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Sr/TRU REMOVAL FROM HANFORD HIGH LEVEL WASTE

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ABSTRACT

The originally proposed removal process for strontium and transuranic species from 241-AN-102 and 241-AN-107 Hanford waste tank supernates was a co-precipitation method. In initial testing, the slurry formed during the strontium and ferric nitrate co-precipitant additions was not filterable. A series of statistically designed tests were performed to evaluate the variables responsible for this poor filterability. These tests also explored strategies to improve the associated decontamination efficiency of the treatment process.

These tests revealed that filterability is negatively influenced by ferric ion added to co-precipitate actinide and lanthanide species. The concentrations of sodium and organic complexants were observed to influence decontamination of the supernate. Furthermore, the amount of at least one organic complexant was correlated to the poor filterability. The americium decontamination factors measured following the maximum iron nitrate addition were marginal at levels of precipitant addition that are of practical interest.

Based on these results, alternative precipitation schemes were investigated. Reported here is the chosen replacement process, a permanganate precipitation process. A statistically designed series of experiments examined the relationship between three responses and five precipitation parameters. The three responses are precipitate filterability, strontium decontamination, and plutonium decontamination. The parameters varied were the initial sodium and hydroxide concentrations of the waste, and the amount of calcium, strontium, and permanganate introduced. The results reveal an optimum set of conditions for decontamination of strontium and plutonium as well as improved filterability.

INTRODUCTION

The mission of B Plant (1) at the Hanford Reservation in Richland, Washington from 1967 through 1985 was to recover Sr-90 from Purex Acidified Sludge and Purex Current Acid Waste (CAW). The B plant mission was also to recover Cs-137 from Redox Neutralized Supernate, Purex Neutralized Supernate, Purex Sludge Supernate, and CAW. Sr-90 was separated from many of these solutions using a solvent extraction process.

This solvent extraction process utilized di-(2-ethylhexyl) phosphoric acid (D_2EHPA) and tributylphosphate (TBP) as the extractants in a normal paraffin hydrocarbon (NPH) diluent. The process was pH sensitive and required a buffering agent. Hydroxyethylene diamine triacetic acid (HEDTA), ethylene diamine tetraacetic acid (EDTA), and citric acid were added to complex many of the di- and trivalent metals in order to prevent their extraction from the aqueous Phase into the organic solvent.

The D_2EHPA-TBP-NPH solvent system used on the production scale was then washed in several stages before recycle. Among the many species present during these stages were glycolic acid, sodium gluconate, and sodium hydroxide. Strontium and the actinide elements (Pu and Am) are present at higher than normal concentrations in the High Level Liquid Waste at Hanford tanks. These elevated elemental concentrations are a direct result of the presence of the complexing agents used in B Plant operation. The resulting complexes are also believed to severely degrade the filterability of the Sr/TRU precipitate. The Waste from this processing is stored in underground storage tanks such as 241-AN-102 and 241-AN-107 at the Hanford Reservation.

The originally proposed BNFL removal process for strontium and transuranic components from 241-AN-102 and 241-AN-107 supernates was a coprecipitation method. Previous experimentation was performed to decontaminate real waste samples using natural strontium nitrate in an isotopic dilution and ferric nitrate to co-precipitate the actinides (2–5). This work was based on earlier investigations by Herting (2) and Orth, et al. (3) In general, the results of the experiments indicated a successful decontamination for Sr-90 and the actinides.

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The objective of the current work was to examine several factors that could potentially improve the filtration and decontamination of the Sr/TRU precipitation process. The research was performed using three phases of statistically designed experimentation. Variables in the first non-radioactive phase included temperature, sodium ion concentration, hydroxide ion concentration, strontium concentration and ferric ion concentration. The second set of experiments examined the influences of several organic complexants in a 241-AN-107 simulant spiked with Sr-85, Pu-239 and Am-241 tracers. The final Phase examined permanganate (6–12) as a precipitation reagent for the strontium and the transuranic elements. Evaluation of this new precipitation scheme was imperative in order to obtain favorable filterability and decontamination simultaneously. These tests were performed on actual radioactive waste from tank 241-AN-102.

EXPERIMENTAL

Simulant Development

Because of the inherent limitations in working with highly regulated radioactive samples a common strategy in scientific evaluation is to prepare simulants that are non-radioactive. These simulants are used for much of the initial foundation building in order to minimize the amount of work actually performed with radioactive tank waste. The simulant is constructed based on extensive review of previous analytical characterizations of the tank of interest. The simulant incorporates trace metals as well as organic species and is designed so as to mimic the actual tank supernate as closely as possible. The composition of a simulant developed as a nonradioactive surrogate of the supernate from Hanford tank 241-AN-107 is presented in Table 1. This simulant was used during the work performed in Phases I and II.

Experimental Design

The JMP software (13) was used to generate all factorial designs. This software was also utilized to model the observed responses as a function of the variables contained in the initial design. Often terms that contributed to the model with less than an 85% confidence were dropped from the model. This strategy allows only the terms that are most likely contributing to a physical description of the filterability to remain. Some primary terms must remain in the model even though their significance of contribution is much less than the 85% threshold. The retention of these parameters is necessitated by higher order terms of sufficient significance for retention that contain that variable of interest. Software validation was

Table I. 241-AN-107 Simulant Composition

Component	Molecular weight	Concentration	Units	Concentration	Units
Acetate	59.04462	1100	mg/Liter	1.86E-02	M
Aluminum	26.98154	386	mg/Liter	1.43E-02	M
Ammonium	18.03846	22	mg/Liter	1.22E-03	M
Barium	137.33	7	mg/Liter	5.42E-05	M
Boron	10.81	35	mg/Liter	3.24E-03	M
Bromide	79.904	1150	mg/Liter	1.44E-02	M
Cadmium	112.41	64	mg/Liter	5.70E-04	M
Calcium	40.08	591	mg/Liter	1.47E-02	M
Carbonate	60.0092	83936	mg/Liter	1.40E+00	M
Cerium	140.12	53	mg/Liter	3.77E-04	M
Chloride	35.453	1830	mg/Liter	5.16E-02	M
Chromium	51.996	176	mg/Liter	3.38E-03	M
Copper	63.546	30	mg/Liter	4.74E-04	M
EDTA	288.20824	5620	mg/Liter	1.95E-02	M
Fluoride	18.9984	133	mg/Liter	7.00E-03	M
Formate	45.01774	10400	mg/Liter	2.31E-01	M
Glycolate	75.04206	18600	mg/Liter	2.48E-01	M
Hydroxide	17.00734	340	mg/Liter	2.00E-02	M
Iron	55.847	1690	mg/Liter	3.03E-02	M
Lanthanum	138.9055	46	mg/Liter	3.28E-04	M
Magnesium	24.305	25	mg/Liter	1.03E-03	M
Manganese	54.938	563	mg/Liter	1.02E-02	M
Molybdenum	95.94	36	mg/Liter	3.73E-04	M
Neodymium	144.24	96	mg/Liter	6.65E-04	M
HEDTA	275.23618	2140	mg/Liter	7.78E-03	M
Nickel	58.69	530	mg/Liter	9.03-03	M
Nitrate	63.0049	230000	mg/Liter	3.71E+00	M
Nitrite	46.0055	61000	mg/Liter	1.33E+00	M
Oxalate	88.0196	826	mg/Liter	9.38E-03	M
Phosphate	94.97136	1110	mg/Liter	1.17E-02	M
Potassium	39.0983	1810	mg/Liter	4.63E-02	M
Selenium	78.96	1	mg/Liter	6.33E-06	M
Sodium	22.9898	195000	mg/Liter	8.48E+00	M
Sulfate	96.0576	8250	mg/Liter	8.59E-02	M
Uranium		127	mg/Liter	1.27E+02	ug/mL
Zinc	65.38	45	mg/Liter	6.93E-04	M
Zirconium	91.22	70	mg/Liter	7.67E-04	M
Nitrilotriacetic Acid	188.11618	561	mg/Liter	2.98E-03	M
Citric Acid	189.09618	8495	mg/Liter	4.49E-02	M
Iminodiacetic Acid	131.08412	5947	mg/Liter	4.54E-02	M
Sodium Gluconate	218.14	43628	mg/Liter	2.00E-01	M

performed on the JMP software used to develop the design. The details of each model are presented in the subsequent discussion.

Testing Method

The Phase I and II nonradioactive tests involved placing 50 mL of the simulant described in Table I into a 200-mL beaker. Prior to this introduction the concentrations of aluminum and hydroxide were adjusted as specified in the experimental design. The solution was stirred with a magnetic stirrer and heated to the required temperature in a water bath (50°C ± 5°C). The proper aliquot of the iron for precipitation was added. This addition was followed after five minutes with the strontium addition. After this final addition, the slurry was stirred for 15 minutes and allowed to cool to room temperature (30°C ± 5°C).

The radioactive tests performed during Phase III involved about 50ml of actual 241-AN-102 supernate at known concentrations of hydroxide and sodium. These samples were equilibrated at 50°C ± 5°C using a water bath. Following this equilibration, the calcium component was added first. The strontium reagent followed this addition five minutes later and finally after another five-minute period the permanganate was introduced. Three minutes after the permanganate was added the sample was placed in a preheated drying oven for four hours at 50°C ± 5°C. Following this aging period the samples were removed and allowed to cool to room temperature (30°C ± 5°C).

Once the Phase III samples were at room temperature they were subjected to three minutes of intense shear at 8,000 rpm from a Braun handmixer. The Braun handmixer was thoroughly rinsed between each experiment. The high shear of the handmixer was not intended to mimic a specified shear condition, rather to introduce a reproducible extreme shear condition prior to filtration.

During all phases the cooled precipitated samples were then filtered. The filterability was measured using a modified ASTM procedure (13). In this procedure, the filtrate was collected through a 0.45-micron nylon filter for 1 minute and volumetrically measured. A portion of the filtrate was collected and diluted 50:1 using 0.1M HCl.

Analysis

These diluted samples were submitted to the Analytical Development Section (ADS) of SRTC for analyses to assist in assessment of the decontamination efficiency of the precipitation process. These analyses included elemental analysis by Inductively Coupled Plasma—Emission spectroscopy, Inductively Coupled Plasma—Mass Spectrometry, gamma spectroscopy, liquid scintillation analysis for strontium-90, and alpha pulse height analysis.

DISCUSSION

Phase I

The first phase of experimentation was conceived to evaluate primary effects associated with the iron/strontium precipitation scheme. The factors investigated in this first design were sodium ion, hydroxide ion, and aluminum concentrations, the total amount of strontium added to the system, and the total amount of iron added to the system. The sodium, hydroxide and aluminum concentrations were selected to span the observed concentration ranges for the 241-AN-102 and 241-AN-107 waste tanks. Lanthanum, cerium and neodymium were used as surrogates for plutonium and americium in this nonradioactive phase of experimentation.

The resulting design is presented in Table II and includes a quarter fraction of the five-factor complete factorial experiment. These eight experiments were conducted in tandem with a center-point. The center point is a test run with all factors at settings equal to the midpoint of their respective ranges. The overall design was a resolution 3 design, which provides unaliased estimates of the main effects. Higher order interactions contain significant convolution of variables.

The measured filtrate flux for these experiments is also shown in Table II. The regressed filtrate data are presented in Table III. As expect, the total iron concentration added to initiate precipitation of the lanthanide ions was statistically significant. A plot of these effects is shown in Figure 1. Interestingly, iron concentration was the only variable revealed to be statistically significant at the 95% confidence level with no other variable significant even at the 85% level.

It had been previously believed that increased ionic strength (sodium level) would decrease the filterability and increased hydroxide ion concentration would increase filterability ref Ionic strength (sodium level) and hydroxide ion concentration did not affect filterability.

Table II. Experimental Matrix for and Results for Phase I

Test No.	Pattern	Na+ (M)	OH- (M)	Al (M)	Sr (M)	Fe (M)	Filtrate Flux (g)
1	−−−−+	5.5	0.4	0.05	0.025	0.075	4.98
2	−−++−	5.5	0.4	0.30	0.075	0.025	7.68
3	−+−+−	5.5	1.0	0.05	0.075	0.025	11.16
4	−++−+	5.5	1.0	0.30	0.025	0.075	4.32
5	+−−++	7.0	0.4	0.05	0.075	0.075	4.32
6	+−+−−	7.0	0.4	0.30	0.025	0.025	7.68
7	++−−−	7.0	1.0	0.05	0.025	0.025	6.84
8	+++++	7.0	1.0	0.30	0.075	0.075	3.66
9	ooooo	6.25	0.7	0.18	0.050	0.050	5.76

Table III. Statistical Model for Filtration Data in Phase I

Term	Estimate	Std Error	t Ratio	Prob > |t|
Intercept	15.8	4.1	3.83	0.03
Na + (M)	−0.94	0.6	−1.55	0.22
OH− (M)	0.42	1.13	0.37	0.73
Al (M)	−3.9	3.6	−1.07	0.36
Sr conc (M)	15.4	18.1	0.85	0.46
Fe conc (M)	−80.2	18.1	−4.42	0.02

The lanthanide concentrations measured in the precipitation tests with the revised 241-AN-107 simulant were used to evaluate the efficiency of the precipitation process on species removal. This evaluation results in determination of process decontamination factors (DFs). These factors are calculated by comparing the ratio of the initial concentration of a give species to the concentration of that species following precipitation. The DF can be considered as a measure of the decontamination efficiency. For instance, if only half of the concentration of a given species remains in solution following precipitation a DF of 1/0.5 or 2 would be obtained. The DF presented in this work includes the ionic strength and caustic adjustments of the feed volume prior to precipitation.

The observed DFs for the lanthanide elements can be found in Table IV. The value of DF for neodymium ranged from a low of 2 to as high as 7.2. The range

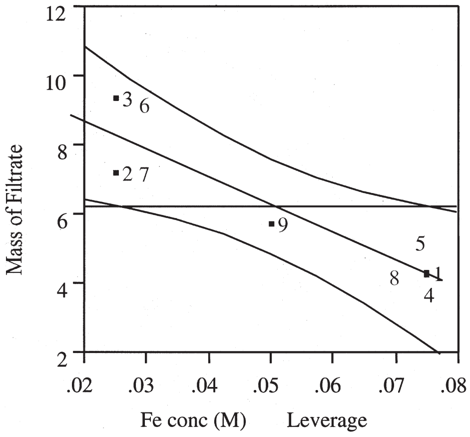

Figure 1. Filtrate Mass versus Iron Concentration for Phase I.

***Table IV**.* Lanthanide Decontamination Factors in Phase I

Test No.	La DF	Ce DF	Nd DF
1	5.3	5.4	3.8
2	6.1	5.8	3.5
3	3.7	3.3	2.2
4	7.2	6.3	4.5
5	4.1	4.2	2.9
6	2.2	2.1	1.8
7	2.2	2.0	1.8
8	4.6	4.3	3.0
9	3.5	1.4	6.0

of DF for lanthanum was from 1.8 to 6.0. This trend of lower DFs for Nd compared to La has been observed in several scoping studies performed at SRTC and may be indicative of the increased charge density on the Nd ion. The decontamination factors measured for cerium spanned from 2 to 6.3.

Statistical modeling of the variables responsible for the observed decontamination factors is provided in Table V. There are some differences between re-

***Table V**.* Statistical Model for Decontamination Factors in Phase I

Term	Estimate	Std Error	t Ratio	Prob > |t|
Lanthanum				
Intercept	10.9	3.0	3.59	0.04
Na + (M)	−1.5	0.45	−3.43	0.04
OH − (M)	0.0	0.84	0.00	1.0
AL (M)	4.8	2.7	1.79	0.17
Sr conc (M)	8.0	13.4	0.60	0.59
Fe conc (M)	35	13.4	2.61	0.08
Cerium				
Intercept	9.9	5.4	1.83	0.16
Na + (M)	−1.4	0.8	−1.73	0.18
OH− (M)	−0.5	1.5	−0.34	0.76
Al (M)	3.6	4.7	0.76	0.50
Sr conc (M)	9.0	23.7	0.38	0.73
Fe conc (M)	35	23.7	1.48	0.24
Neodymium				
Intercept	6.5	5.5	1.19	0.32
NA + (M)	−0.75	0.8	−0.93	0.42
OH− (M)	−0.16	1.5	−0.10	0.92
Al (M)	2.1	4.8	0.43	0.69
Sr conc (M)	−1.5	24.3	−0.06	0.95
Fe conc (M)	24.5	24.3	1.01	0.39

sults for each of the lanthanide elements; however, the primary effect of each of the variables is the same. In the lanthanum results, sodium level was statistically significant at a 5% significance level and iron concentration was nearly significant. The magnitude of the effect for each of these variables is shown in Figure 2 and was as expected. Sodium ion increases resulted in a slight decrease in the DF

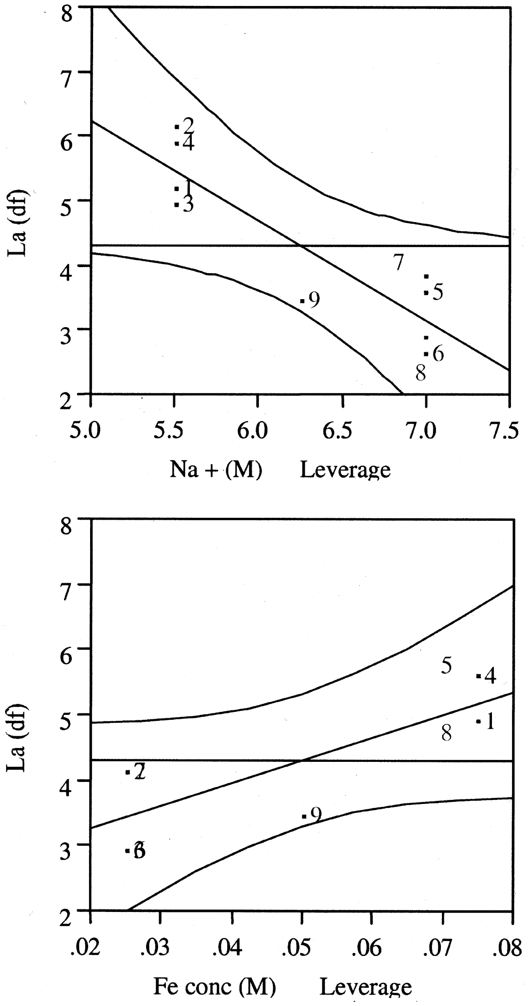

Figure 2. Sodium and Iron Statistical Plots for DF Phase I.

(estimate of slope of DF vs. [Na] = −1.5). An increase in iron concentration showed a large increase in the DF (estimate of DF vs. [Fe] = 35). Additionally, hydroxide ion did not have an effect on the DF obtained for lanthanum, neodymium, or cerium.

The results for cerium and neodymium are not statistically significant but the estimates from the fitted models support the same conclusion. In the results for cerium DF, there were no statistically significant variables. However, the magnitudes of the estimates are nearly identical to those for lanthanum. In the neodymium results, there are no significant effects and the estimates are slightly different but of the same direction. This delta for neodymium may be indicative of its higher charge density due to its smaller size. The results of these tests indicate that successful decontamination of the actinide surrogates (La, Ce, and Nd) can be obtained. The optimum conditions would be to utilize high concentrations of ferric nitrate (0.075 M) and a low sodium ion concentration (5.5 M).

Phase II

The second phase of experimentation was designed determine the effects of several variables on filterability, Sr-90 decontamination and TRU decontamination that were not evaluated during the first phase. The design utilized for this study included a quarter fraction of the six-factor complete factorial experiment. The resulting 16 tests along with two midpoint tests are presented in Table VI. The design is a resolution 4 design that provides unaliased estimates of all main effects and some two-way interactions.

Specifically, the objective of Phase II was to determine the influence of each organic complexant on the filterability of the Sr/TRU precipitate. The levels for each primary variable were the same as in Phase I. The levels of organic complexants were established to interrogate the range of actual concentrations measured in the 241-AN-102 and 241-AN-107 tanks. Three other variables were studied and were the sodium, aluminum, and hydroxide concentrations.

During Phase II tests, simulated 241-AN-107 waste was spiked with Sr-85, Am-241 and Pu-239 radiotracers on the order of 10^5 dpm/mL. Various levels of organic complexing agents were added according to the experimental matrix. The effects of these organic agents on the filterability of the Sr/TRU precipitation process were examined along with the decontamination of the radiotracers.

The results of the filtration portion of the Phase II tests are shown in Table VI. In general, the filterability of the precipitates formed in this phase was poor. The filtration data shows six conditions in which little or no filtrate was obtained. These conditions span the sodium and hydroxide conditions used in the tests. Additionally, the mid point filtration data showed a very low filtrate flux.

***Table VI*.** Experimental Design Phase II

Pattern	Test No.	Na	OH	Al	Fe Conc	EDTA Gp.	Gluconate	Filtrate vol (mL)
−−−−−−	1	5.5	0.4	0.05	0.02	−1	−1	19.5
−−−+++	2	5.5	0.4	0.05	0.1	1	1	1
−−+−−+	3	5.5	0.4	0.3	0.02	−1	1	0
−−−+−	4	5.5	0.4	0.3	0.1	1	−1	19
−+−−+−	5	5.5	1	0.05	0.02	1	−1	32.3
−+−+−+	6	5.5	1	0.05	0.1	−1	1	1
−++−++	7	5.5	1	0.3	0.02	1	1	1
−+++−−	8	5.5	1	0.3	0.1	−1	−1	16.4
+−−−++	9	7	0.4	0.05	0.02	1	1	0
+−−+−−	10	7	0.4	0.05	0.1	−1	−1	9.4
+−+−+−	11	7	0.4	0.3	0.02	1	−1	7.2
+−++−+	12	7	0.4	0.3	0.1	−1	1	10
++−−−+	13	7	1	0.05	0.02	−1	1	0
++−++−	14	7	1	0.05	0.1	1	−1	7.2
+++−−−	15	7	1	0.3	0.02	−1	−1	5.3
++++++	16	7	1	0.3	0.1	1	1	0
Oooooo	17	6.25	0.6	0.175	0.06	0	0	2.9
Oooooo*	18	6.25	0.6	0.175	0.075	0	0	3.3

*Volumes measured after one minute filtration.

Organic levels based on 8.7 M sodium ion in starting salt solution concentrations were:

Organic	Level −1	Level 0	Level +1
EDTA	0.0075	0.022	0.037
HEDTA	0.0078	0.023	0.039
NTA	0.0	0.004	0.0073
IDA	0.0375	0.113	0.188
Glycolate	0.07	0.21	0.35
Citrate	0.0128	0.038	0.064
Gluconate	0.0	0.009	0.018

***Table VII*.** Statistical Model for Filtration in Phase II

Term	Estimate	Prob > |t|
Intercept	35.4	0.04
Sodium	−4.3	0.09
Hydroxide	0.01	0.99
Aluminum	−5.75	0.69
Fe Conc.	−4.5	0.92
EDTA Group	0.38	0.83
GLuconate Group	−6.45	0.01

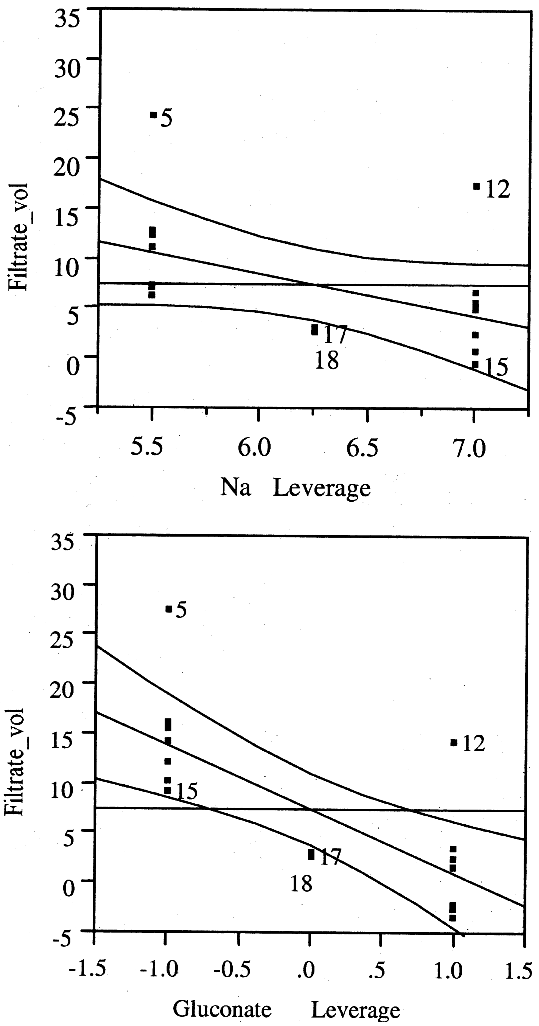

Figure 3. Statistical Plot for the Gluconate Group and the Sodium Levels for Phase II.

This regressed data are presented in Table VII. The concentration of the gluconate group agents was shown to be a statistically significant variable. The group of complexing agents included gluconate, glycolate, and citrate. This group had a negative impact on filterability, i.e., increased level decrease filterability. The magnitude of the model coefficient is 6.5 and the sign is negative. This result is somewhat surprising since increased gluconate levels forms soluble complexes with iron and should have provided for better filtration performance with corresponding reduction in the TRU DF. The citrate component should not have an effect; however, glyconate could potentially act as a surfactant. The concentration of the gluconate group spanned the concentrations of thee organic species in the real 241-AN-102 and 241-AN-107 wastes. This presence of the organic agents could peptize the precipitate.

Additionally, the sodium level was significant, but only at a 10% level. The Phase II data model predicts poorer filterability at high sodium levels. This is indicative of the high ionic strength of the solution. Shown in Figure 3 are the statistical plots for gluconate group and sodium levels. This data clearly indicates the glycolate/gluconate concentrations present in the real 241-AN-102 and 241-AN-107 wastes will affect the filterability of the ferric hydroxide precipitate. Without removal of the glycolate/gluconate, the ferric hydroxide precipitate can not be filtered in the 241-AN-102 and 241-AN-107 solutions.

The decontamination factors (DFs), neglecting the effect of dilution, that were obtained in the Phase II tests for Sr-85, Am-241, and Pu-239 are shown in Table VIII. The starting, spiked concentrations were nominally 10^5 dpm/mL. The DFs for Sr ranged from 4.5 to 52.6. The DFs for the actinides ranged from 1 to 3 for Am and 1 to 12 for Pu.

Regression of DF data for strontium revealed only one statistically significant variable, the concentration of the EDTA group. Specifically, an increase in

Table VIII. Decontamination Factors from Phase II

Test No.	Sr DF	Am	Pu
1	32.2	—	6.6
2	29.3	1.5	2.2
3	37.8	3.0	1.3
4	10.0	1.4	5.6
5	7.5	3.3	2.4
6	13.2	1.4	1.2
7	4.8	1.0	1.0
8	39.2	—	—
9	10.8	1.3	1.7
10	52.6	—	3.6
11	4.5	1.5	4.6
12	24.0	2.9	1.3
13	15.7	0.9	11.9
14	32.9	1.8	1.0
15	26.6	—	1.0
16	14.3	1.4	1.3
17	21.2	2.3	3.3
18	17.0	1.3	1.4

the concentration of the EDTA group (EDTA, HEDTA, IDA, and NTA) caused a decrease in the DF for strontium. Figure 4 displays the statistical plot of the strontium DF data. Strontium is known to complex with EDTA and the other members of this organic grouping. Because only a single level of non-radioactive strontium was added in these tests, the data imply that some of this strontium was complexed by the chelants. This would effectively lower the isotope dilution effect of adding non-radioactive strontium. The statistical analysis of the actinide DF data did not reveal any variable as significant. This observation warrants further experimental evaluation due to a possible masking in the effects of the process variables.

Phase III

The final phase of testing was constructed to assist in evaluation of a new precipitation scheme involving a sodium permanganate addition. Exploration of this new scheme was in search for improved filterability and decontamination. The design consists of 25 experimental trials that are presented in Table IX. The first 16 experiments are a quarter factorial design constructed to support the estimation of the overall average, all major effects, and all two-way interactions. However, fitting a model with these 16 terms only would leave no degrees of freedom for estimating error in the model or experimental process. In addition, a nonlinear response could not be detected or modeled with only these data points.

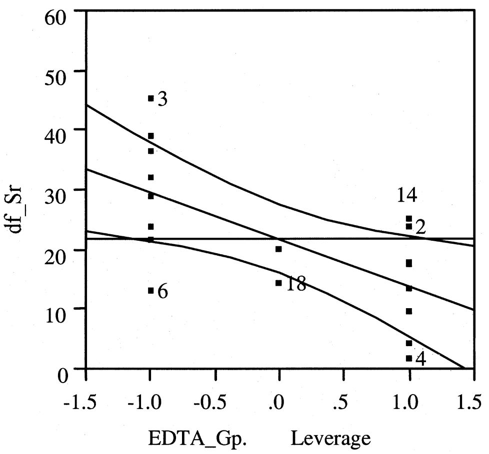

Figure 4. Statistical Plot of Sr DF Data for Phase II.

Table IX. Experimental Design for Phase III

Expt	Pattern	[Mn]	[Ca]	[OH]	[Sr]	[Na]	Volume (ml)	Pu-total DF	Sr DF
1	++−+−	0.05	0.012	0.5	0.075	6	13	2.7	53
2	00000	0.04	0.006	0.75	0.05	6.5	13	2	3.2
3	+−+−+	0.05	0	1	0.02	7	11.5	2	13.6
4	+++−−	0.05	0.012	1	0.075	6	18	0.9	17
5	+++−−	0.05	0.012	1	0.02	6	18	2.5	17
6	−+−++	0.03	0.012	0.5	0.075	7	9	2.4	46.2
7	0−000	0.04	0	0.75	0.05	6.5	16.5	2.1	41.1
8	+−−−	0.05	0	0.5	0.02	6	14.5	1.5	29
9	0+000	004	0.012	0.75	0.05	6.5	14.5	2.5	15.6
10	0+000	0.04	0.012	0.75	0.05	6.5	13	2.2	32.2
11	0−000	0.04	0	0.75	0.05	6.5	15	1.7	37
12	−0000	0.03	0.006	0.75	0.05	6.5	12.5	1.6	33.6
13	−−+++	0.03	0	1	0.075	7	17	1	59.3
14	−−−−+	0.03	0	0.5	0.02	7	14.5	1.9	11
15	−−−+−	0.03	0	0.5	0.075	6	19	2.3	81.4
16	−−0+0	0.03	0	0.75	0.075	6.5	16	1.6	74.5
17	+0000	0.05	0.006	0.75	0.05	6.5	16	2.2	35.2
18	+−−++	0.05	0	0.5	0.075	7	17	2.1	38.9
19	−+−−−	0.03	0.012	0.5	0.02	6	16	1.6	15
20	−++−+	0.03	0.012	1	0.02	7	20	0.5	9.9
21	−+0−0	0.03	0.012	0.75	0.02	6.5	15	1.6	7
22	++−−+	0.05	0.012	0.5	0.02	7	13	1.8	16
23	+−++−	0.05	0	1	0.02	6	21.5	2.1	65
24	+0000	0.05	0.006	0.75	0.05	6.5	16	2.2	41
25	+++++	0.05	0.012	1	0.075	7	12.5	1.8	55.2
26	−−+−−	0.03	0	1	0.02	6	22	1.9	14.9

* Run 22 is an extra run not originallyincluded in design

* Concentration are in molar units

To address these limitations, the design was modified by adding 9 more experiments. This design allows for the investigation of a curvilinear effect due to calcium and/or manganese and for the estimation of process reproducibility. This estimation of error also provides for an opportunity to more thoroughly test for a lack of fit for the fitted models. The order of those experiments was randomized to minimize systematic error contribution from the experimental procedure. This was a resolution 4 design that provides estimates of all main effects and some two-way interactions.

Table IX contains the filtration results measured for each of the precipitated and sheared radioactive 241-AN-102 samples prepared during Phase III. The mass results were measured on a balance in the shielded cells. The volumes were measured by transferring the filtrate into a 50-ml graduated cylinder and using a monocle to estimate the fluid level. Because the mass measurements are more reproducible in the cell environment compared to volume measurement a decision was made to focus on this observable as a means for modeling the filterability as a function of the design parameters.

The filterability results were used to perform a statistical analysis. The resulting model relating filterability of the precipitated slurry to the five precipitation parameters is provided in Table X. The values shown this table are the

***Table X*.** Statistical Model for Phase III

	Filterability RSquare		0.81	
Term	Estimate	Std Error	t Ratio	Prob > |t|
Intercept	19.690638	0.403723	48.77	<.0001
[Mn]	−0.511698	0.449684	−1.14	0.2719
[Ca]	−1.089157	0.440793	−2.47	0.0251
[OH]	2.245	0.512155	4.38	0.0005
[Mn]*[OH]	−1.011375	0.512155	−1.97	0.0658
[Ca]*[OH]	1.0005	0.512155	1.95	0.0685
[Sr]	−0.222928	0.487868	−0.46	0.6539
[Mn]*[Sr]	0.8703032	0.487868	1.78	0.0934
[Ca]*[Sr]	−1.695352	0.487356	−3.48	0.0031
[Na]	−2.062625	0.512155	−4.03	0.0010
	Sr-90 DF RSquare	0.89		
Term	Estimate	Std Error	t Ratio	Prob > |t|
Intercept	20.158595	5.532757	3.64	0.0022
[Mn]	−0.32781	2.005027	−0.16	0.8722
[Ca]	−3.798486	1.996236	−1.90	0.0752
[Sr]	21.491097	2.189492	9.82	<.0001
[Mn]*[Sr]	−4.428597	2.189492	−2.02	0.0602
[Na]	−5.52462	2.312316	−2.39	0.0295
[Ca]*[Na]	2.9128801	2.312316	1.26	0.2258
[Mn]*[Mn]	10.89781	4.42169	2.46	0.0254
[Ca]*[Ca]	7.076756	4.854153	1.46	0.1642
	Pu-DF RSquare	0.86		
Term	Estimate	Std Error	t Ratio	Prob > |t|
Intercept	1.9547456	0.046455	42.08	<.0001
[Mn]	0.171568	0.051744	3.32	0.0047
[Ca]	0.1035714	0.050513	2.05	0.0582
[OH]	−0.125	0.058932	−2.12	0.0510
[Sr]	0.1892857	0.055845	3.39	0.0040
[Na]	−0.225	0.058932	−3.82	0.0017
[OH]*[Mn]	0.1625	0.058932	2.76	0.0147
[Sr]*[Ca]	0.1759086	0.056079	3.14	0.0068
[Sr]*[OH]	−0.1375	0.058932	−2.33	0.0340
[Na]*[Ca]	−0.125	0.058932	−2.12	0.0510
[Na]*[OH]	−0.2375	0.058932	−4.03	0.0011

model estimates (coefficients) of the linear response model, the standard errors of the estimates, the statistical t ratio's, and the significance levels. For a parameter to be statistically significant, the significance level should be less than or equal to 0.05.

The resulting model clearly describes the experimentally obtained filterability data well. A strategy was developed to find the optimum filterability response for the five variable parameter space examined. The method implemented for this work consisted of several steps. The first step was to plot the predicted filterability as a function of the measured filterability. This plot is shown in Figure 5. The actual data points are shown on the graph as well as the 95% confidence intervals (lines). The experiment numbers corresponding to the extremes are shown on the figure. The conditions that correspond to this extreme (highest and lowest) filterability were analyzed for opposing contribution to the extremes.

Evaluation of the conditions associated with the extremes, presented in Table XI, show that high filterability experiments contained the high level of hydroxide and the low level of calcium. On the other hand, the conditions affiliated with the low filterability extreme are opposite to those of the high extreme. Namely, the level of calcium is high and the level of hydroxide is low for the poor filterability experiments. Once the opposing conditions associated with the extremes were identified the next step in the deconvolution was to hold those two variables constant.

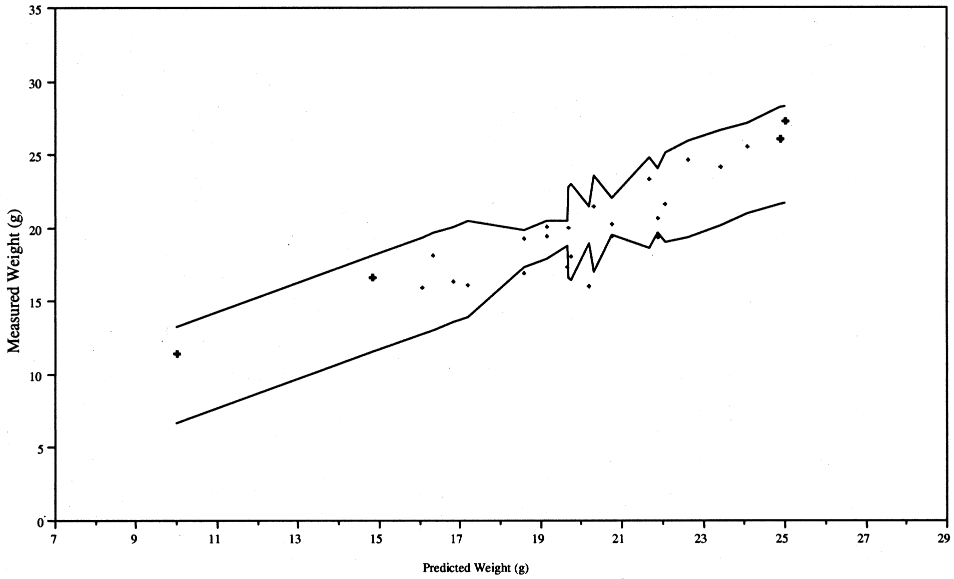

Figure 5. Predicted vs. Measured Filterability for Phase III.

Table XI. Extreme Conditions for Predicted Responses in Phase III

Filtration Data Extreme	[Mn]	[Ca]	[OH]	[Sr]	[Na]
Low	1	1	−1	−1	1
High	−1	−1	1	−1	−1
Optimum	1 or −1	−1	1	1 or −1	−1
Sr-90 DF Extreme	**[Mn]**	**[Ca]**	**[OH]**	**[Sr]**	**[Na]**
Low	−1	1	1	1	1
High	−1	−1	−1	1	−1
Optimum	−1	−1	−1 or 1	1	−1
PU DF Extreme	**[Mn]**	**[Ca]**	**[OH]**	**[Sr]**	**[Na]**
Low	−1	−1	1	1	1
High	1	1	−1	1	−1
Optimum	1	1	−1	1	−1

Based on this evaluation a unified story emerges describing the optimum conditions for filterability. This interpretation suggests the conditions presented in Table XI are most beneficial for filterability. More specifically the results suggest that the hydroxide level should be high and the sodium and calcium concentrations should be at the lower level. Note that the favorable levels for strontium and manganese are most favorable when incorporated at the same extreme. Namely, either both are high or low.

The next response of interest for the new precipitation scheme is presented in Table IX. This table contains the strontium-90 decontamination factors determined from the precipitated and sheared 241-AN-102 samples. The decontamination factor presented is calculated by simply comparing the ratio of the initial Sr-90 activity to the final activity. For example if 50% of the activity were not present relative to the feed the accompanying DF would be two. This calculation does not take into account issues such as dilution involved in various activities such as compositing or precipitating. The worst case scenario in dilution of the final activity affiliated with addition of the precipitants is about 9%.

The Sr-90 decontamination results were used to perform a statistical analysis. The resulting model relating Sr-90 DF of the precipitated slurry to the five precipitation parameters is provided in Table X. The criterion for keeping terms in the model is identical to those used in the previous filtration modeling section.

The values shown in this table are the model estimates (coefficients) of the linear response model, the standard errors of the estimates, the statistical t ratio's, and the significance levels. The resulting model clearly describes the experimentally obtained Sr-90 decontamination efficiency data well. This fit is evidenced by the residuals square and the fact that all terms are important at the 95% confidence level with the exception of the primary sodium term which is retained for the previously discussed reason.

As in the interpretation of the Phase III filtration work, a strategy was developed to find the optimum Sr-90 DF response for the five variable parameter space examined. The method implemented for this evaluation consisted of several steps. The first was to plot the predicted decontamination as a function of the measured decontamination. This plot is shown in Figure 6.

The data used for the next step in the deconvolution are shown in Table XI. By evaluating the conditions associated with the extremes it can be seen that the experimental conditions which yield the highest Sr-90 DF contained the low level of hydroxide and the high level of calcium. On the other hand, the conditions affiliated with the low filterability extreme are opposite to those of the high extreme. Namely, the level of calcium is low and the level of hydroxide is high for the poor Sr-90 DF experiments. Once the opposing conditions associated with the extremes were identified the next step in the analysis was to hold these two variables constant. The effects of the other three variables were then evaluated.

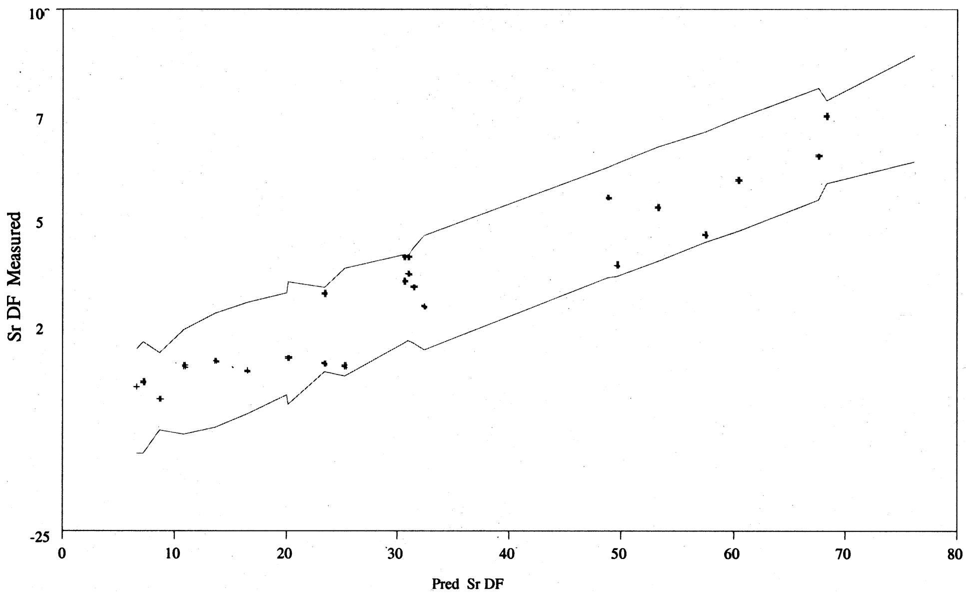

Figure 6. Predicted vs. Measured Sr DF for Phase III.

Based on this evaluation, a unified story emerges for the optimum conditions for Sr-90 DF. This interpretation suggests the conditions presented in Table XI are most beneficial for decontamination of strontium. More specifically the results suggest that the strontium levels should be high and the sodium, calcium, and manganese concentrations should be at their low levels. Hydroxide does not enter into the model and may be any value.

The final response for the Phase III work presented in this manuscript is the plutonium decontamination factors. These values are presented in Table IX. The plutonium concentration was measured using alpha-PHA counting for the initial feeds and the precipitated, sheared and filtered samples. The plutonium value used to calculate the decontamination factor was for the total of isotopes 238, 239, and 240. The decontamination factor presented is calculated by simply comparing the ratio of this total plutonium activity to the activity in the final sample after pretreatment. For example if 50% of the activity were not present relative to the feed the accompanying DF would be two. This calculation does not take into account issues such as dilution involved in various activities such as compositing or precipitating. The worst case scenario in dilution of the final activity affiliated with addition of the precipitants is about 9%.

The Pu decontamination results were used to perform a statistical analysis. The resulting model relating this DF of the precipitated slurry to the five precipitation parameters is provided in Table XI. The values shown in this table are the model estimates (coefficients) of the linear response model, the standard errors of the estimates, the statistical t ratio’s, and the significance levels.

As previously used to interpret the Phase III strontium DF and filterability data, a plot of the predicted decontamination as a function of the measured decontamination was constructed for plutonium. This plot is shown in Figure 7. The data used for this analysis of plutonium decontamination are shown in Table IX. By evaluating the conditions associated with the extremes it can be seen that the experimental conditions which yield the highest DF contained the low level of sodium and the high level of manganese. On the other hand, the conditions affiliated with the low filterability extreme are opposite to those of the high extreme. Namely, the level of manganese is low and the level of sodium is high for the poor Pu DF extreme. Once the opposing conditions associated with the extremes were identified these two variables were held constant and the effects of the other three variables were evaluated.

Based on this evaluation, the optimum conditions for Pu DF emerge. This interpretation suggests the conditions presented in table XI are most beneficial for decontamination of plutonium. More specifically the results suggest that the hydroxide and sodium levels should be low and the strontium, calcium, and manganese concentrations should be at their high levels.

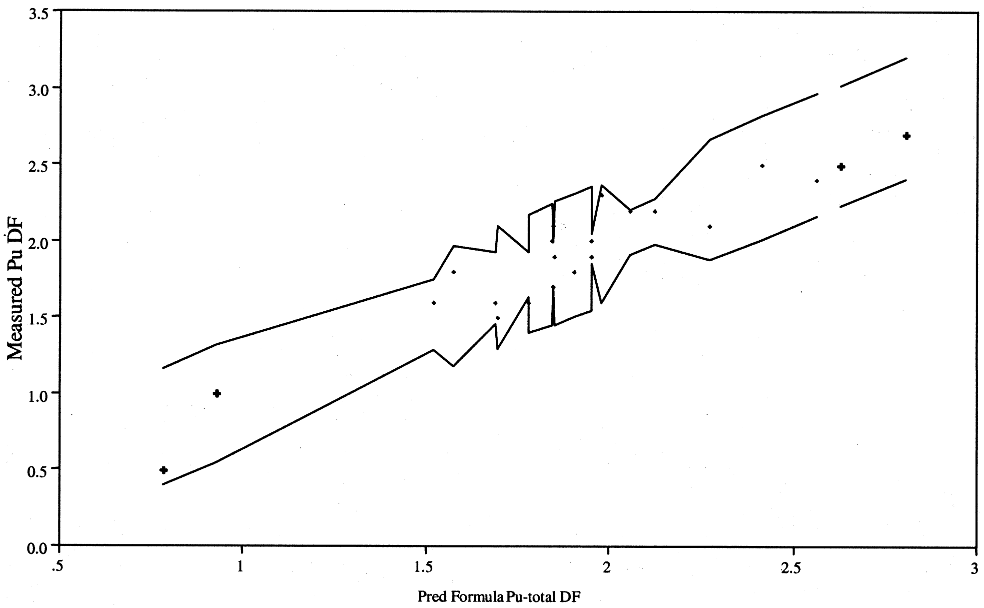

Figure 7. Predicted vs. measured Pu DF for Phase III.

CONCLUSIONS

Three sets of statistically designed experiments have been performed to evaluate the filterability and decontamination efficiency for a diverse range of precipitant and waste solution characteristics. These tests were performed on non-radioactive simulants, radioactive spiked simulants, and actual waste tank supernate from Hanford.

The tests performed during Phase I showed sodium level was important. The effect was a reduction in filterability at higher sodium levels. These tests also displayed a detrimental effect on filterability from the concentration of ferric nitrate added during the precipitation. In order to obtain acceptable filter performance, the amount of ferric nitrate added would be insufficient to remove the required amount of actinide ion for further processing. Overall, the outcome of Phase I suggested further examination of the co-precipitation process would be necessary in order to develop a process of practical use.

The results during Phase II indicated that one of the organic complexants present in the waste supernate is also detrimental to the filterability of the Sr/TRU precipitate. This effect is potentially related to the large concentration of glycolate in the slurry. At sufficient concentrations peptization is a potential process responsible for the poor filterability characteristics of the slurry. Overall, the process and chemical variables are better understood following these series of tests. Alternative precipitating agents such as other transition metals or oxidants have been examined to replace the ferric nitrate co-precipitation of the actinide ions.

An improved precipitation process was developed that implements a strontium isotopic dilution, a sodium permanganate oxidation, and under certain conditions addition of calcium. A series of statistically designed tests examined the relationship between the responses of interest and five precipitation parameters. The resulting computer models indicate the conditions that will provide sufficient DF for strontium and plutonium. The filterability response improved and was also modeled.

Future work will focus on evaluating the effect of this new precipitation scheme on decontamination efficiency of americium. The results for filterability and all radionuclide decontamination processes will then be unified into a model that describes the overall process. Tests will also be performed to evaluate the robustness of the process with regard to precipitation temperature, reagent addition timings and other process variations. These future studies are currently underway and will be reported shortly.

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