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FLOWSHEET DEVELOPMENT FOR THE NEW NEPTUNIUM OXALATE PRECIPITATION SYSTEM

INTRODUCTION

The HB-Line facilities now under construction will use a new two-stage semi-continuous precipitation system[1] to provide product versatility and to maintain consistent control over product characteristics. A procedure has been demonstrated that produces neptunium (IV) oxalate particles that filter well and readily calcine to the oxide. The laboratory precipitations were small scale using a 1/100th scale model of the new HB-Line neptunium (IV) oxalate precipitation system. This memorandum summarizes laboratory development work and provides flowsheet guidelines for neptunium (IV) oxalate precipitation in the new HB-Line.

SUMMARY

Results of the laboratory scale two-stage precipitation work show that neptunium (IV) oxalate and oxide particle size increase with higher precipitation temperatures. For a given solubility, particle size decreased as the absolute concentrations of oxalic and nitric acid increased. Large particles could be produced from either cationic or anionic precipitation conditions. Increasing residence time in the first stage precipitator did not significantly increase particle size. Based on these small scale tests and present product requirements, the following flowsheet guidelines are provided to assist in start-up of the new HB-Line.

FLOWSHEET GUIDELINES

The neptunium (IV) oxalate precipitations used a two-stage precipitation system. The precipitation experiments were designed to investigate the powder characteristics of neptunium (IV) oxalate precipitates over a wide range of process variables.

The flowsheet suggestions outlined in Table 1 are derived from the statistical analysis of the results of these precipitation experiments. Table 1 shows an "optimum" flowsheet and two alternative flowsheets. These are described below.

"Optimum" Flowsheet

The "optimum" flowsheet is a set of precipitation conditions which:

- Maximizes neptunium (IV) oxalate particle size for the two-stage precipitation design.
- Minimizes the volume percent of "fines".
- Minimizes total waste volumes.
- Maintains filtrate losses below 10 mg/l.
- Meets design batch sizes of 1.0 kg neptunium
- Operates the two-stage precipitation system in a batch mode.

The advantages of the "optimum" flowsheet are maximum neptunium (IV) oxalate particle size and minimum volume percent of "fines." These oxalate characteristics contribute to good filtration. The "optimum" flowsheet minimizes waste volumes and maintains filtrate losses below 10 mg/l, thus reducing the amount of recycle material.

In the "optimum" flowsheet, filtrate losses are minimized in two ways. Since the second stage precipitator is maintained at high temperature during precipitation, the slurry spends a longer time at a higher temperature where the reduction of neptunium (V) to neptunium (IV) is rapid and complete.[7] The presence of neptunum (V) results in higher filtrate losses. Also, in the "optimum" flowsheet, the filtration is performed at ambient temperatures where the equilibrium solubility is less than 10 mg/l.

The signifcant feature of the "optimum" flowsheet is that filtrate losses as low as 10 mg/l can be achieved by operating the two-stage precipitation system in a batch mode.

The "optimum" flowsheet is determined using the statistically significant factor effects in Tables 6 through 8.

Alternate Flowsheet 1

The "Alternate Flowsheet 1" in Table 1, is the same as the "optimum" flowsheet except the filtration is performed at 60°C instead of ambient. Filtration at 60°C will result in neptunium losses to the filtrate of approximately 50 to 100 mg/l (approximately 1 to 2 % losses per run). This flowsheet is a semi-continuous version of the "optimum" flowsheet.

Advantages associated with "Alternate Flowsheet 1" are increased throughput from semi-continuous operation and reduced cycle time by elimination of a cooling cycle. The main disadvantage of this flowsheet, compared with the "optimum" flowsheet, is the relatively higher neptunium losses to the filtrate.

Alternate Flowsheet 2

The "Alternate Flowsheet 2" in Table 1, maintains the second stage precipitator at ambient temperature with continuous filtration during the precipitation run. Nitric acid concentrations, in the neptunium feed, of approximately 4.0 M are required to achieve a rapid and complete[7] reduction of neptunium (V) to neptunium (IV). This flowsheet takes advantage of the lower solubility of neptunium (IV) oxalate at ambient temperatures.

Potential disadvantages of "Alternate Flowsheet 2" are decreased particle sizes of oxalate and oxides of approximately 30 to 40 % and 10 to 15% respectively. The decreased particle sizes are due to increased nitric acid concentration in the neptunium feed and lower temperature in the second stage precipitator. The decreased particle size is based on the statistically significant factor effects in Tables 6 through 8.

DISCUSSION

EXPERIMENTAL METHODS

Solubility Tests

Pure solutions of neptunium (IV) in dilute nitric acid required for solubility and precipitation studies were prepared by dissolving neptunium oxide obtained from HB-Line and purifying by anion exchange.

The equilibrium solubility of neptunium oxalate in nitric/oxalic acid solutions was determined at room temperature, 45°C, and 60°C. In this procedure, neptunium oxalate was precipitated from solutions of various concentrations of oxalic and nitric acids. The nitric/oxalic acid solutions represented a wide range of free oxalate ion concentration. After equilibration, the solutions were analyzed to determine the solubility of neptunium oxalate. Neptunium analysis were performed by standard alpha counting techniques.

Precipitation Tests

All precipitations were performed using a two stage semi-continuous precipitation system[1] (see Figure 1). A series of precipitation experiments were used to identify the significant process variables affecting precipitate characteristics. Response variables in these experiments were the neptunium oxalate and oxide particle size distributions, plating in the precipitators, and extent of precipitation in the first stage precipitator. The major process variables of interest were:

Process Variable	**Range**
• Neptunium feed concentration to the first stage precipitator.	10 - 20 gm/1
• Nitric acid concentration in the neptunium feed.	1 - 3.5M

Oxalic acid concentration to the first stage precipitator.	0.45 - 0.9M
Temperature in the first stage precipitator.	2 - 10 min
Temperature in the second stage precipitator.	25 - 60°C
Oxalic/nitric ratio (i.e. R_s value)	oxalic - oxalic lean rich

Experimental flow rates for the two stage semi-continuous precipitation system were determined (see Appendix 1) as functions of the process variables. A two-level factorial screening design[3] was used to set up process parameters for the precipitation experiments.

Neptunium Oxalate Flowsheet Development

General Background

Phase II of the New HB-Line Project is the new facility for the production of neptunium oxide via oxalate precipitation/calcination. Characteristics of the oxide depend on the precursor neptunium oxalate. Primary objectives of the new two-stage semi-continuous precipitation system were to provide product versatility and to maintain consistent control over process parameters.

Different solution conditions during precipitation influence particle size distributions and particle morphologies. The two-stage semi-continuous precipitation system (see Figure 1) was designed to operate at essentially constant solubility conditions. Constant solubility maintains consistent control over solution conditions (i.e. constant concentration profiles).

The neptunium (IV) oxalate development work identified process variables which significantly affect product characteristics using the two-stage semi-continuous precipitation system.

Equilibrium Solubility Measurements

Equilibrium solubility data are shown in Figure 2. Neptunium (IV) oxalate was precipitated from solutions of various concentrations of oxalic and nitric acid. The data show that neptunium (IV) oxalate solubility is a function of the free oxalate ion concentration. Equilibria between neptunium (IV) oxalate complexes account for the varying solubility. Four oxalate complexes have been reported.[5,6] Minimum solubility resulted when the formation of the highly insoluble di-oxalate complex was favored. Increased solubility resulted from the formation of cationic or anionic complexes as the free oxalate ion was varied from optimum values.

The following complex equilibria have been used to develop a mathematical model of the equilibrium solubility of neptunium oxalate as a function of free oxalate ion concentration.

$$Np(C_2O_4)_2 \cdot 6H_2O \text{ (solid)} \rightleftharpoons Np(C_2O_4)_2^0 \text{ (soln)} \quad (1)$$

$$Np(C_2O_4)_2^0 + 2H^+ \rightleftharpoons Np(C_2O_4)^{+2} + H_2C_2O_4 \quad (2)$$

$$Np(C_2O_4)_2^0 + H_2C_2O_4 \rightleftharpoons Np(C_2O_4)_3^{-2} + 2H^+ \quad (3)$$

The neptunium (IV) oxalate solubility can be expressed (i.e., moles/liter) as;

$$[Np^{+4}] \text{ total} = a_0 + a_1/R_s + a_2R_s \quad (4)$$

where R_s is proportional to the free oxalate ion concentration and a_0, a_1, and a_2 are least square coefficients based on the solubility model. Table 2 summarizes the experimentally determined coefficients at 22, 45, and 60°C.

Precipitation Procedures

Neptunium (IV) oxalate was precipitated from neptunium (IV) nitrate solutions containing about 10 to 25 grams of neptunium per liter in 1.0 to 3.5 M nitric acid. The neptunium feed solution contained 0.05 M hydrazine to stabilize the neptunium (IV) valence state. Ascorbic acid was added before precipitation to reduce any neptunium (V) to neptunium (IV). The prescence of neptunium (V) results in higher losses to the filtrate. The neptunium oxalate precipitations were on a 2.0 to 5.0 gram scale.

Precipitation Screening Designs

The main use of a screening design is to efficiently identify the few really important variables among a larger number of possible variables with a minimum number of experiments. A detailed explanation and analysis[3,4] of the two-level factorial experimental designs may be found in Appendix 2. Table 3 shows the experimental screening design[3] used for the neptunium (IV) oxalate precipitations.

Precipitation Response Variables

The particle size distributions of neptunium oxalate and neptunium oxide were used to evaluate the quality of precipitates formed under a given set of conditions. Measures used to evaluate quality were: mode, median, percent of particles less than 5μm, and percent of particles greater than 20μm. Particle size distributions were determined by Coulter Counter analysis.

The mode of the particle size distribution was used as a measure of precipitate quality because it is not influenced by extreme observations. The mode is simply the size that occurs most frequently. The median is the mid-point of the particle size distribution and is somehwat sensitive to extreme values. The mean is very sensitive to extreme values. The percentage of particles less than 5.0μm was used to evaluate the formation of fines. This measure may be useful regarding filtration characteristics of the oxalate.

The extent of plating in the precipitators was simply noted as none, light or heavy. This was a qualitative observation.

Vessel Agitation

A series of agitation[8] tests were performed on the 1/100th scale model precipitation system. These tests involved observation of $NaOH/HNO_3$ neutralization reactions using colored indicators. The rate of color change in the precipitation system is limited by mixing kinetics and not neutralization kinetics. The neutralization reactions are very fast. Bulk mixing times of less than 5 seconds were typical in the first and second stage precipitation vessels.

Three bladed marine[8] type impellers were used in both vessels. Tip speeds of the agitators in the first and second stage precipitators were the same as tip speeds used in previous neptunium (IV) oxalate work.[7] One inch and three inch diameter marine type impellors were used in the first and second stage precipitators respectively.

PRECIPITATION RESULTS

Effect of Temperature

Table 4 shows data obtained in the neptunium (IV) oxalate precipitation experiments. The particle size is strongly influenced by the temperature during precipitation. Larger oxalate particles were obtained when both precipitators were at the higher temperature. The higher precipitation temperatures provided better particle growth and reduced amount of fines (i.e., the percent of material less than 5.0µm). This effect is shown in Table 7. Particle sizes were routinely between 25µm and 40µm.

When both precipitators were at room temperature, the oxalate particle sizes were typically less than 16µm.

When the precipitators were operated at different temperatures the results varied. When the first stage precipitator was at 60°C and the second stage at ambient, the oxalate particle sizes varied between 15 and 25µm. When the first stage precipitator was at ambient and the second stage at 60°C the oxalate particle sizes varied between 20 and 30µm.

The rate of reduction of neptunium (V) to neptunium (IV) increases at higher temperatures.[7]

Effect of Nitric Acid Concentration

Neptunium (IV) oxalate particle size decreases with high nitric acid concentration in the neptunium (IV) feed stream. This effect is statistically significant as shown in Table 6. Nitric acid concentration ranged from 1.0 to 3.5 M in these tests.

The lower limit of 2.0 M nitric acid in the neptunium feed given in the recommended flowsheet is to prevent precipitation of ascorbic acid degradation product in the feed during a precipitation run. The rate of reduction of neptunium (V) increases with increasing nitric acid concentration.[7]

Effect of Neptunium Concentration

Precipitation of neptunium (IV) oxalate from feed solutions containing 10 to 25 g/l neptunium produced low filtrate losses and slurries that filtered well. The overall effect of neptunium concentration on particle size is not statistically significant.

Effect of Oxalic Acid Concentration

Oxalic acid concentration in the feed streams was varied between 0.45 and 0.9 M. Plating observed in the first stage precipitator decreased with higher concentrations of oxalic acid. This effect was statistically significant as shown in Table 8.

Effect of Oxalic/Nitric Ratio

Large particles can be produced from precipitation conditions on both sides of the solubility minimum (i.e., cationic vs anionic.) However, cationic precipitation conditions, in general, produce significantly higher throughputs and lower total volumes for a given design. Anionic precipitation conditions significantly reduced the rate of precipitation in the first stage precipitator by forming strong oxalate complexes with neptunium (see Table 8).

In is expected that the morphology of precipitates produced under these different conditions will be different but morphology information will not be available for these studies until a contained scanning electron microscope (SEM) is available.

Effect of Residence Time

The effect of residence time in the first stage precipitator on particle size was not statistically significant in these studies. The range of first stage residence times was 2.0 to 7.0 minutes.

Ascorbic Acid Degradation

Excessive degradation of ascorbic acid was observed during the neptunium valence adjustment from neptunium (V) to neptunium (IV) at high temperatures. The ascorbic acid degradation product precipitated in the feed tanks. However, the sludge which formed was soluble in 3.0 to 4.0 M nitric acid.

It is recommended that valence adjustment of neptunium (V) to neptunium (IV) be performed just before precipitation at room temperature with the nitric acid concentration at least 2.0 M. This solution will be stable to precipitation of ascorbic acid degradation product for at least 4 hours.

CONCLUSIONS

The particle size of the neptunium (IV) oxalate precipitates are very sensitive to precipitation temperatures and concentrations of oxalic and nitric acids during precipitation. In general, larger particles were produced when precipitation temperatures in both vessels were at 60°C. The nitric acid concentration in the neptunium (IV) nitrate feed solution must be at least 2.0 M to prevent precipitation of ascorbic acid degradation product. The effect of residence time on particle size was not statistically significant in these studies.

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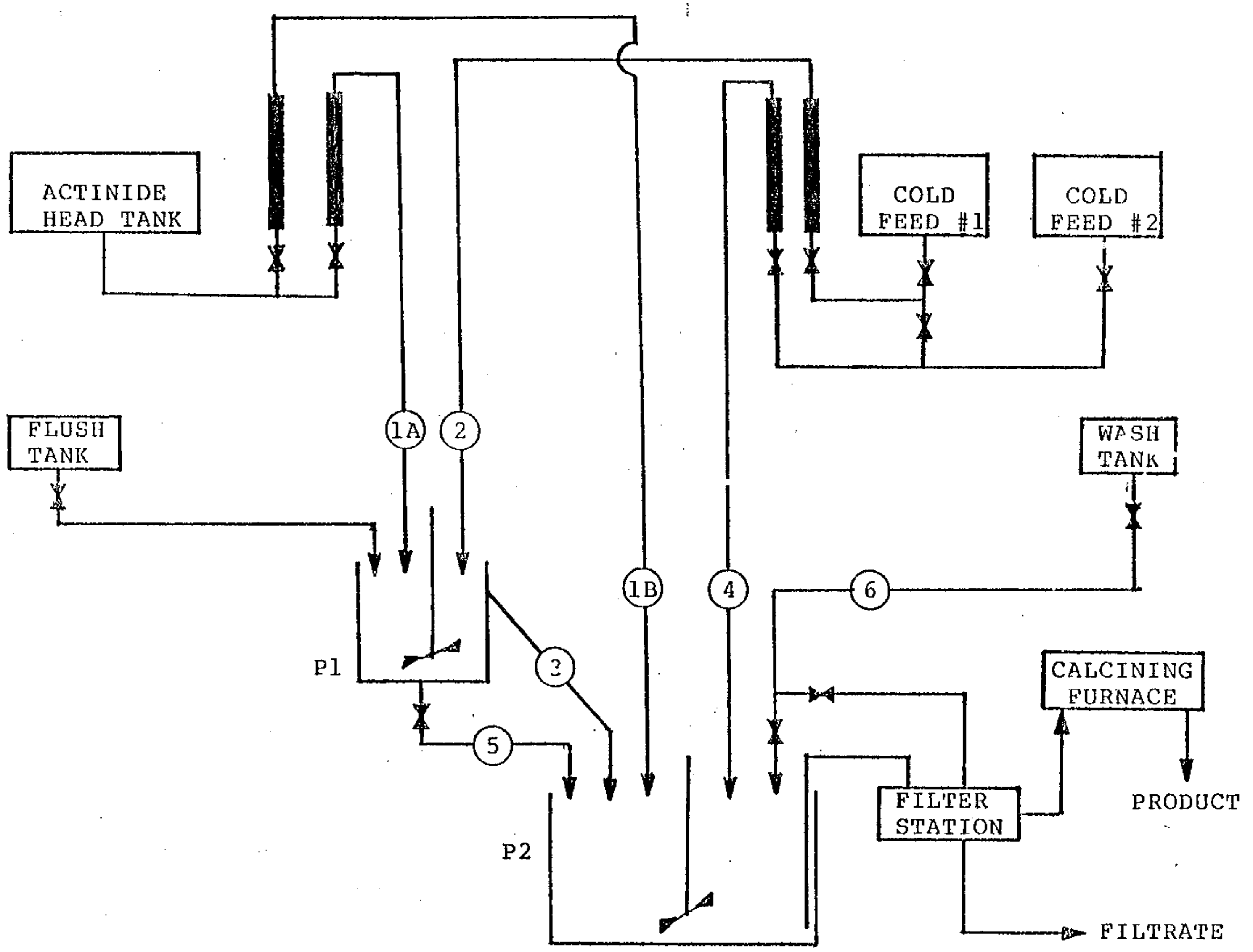

FIGURE 1. TWO STAGE PRECIPITATION SYSTEM

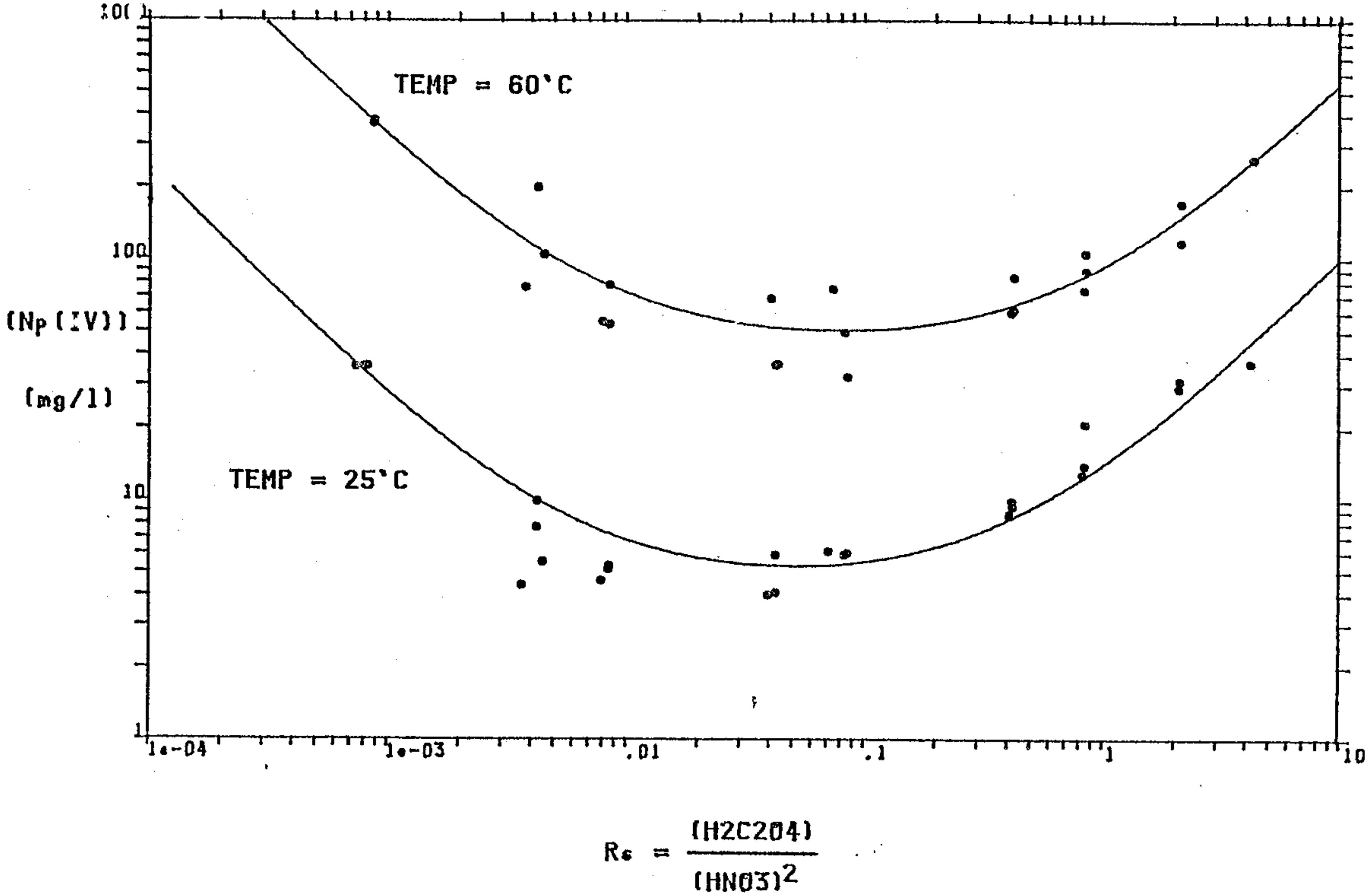

FIGURE 2. NEPTUNIUM (IV) SOLUBILITY

TABLE 1

Neptunium (IV) Oxalate Flowsheets

Process Variable	Optimum	Alternate #1	Alternate #2
Temperature During Precipitation			
First Stage	50 - 60°C	Same	Same
Second Stage	50 - 60°C	Same	Ambient
Filtration Temperature	Ambient	50 - 60°C	Ambient
Nitric Acid In Actinide Feed	2.0 - 3.0 M	Same	>4.0 M
Neptunium Feed	0.05 M Hydrazine 0.03 M Ascorbic Acid	Same	Same
Oxalic Acid	0.45 - 0.9 M	Same	Same
Oxalic to Nitric Ratio	<0.005	Same	Same

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* The lower limit of 50°C for precipitation temperature is to assure complete and rapid[7] reduction of neptunium (V) to neptunium (IV).

TABLE 2

Least Squares Coefficients for Solubility Data

Coeff.	Temperature (°C) 22	45	60
a_0	1.6×10^{-5}	5.6×10^{-5}	1.7×10^{-4}
a_1	1.3×10^{-7}	1.4×10^{-6}	1.5×10^{-6}
a_2	3.3×10^{-5}	2.6×10^{-4}	2.0×10^{-4}

TABLE 3

Precipitation Screening Design

Run #	Temp P1 (°C)	$[Np]_f$ (g/l)	$[HNO_3]_f$ (M)	Res. Time (Min)	R_s	Temp P2 (°C)	$[H_2C_2O_4]_f$ (M)
R-1	22	10	3.5	2.0	anion	60	0.9
R-2	22	20	3.5	7.0	anion	22	0.45
R-3	60	20	3.5	2.0	cation	22	0.9
R-4	60	10	3.5	2.0	anion	22	0.45
R-5	60	20	1.0	7.0	cation	22	0.45
R-6	22	10	1.0	2.0	cation	22	0.45
R-7	60	10	1.0	2.0	cation	60	0.9
R-8	22	10	3.5	7.0	cation	22	0.9
R-9	60	20	1.0	2.0	anion	60	0.45
R-10	22	10	1.0	7.0	anion	60	0.45
R-11	22	20	1.0	2.0	anion	22	0.9
R-12	22	20	1.0	7.0	cation	60	0.9
R-13	60	10	3.5	7.0	cation	60	0.45
R-14	60	20	3.5	7.0	anion	60	0.9
R-15	22	20	3.5	2.0	cation	60	0.45
R-16	60	10	1.0	7.0	anion	22	0.9

TABLE 4

Median and Mode for Neptunium Oxalates and Oxides

Run #	Oxalate Mode (μm)	Oxide Mode (μm)	Oxalate Median (μm)	Oxide Median (μm)
R-1	16.8	7.8	15.1	8.5
R-2	16.0	10.1	14.4	10.2
R-3	20.2	8.7	18.4	9.3
R-4	16.0	8.0	16.3	8.6
R-5	32.0	10.9	29.8	11.2
R-6	20.2	20.2	15.7	13.0
R-7	40.3	10.1	38.6	12.7
R-8	14.9	8.0	15.6	9.0
R-9	29.8	16.0	25.3	13.5
R-10	32.0	8.0	30.1	9.2
R-11	16.0	9.4	15.8	8.9
R-12	20.2	12.7	20.8	11.8
R-13	25.4	12.7	28.1	12.7
R-14	20.2	8.0	20.8	11.9
R-15	16.0	6.3	16.8	7.9
R-16	12.7	6.3	13.7	8.1

TABLE 5

Particle Size Distribution Data for Neptunium Oxalate and Oxide

Run #	Oxalate % <5 µm	Oxalate % >30 µm	Oxide % <5 µm	Oxide % >20 µm
R-1	1.8	3.3	13.0	5.0
R-2	6.7	0.0	10.0	8.7
R-3	3.7	14.7	13.3	8.0
R-4	4.2	1.0	18.0	2.2
R-5	0.5	44.3	14.0	12.7
R-6	5.7	4.0	17.0	27.0
R-7	1.3	61.3	10.7	28.7
R-8	2.2	3.0	11.0	8.0
R-9	2.3	29.7	11.0	20.7
R-10	2.7	46.7	12.3	12.0
R-11	1.7	3.0	12.0	1.7
R-12	1.7	12.0	11.0	12.7
R-13	2.5	36.0	6.7	17.7
R-14	1.2	27.7	14.3	4.3
R-15	1.7	12.7	16.0	2.8
R-16	3.3	4.3	16.3	5.7

TABLE 6

Analysis of the Mode and Median of the Particle Size Distribution

	Temp P1 (°C)	$[Np]_f$ (g/l)	$[HNO_3]_f$ (M)	Res. Time (Min)	R_s	Temp P2 (°C)	$[H_2C_2O_4]_f$ (M)
Oxalate Mode	5.5	-0.3	-6.5**	0.4	-3.1	8.0**	-3.4
	MFE = 6.2	**Average Mode Size = 22.5μm**					
Oxalate Median	5.9**	-1.4	-5.5**	1.4	-4.1	7.0**	-2.2
	MFE = 5.3	**Average Median Size = 20.9μm**					
Oxide Mode	-0.15	0.34	-2.6	-0.9	-2.0	-0.17	-2.4
	MFE = 3.6	**Average Mode Size = 10.3μm**					
Oxide Median	1.2	0.4	-1.3	0.2	-1.1	1.3	-0.8
	MFE = 1.9	**Average Median Size = 10.4μm**					

Note: MFE is the minimum factor effect at 90% confidence limits for 8 degrees of freedom

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** Statistically signifcant factor effects are denoted by the double asterisk.

TABLE 7

Analysis of the Variables Affecting the Formation of Fines

	Temp P1 (°C)	$[Np]_f$ (g/l)	$[HNO_3]_f$ (M)	Res. Time (Min)	R_s	Temp P2 (°C)	$[H_2C_2O_4]_f$ (M)
Oxalate							
% <5.0	-0.7	-0.5	0.6	-0.2	0.6	-1.6**	-1.2
	MFE = 1.56	**Average % <5 m = 2.7%**					
% > 30	16.7**	-1.9	-13.3	5.6	-9.0	19.3**	-5.7
	MFE = 13.6	**Average % > 30 m = 19.0%**					
Oxide							
% < 5.0	0.3	-0.4	-0.3	-1.99	0.9	-2.1	-0.4
	MFE = 3.2	**Average % < 5 m = 12.9%**					
% > 20	2.8	-4.3	-8.1**	-1.8	-7.2**	3.7	-3.7
	MFE = 6.6	**Average % > 20 m = 11.1%**					

Note: MFE is the minimum factor effect at 90% confidence limits for 8 degrees of freedom

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** Statistically signifcant factor effects are denoted by the double asterisk.

TABLE 8

Significant Variables Affecting Plating in Pl and Reaction Kinetics

	Temp Pl (°C)	$[Np]_f$ (g/l)	$[HNO_3]_f$ (M)	Res. Time (Min)	R_s	Temp P2 (°C)	$[H_2C_2O_4]_f$ (M)
Plating in Pl	0.0	0.3	0.0	0.0	-0.3	-	-0.8**

MFE = 0.4   Average response = 0.4

	Temp Pl (°C)	$[Np]_f$ (g/l)	$[HNO_3]_f$ (M)	Res. Time (Min)	R_s	Temp P2 (°C)	$[H_2C_2O_4]_f$ (M)
Reaction Kinetics	-0.7**	1.5**	0.8	-1.4	-1.6**	0.1	-0.4

MFE = 1.48   Average g/l/min loss = 1.3 g/l/min

Note: MFE is the minimum factor effect at 90% confidence limits for 8 degrees of freedom

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** Statistically signifcant factor effects are denoted by the double asterisk.

APPENDIX 1

DETERMINING FLOW RATIOS FOR THE SEMI-CONTINUOUS PRECIPITATION SYSTEM

Flow Ratio for the First Stage Precipitator

The stream designations for the two-stage semi-continuous precipitation are given in Figure 1. The flow ratio for the first stage precipitator is the determined as the flow rate of the oxalic acid stream to the flow rate of the actinide stream. Thus the streams can be adjusted for any residence time or throughput rate. The flow ratio can be determined by substituting into the following design equations:

$$\frac{V_2}{V_1} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

where

$$A = [H_2C_2O_4]_2 + 2[Np]_3 - 16R_{s1}[Np]_3{}^2$$

$$B = [H_2C_2O_4]_2 + 4[Np]_3 - 2[Np]_1$$

$$C = -\left(2([Np]_1-[Np]_3) + R_{s1}([HNO_3]_1 + 4([Np]_1 - [Np]_3)^2\right)$$

Flow Ratio for Adjustment Stream

The flow rate for the second stage adjustment stream is given as the ratio of the flow rate of the solubility adjustment stream to the flow rate of the actinide. Absolute flow rates may be determined by setting vessel capacity, residence time, or throughput rate. The flow ratio for the second stage adjustment stream can be determined by substituting in the following design equations:

$$\frac{V_4}{V_3} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

where

where

$$A = \left([H_2C_2O_4]_4 + 2[Np]_4\right) - 16R_{s2}[Np]_4{}^2$$

$$B = \left([H_2C_2O_4]_3 - 2[Np]_3 + 4[Np]_4 + [H_2C_2O_4]_4\right)$$

$$C = \left([H_2C_2O_4]_3 - 2[Np]_3 + 2[NP]_4\right)$$
$$- R_{s2}\left([HNO_3]_3 + 4[NP]_3 - 4[NP]_4\right)^2$$

and

$$V_3 = V_1\left(1 + \frac{V_2}{V_1}\right)$$

APPENDIX 1 (cont'd)

Determining Flow Ratios for The Semi-continuous Precipitation System

List of Variables

$[Np]_1$ ... Neptunium feed concentration in stream #1

$[HNO_3]_1$ ... Nitric acid concentration in the neptunium feed

$[H_2C_2O_4]_2$ ... Oxalic acid feed concentration to the first stage precipitator

$[Np]_3$ ... Unprecipitated neptunium concentration in the overflow line

$[H_2C_2O_4]_3$ ... Oxalic acid concentration in the overflow stream

$[HNO_3]_3$ ... Nitric acid concentration in the overflow stream

R_s ... Ratio of oxalic acid concentration to the concentration of nitric acid squared. This is the free oxalate ion concentration.

$[NP]_4$ ... Unprecipitated neptunium concentration in the second stage precipitator. This may be a close to the equilibrium solubility value.

$[H_2C_2O_4]_4$ ... Oxalic acid concentration to the second stage precipitator. This is the adjustment stream.

APPENDIX 2

TWO-LEVEL FACTORIAL DESIGNS

Experimental Designs

Two-level factorial experimental designs[2] permit estimation of the effects of several factors simultaneously. This is accomplished by making experimental runs at all combinations of "p" factors, with "2" levels per factor. These two-level factorial experiments are easy to design and analyze, are readily adaptable to both continuous and discrete factors, and provide adequate prediction models for factor relationships that have no strong curvature (maximum or minimum) in the experimental region. For continuous variables, the higher value is coded "+" and the lower value coded "-". The coding for the sixteen run fractional factorial screening design used in the neptunium (IV) oxalate precipitation experiments is given in Table 2.

Use of these designs permits estimation of factor effects more precisely than a one-at-a time testing because of the hidden replication included. Systematic error is kept to a minimum by replication of design points and randomization of the trails before running.

If a computed factor effect is larger in absolute value than the "minimum significant factor effect," the experimenter can safely conclude that the true effect is nonzero.

The computed factor effects represent the difference between response at the high and low levels of the factor. If the factor is divided by the difference of the high and low levels of the factors, the result will be the change in the response for a unit change in the factor.

APPENDIX 2 (cont'd)

TWO-LEVEL FACTORIAL DESIGNS

The model underlying the two-level factorial is of the form

$$y = a_0 + a_1x_1 + a_2x_2 + \ldots a_px_p$$
$$+ a_{12}x_1x_2 + a_{13}x_1x_3 + \ldots + a_{p-1,p}x_{p-}x_p$$
$$+ \text{higher order interactions}$$

where

y = predicted response for: particle size distributions, plating in the precipitators, and extent of precipitation in the first stage precipitator.

x_j = (factor level - (Hi + Lo)/2)/(Hi - Lo)/2

a_j = (factor effect for x_j)/2

a_{ij} = (interaction effect for x_i, x_j)/2

The fractional factorial screening design used in the neptunium (IV) oxalate precipitation experiments can be viewed as an estimate of the constant and linear terms of this general polynomial model of the precipitation system. The analysis of this type of screening design is simply multivariable linear regression.

Interpretation of the Screening Design Analysis

The computed factor effects are the coefficients of a linear multivariable model. If the sign of the computed factor effect is negative for a given response variable the response decreases as the variable increases. In other words the response and the variable are inversely related. If the computed factor effect is positive the response and the variable are directly related.

The magnitude of the computed factor effect compared with the "minimum factor effect" determines the level of significance of the variable at a certain level of confidence. Thus the analysis produces a relative ordering of significance among the variables. The results from screening designs are often used to design further experiments.