910	UOP	CST powder Lot #899371998000001
CST IE-911	UOP	CST engineered form Lot #899902081000009
DM1-11-1	TAMU	CST prepared for maximum Sr²⁺ uptake
EAB-II-23	TAMU	pharmacosiderite in K⁺ form
DM-1-25	TAMU	pharmacosiderite in Na⁺ form

Tables 4.4.2 and 4.4.3 provide the DF and K_d values, respectively, after 24 hours and 7 days of contact for each of the alternate sorbents listed in Table 4.4.1 except for the first three ST samples. As reported previously, the first three samples exhibited lower strontium and actinide removal characteristics than that for MST.^{29,30}

Table 4.4.2 Decontamination Factors for Alternate Sorbent Materials

Sorbent	Decontamination Factor							
	Sr 24 h	Sr 7d	Pu 24 h	Pu 7d	U 24 h	U 7d	Np 24 h	Np 7d
MST #33180*	1.30E+02	1.40E+02	1.29E+01	3.66E+01	1.20E+00	1.50E+00	3.70E+00	7.44E+00
MST #33180	1.51E+02	3.05E+02	1.13E+01	3.23E+01	1.14E+00	1.36E+00	3.47E+00	8.08E+00
SrTreat #48	4.20E+00	4.08E+01	1.40E+00	1.81E+00	9.33E-01	9.97E-01	9.37E-01	1.33E+00
SrTreat #49	1.07E+02	5.91E+02	1.74E+00	2.90E+00	9.31E-01	1.02E+00	1.06E+00	1.73E+00
CST IE-910	1.06E+01	1.59E+01	1.28E+00	1.16E+00	9.58E-01	9.56E-01	1.00E+00	1.16E+00
CST IE-911	5.81E+00	1.97E+01	1.95E+00	3.39E+00	1.00E+00	1.12E+00	1.13E+00	2.00E+00
MST #33180	3.23E+01	4.31E+01	4.93E+00	1.44E+01	1.12E+00	1.22E+00	1.98E+00	2.47E+00
SrTreat #8	8.74E+01	1.96E+02	2.01E+00	8.20E+01	1.20E+00	2.26E+00	1.43E+00	1.13E+01
TAMU DM1-11-1	2.61E+01	4.76E+01	1.30E+00	1.82E+00	1.17E+00	1.24E+00	1.23E+00	1.45E+00
MST #33180	1.58E+02	1.90E+02	1.03E+01	2.96E+01	2.08E+00	1.36E+00	5.56E+00	1.34E+01
ST-RC-4-23B	1.09E+02	9.91E+01	3.54E+00	9.11E+00	1.50E+00	1.52E+00	3.47E+00	7.04E+00
ST-RC-4-64B	2.91E+02	4.73E+02	7.69E+00	5.69E+01	1.80E+00	2.71E+00	2.81E+00	1.24E+01
ST-39287-5A	7.60E+01	1.78E+02	1.09E+01	2.56E+01	2.92E+00	2.43E+00	4.19E+00	1.31E+01
ST-39287-5B	2.55E+01	6.07E+01	3.08E+01	5.81E+01	2.04E+00	2.23E+00	5.44E+00	1.72E+01
MST #33180	1.07E+02	1.41E+02	9.21E+00	2.11E+01	1.40E+00	1.74E+00	2.02E+00	6.42E+00
MST #33470	3.62E+00	2.81E+01	2.36E+00	1.29E+01	1.14E+00	1.34E+00	1.37E+00	3.68E+00
MST #TNX	1.14E+01	3.17E+01	3.87E+00	1.37E+01	1.15E+00	1.18E+00	1.50E+00	3.02E+00
TAMU DM1-25	8.73E+01	1.53E+02	4.21E+00	2.47E+02	1.27E+00	3.20E+00	1.61E+00	2.09E+01
TAMU EABII-23	2.91E+01	7.73E+01	1.69E+00	1.91E+01	1.13E+00	1.34E+00	1.27E+00	3.01E+00

* data reported in WSRC-TR-2000-00142 (reference 3)

Table 4.4.3 Distribution Constants (K_d) for Alternate Sorbent Materials

Sorbent	Distribution Constant (mL/g)							
	Sr 24 h	Sr 7d	Pu 24 h	Pu 7d	U 24 h	U 7d	Np 24 h	Np 7d
MST #33180*	3.23E+05	3.48E+05	2.98E+04	8.90E+04	5.00E+02	1.25E+03	6.75E+03	1.61E+04
MST #33180	3.75E+05	7.61E+05	2.58E+04	7.85E+04	3.48E+02	9.06E+02	6.18E+03	1.77E+04
SrTreat #48	6.97E+03	8.67E+04	8.80E+02	1.77E+03				7.19E+02
SrTreat #49	2.22E+05	1.23E+06	1.54E+03	3.97E+03		4.52E+01	1.34E+02	1.52E+03
CST IE-910	8.82E+03	1.37E+04	2.57E+02	1.46E+02			4.46E+00	1.45E+02
CST IE-911	4.34E+03	1.68E+04	8.60E+02	2.15E+03		1.08E+02	1.15E+02	9.00E+02
MST #33180	7.83E+04	1.05E+05	9.85E+03	3.36E+04	3.08E+02	5.62E+02	2.45E+03	3.69E+03
SrTreat #8	3.52E+05	7.95E+05	4.10E+03	3.30E+05	8.05E+02	5.14E+03	1.76E+03	4.20E+04
TAMU DM1-11-1	5.42E+04	1.01E+05	6.47E+02	1.76E+03	3.73E+02	5.11E+02	4.97E+02	9.82E+02
MST #33180	3.92E+05	4.72E+05	2.33E+04	7.14E+04	2.71E+03	8.88E+02	1.14E+04	3.11E+04
ST-RC-4-23B	2.23E+05	2.03E+05	5.25E+03	1.68E+04	1.03E+03	1.08E+03	5.11E+03	1.25E+04
ST-RC-4-64B	5.53E+05	9.01E+05	1.28E+04	1.07E+05	1.53E+03	3.27E+03	3.46E+03	2.18E+04
ST-39287-5A	9.56E+04	2.26E+05	1.26E+04	3.13E+04	2.45E+03	1.83E+03	4.06E+03	1.55E+04
ST-39287-5B	4.70E+04	1.15E+05	5.72E+04	1.10E+05	1.99E+03	2.36E+03	8.52E+03	3.12E+04
MST #33180	2.65E+05	3.51E+05	2.06E+04	5.04E+04	1.01E+03	1.86E+03	2.56E+03	1.36E+04
MST #33407	6.57E+03	6.80E+04	3.41E+03	2.98E+04	3.47E+02	8.52E+02	9.38E+02	6.71E+03
MST #TNX	2.59E+04	7.63E+04	7.14E+03	3.16E+04	3.64E+02	4.51E+02	1.25E+03	5.01E+03
TAMU DM1-25	9.13E+04	1.60E+05	3.40E+03	1.60E+05	2.88E+02	2.33E+03	6.45E+02	2.11E+04
TAMU EABII-23	3.37E+04	9.14E+04	8.22E+02	2.16E+04	1.56E+02	4.13E+02	3.21E+02	2.41E+03

* data reported in WSRC-TR-2000-00142 (reference 3)

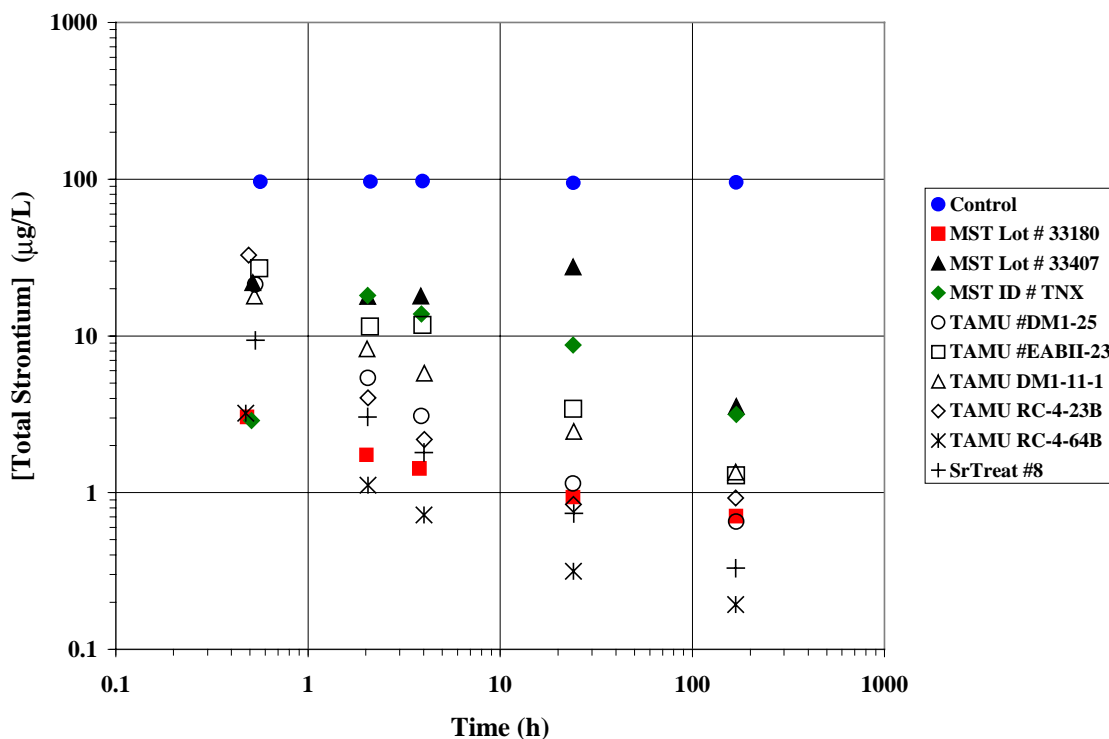
blanks indicate no measurable sorbate removal (DF less than or equal to 1)

4.4.1 Strontium Removal

Figure 4.4.1 presents a plot of the strontium concentration versus time for selected alternate sorbent materials. Samples that exhibited removal characteristics clearly better than any of the MST samples included the TAMU ST sample (ST-RC-4-64B) and the SrTreat[®] Lot #8 sample. The two pharmacosiderite samples, the other ST sample and the modified CST sample exhibited removal characteristics within the range spanned by the three different MST samples.

Comparing the two TAMU ST samples, ST-RC-4-23B and ST-RC-4-64B, we find that strontium removal kinetics and capacity proved better for the sample having less crystallinity (ST-RC-4-64B). For the two pharmacosiderites, the results indicate greater strontium removal for the sodium form (DM-1-25) compared to that for the potassium form (EAB-II-23). The modified CST sample (DM1-11-1) exhibited increased removal kinetics and capacity compared to the previously tested commercially available CST powder and engineered form.

Figure 4.4.1 Strontium Removal with MST, ST, CST and Pharmacosiderite Materials



4.4.2 Plutonium Removal

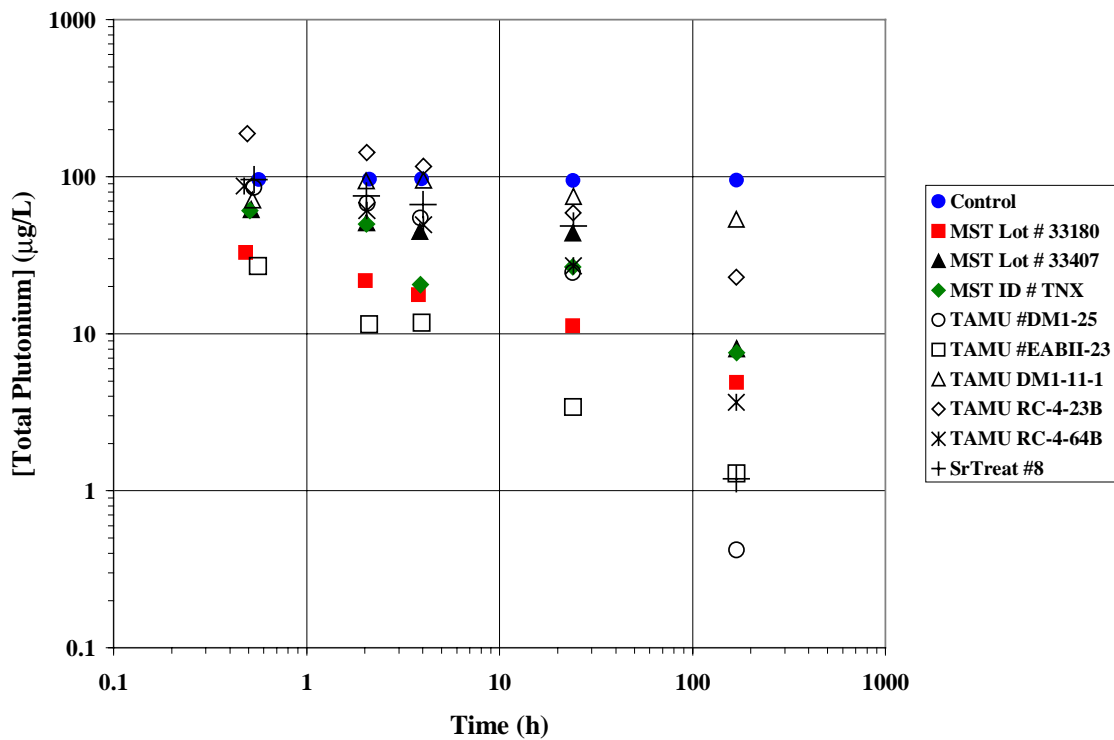
Figure 4.4.2 presents a plot of the plutonium concentration versus time for selected alternate sorbent materials. The pharmacosiderite sample in the K^+ form exhibited removal kinetics better than the MST samples. The Na^+ form of the pharmacosiderite sample, one of the ST samples (ST-RC-4-64B) and the SrTreat[®] Lot #8 sample exhibited removal capacities within the range spanned by the three different MST samples. Note however, that the plutonium K_d value after 24 hours of contact (see Table 4.4.2) did not approach that of the best MST sample (#33180) for any of the alternate sorbent samples. The pharmacosiderite samples have a relatively low titanium content and when the weight of sorbent is factored into the determination of the K_d value, the 24-hour K_d value falls well below that of the MST #33180 sample.

Comparing the two TAMU ST samples, ST-RC-4-23B and ST-RC-4-64B, we find that the less crystalline sample exhibited greater plutonium capacity and faster kinetics. For the two pharmacosiderites, the results indicate a faster removal rate for the potassium form than the sodium form. This finding is opposite to that observed with strontium removal kinetics (see section 4.4.1). Based on the 7-day results, the sodium form (DM1-25) appears to have a higher equilibrium capacity for plutonium than that of the potassium form (EAB-II-23). Unlike that observed for strontium, the modified CST sample (DM1-11-1) exhibited little affinity for plutonium. The low affinity of the CST

sample for plutonium is very similar to that previously observed with CST IE-910 powder.

The SrTreat[®] Lot #8 sample exhibited a much higher equilibrium capacity for plutonium compared to the previously tested samples (see Tables 4.4.1 and 4.4.2). Note however, that the plutonium removal kinetics proved considerably slower than that for the best of the MST samples. The measured DF for plutonium after 24 hours of contact fell well below the values needed to achieve the necessary DFs for the average and bounding waste cases.

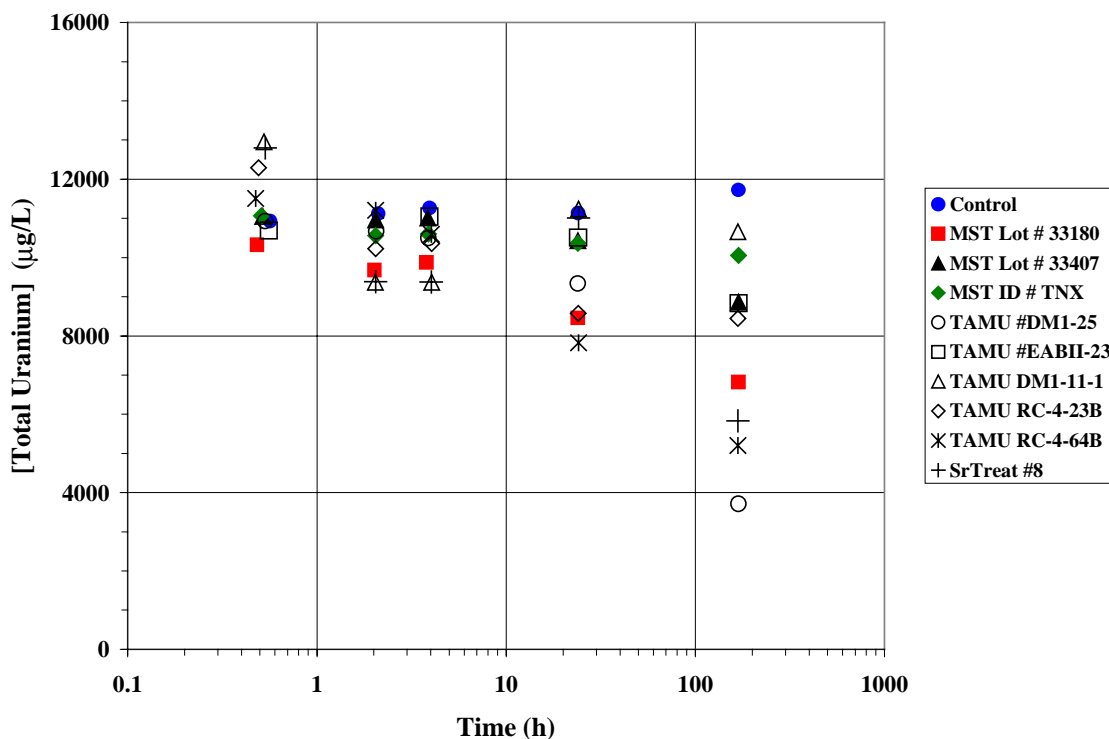
Figure 4.4.2 Plutonium Removal with MST, ST, CST and Pharmacosiderite Materials



4.4.3 Uranium Removal

Figure 4.4.3 presents a plot of the uranium concentration versus time for selected alternate sorbent materials. None of the samples exhibited removal characteristics clearly better than the MST samples during the first 24 hours of contact. After 168 hours of contact, the modified CST, the less crystalline ST and the SrTreat[®] samples removed more uranium than any of the MST samples (see Figure 4.4.3). The uranium removal characteristics for these three materials result in higher K_d values after 7-days of contact than those measured for the MST samples (see Table 4.4.2)..

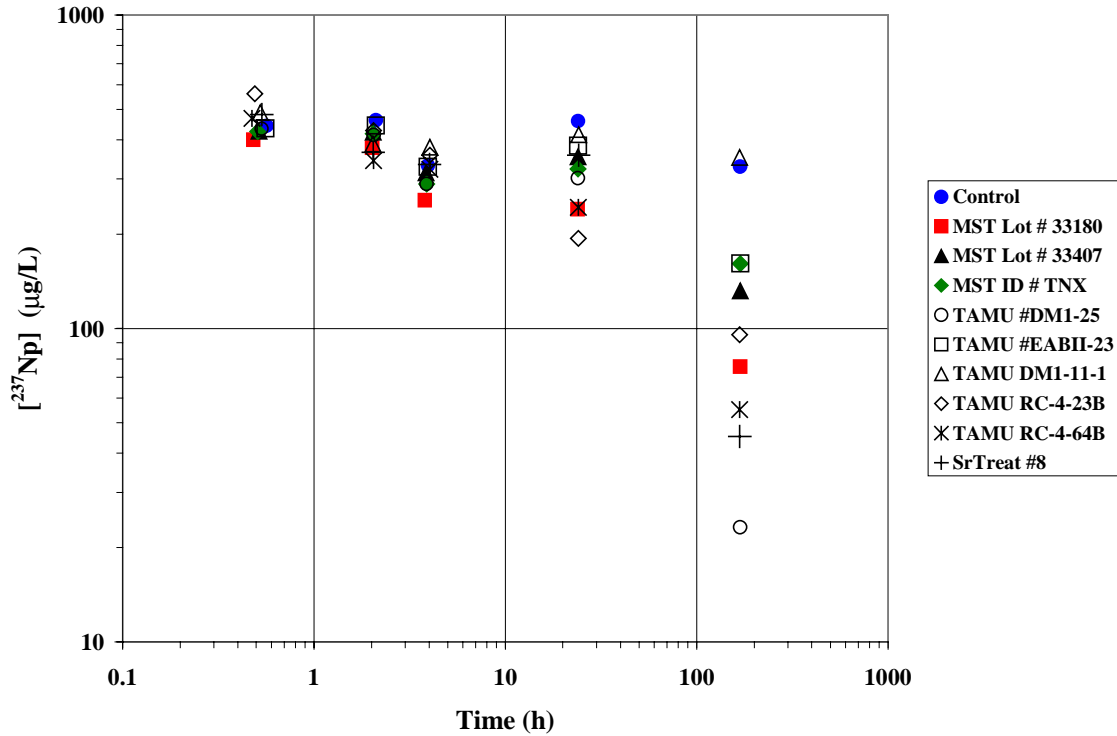
Figure 4.4.3 Uranium Removal with MST, ST, CST and Pharmacosiderite Materials



4.4.4 Neptunium Removal

Figure 4.4.4 presents a plot of the ²³⁷Np concentration versus time for selected alternate sorbent materials. None of the samples exhibited neptunium removal characteristics clearly better than any of the MST samples. However, SrTreat[®] Lot #8 sample, and the two TAMU ST samples (ST-RC-4-23B and ST-RC-4-64B) exhibited comparable removal characteristics to the best of the MST samples. The pharmacosiderite sample in the Na⁺ form exhibited a higher capacity than the pharmacosiderite sample in the K⁺ form. The CST sample (DM1-11-1) exhibited very low affinity for removing neptunium from the alkaline salt solution.

Figure 4.4.4 Neptunium Removal with MST, ST, CST and Pharmacosiderite Materials



4.4.5 Alternate Sorbent Conclusions

Results of the screening tests indicate that sodium nonatitanate and pharmacosiderite materials exhibit as good or better performance than MST samples. Sodium nonatitanate samples exhibiting good performance included the TAMU sample #ST-RC-4-64B and the Fortum SrTreat[®] #8 samples. Both of the pharmacosiderite samples exhibited good strontium and actinide separation performance. With the exception of plutonium, the sodium form (DM-1-25) of the pharmacosiderite exhibited better performance characteristics than the potassium form (EAB-II-23).

5.0 Quality Assurance

This work used the following task plan.

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.

This document provides deliverables for the affects of solution composition and plutonium and neptunium oxidation states and the performance of alternate sorbent materials requested in the authorizing task request,

Savannah River Site Salt Processing Project Research and Development Program Plan, PNNL-13253, Rev. 1, November 2000.

Notebooks WSRC-NB-2000-00120 (D. T. Hobbs), WSRC-NB-2001-00011 (D. T. Hobbs), WSRC-NB-2001-00168 (M. J. Barnes) and WSRC-NB-2001-00124 (K. M. Marshall) contain the experimental data obtained from this work.

6.0 References

- ¹ R. A. Dimena, H. H. Elder, J. R. Fowler, R. C. Fowler, M. V. Gregory, T. Hang, R. A. Jacobs, P. K. Paul, J. A. Pike, P. L. Rutland, F. G. Smith III, S. G. Subosits, G. A. Taylor and S. G. Campbell, "Bases, Assumptions, and Results of the Flowsheet Calculations for the Short List Salt Disposition Alternatives," WSRC-RP-99-00006, Rev. 2, April, 4, 2001.
- ² Savannah River Site Salt Processing Project Research and Development Program Plan, PNNL-13253, Rev. 1, November 2000.
- ³ D. T. Hobbs, M. S. Blume, H. L. Thacker, "Phase V Testing of Monosodium Titanate Adsorption Kinetics," WSRC-TR-2000-00142, May 24, 2000.
- ⁴ D. T. Hobbs, M. S. Blume, H. L. Thacker, "Screening Evaluation of Sodium Nonatitanate for Strontium and Actinide Removal from Alkaline Salt Solution, WSRC-TR-2000-00361, October 2, 2000.
- ⁵ D. T. Hobbs, M. S. Blume, H. L. Thacker, "Screening Evaluation of Alternate Sorbents and Methods for Strontium and Actinide Removal from Alkaline Salt Solution, WSRC-TR-2001-00072, February, 2001.
- ⁶ David T. Hobbs and David G. Karraker, "Recent Results on the Solubility of Uranium and Plutonium in Savannah River Site Waste Supernate," *Nuclear Technology*, **1996** (114), 318 – 324.
- ⁷ C. H. Delegard, "Solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in Alkaline Hanford High-Level Waste Solution," *Radiochem. Acta*, **41** (1987), 11.
- ⁸ *Comprehensive Inorganic Chemistry*, J. C. Bailar, ed., Pergammon Press, New York, 1973, Vol. 5, p. 465-635.
- ⁹ D. T. Hobbs and R. L. Pulmano, "Phase IV Simulant Testing Monosodium Titanate Adsorption Kinetics," WSRC-TR-99-00219, Rev. 0, June 29, 1999.
- ¹⁰ D. T. Hobbs and R. L. Pulmano, "Phase IV Testing of Monosodium Titanate Adsorption with Radioactive Waste," WSRC-TR-99-00286, Rev. 0, September 3, 1999.
- ¹¹ J. B. Harris, "Specification for Procurement of Monosodium Titanate," Specification No. Z-SPP-H-00001, Rev. 2, May 1992.
- ¹² D. T. Hobbs and T. B. Edwards, "Solubility of Uranium in Alkaline Salt Solutions (U)," WSRC-TR-93-454, March 29, 1994.
- ¹³ D. T. Hobbs and T. B. Edwards, "Solubility of Plutonium in Alkaline Salt Solutions (U)," WSRC-TR-93-131, February 26, 1993.
- ¹⁴ J. M. Cleveland, *The Chemistry of Plutonium*, Gordon & Breach, 579, pp. 49-52 (1970), (Am. Nucl. Soc. Reprint 1979).
- ¹⁵ A. G. Burney and R. M. Harbour, *Radiochemistry of Neptunium*, NAS-NS-3060, 150, p. 189, Technical Information Center, USAEC (1974).

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- ¹⁶ Procedure Manual L16.1, Analytical Development Section, Analytical Operating Procedures (U).
- ¹⁷ Procedure Manual L16.1, Analytical Development Section, Analytical Operating Procedures (U), ADS-2420, Rev. 3.
- ¹⁸ Procedure Manual L16.1, Analytical Development Section, Analytical Operating Procedures (U), ADS-1455, Rev. 1.
- ¹⁹ Procedure Manual L16.1, Analytical Development Section, Analytical Operating Procedures (U), ADS-2453, Rev. 0.
- ²⁰ T. B. Edwards, "A Revised, Statistically Designed Test Matrix for Studying MST Performance (U)," SRT-SCS-2001-00019, May 1, 2001.
- ²¹ J. A. Cornell, *Experiments with Mixtures*, Second Edition, John Wiley & Sons, New York, 1990.
- ²² D. T. Hobbs, T. B. Edwards, and S. D. Fleischman, "Solubility of Plutonium and Uranium in Alkaline Salt Solution (U)", WSRC-TR-93-056, February 12, 1993.
- ²³ SAS Institute, Inc., "JMP Statistics and Graphics Guide: Version 4 of JMP," SAS Institute, Inc., Cary, NC, 2000.
- ²⁴ K. Bourikas, T. Hiemstra and W. H. Van Riemsdijk, "Ion Pair Formation and Primary Charging Behavior of Titanium Oxide (Anatase and Rutile), *Langmuir*, **2001**, 17(3), 749-756.
- ²⁵ M. C. Duff, D. B. Hunter, D. T. Hobbs, M. J. Barnes and S. D. Fink, "Characterization of Sorbed Uranium, Plutonium and Neptunium on Monosodium Titanate", WSRC-TR-2001-00467, Rev. 0, October 1, 200.
- ²⁶ F. L. Slejko, *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application*, Tall Oaks Publishing, Inc., Voorhees, New Jersey, 1985, 18 – 22.
- ²⁷ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry A Comprehensive Text*, Third Edition, Interscience Publishers, New York, 1972, 652 – 680.
- ²⁸ M. C. Duff, D. B. Hunter, D. T. Hobbs, M. J. Barnes and S. D. Fink, "Characterization of Sorbed Uranium, Plutonium and Neptunium on Monosodium Titanate", WSRC-TR-2001-00356, Rev. 0, September 19, 2001.
- ²⁹ D. T. Hobbs, M. S. Blume, H. L. Thacker, "Screening Evaluation of Sodium Nonatitanate for Strontium and Actinide Removal from Alkaline Salt Solution, WSRC-TR-2000-00361, October 2, 2000.
- ³⁰ D. T. Hobbs, M. S. Blume, H. L. Thacker, "Screening Evaluation of Alternate Sorbents and Methods for Strontium and Actinide Removal from Alkaline Salt Solution, WSRC-TR-2001-00072, February, 2001.

Appendix 1**Plutonium (IV) Concentration Data**

Time	Pu(IV) Concentration (µg/L)			Average
	Test Pu(IV)-1	Test Pu(IV)-2	Test Pu(IV)-3	
0	37.26			37.26
1.0	15.06	14.42	13.91	14.46
2.0	11.60	11.77	12.53	11.97
4.0	10.25	9.72	9.85	9.94
29.6	1.33	4.85	4.31	3.50
48.0	3.14	3.97	2.40	3.17
168	1.48	1.65	4.90	2.68

Plutonium (VI) Concentration Data

Time	Pu(VI) Concentration (µg/L)			Average
	Test Pu(VI)-1	Test Pu(VI)-2	Test Pu(VI)-3	
0	712.04			712.04
1.1	239.90	197.79	239.90	225.86
2.1	202.89	193.96	204.17	200.34
4.0	172.27	164.61	172.27	169.72
29.7	81.92	72.99	76.56	77.16
48.0	61.51	55.13	60.23	58.95
168	25.65	24.12	26.03	25.27

Neptunium (IV) Concentration Data

Time	Np(IV) Concentration (µg/L)			Average
	Test Np(IV)-1	Test Np(IV)-2	Test Np(IV)-3	
0	1159.4			1159.42
1.2	519.4	532.7	556.7	536.23
2.1	643.7	691.7	702.6	679.31
4.1	530.3	567.1	540.5	545.95
29.7	242.0	259.2	287.6	262.95
48.1	191.7	203.4	194.3	196.46
168	35.1	53.3	33.4	40.63

Neptunium (V) Concentration Data

Time	Np(V) Concentration (µg/L)			Average
	Test Np(V)-1	Test Np(V)-2	Test Np(V)-3	
0	1259.0			1259.00
1.1	647.4	669.2	670.0	662.20
2.1	879.1	848.6	868.6	865.41
4.0	769.8	758.0	866.1	797.95
29.7	327.3	388.3	386.0	367.19
48.1	295.1	312.7	382.5	330.11
168	61.7	134.0	169.6	121.73

Appendix 2

We designated the eleven (11) experiments Trials 1 through 11. The first 6 used conditions selected from the set of extreme vertices (EVs) that bound the mixture region of interest in this study. Trials 7 and 8 represent duplicates of the centroid of the mixture region. Trial 9 was this centroid spiked with trace amounts of the minor salts, Trial 10 contained no MST (a control), and Trial 11 duplicated a Phase V trial. The following plot shows the symbols, colors, and trial labels used in the following analyses.

Exhibit 1: Colors and Symbols Used to Represent the 11 Experimental Trials

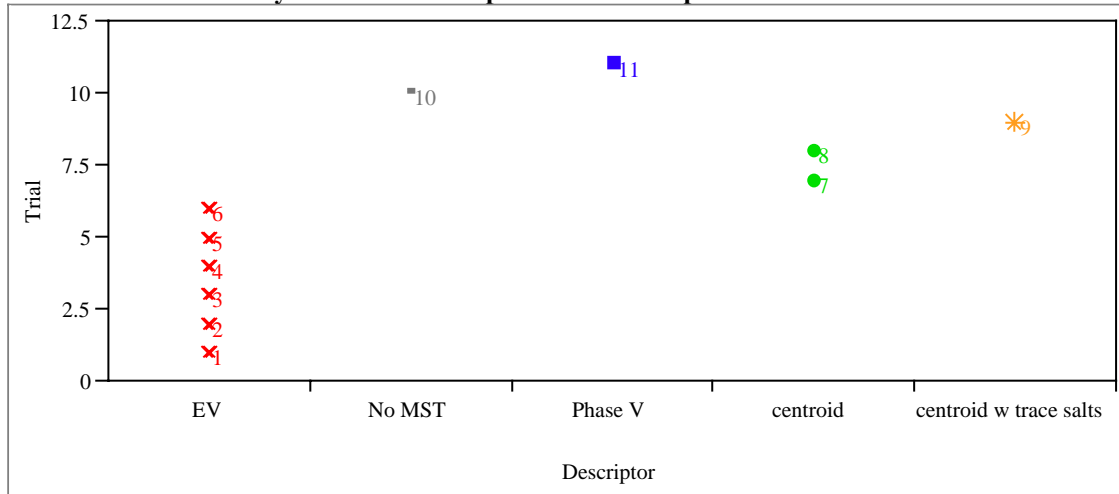


Exhibit 2: Correlations and Scatter Plot of Design Points in Normalized Ionic Strength Space

Correlations

	NaNO3 (Nis)	Free NaOH (Nis)	NaNO2 (Nis)	NaAl(OH)4 (Nis)	Na2CO3 (Nis)	Na2SO4 (Nis)
NaNO3 (Nis)	1.0000	-0.6658	-0.1654	0.0621	-0.1745	-0.2294
Free NaOH (Nis)	-0.6658	1.0000	-0.1433	-0.1843	-0.1292	-0.4232
NaNO2 (Nis)	-0.1654	-0.1433	1.0000	-0.1035	0.4009	-0.0380
NaAl(OH)4 (Nis)	0.0621	-0.1843	-0.1035	1.0000	-0.1143	-0.0439
Na2CO3 (Nis)	-0.1745	-0.1292	0.4009	-0.1143	1.0000	-0.1140
Na2SO4 (Nis)	-0.2294	-0.4232	-0.0380	-0.0439	-0.1140	1.0000

Scatterplot Matrix

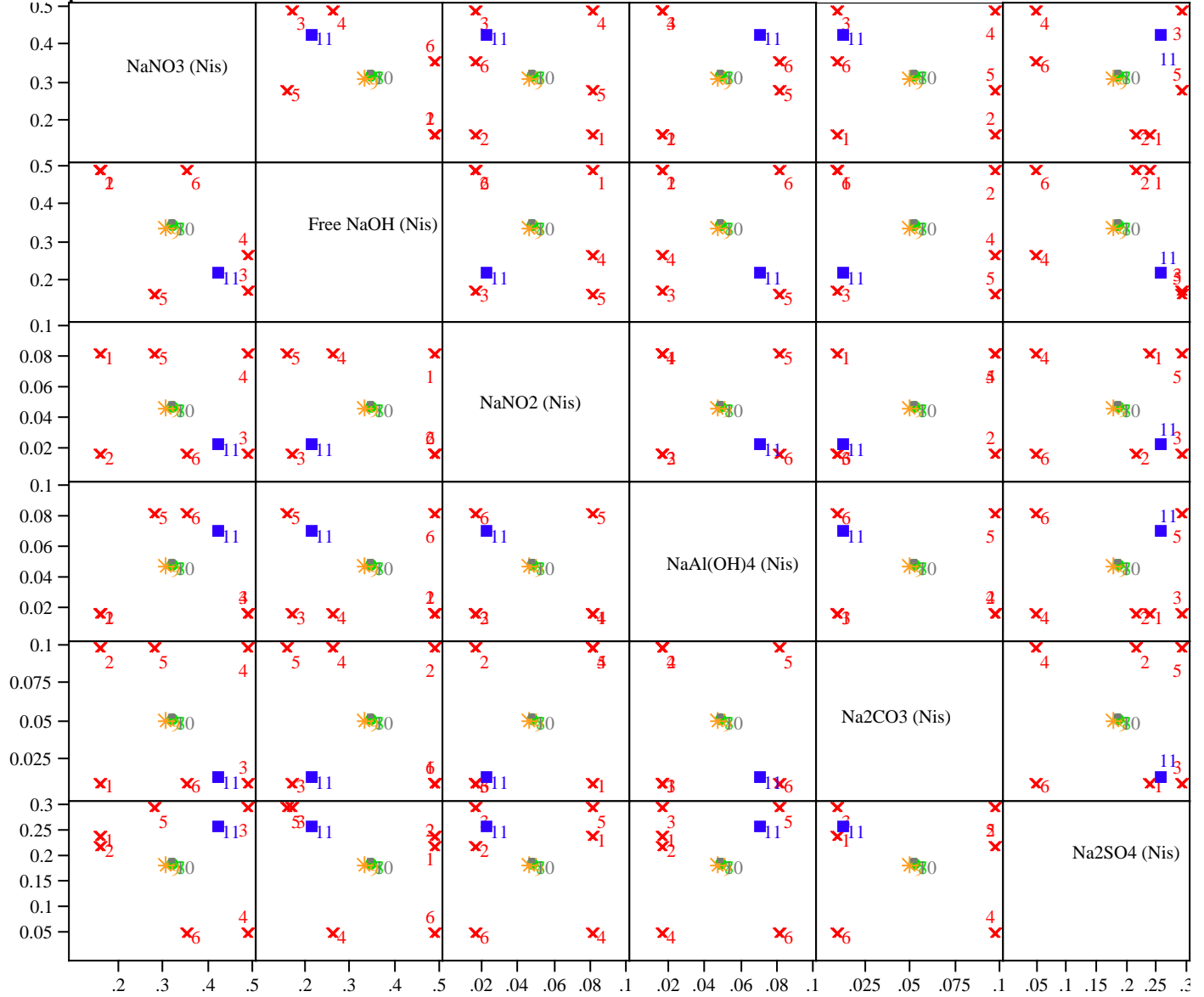


Exhibit 3: Sr DF-24h by Trial Descriptor

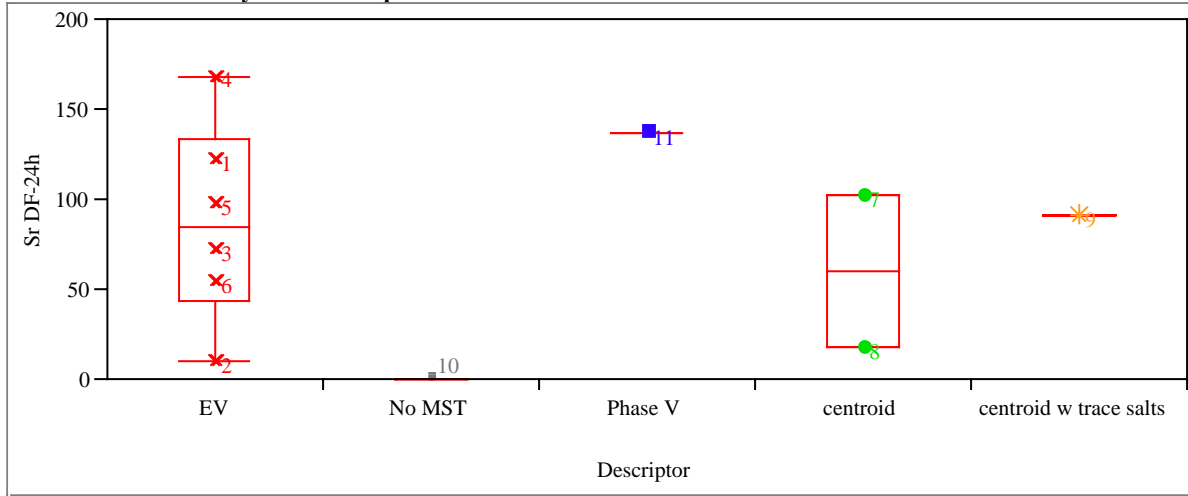


Exhibit 4: Sr DF-7d by Trial Descriptor

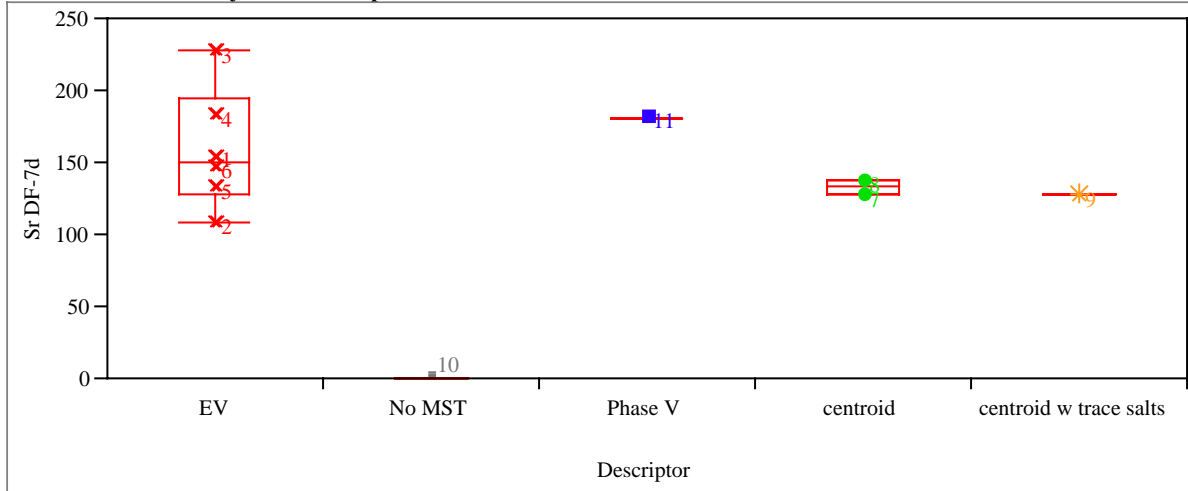


Exhibit 5: Pu DF-24h by Trial Descriptor

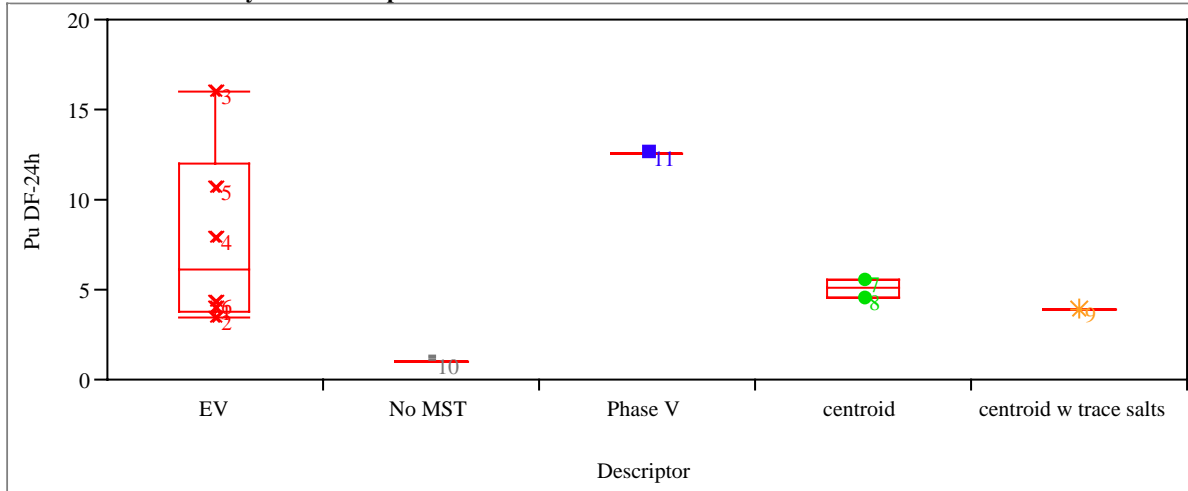


Exhibit 6: Pu DF-7d by Trial Descriptor

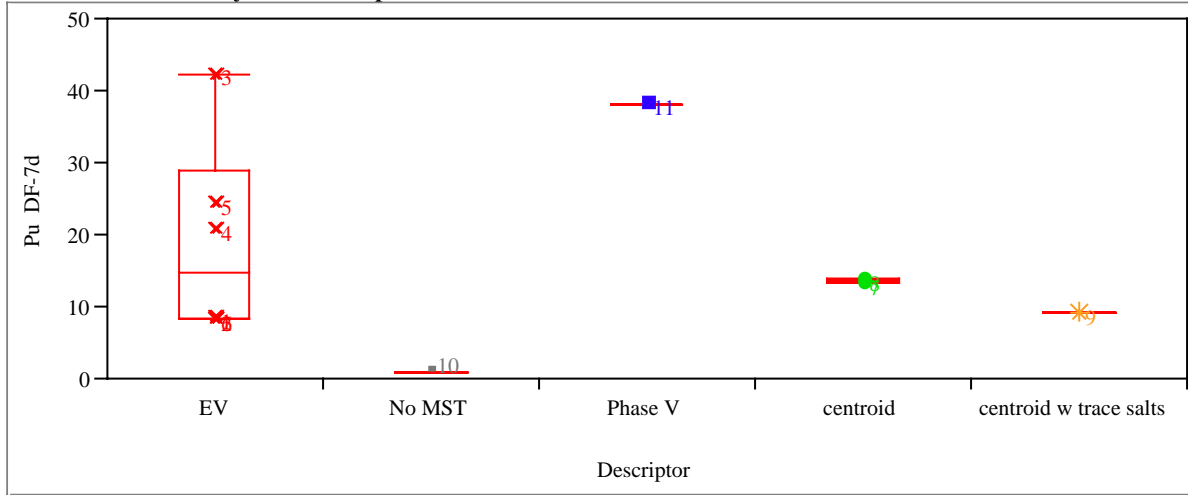


Exhibit 7: U DF-24h by Trial Descriptor

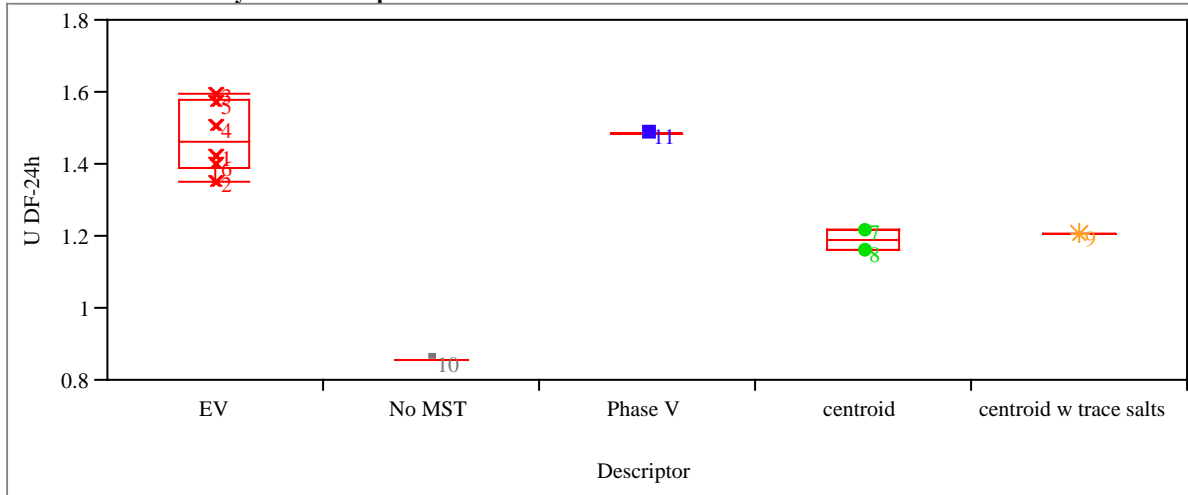


Exhibit 8: U DF-7d by Trial Descriptor

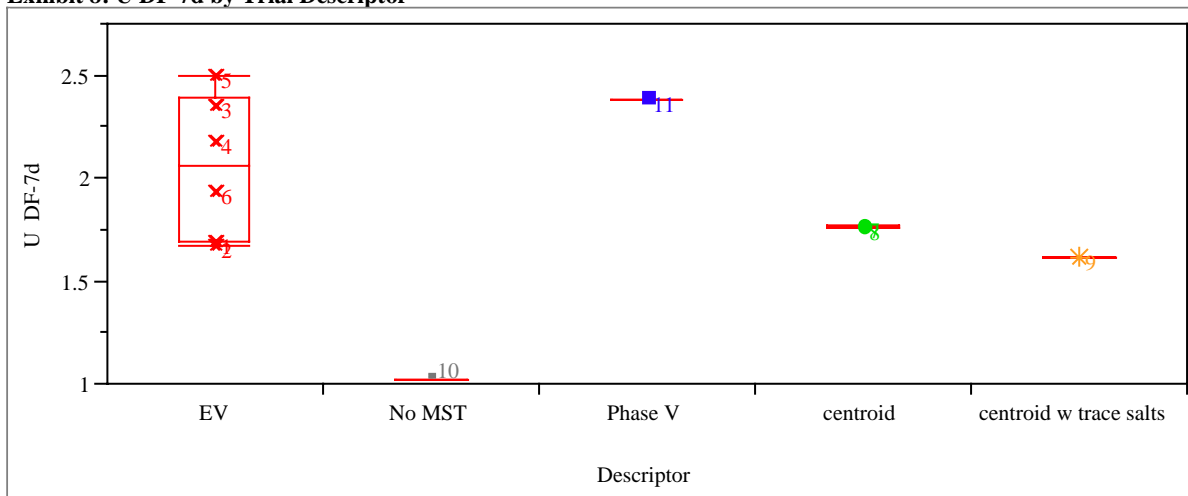


Exhibit 9: Np DF-24h by Trial Descriptor

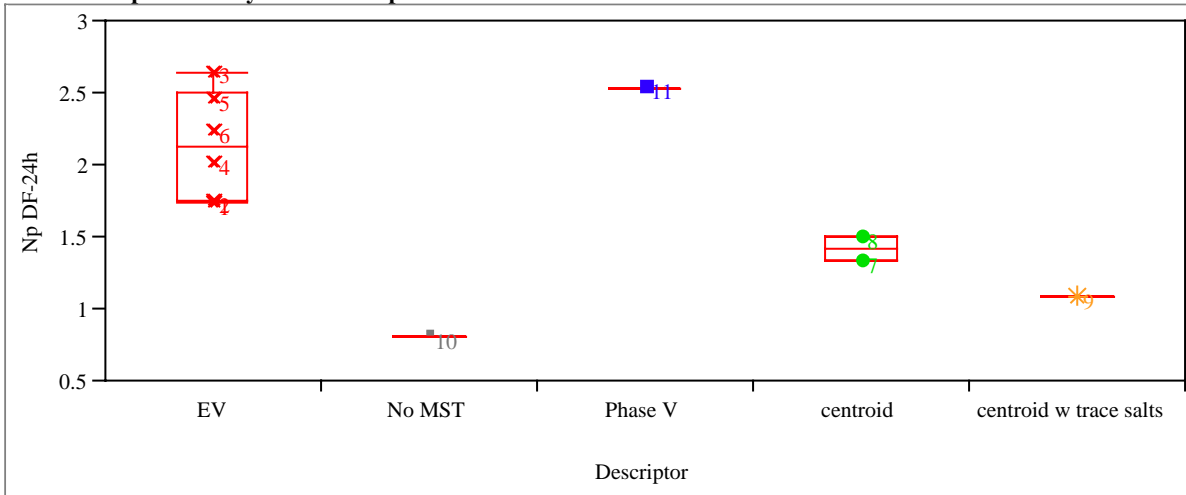


Exhibit 10: Np DF-7d by Trial Descriptor

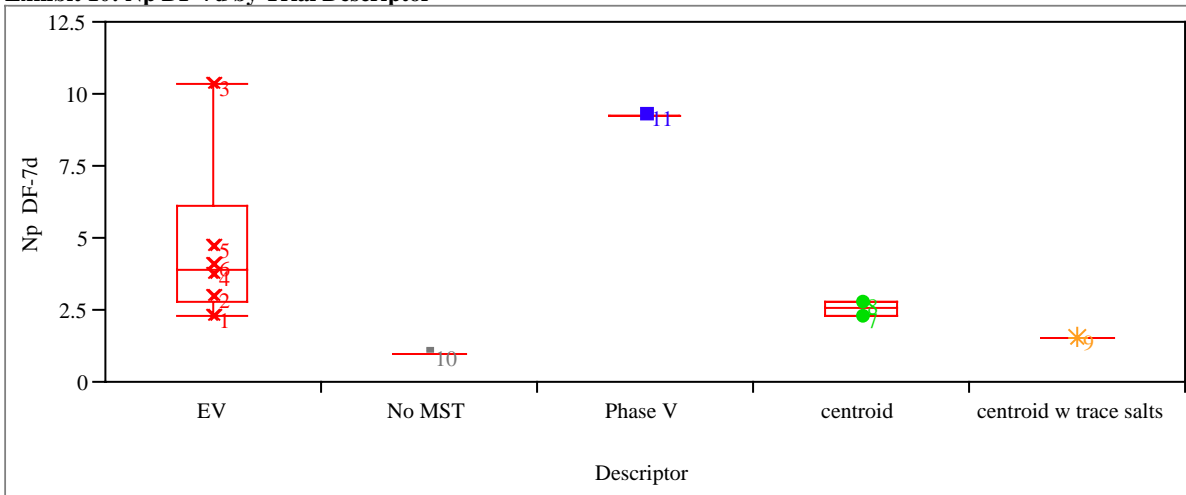


Exhibit 11: Correlations Between and Scatter Plots for Decontamination Factor Values Over the Eleven Trials

Correlations

	Sr DF-24h	Sr DF-7d	Pu DF-24h	Pu DF-7d	U DF-24h	U DF-7d	Np DF-24h	Np DF-7d
Sr DF-24h	1.0000	0.6078	0.4584	0.4589	0.6014	0.5879	0.4063	0.2970
Sr DF-7d	0.6078	1.0000	0.7652	0.7662	0.8580	0.8177	0.7689	0.7221
Pu DF-24h	0.4584	0.7652	1.0000	0.9853	0.7642	0.8767	0.8325	0.9326
Pu DF-7d	0.4589	0.7662	0.9853	1.0000	0.7153	0.8474	0.7984	0.9466
U DF-24h	0.6014	0.8580	0.7642	0.7153	1.0000	0.9127	0.9142	0.6932
U DF-7d	0.5879	0.8177	0.8767	0.8474	0.9127	1.0000	0.9156	0.7762
Np DF-24h	0.4063	0.7689	0.8325	0.7984	0.9142	0.9156	1.0000	0.8498
Np DF-7d	0.2970	0.7221	0.9326	0.9466	0.6932	0.7762	0.8498	1.0000

Scatterplot Matrix

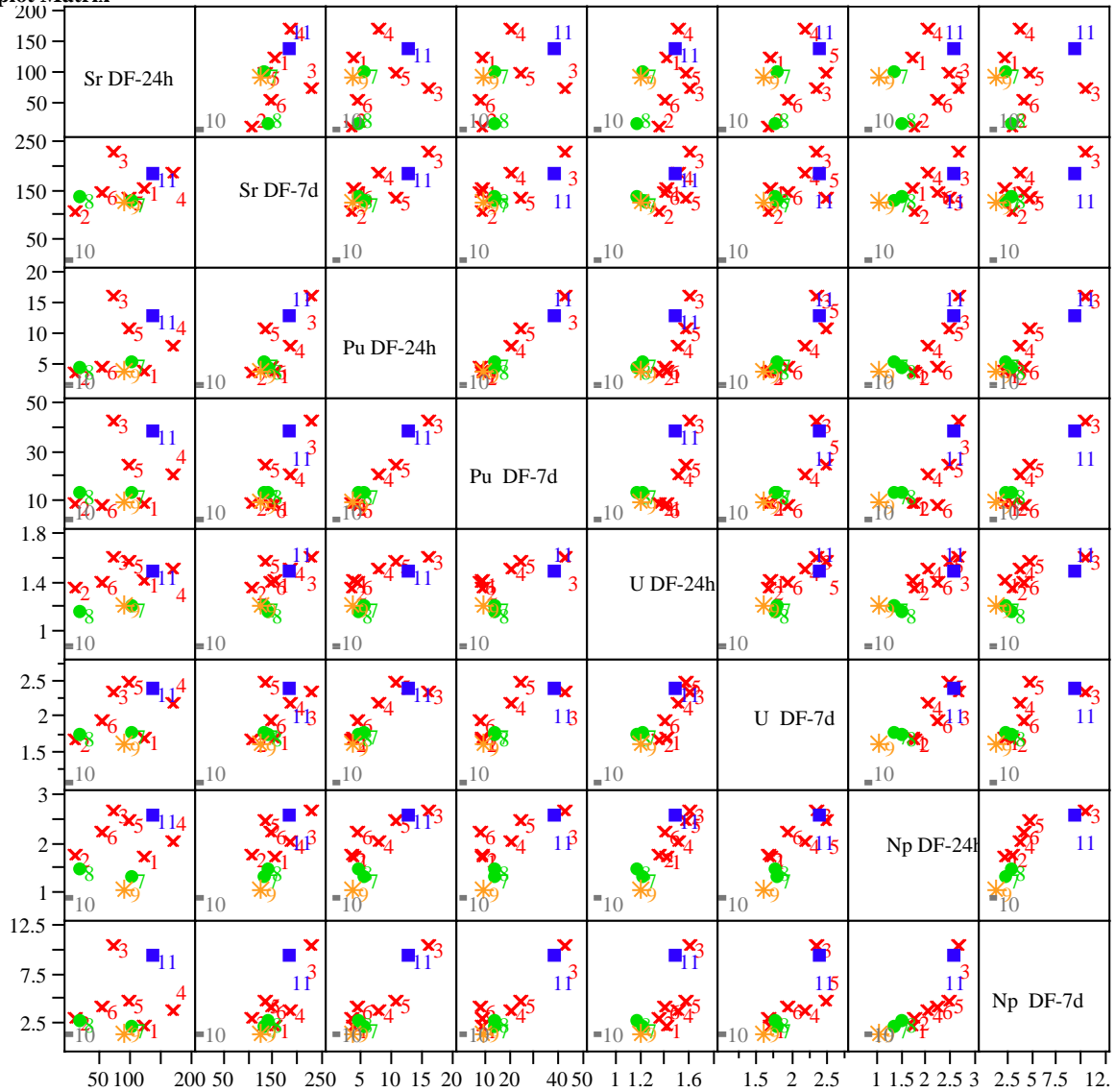
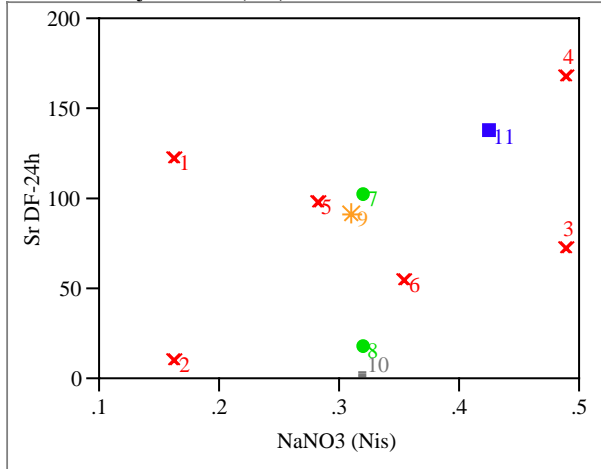
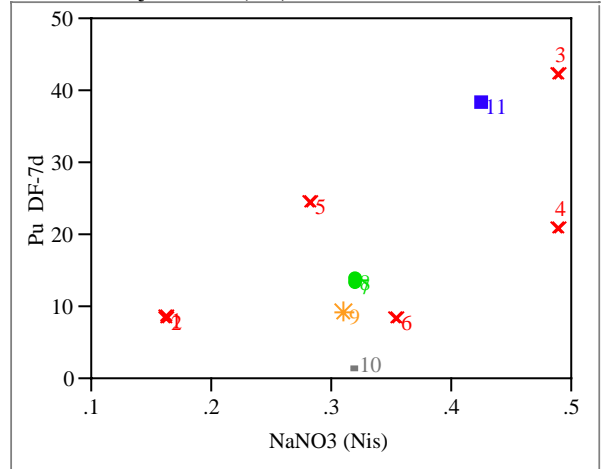


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

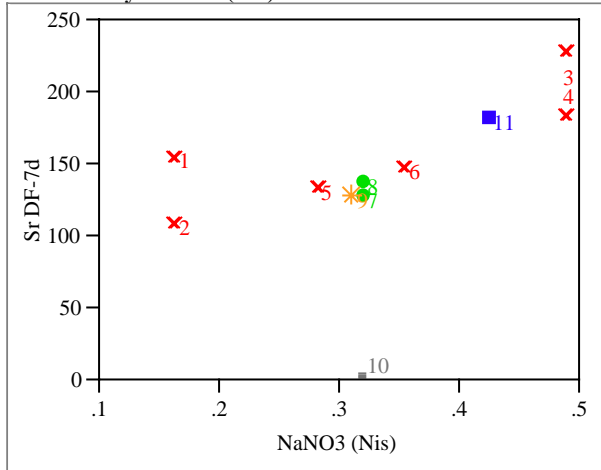
Sr DF-24h By NaNO3 (Nis)



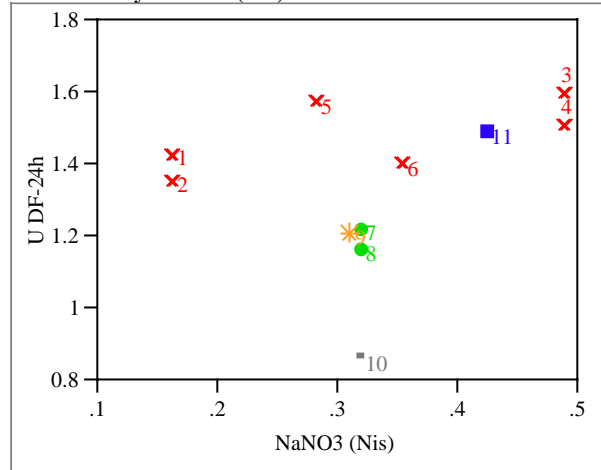
Pu DF-7d By NaNO3 (Nis)



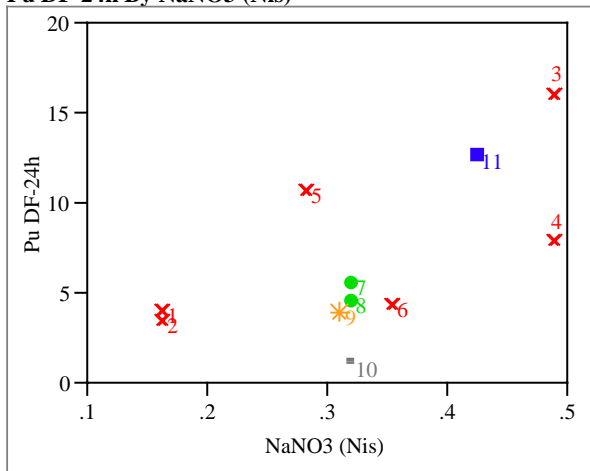
Sr DF-7d By NaNO3 (Nis)



U DF-24h By NaNO3 (Nis)



Pu DF-24h By NaNO3 (Nis)



U DF-7d By NaNO3 (Nis)

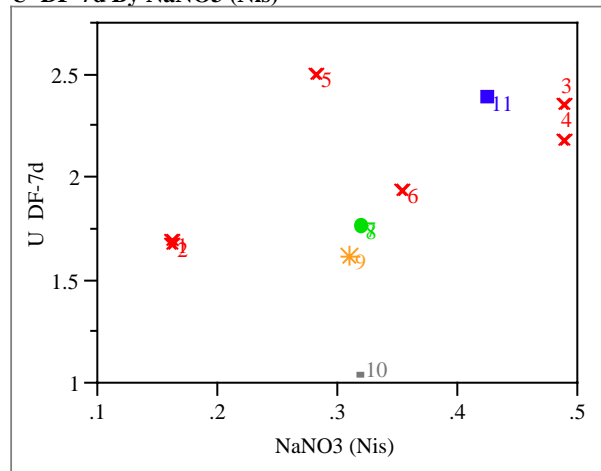
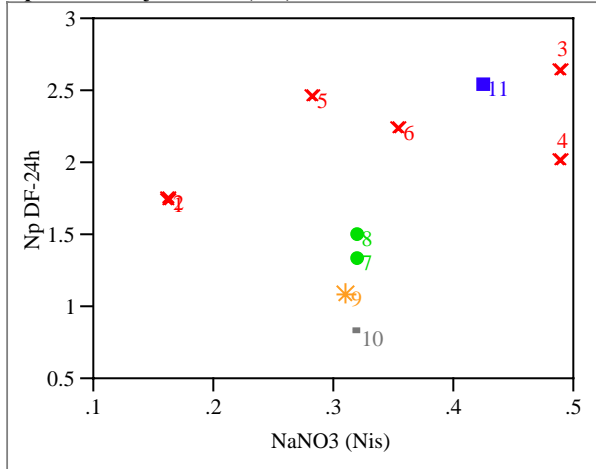
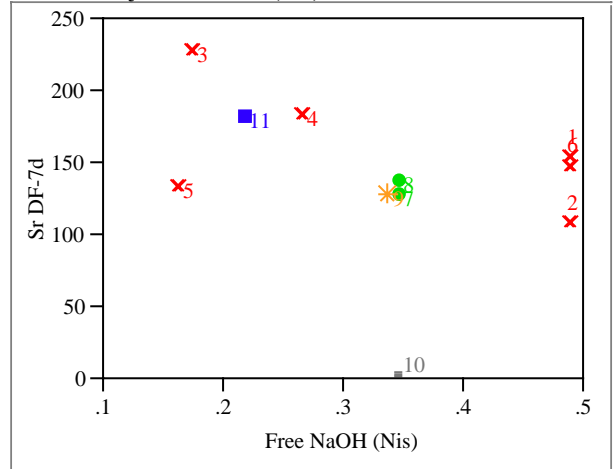


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

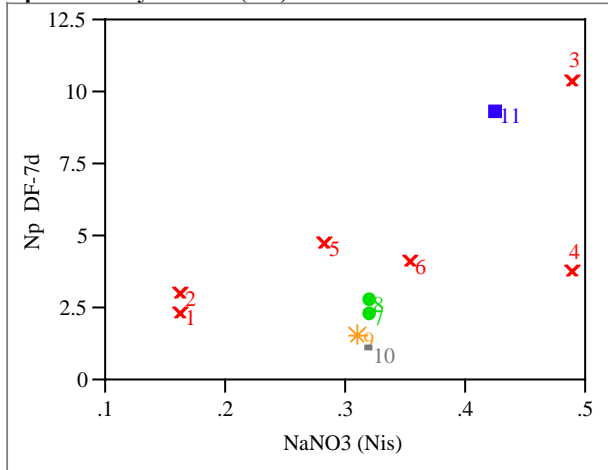
Np DF-24h By NaNO3 (Nis)



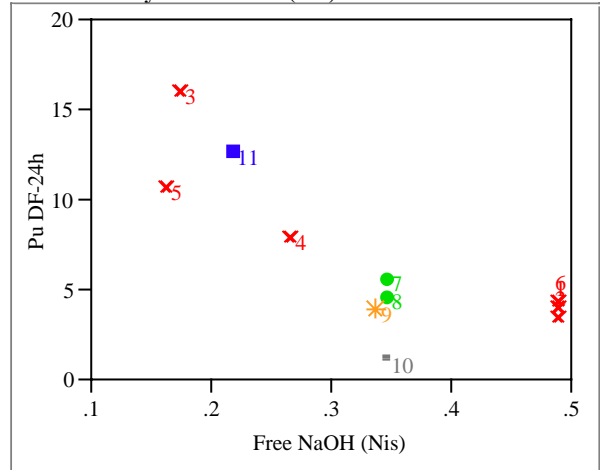
Sr DF-7d By Free NaOH (Nis)



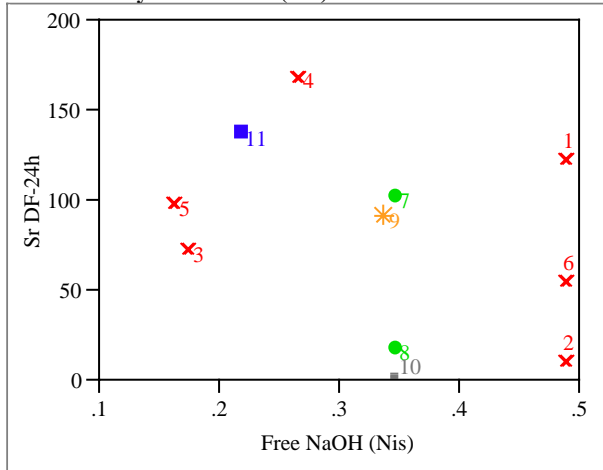
Np DF-7d By NaNO3 (Nis)



Pu DF-24h By Free NaOH (Nis)



Sr DF-24h By Free NaOH (Nis)



Pu DF-7d By Free NaOH (Nis)

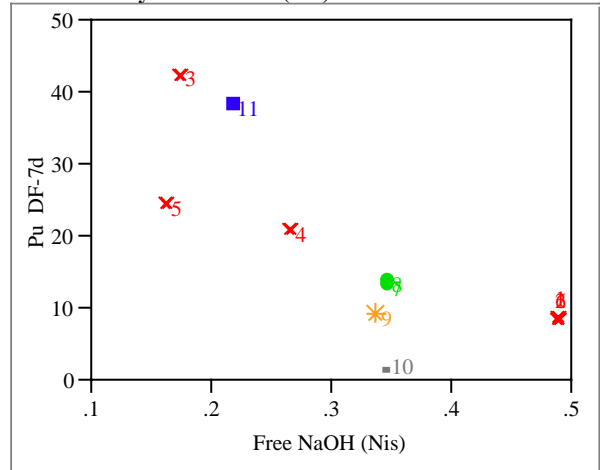
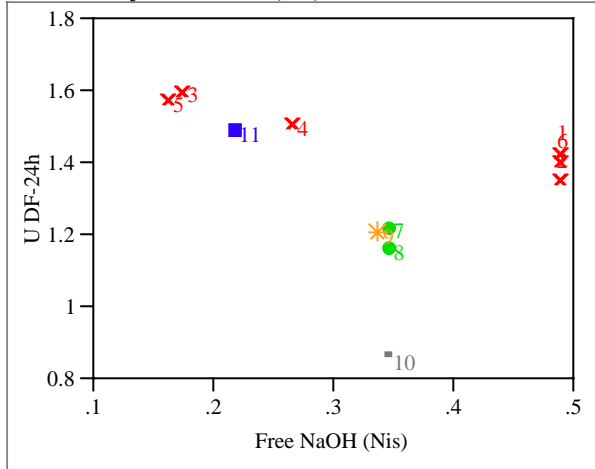
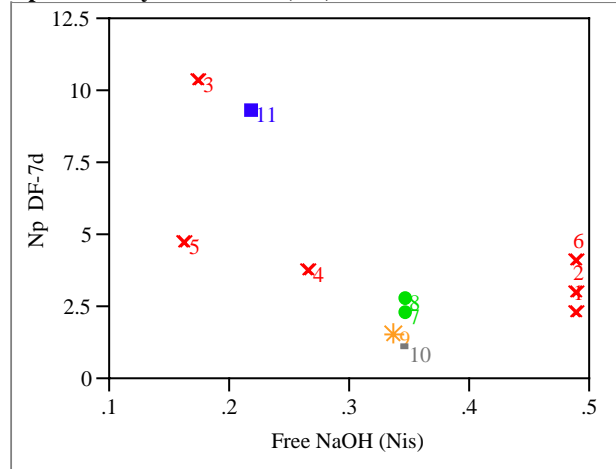


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

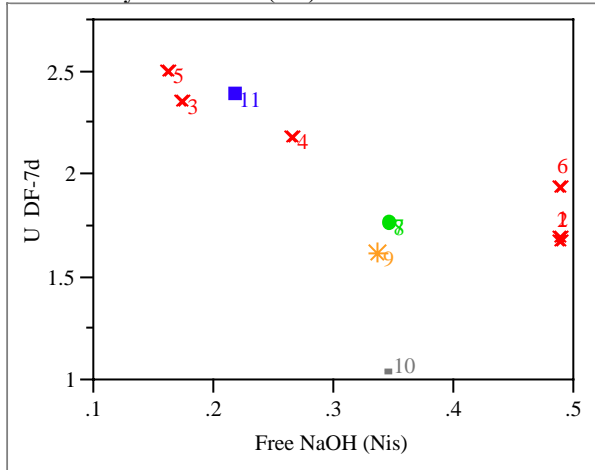
U DF-24h By Free NaOH (Nis)



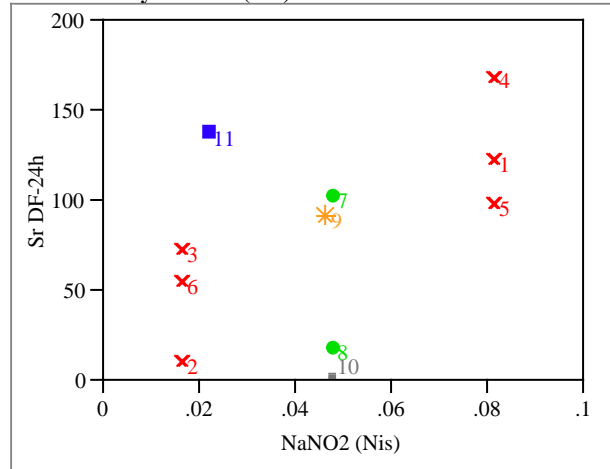
Np DF-7d By Free NaOH (Nis)



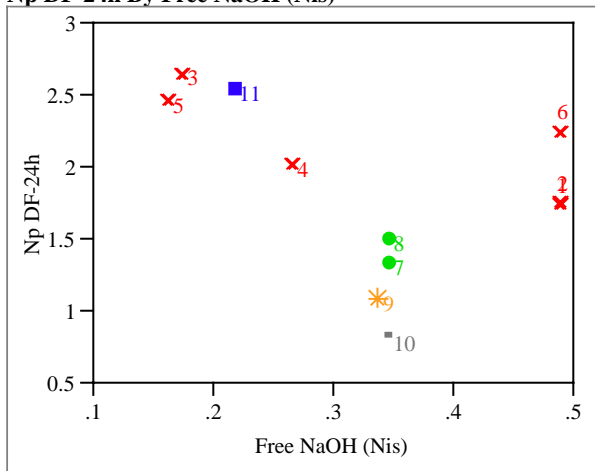
U DF-7d By Free NaOH (Nis)



Sr DF-24h By NaNO2 (Nis)



Np DF-24h By Free NaOH (Nis)



Sr DF-7d By NaNO2 (Nis)

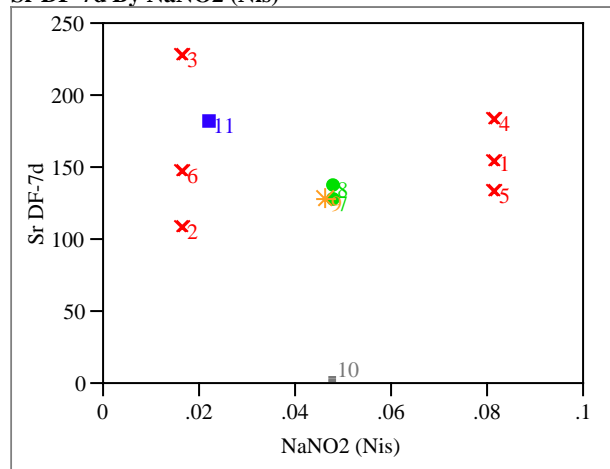
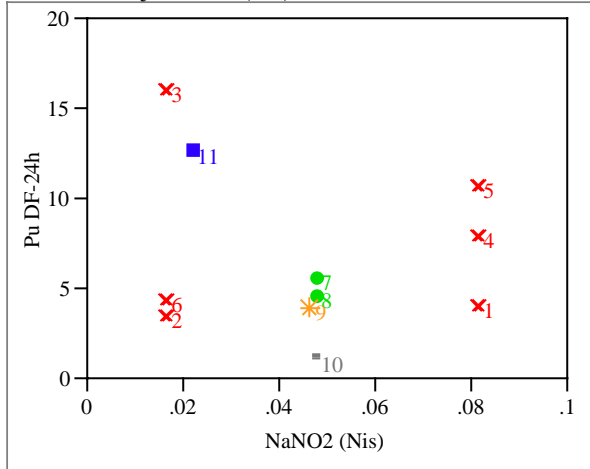
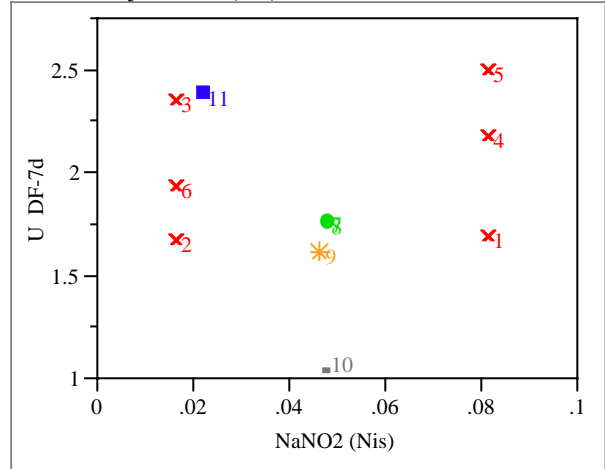


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

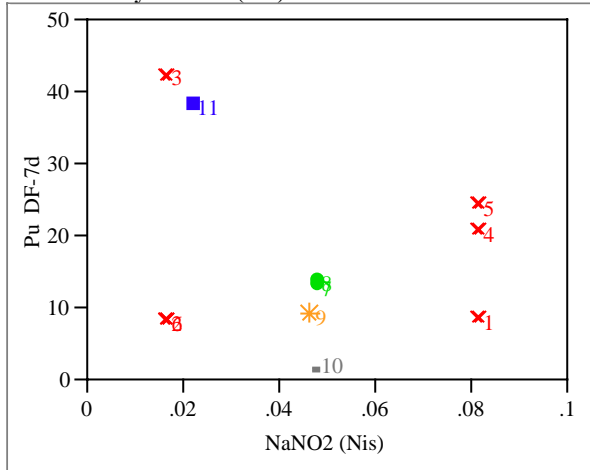
Pu DF-24h By NaNO2 (Nis)



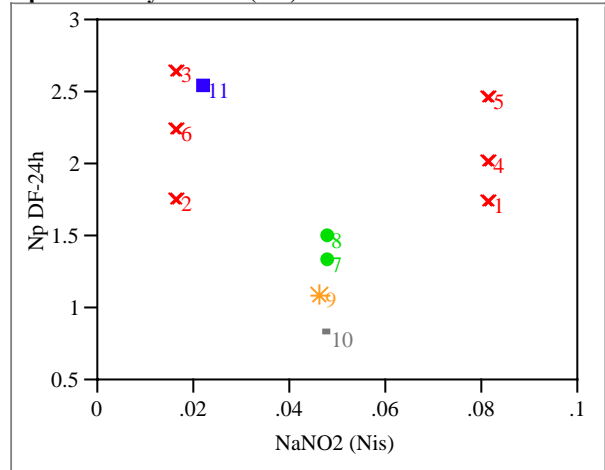
U DF-7d By NaNO2 (Nis)



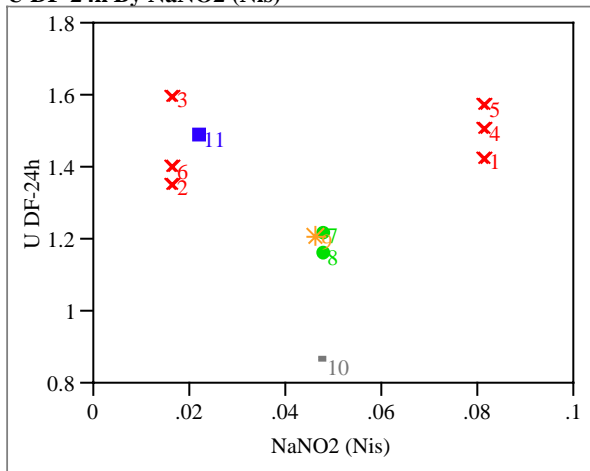
Pu DF-7d By NaNO2 (Nis)



Np DF-24h By NaNO2 (Nis)



U DF-24h By NaNO2 (Nis)



Np DF-7d By NaNO2 (Nis)

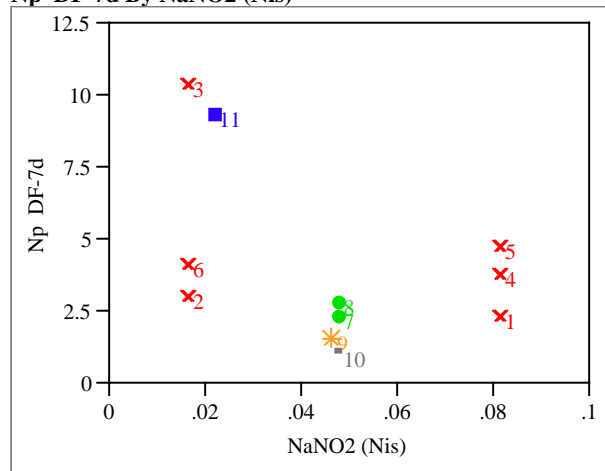
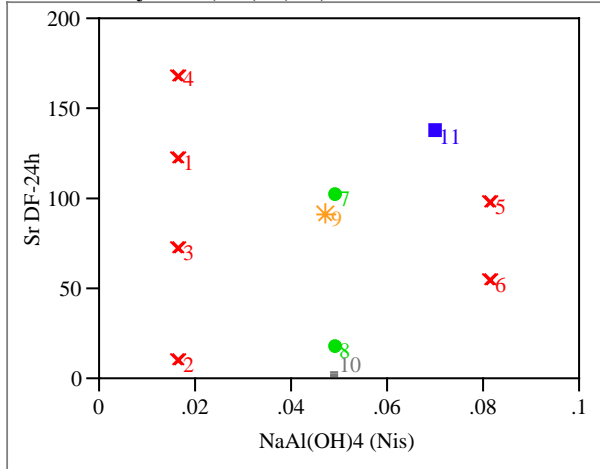
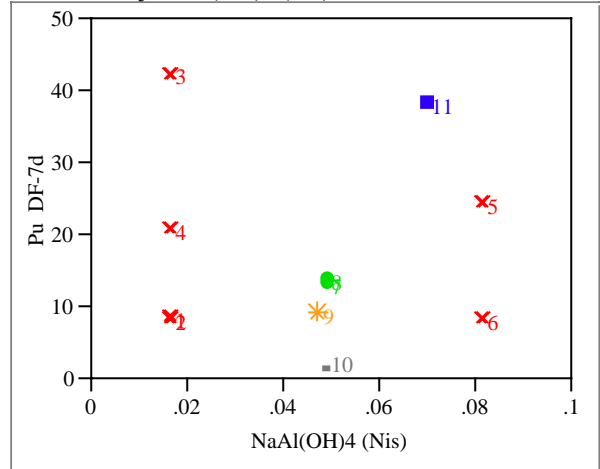


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

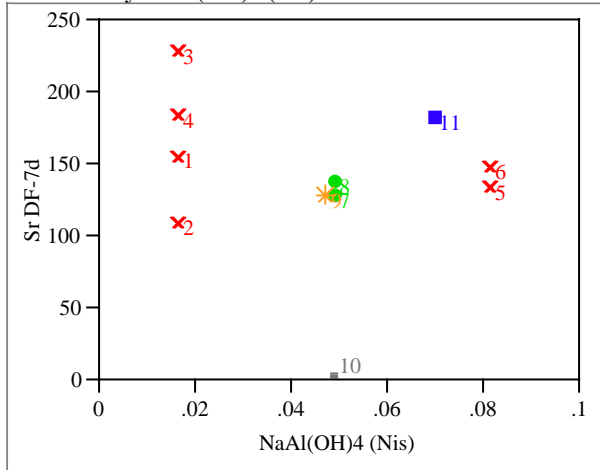
Sr DF-24h By NaAl(OH)4 (Nis)



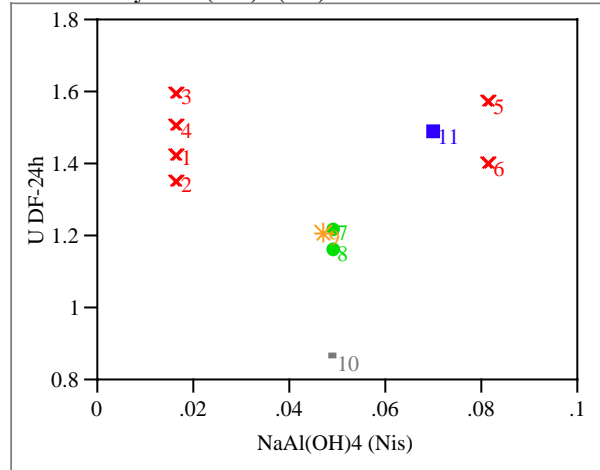
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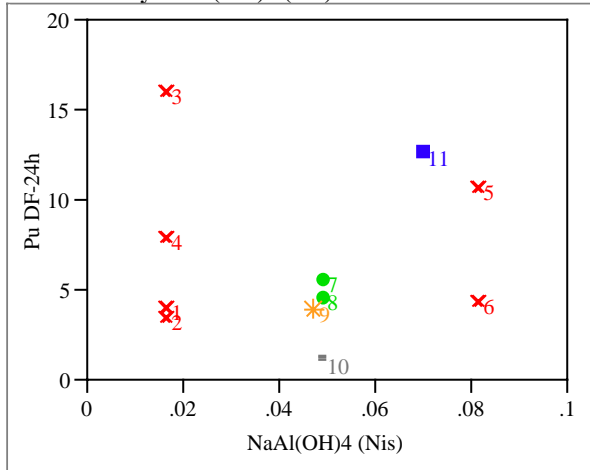
Sr DF-7d By NaAl(OH)4 (Nis)



U DF-24h By NaAl(OH)4 (Nis)



Pu DF-24h By NaAl(OH)4 (Nis)



U DF-7d By NaAl(OH)4 (Nis)

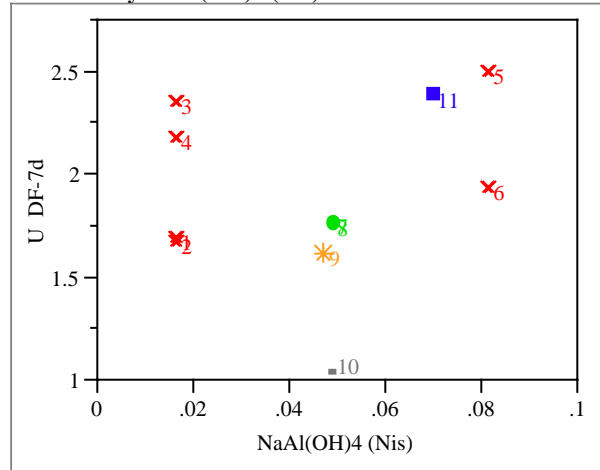
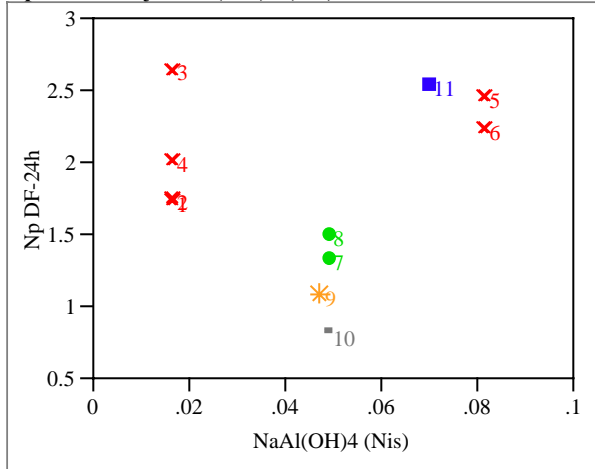
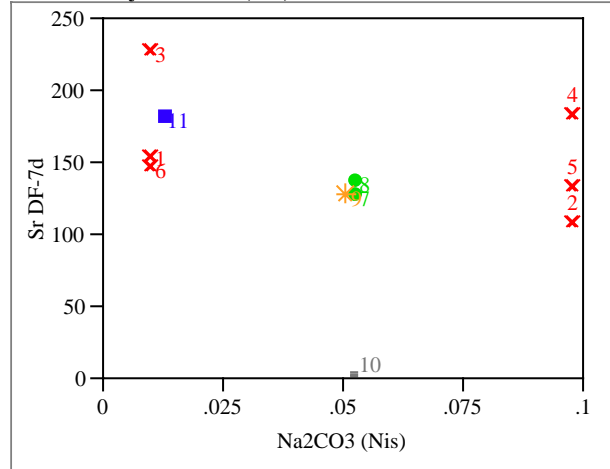


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

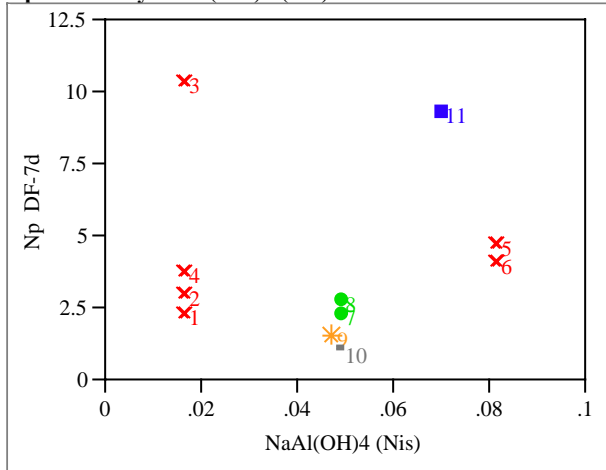
Np DF-24h By NaAl(OH)4 (Nis)



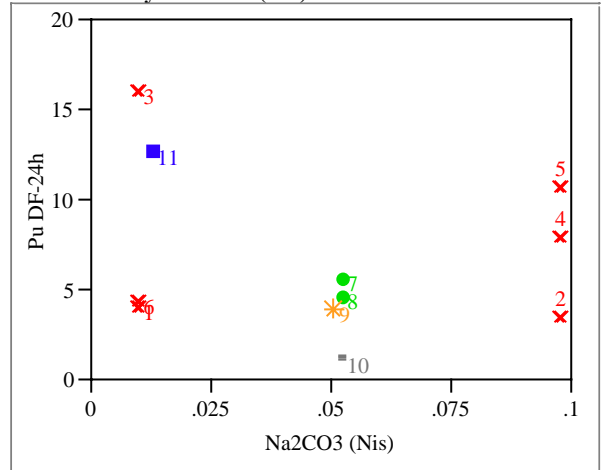
Sr DF-7d By Na2CO3 (Nis)



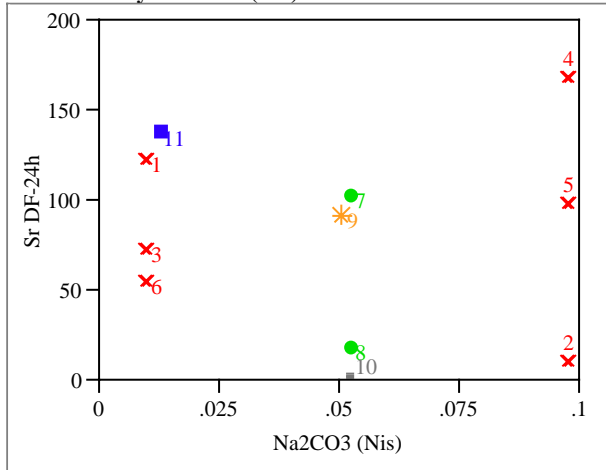
Np DF-7d By NaAl(OH)4 (Nis)



Pu DF-24h By Na2CO3 (Nis)



Sr DF-24h By Na2CO3 (Nis)



Pu DF-7d By Na2CO3 (Nis)

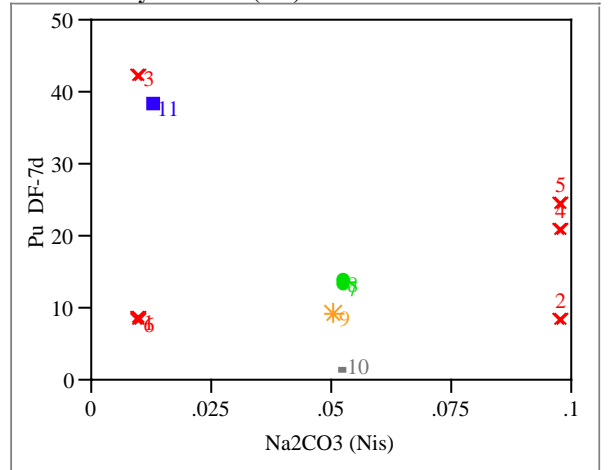
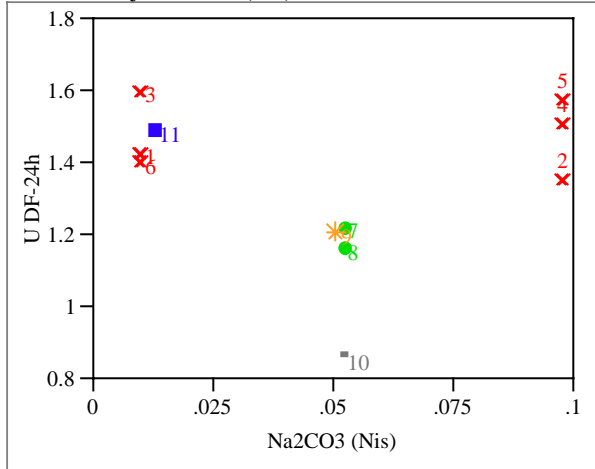
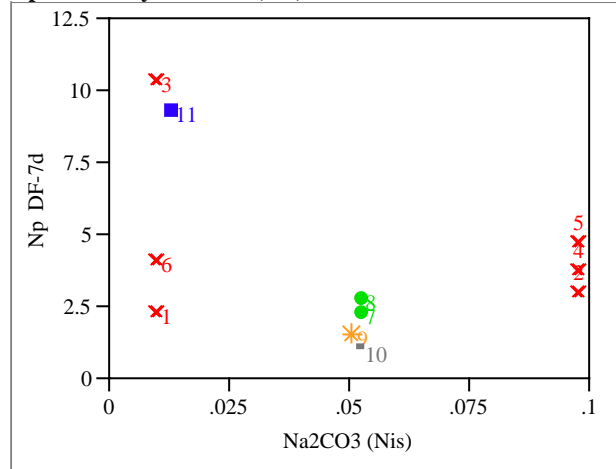


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

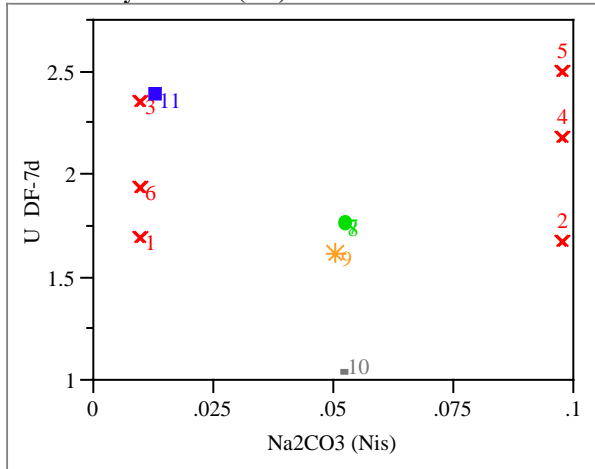
U DF-24h By Na₂CO₃ (Nis)



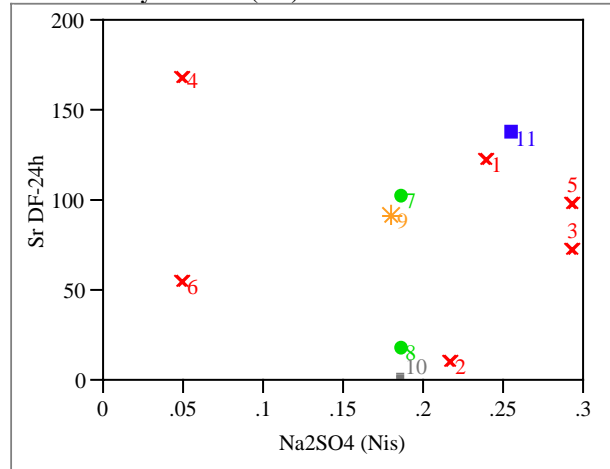
Np DF-7d By Na₂CO₃ (Nis)



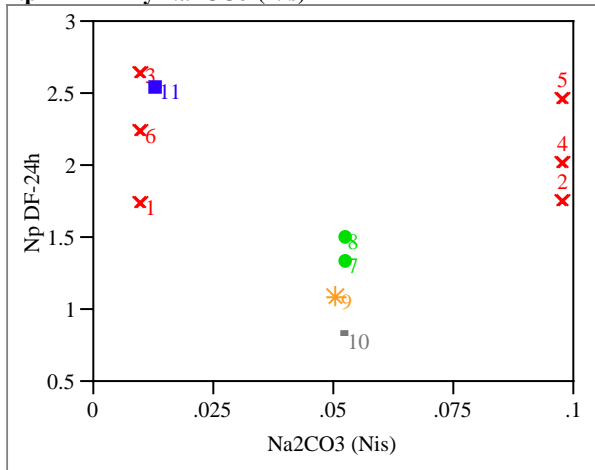
U DF-7d By Na₂CO₃ (Nis)



Sr DF-24h By Na₂SO₄ (Nis)



Np DF-24h By Na₂CO₃ (Nis)



Sr DF-7d By Na₂SO₄ (Nis)

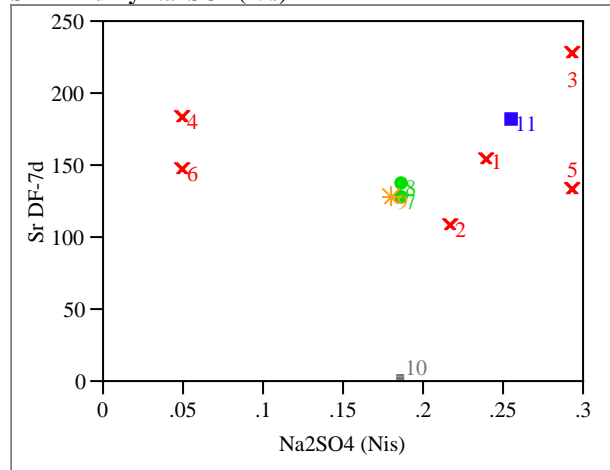
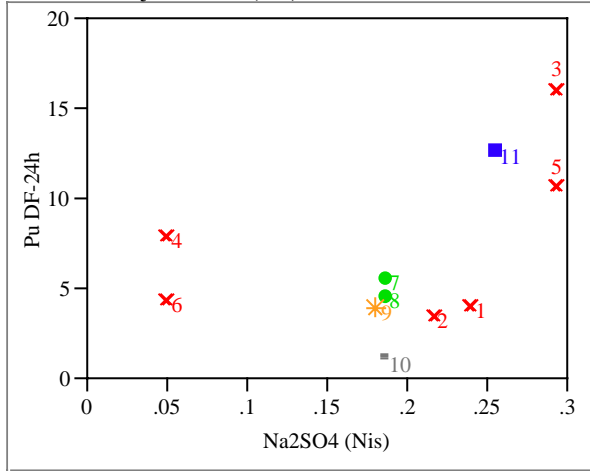
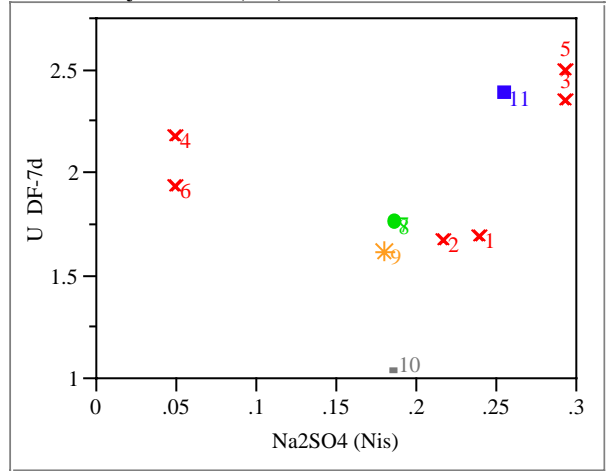


Exhibit 12: Plots of Decontamination Factors (DFs) versus Normalized Ionic Strength Fractions

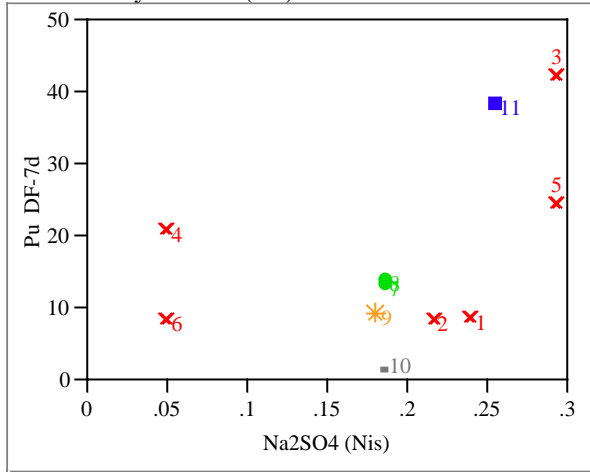
Pu DF-24h By Na2SO4 (Nis)



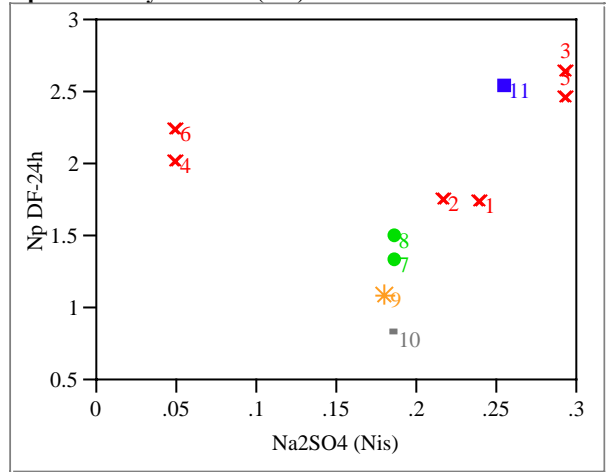
U DF-7d By Na2SO4 (Nis)



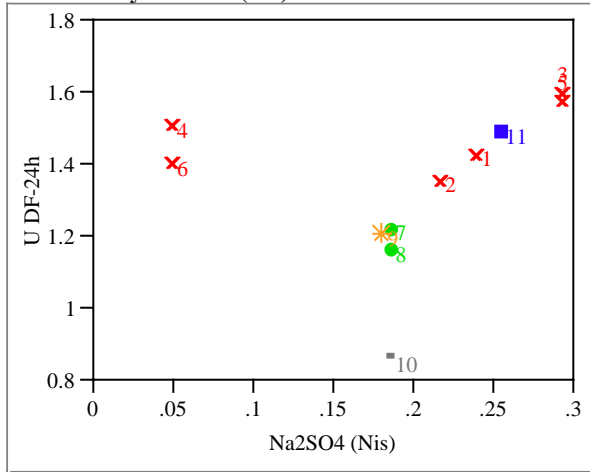
Pu DF-7d By Na2SO4 (Nis)



Np DF-24h By Na2SO4 (Nis)



U DF-24h By Na2SO4 (Nis)



Np DF-7d By Na2SO4 (Nis)

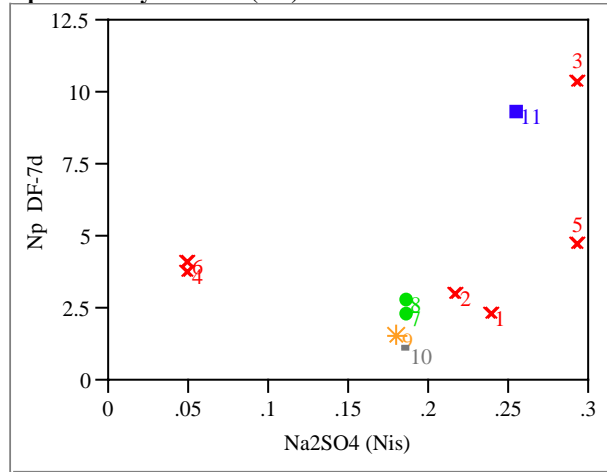
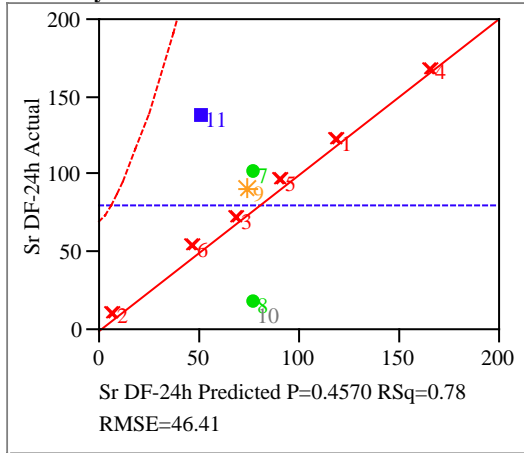
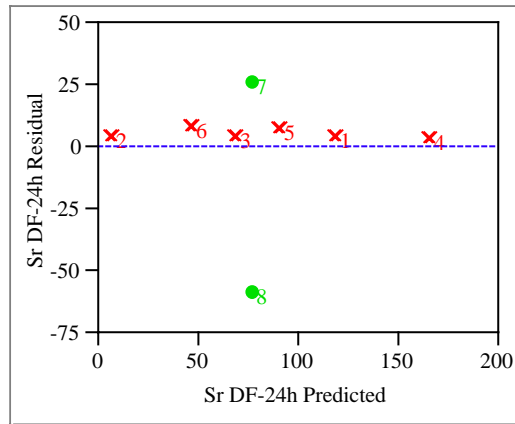


Exhibit 13: Linear Model Relating Strontium (Sr) DF-24h to the Six Primary Salt Solutions Components

**Response Sr DF-24h
Actual by Predicted Plot**



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.783292
RSquare Adj	0.241524
Root Mean Square Error	46.41023
Mean of Response	81.15029
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	15570.673	3114.13	1.4458
Error	2	4307.819	2153.91	Prob > F
C. Total	7	19878.492		0.4570

Tested against reduced model: Y=mean

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	727.4010	727.40	0.2032
Pure Error	1	3580.4184	3580.42	Prob > F
Total Error	2	4307.8195		0.7304
				Max RSq
				0.8199

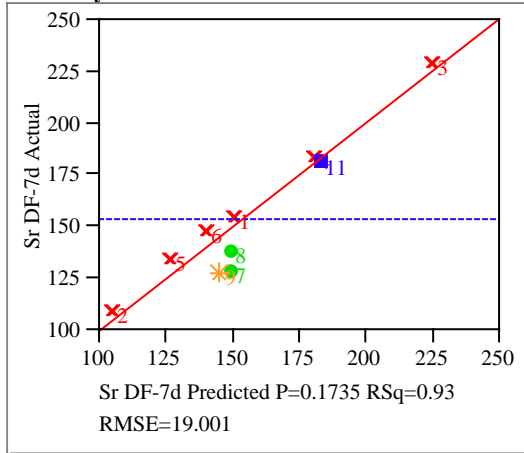
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed	0	0	.
NaNO3 (Nis)	155.78347	101.6782	1.53	0.2652
Free NaOH (Nis)	3.1459008	87.78354	0.04	0.9747
NaNO2 (Nis)	1457.2522	600.0041	2.43	0.1358
NaAl(OH)4 (Nis)	-345.7717	584.4639	-0.59	0.6141
Na2CO3 (Nis)	-216.0979	444.6861	-0.49	0.6750
Na2SO4 (Nis)	-81.29	153.0583	-0.53	0.6484

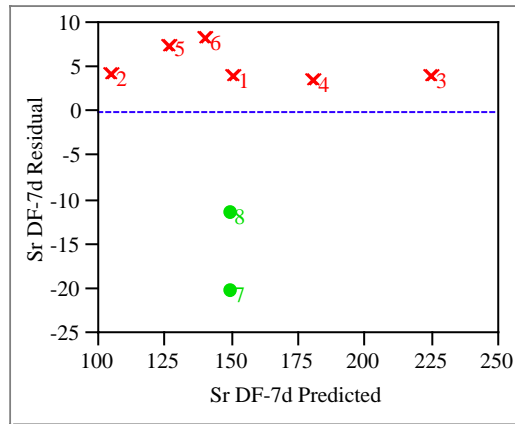
Exhibit 14: Linear Model Relating Strontium (Sr) DF-7d to the Six Primary Salt Solutions Components

Response Sr DF-7d

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.926624
RSquare Adj	0.743182
Root Mean Square Error	19.00081
Mean of Response	153.2807
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	9118.4457	1823.69	5.0513
Error	2	722.0618	361.03	Prob > F
C. Total	7	9840.5075		0.1735

Tested against reduced model: Y=mean

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	683.84450	683.844	17.8936
Pure Error	1	38.21730	38.217	Prob > F
Total Error	2	722.06180		0.1478
				Max RSq
				0.9961

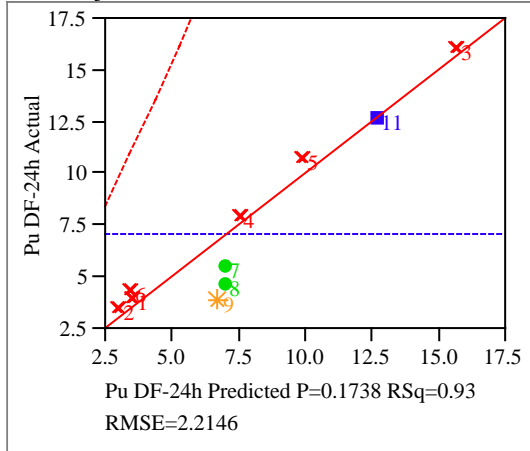
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed 0	0	.	.
NaNO3 (Nis)	328.91168	41.62807	7.90	0.0156
Free NaOH (Nis)	81.797327	35.93946	2.28	0.1506
NaNO2 (Nis)	259.1237	245.6477	1.05	0.4021
NaAl(OH)4 (Nis)	-331.4975	239.2854	-1.39	0.3002
Na2CO3 (Nis)	-276.1282	182.0589	-1.52	0.2686
Na2SO4 (Nis)	182.85458	62.66362	2.92	0.1001

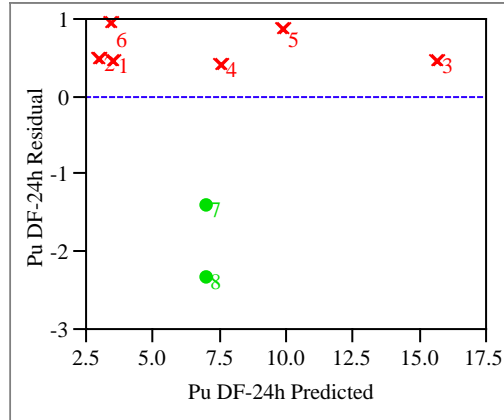
Exhibit 15: Linear Model Relating Plutonium (Pu) DF-24h to the Six Primary Salt Solutions Components

Response Pu DF-24h

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.926495
RSquare Adj	0.742732
Root Mean Square Error	2.214636
Mean of Response	7.117602
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	123.64012	24.7280	5.0418
Error	2	9.80922	4.9046	Prob > F
C. Total	7	133.44934		0.1738

Tested against reduced model: Y=mean

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

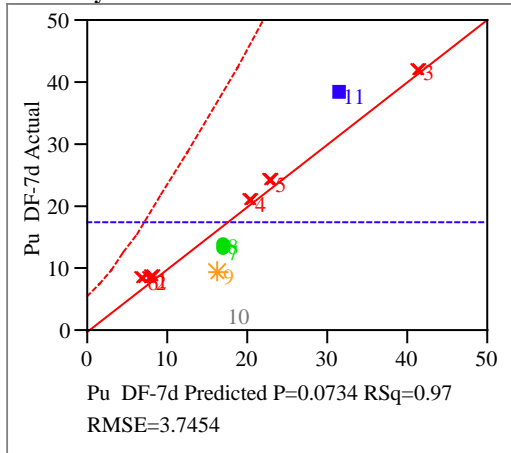
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	9.3797627	9.37976	21.8409
Pure Error	1	0.4294581	0.42946	Prob > F
Total Error	2	9.8092208		0.1342
				Max RSq
				0.9968

Parameter Estimates

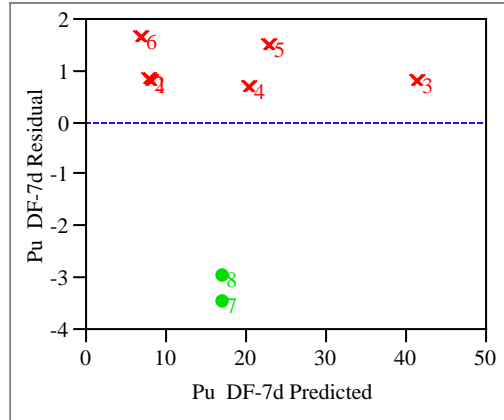
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed 0	0	.	.
NaNO3 (Nis)	21.483399	4.851951	4.43	0.0474
Free NaOH (Nis)	-10.01745	4.188916	-2.39	0.1392
NaNO2 (Nis)	-9.504671	28.63141	-0.33	0.7715
NaAl(OH)4 (Nis)	-2.801132	27.88985	-0.10	0.9292
Na2CO3 (Nis)	-6.919366	21.21984	-0.33	0.7753
Na2SO4 (Nis)	24.292712	7.303744	3.33	0.0797

Exhibit 16: Linear Model Relating Plutonium (Pu) DF-7d to the Six Primary Salt Solutions Components

**Response Pu DF-7d
Actual by Predicted Plot**



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.969987
RSquare Adj	0.894954
Root Mean Square Error	3.745429
Mean of Response	17.6535
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	906.75302	181.351	12.9275
Error	2	28.05647	14.028	Prob > F
C. Total	7	934.80949		0.0734

Tested against reduced model: Y=mean

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	27.944001	27.9440	248.4568
Pure Error	1	0.112470	0.1125	Prob > F
Total Error	2	28.056471		0.0403
				Max RSq
				0.9999

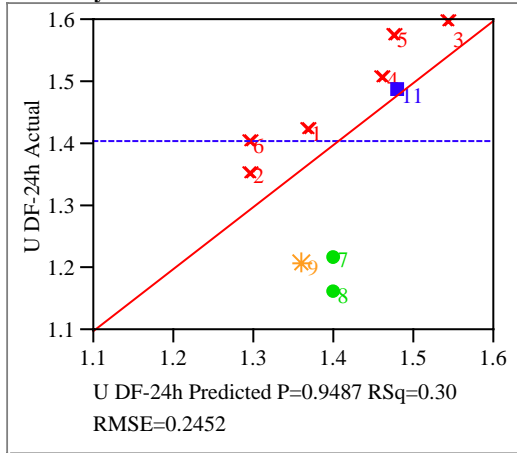
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed 0	0	.	.
NaNO3 (Nis)	59.56008	8.2057	7.26	0.0185
Free NaOH (Nis)	-26.2868	7.084364	-3.71	0.0656
NaNO2 (Nis)	-35.86907	48.42192	-0.74	0.5360
NaAl(OH)4 (Nis)	-44.60449	47.16778	-0.95	0.4441
Na2CO3 (Nis)	-13.21168	35.88734	-0.37	0.7481
Na2SO4 (Nis)	62.338539	12.35221	5.05	0.0371

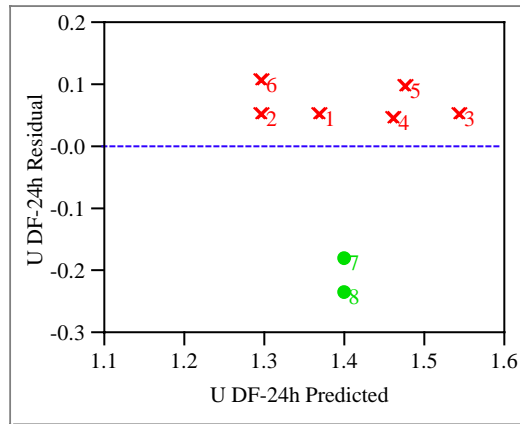
Exhibit 17: Linear Model Relating Uranium (U) DF-24h to the Six Primary Salt Solutions Components

Response U DF-24h

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.304711
RSquare Adj	-1.43351
Root Mean Square Error	0.245179
Mean of Response	1.405462
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	0.05268898	0.010538	0.1753
Error	2	0.12022587	0.060113	Prob > F
C. Total	7	0.17291485		0.9487

Tested against reduced model: Y=mean

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	0.11868997	0.118690	77.2772
Pure Error	1	0.00153590	0.001536	Prob > F
Total Error	2	0.12022587		0.0721
				Max RSq
				0.9911

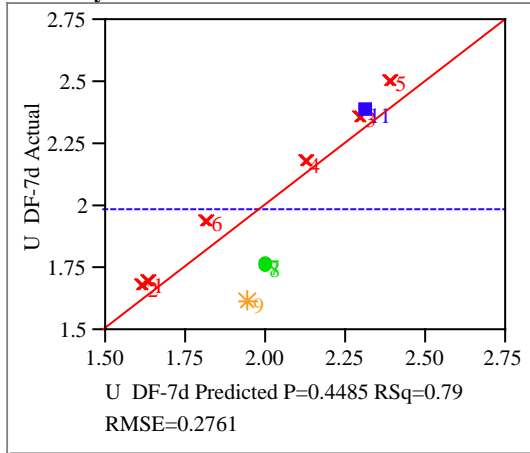
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed 0	0	.	.
NaNO3 (Nis)	1.6654684	0.537153	3.10	0.0902
Free NaOH (Nis)	1.0349979	0.463749	2.23	0.1553
NaNO2 (Nis)	2.0225676	3.169746	0.64	0.5887
NaAl(OH)4 (Nis)	0.9114191	3.087649	0.30	0.7957
Na2CO3 (Nis)	1.1121986	2.34922	0.47	0.6825
Na2SO4 (Nis)	1.6695054	0.808588	2.06	0.1750

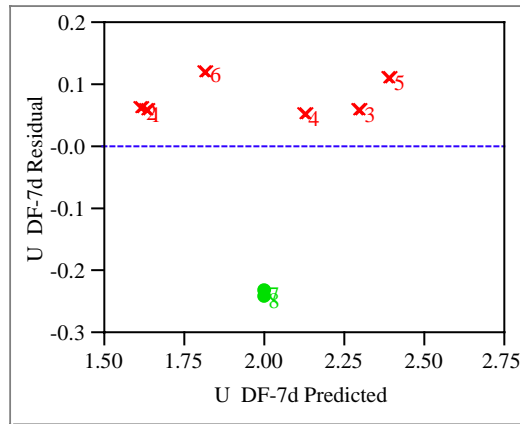
Exhibit 18: Linear Model Relating Uranium (U) DF-7d to the Six Primary Salt Solutions Components

Response U DF-7d

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.788156
RSquare Adj	0.258546
Root Mean Square Error	0.27614
Mean of Response	1.985293
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	0.56739411	0.113479	1.4882
Error	2	0.15250662	0.076253	Prob > F
C. Total	7	0.71990073		0.4485

Tested against reduced model: Y=mean

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	0.15245141	0.152451	2761.621
Pure Error	1	0.00005520	0.000055	Prob > F
Total Error	2	0.15250662		0.0121
				Max RSq
				0.9999

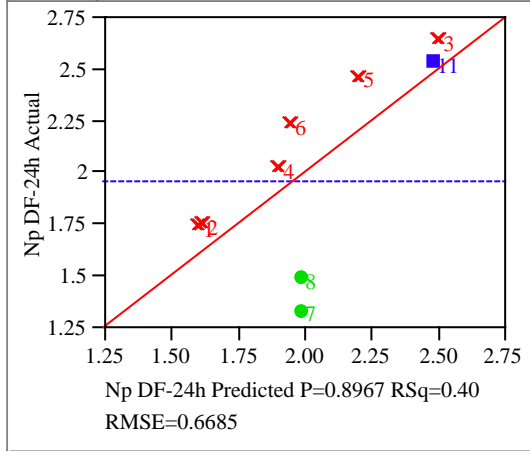
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed	0	0	.
NaNO3 (Nis)	2.7321177	0.604983	4.52	0.0457
Free NaOH (Nis)	0.6142553	0.52231	1.18	0.3606
NaNO2 (Nis)	2.5755196	3.570013	0.72	0.5456
NaAl(OH)4 (Nis)	4.4898721	3.477549	1.29	0.3258
Na2CO3 (Nis)	2.3230774	2.645874	0.88	0.4725
Na2SO4 (Nis)	2.4297437	0.910694	2.67	0.1164

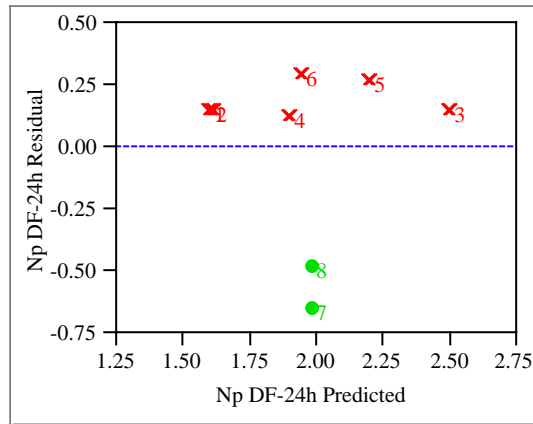
Exhibit 19: Linear Model Relating Neptunium (Np) DF-24h to the Six Primary Salt Solutions Components

Response Np DF-24h

Actual by Predicted Plot



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.40333
RSquare Adj	-1.08834
Root Mean Square Error	0.668546
Mean of Response	1.965631
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	0.6042551	0.120851	0.2704
Error	2	0.8939088	0.446954	Prob > F
C. Total	7	1.4981639		0.8967

Tested against reduced model: Y=mean

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

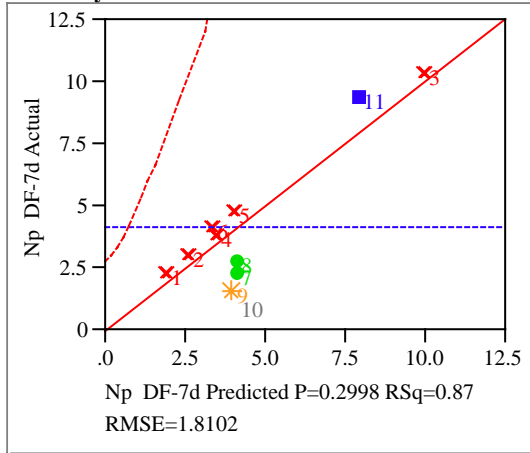
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	0.88001807	0.880018	63.3531
Pure Error	1	0.01389068	0.013891	Prob > F
Total Error	2	0.89390875		0.0796
				Max RSq
				0.9907

Parameter Estimates

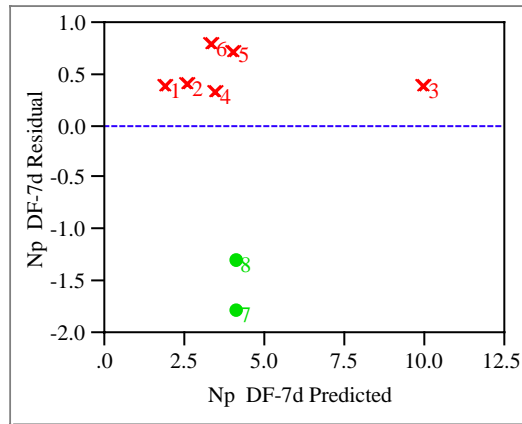
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed 0	0	.	.
NaNO3 (Nis)	2.9699234	1.46469	2.03	0.1798
Free NaOH (Nis)	0.7864903	1.264535	0.62	0.5974
NaNO2 (Nis)	-0.3855	8.643151	-0.04	0.9685
NaAl(OH)4 (Nis)	4.5172419	8.419291	0.54	0.6453
Na2CO3 (Nis)	0.5726724	6.40577	0.09	0.9369
Na2SO4 (Nis)	2.85479	2.204829	1.29	0.3247

Exhibit 20: Linear Model Relating Neptunium (Np) DF-7d to the Six Primary Salt Solutions Components

**Response Np DF-7d
Actual by Predicted Plot**



Residual by Predicted Plot



Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.86712
RSquare Adj	0.53492
Root Mean Square Error	1.810206
Mean of Response	4.193309
Observations (or Sum Wgts)	8

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	42.766664	8.55333	2.6102
Error	2	6.553692	3.27685	Prob > F
C. Total	7	49.320356		0.2998

Tested against reduced model: Y=mean

Lack Of Fit

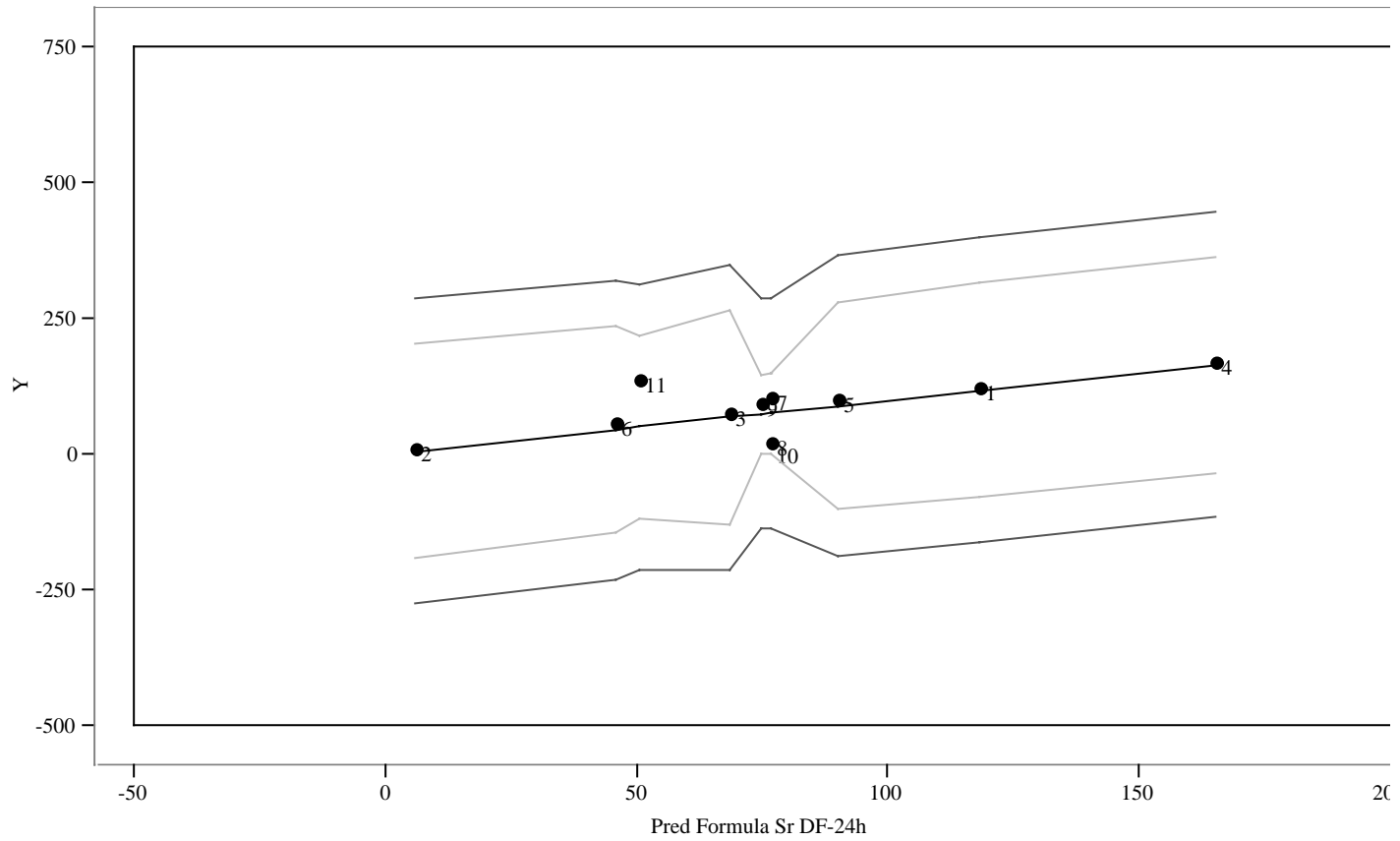
Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	6.4335152	6.43352	53.5339
Pure Error	1	0.1201766	0.12018	Prob > F
Total Error	2	6.5536918		0.0865
				Max RSq
				0.9976

Parameter Estimates

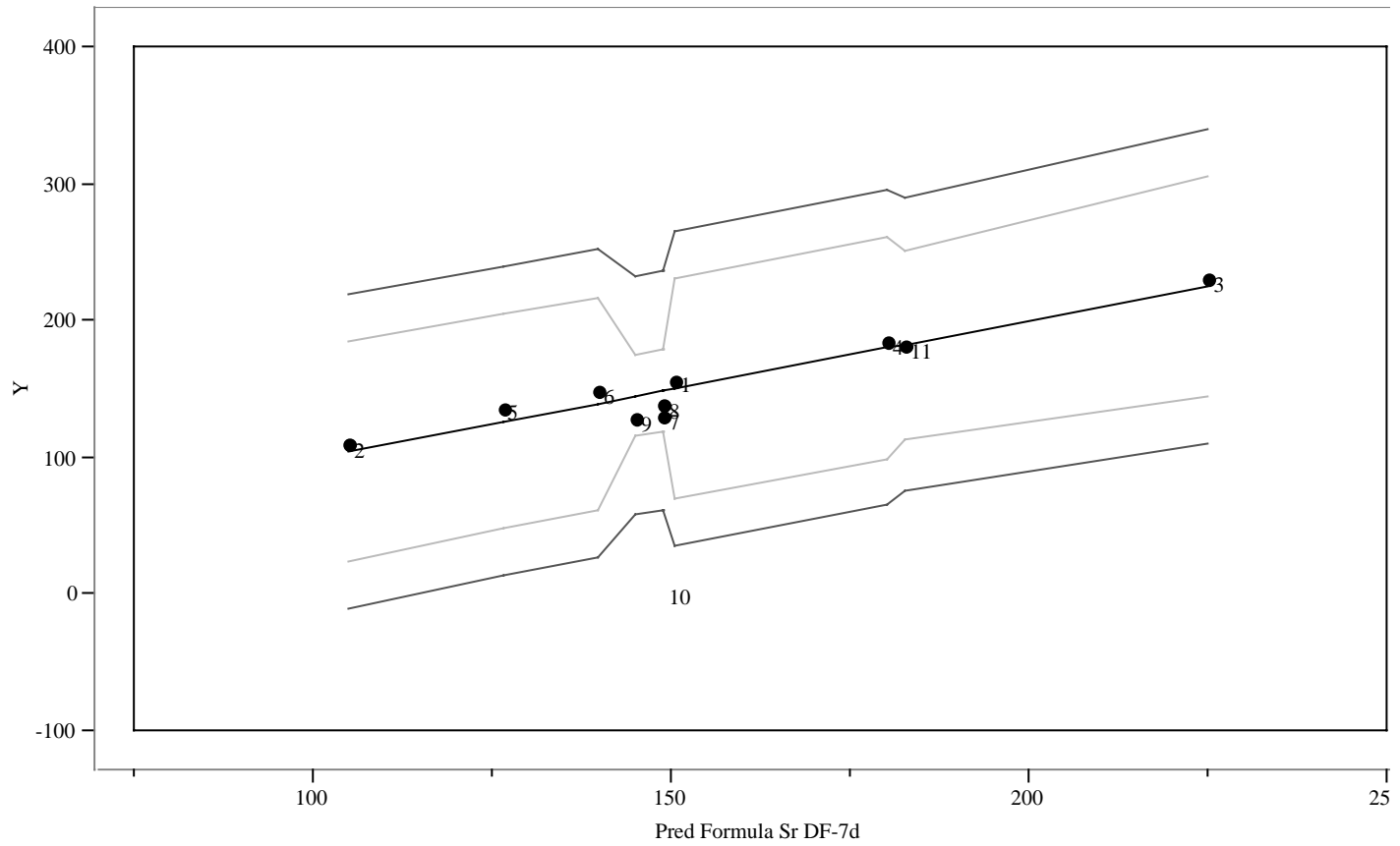
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	Zeroed	0	0	.
NaNO3 (Nis)	13.989464	3.965903	3.53	0.0718
Free NaOH (Nis)	-2.723434	3.42395	-0.80	0.5098
NaNO2 (Nis)	-28.89155	23.40284	-1.23	0.3424
NaAl(OH)4 (Nis)	-5.423186	22.7967	-0.24	0.8341
Na2CO3 (Nis)	-9.571154	17.34474	-0.55	0.6365
Na2SO4 (Nis)	14.582325	5.969958	2.44	0.1346

Exhibit 21: Predicted versus Actual Sr DF-24h with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



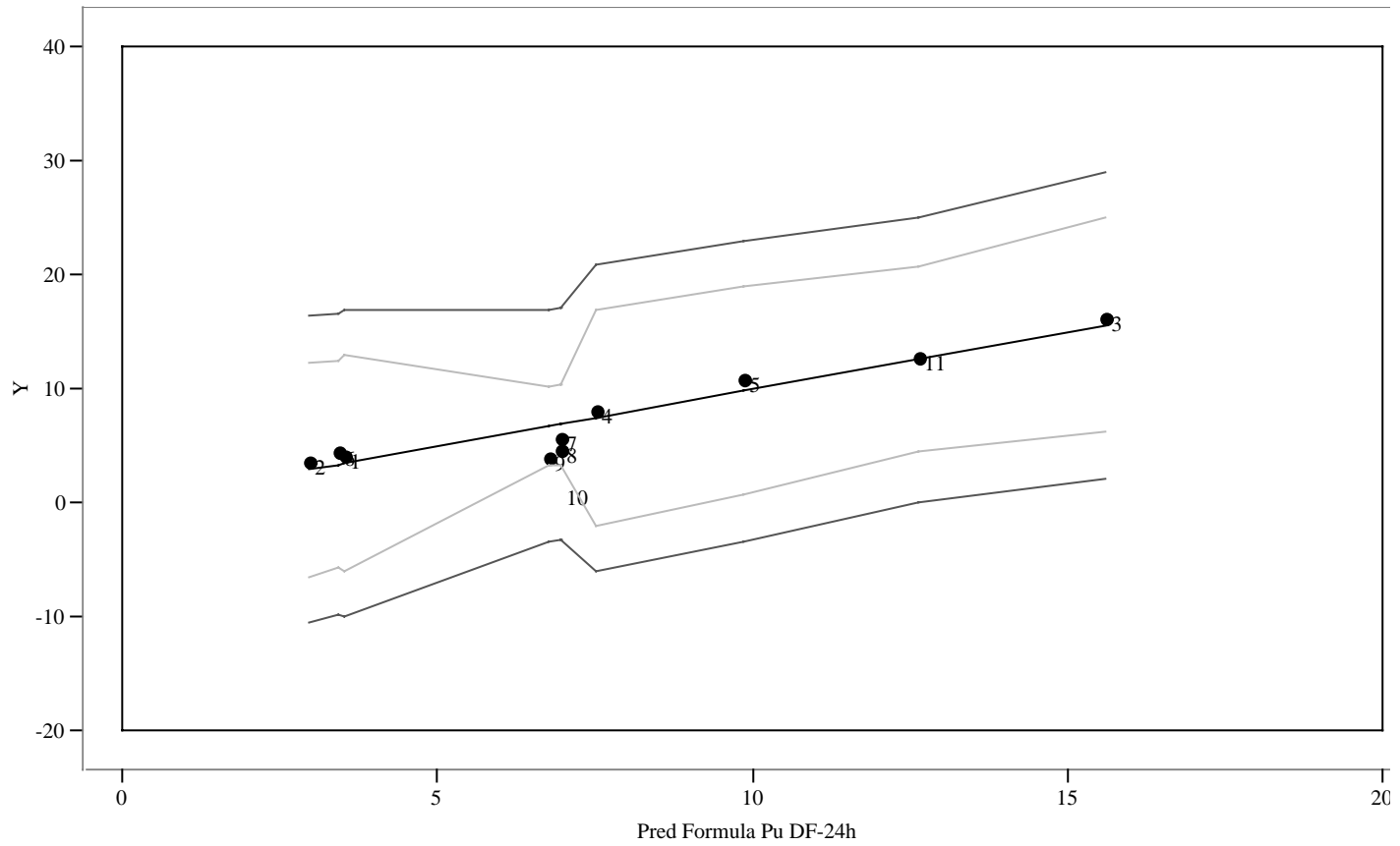
- Y ● *Sr DF-24h*
- Pred Formula Sr DF-24h
- Lower 95% Mean Sr DF-24h
- Upper 95% Mean Sr DF-24h
- Lower 95% Indiv Sr DF-24h
- Upper 95% Indiv Sr DF-24h

Exhibit 22: Predicted versus Actual Sr DF-7d with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



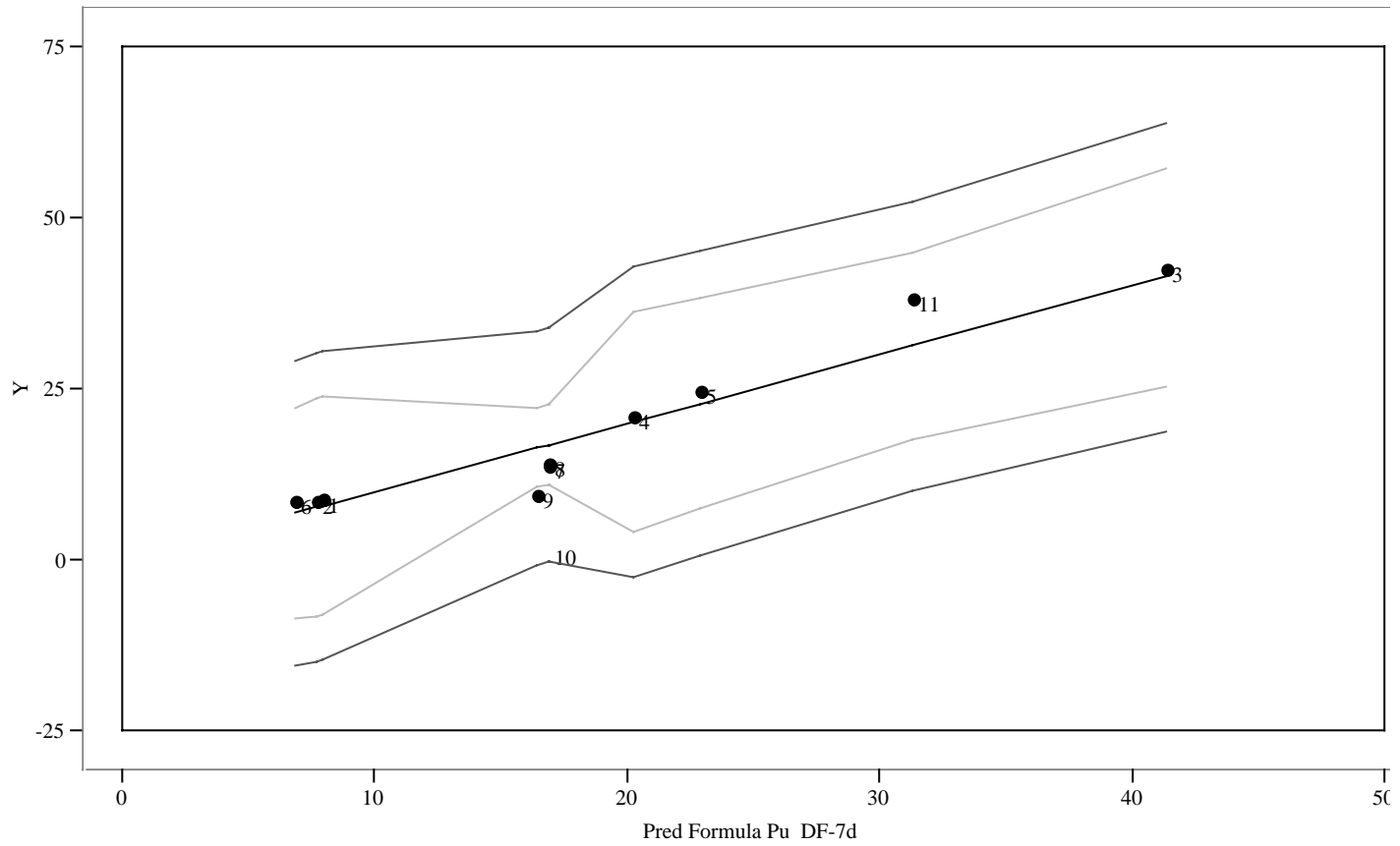
- Y ● *Sr DF-7d*
- Pred Formula Sr DF-7d
- Lower 95% Mean Sr DF-7d
- Upper 95% Mean Sr DF-7d
- Lower 95% Indiv Sr DF-7d
- Upper 95% Indiv Sr DF-7d

Exhibit 23: Predicted versus Actual Pu DF-24h with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



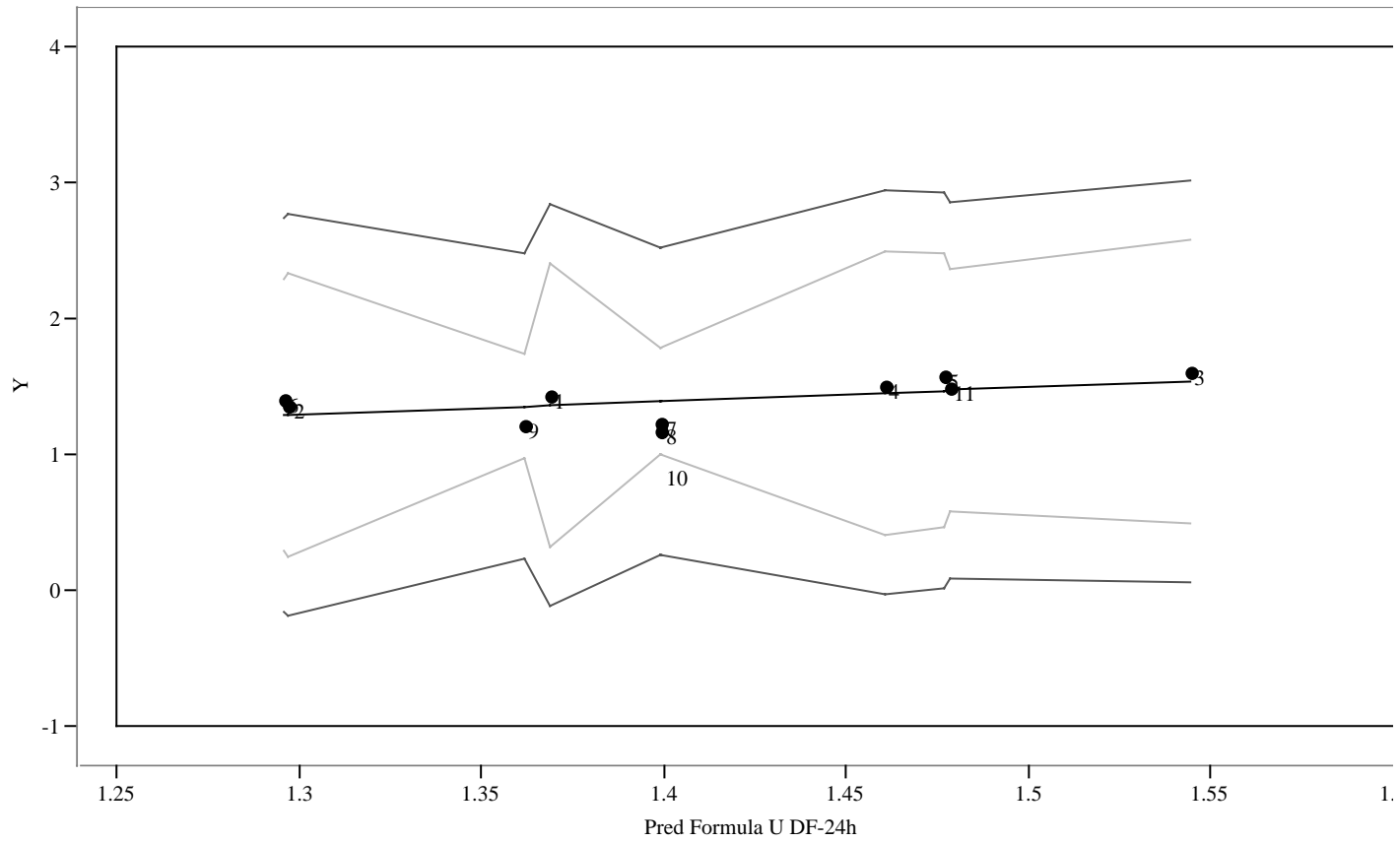
- Y ● Pu DF-24h
- Pred Formula Pu DF-24h
- Lower 95% Mean Pu DF-24h
- Upper 95% Mean Pu DF-24h
- Lower 95% Indiv Pu DF-24h
- Upper 95% Indiv Pu DF-24h

Exhibit 24: Predicted versus Actual Pu DF-7d with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



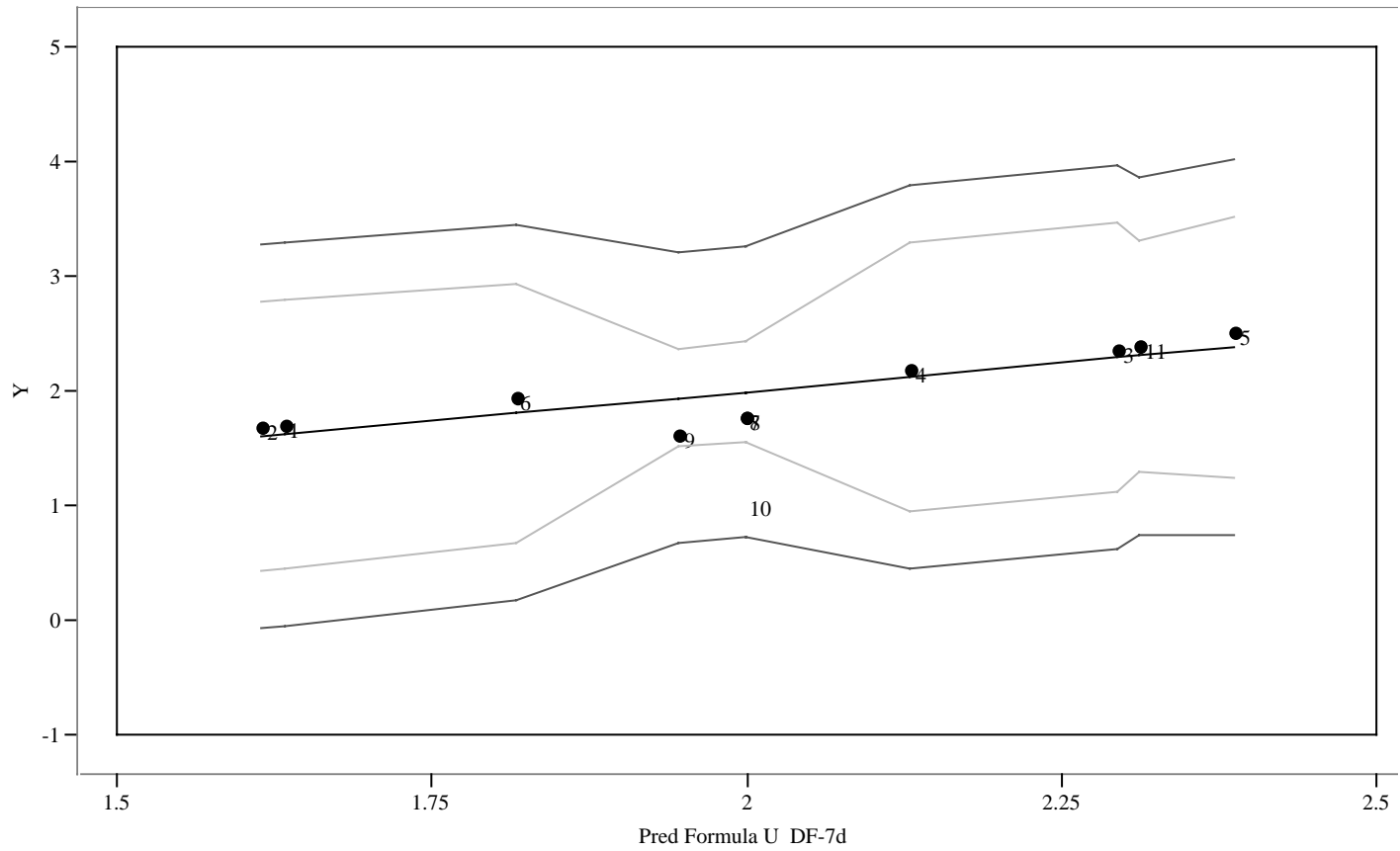
- Y ● Pu DF-7d
- Pred Formula Pu DF-7d
- Lower 95% Mean Pu DF-7d
- Upper 95% Mean Pu DF-7d
- Lower 95% Indiv Pu DF-7d
- Upper 95% Indiv Pu DF-7d

Exhibit 25: Predicted versus Actual U DF-24h with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



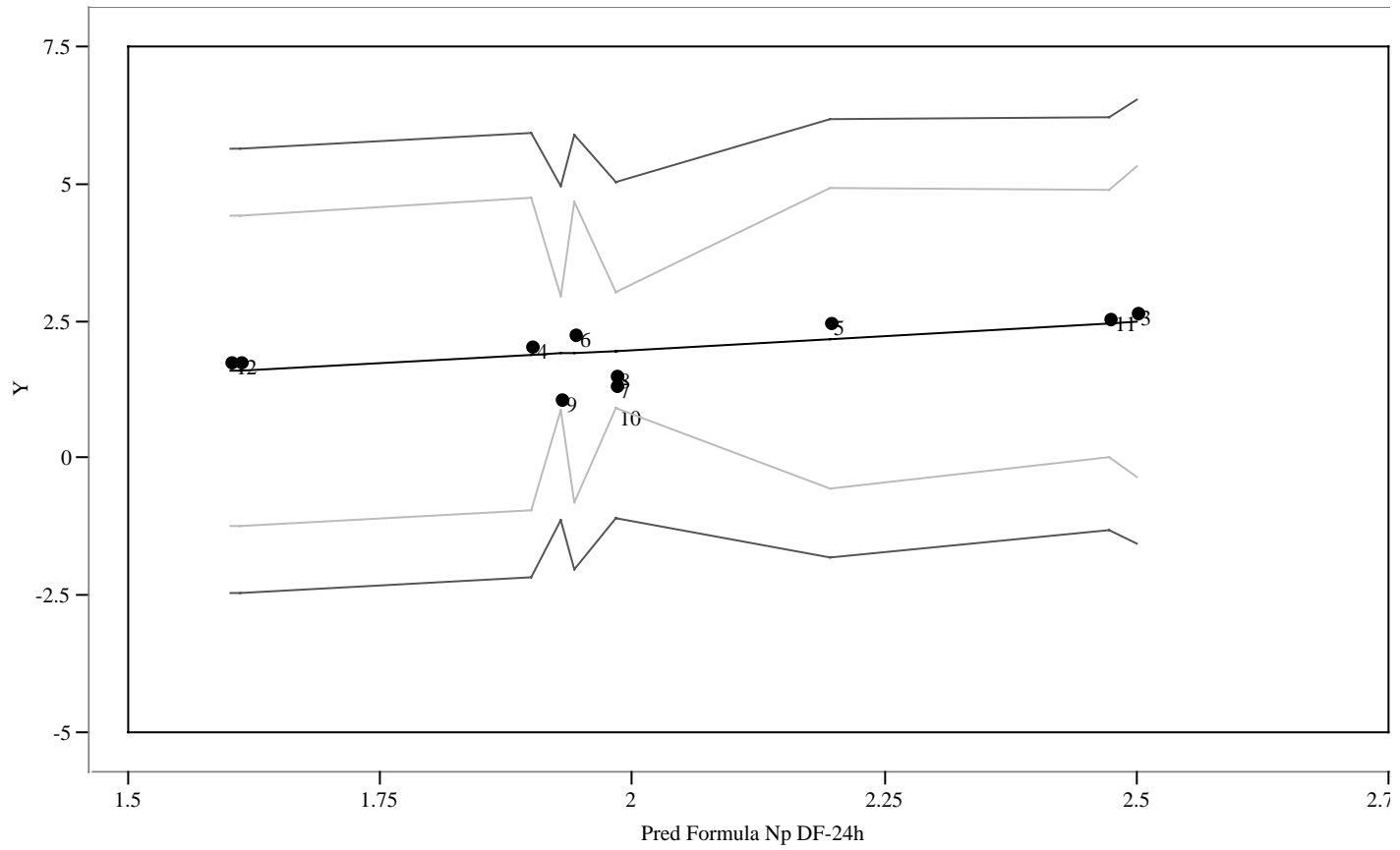
- Y ● U DF-24h
- Pred Formula U DF-24h
- Lower 95% Mean U DF-24h
- Upper 95% Mean U DF-24h
- Lower 95% Indiv U DF-24h
- Upper 95% Indiv U DF-24h

Exhibit 26: Predicted versus Actual U DF-7d with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



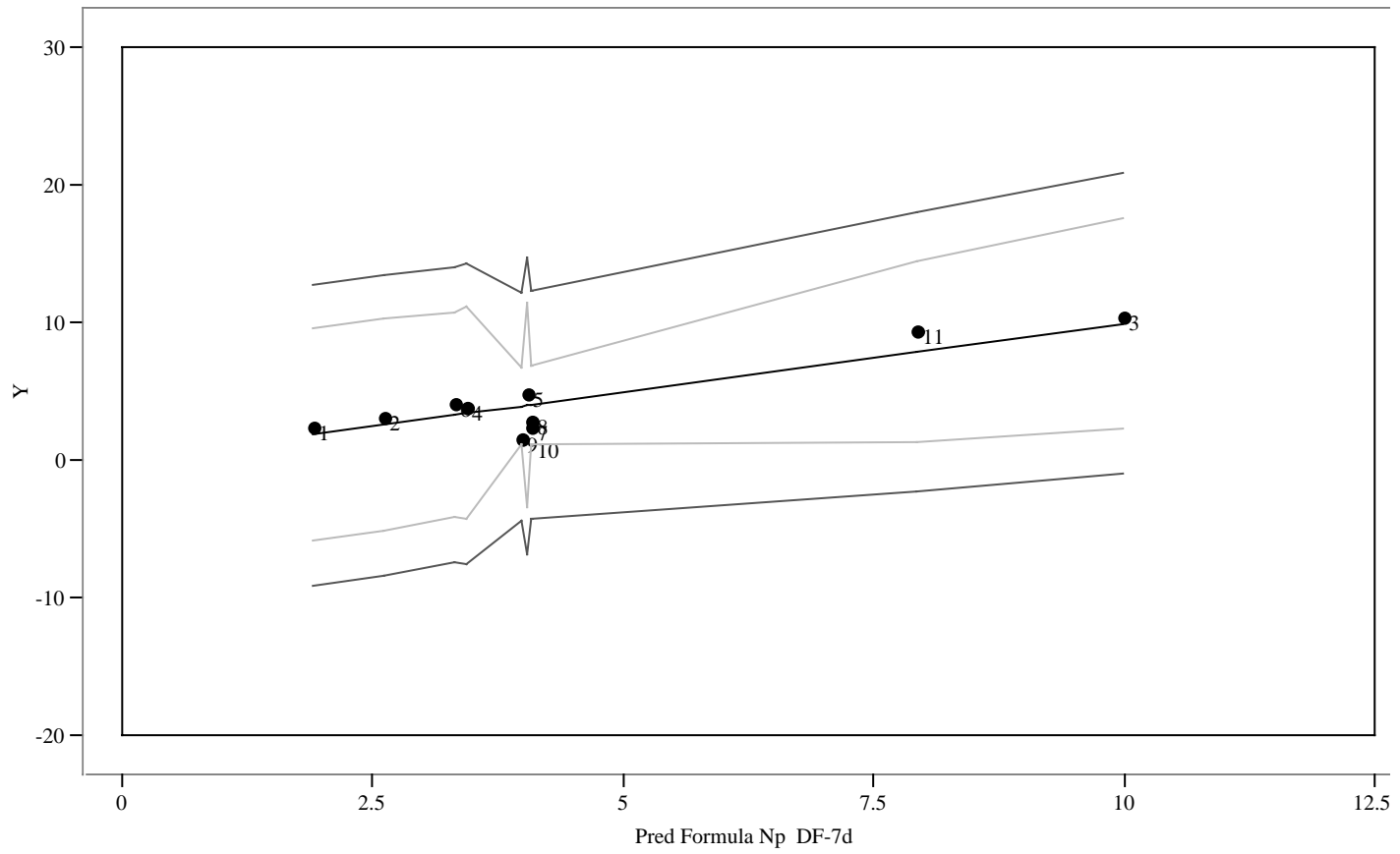
- Y ● U DF-7d
- Pred Formula U DF-7d
- Lower 95% Mean U DF-7d
- Upper 95% Mean U DF-7d
- Lower 95% Indiv U DF-7d
- Upper 95% Indiv U DF-7d

Exhibit 27: Predicted versus Actual Np DF-24h with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



- Y ● Np DF-24h
- Pred Formula Np DF-24h
- Lower 95% Mean Np DF-24h
- Upper 95% Mean Np DF-24h
- Lower 95% Indiv Np DF-24h
- Upper 95% Indiv Np DF-24h

Exhibit 28: Predicted versus Actual Np DF-7d with Predicted Line, Confidence Intervals, and Prediction Intervals for Individual DFs



- Y ● Np DF-7d
- Pred Formula Np DF-7d
- Lower 95% Mean Np DF-7d
- Upper 95% Mean Np DF-7d
- Lower 95% Indiv Np DF-7d
- Upper 95% Indiv Np DF-7d

Distribution: *[C. Canada to add)*