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AN IMPROVED PLUTONIUM TRIFLUORIDE PRECIPITATION FLOWSHEET

INTRODUCTION

Actinide Technology Division is currently engaged in a precipitation development program in support of the FB-Line upgrade projects. The focus of our continuing efforts is to provide technical recommendations to assist in the startup and optimum operation of these facilities. A key feature of the precipitation development program has been a two-stage precipitation study which has provided the fundamental understanding needed for detailed control of the plutonium trifluoride precipitation process. The purpose of this memorandum is to describe and discuss the results of these precipitation studies and recommend new flowsheet conditions for improved plutonium trifluoride precipitation.

SUMMARY

The plutonium trifluoride two-stage precipitation study has been completed. A series of precipitation experiments was used to identify the significant process variables affecting precipitation performance. A mathematical model of the precipitation process was developed which is based on the formation of plutonium fluoride complexes. The precipitation model relates all process variables, in a single equation, to a single parameter which can be used to control the performance of the plutonium trifluoride precipiation process. Recommendations have been made which will optimize the FB-Line plutonium trifluoride precipitation process.

RECOMMENDATIONS

The recommended conditions for optimum plutonium trifluoride precipitation, using a two-stage precipitation system, are summarized below.

$[Pu]_{feed} = 25\text{-}35\ g/L\ ,\ [H^+] = 2\text{-}3\ M$

1. The "as mixed" total fluoride in the first stage precipitator should be in the range of 0.10 to 0.15 M to minimize "plating" in the first stage precipitator and to maximize particle size in the second stage precipitator.
2. The "as mixed" total fluoride in the second stage precipitator should be in the range of 0.7 to 1.0 M to minimize losses from precipitation and complexation.
3. The residence time in the second stage precipitator should be at 10 to 15 minutes to insure maximum precipitation and minimum filtrate losses.

These recommended conditions can best be accomplished in the FB-Line by decreasing the hydrofluoric acid flow rate to the first stage precipitator from the current 185 ml/minute to 25 ml/minute. The hydrofluoric acid flow rate to the second stage precipitator should then be increased from 185 ml/minute to 345 ml/minute to meet condition number 2. Successful implementation of these recommendations will require concerted efforts between SRL and SRP. A detailed description and discussion of the proposed plant test will be tranmitted to SRP to augment and assist in this effort.

DISCUSSION

BACKGROUND

Different solution conditions during precipitation influence particle characteristics of the precipitated material[1-4]. These particle characteristics determine the performance of the precipitation process. For example, in most precipitation processes, conditions of high supersaturation promote crystal nucleation whereas conditions of low supersaturation promote crystal growth. Precipitation conditions which predominately favor nucleation can result in excess "fines" generation which can plug filter frits and increase product filtration times. Precipitation conditions which predominately favor crystal growth can result in "plating" on interior surfaces. Plated material builds up and eventually flakes off resulting in plugged process lines. In addition, plated material increases background radiation exposure to personnel.

Successful precipitation processes ultimately optimize the conditions of supersaturation to provide sufficient nuclei which can be grown to larger particles while avoiding excess nucleation (fines) or growth (plating) conditions. In general, selection of these optimum precipitation conditions depends in part on precipitation equipment, feed streams, precipitation solubility, precipitation kinetic relations, and mixing.

TWO-STAGE PRECIPITATION SYSTEMS

Figure 1 shows a diagram of a two-stage precipitation system. The flow rates to each stage of the two-stage system are determined[5] by specifying input concentrations, residence time, solubility conditions in each precipitator, vessel capacities and product throughput.

An important feature of the two-stage precipitation system is that solution conditions can be held constant during precipitation[5]. This means that consistent control of the solution conditions can be maintained, allowing consistent control over the particle characteristics of the precipitated material.

EXPERIMENTAL METHODS

"As Mixed" Variables

There are a number of independent variables used in this study that are denoted as "as mixed" quantities (subscript "am"). In general, this terminology denotes a quantity before reaction but after dilution. As an example, the "as mixed" plutonium concentration and "as mixed" total fluoride concentration to the first stage precipitator are given by:

$$[Pu]_{am} = [Pu]_1 \dot{v}_1/(\dot{v}_1+\dot{v}_2)$$

and

$$[HF]_{am} = [HF]_2 \dot{v}_2/(\dot{v}_1+\dot{v}_2)$$

where

$[Pu]_1$ = Plutonium nitrate concentration in stream #1.

$[HF]_2$ = Hydrofluoric acid concentration in stream #2.

$\dot{v}_1$ = Volumetric flow rate of stream #1.

$\dot{v}_2$ = Volumetric flow rate of stream #2

Other "as mixed" quantities can be defined in an analogous fashion.

Equilibrium Solubility Determination

The equilibrium solubility of plutonium hydrofluoric/nitric acid solutions was determined at 22° C. Plutonium trifluoride was precipitated from solutions containing a mixture of known hydrofluoric acid and nitric acid concentrations. After equilibration, the solutions were analyzed to determine the concentration of plutonium.

Rapid Nucleation Tests

The rapid nucleation region of plutonium trifluoride in nitric/hydrofluoric acid was determined at 22°C using direct strike methods. Plutonium trifluoride was precipitated from aqueous solutions by rapid addition of hydrofluoric acid to a plutonium nitrate solution of known composition. The rapid nucleation region was determined as the point at which the solution approached instantaneous cloudiness upon rapid addition of hydrofluoric acid.

Precipitation Tests

All precipitations were performed using a small scale two-stage precipitation system (Figure 1). A series of precipitation experiments was used to identify the significant process variables affecting precipitation kinetics, precipitate characteristics, and the extent of "plating" in the first stage precipitator. Response variables in these experiments were plutonium trifluoride particle size distributions in the second stage precipitator, extent of precipitation (conversion) in the first stage precipitator, and the quantity of "plated" material in the first stage precipitator. The major process variables of interest were:

Process Variable	Range
Plutonium concentration in the feed.	27.5 , 7.5 g/L
Nitric acid concentration in the plutonium feed.	2.4 , 6.5 M
Total fluoride to the first stage precipitator.	0.0 - 2.5 M

Table 1 shows the actual experimental design used in these tests.

Precipitation Procedures

Plutonium trifluoride was precipitated from plutonium nitrate solutions containing 27.5 and 7.5 grams of plutonium per liter in 2.4 and 6.5 M total nitric acid, respectively. The plutonium feed solution contained 0.03 M excess ascorbic acid and 0.22 M sulfamic acid to maintain the plutonium in the +3 valence state[6]. The plutonium trifluoride precipitations were on a 6.0 gram scale.

Precipitation Response Variables

The steady-state conversion in the first stage precipitator was monitored by measuring the unprecipitated plutonium in the overflow from the first stage precipitator at steady-state. The slurry was sampled and immediatley filtered through a micropore membrane filter into a known volume of strong nitric acid to quench further precipitation. The solution was then analyzed for total plutonium using standard alpha counting techniques.

The extent of "plating" in the first stage precipitator was monitored by measuring the total amount of plutonium trifluoride plated out during each precipitation test. At the end of each precipitation test, the plated material was completely dissolved in a known aliquot of aluminum nitrate. The resulting solution was then analyzed for total plutonium using standard alpha techniques.

The particle size distributions of plutonium trifluoride were used to evaluate the quality of precipitates formed under a given set of solution conditions. Measures used to evaluate the quality were: mode, median, and volume percent of particles less than 5 microns. Particle size distributions were determined by Coulter Counter analysis.

Plutonium Trifluoride Flowsheet Development

Equilibrium Solubility Tests

Equilibrium solubility data are tabulated in Table 2. Figure 2 shows these data as a function of free fluoride ion concentration at three different hydrogen ion concentrations. Equilibria between plutonium (III) fluoride complexes account for the varying solubility[6]. Minimum solubility occurs when the highly insoluble trifluoride complex is favored. Increased solubility results from the formation of cationic or anionic complexes as the free fluoride ion concentration varies from optimum values.

Rapid Nucleation Tests

Rapid nucleation data are tabulated in Table 3. Figure 2 shows these data as a function of free fluoride ion concentration. The composite plot shows the superposition of the rapid nucleation line and the equilibrium solubility data. Note the region at low free fluoride ion concentrations where the equilibrium solubility line and the rapid nucleation line do not coincide. Spontaneous precipitation does not occur in this region. That is, rapid addition of hydrofluoric acid to a solution of plutonium nitrate will not immediately precipitate. However, precipitation will occur after a suitable digestion period. This region is called the metastable region[3,4].

Precipitation Model

The following consecutive reactions were used to develop a chemical kinetic model[5] of the plutonium trifluoride precipitation process:

$$Pu^{+3} + F^{-} \xrightarrow{k_1} PuF^{+2} \qquad (1)$$

$$PuF^{+2} + F^{-} \xrightarrow{k_2} PuF_2^{+1} \qquad (2)$$

$$PuF_2^{+1} + F^{-} \xrightarrow{k_3} PuF_3^{o} \qquad (3)$$

$$PuF_3^{o} \xrightarrow{k_4} PuF_3 \downarrow \qquad (4)$$

The resulting chemical kinetic model predicts the first stage conversion to be given by:

$$X_s = \frac{k_1' K_a}{[Pu^{+3}]_{am}\left(\frac{[H^+]}{\tau} + k_1' K_a \right)} \left([HF]_{am} - [HF]_{cpx} \right) \qquad (5)$$

where

X_s = Steady-state conversion in the first stage precipitator.

$[Pu^{+3}]_{am}$ = Total plutonium before reaction.

= First stage residence time.

$[HF]_{am}$ = Total fluoride in the first stage before reaction.

$[HF]_{cpx}$ = Total complexed fluoride.

$[H^+]$ = Hydrogen ion concentration.

K_a = Dissociation constant of hydrofluoric acid.

Interpretation of the Precipitation Model[5]

In general, the precipitation model shows the steady-state conversion in the first stage precipitator as a complex function of "as mixed" quantities, the precipitation rate constant, and the first stage residence time. For a given "as mixed" plutonium concentration, the first stage conversion is a strong function of the "as mixed" total fluoride concentration and a "weaker" function of the hydrogen ion concentration and first stage residence time.

The model shows that the steady-state first stage conversion increases directly as the "as mixed" total fluoride concentration increases. However, the first stage conversion decreases as the ratio of hydrogen ion concentration to first stage residence time increases. This latter effect depends on the magnitude of the rate constant. Thus, if the ratio of the hydrogen ion concentration to first stage residence time is small compared to the rate constant, the effect of the hydrogen ion concentration on first stage conversion will be greatly reduced. Consequently, long residence times can be used to directly suppress effects due to hydrogen ion concentration.

PRECIPITATION RESULTS

Data Analysis

Table 4 shows the actual flow rates and "as mixed" concentrations from the precipitation experiments. Table 5 shows the first stage conversion, grams of plated material in the first stage precipitator, and filtrate losses for each precipitation test. Particle size distribution data from the second stage precipitator are given in Table 6.

Figure 3 shows the actual steady-state first stage conversion data as a function of "as mixed" total fluoride. The solid lines through the data points are least square lines generated from the data using the precipitation model at each plutounium concentration and hydrogen ion concentration. Equation 5 provides the basis of a least square model of the form:

$$Y = a_o + a_1 X \pm \sigma \qquad (6)$$

where

Y = Steady-state conversion

X = "As Mixed" total fluoride

σ = Standard deviation in Table 7 and

$$a_0 = \frac{k_1' K_a [HF]_{cpx}}{[Pu^{+3}]_{am}\left(\frac{[H^+]}{\tau} + k_1' K_a \right)} \quad (7)$$

$$a_1 = \frac{k_1' K_a}{[Pu^{+3}]_{am}\left(\frac{[H^+]}{\tau} + k_1' K_a \right)} \quad (8)$$

a_0 and a_1 are least square coefficients determined from the experimental data.

Table 7 summarizes the experimentally determined least square coefficients at total plutonium concentrations of 27.5 and 7.5 grams per liter and total hydrogen ion concentrations of 2.0 and 5.2 M, respectively. Table 7 also shows the correlation coefficient and standard deviation of the least square fit of the precipitation model to the precipitation data at each set of concentrations.

Figures 4 and 5 confirm that particle size distribution parameters in the second stage precipitator are directly related to the first stage conversion and "as mixed" total fluoride. Figure 4 shows the mean and median of the second stage particle size distributions as a function of "as mixed" total fluoride for each plutonium concentration. Figure 5 shows the median of the second stage particle size distributions and the first stage conversion as a function of the "as mixed" total fluoride concentration.

Figure 6 confirms that the extent of "plating" in the first stage precipitator is directly related to the "as mixed" total fluoride concentration in the first stage precipitator. Figure 6 shows the extent of "plating" in the first stage precipitator as a function of the "as mixed" total fluoride concentration for different plutonium and hydrogen ion concentrations.

Precipitation Performance

In general, the overall performance of the plutonium trifluoride precipitation process is determined by the extent of plating in the precipitators, particle characterisitics of the precipitated material, and filtrate losses. An optimum precipitation flowsheet, therefore, minimizes plating and filtrate losses while maximizing particle size distribution parameters in order to achieve good filtration performance.

Figures 7 and 8 show the optimum conditions for precipitation of 27.5 g/L and 7.5 g/L plutonium solutions in 2.0 M and 5.2 M total hydrogen ion concentration, respectively. Figure 7 shows that minimum plating in the first stage precipitator and maximum particle size in the second stage precipitator occur at "as mixed" total fluoride concentrations of 0.1 M or less. Conversion in the first stage precipitator is zero under these conditions. The concentrations shown in Figure 7 represent the normal FB-Line process concentrations. Currently the FB-Line precipitation process is operated at an "as mixed" total fluoride concentration of approximately 0.70 M. Under these conditions, significant plating occurs in the first stage, particle size in the second stage is only 6-7 microns, and conversion in the first stage is nearly 100 percent. This is shown in Figure 7.

Figure 8 shows that minimum plating in the first stae precipitator and maximum particle size in the second stage precipitator occurs at "as mixed" total fluoride concentrations of 0.5 M or less. Conversion in the first stage precipitator can be as high as 20-30 percent under these conditions. The concentrations in this example represent a "slow" precipitation since the rate of precipitation depends on both the concentrations of plutonium and free fluoride ion. The plutonium concentration is low while the high hydrogen ion concentration suppresses free fluoride ion concentration. Consequently, the overall rate of precipitation is decreased.

However, Figure 8 also shows that minimum plating and maximum particle size can be achieved at "as mixed" concentrations of 2.5 M or greater. Conversion in the first stage precipitator is 100 percent under these conditions. This case is the "two-stage" equivalent of a batch reverse strike. The large particle size in the second stage is due to agglomeration of small particles and no plating occurs in the first stage precipitator since the precipitation conditions are predominatley nucleation conditions. A significant disadvantage of this flowsheet is the large filtrate volumes (filtrate losses) which are generated.

"As Mixed" Total Fluoride Concentration

The previous discussion showed that the overall performance of the plutonium trilfluoride process is controlled by the "as mixed" total fluoride ion concentration in the first stage precipitator.

In general, as the "as mixed" total fluoride concentration varies between optimum values, the plating in the first stage precipitator rises very sharply, reaches a maximum and then begins to slowly decrease as the total fluoride concentration increases. Maximum plating is reached at approxmately 0.5 M and 1.0 M total fluoride for total plutonium concentration of 27.5 g/L - 2.0 M total hydrogen ion and 7.5 g/L - 5.2 M total hydrogen ion, respectively. The current FB-Line conditions are 0.6-0.7 M "as mixed" total fluoride. The extent of plating in the FB-Line is very near the maximum under these conditions.

In general, the first stage conversion increases directly with an increase in "as mixed" total fluoride. The "as mixed" total fluoride must be increased beyond the equilibrium solubility into the rapid nucleation region to attain conversion in the first stage preciptator. After 100 percent conversion reached, further increases in the total fluoride have no further effect on conversion. The FB-Line currently operates at nearly 100 percent conversion in the first stage precipitator.

The particle size in the second stage precipitator is a function of "as mixed" total fluoride, plutonium concentration, hydrogen ion concentration, and residence time. These variables are all related through the first stage conversion. Figure 7 shows the second stage particle size for 27.5 g/L plutonium - 2.0 M total hydrogen ion (FB-Line concentrations). As the total fluoride is varied, the particle size initially rises very rapidly and reaches a maximum of approximately 10-12 micron at 0.1 M total fluoride before beginning to decrease to 5-6 micron at 0.6-0.7 M "as mixed" total fluoride concentration (current FB-Line conditions). The particle size of the plutonium trifluoride product in the FB-Line is nominally 6 micron.

Figure 8 shows the particle size for 7.5 g/L plutonium - 5.2 M total hydrogen ion. As the total fluoride is varied, the particle size initially rises very rapidly, however, further addition of fluoride increases the particle size. This latter affect is due to agglomeration of "fines" produced under high fluoride conditions.

"As Mixed" Plutonium Concentration

The overall effect of varying the "as mixed" plutonium feed concentration is illustrated in Figure 9. As the plutonium feed concentration is increased, the first stage conversion decreases. The particle size distribution parameters and plating characteristics will change accordingly. It is expected that plutonium feed concentration will not vary over a large range. The current FB-Line plutonium feed concentration is nominally 25-35 g/L in 2.0-3.0 M total hydrogen ion.

Nitric Acid Concentration

Figure 9 illustrates the effect of varying the total nitric acid concentration in the plutonium feed. As the nitric acid concentration increases the first stage conversion decreases. This effect is due to hydrogen ion suppression of free fluoride ion concentration which in turn decreases the overall rate of precipitation.

Hydrogen ion concentration is maintained through the dissociation of nitric acid. The dissociation constant of nitric acid[9] is 21.5. Thus, nitric acid is not totally dissociated and the hydrogen ion concentration must be calculated using the following quadratic formula:

$$[H^+] = \frac{-K_s + \sqrt{K_s^2 + 4K_s[HNO_3]_t}}{2} \qquad (9)$$

where

K_s = The dissociation constant of nitric acid

$[H^+]$ = Hydrogen ion concentration

$[HNO_3]$ = Total nitric acid concentration

Since the dissociation constant of nitric acid is 21.5, it can be shown that the hydrogen ion concentration remains essentially constant during precipitation. This buffering action results from the following chemical equilibria:

$$Pu(NO_3)_3 \rightleftharpoons Pu^{+3} + 3NO_3^- \qquad (10)$$

$$HF \rightleftharpoons H^+ + F^- \qquad (11)$$

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \qquad (12)$$

$$Pu^{+3} + 3F^- \rightleftharpoons PuF_3 \downarrow \qquad (13)$$

Note that plutonium nitrate is a source of nitrate ion and a sink for free fluoride ion. Hydrofluoric acid is a source of hydrogen ion and free fluoride ion. Nitric acid is both a source and a sink for hydrogen ion, nitrate ion, and molecular nitric acid. The overall effect is that hydrogen ion concentration remains constant during precipitation and molecular nitric acid increases as the precipitation proceeds.

Residence Time

The effect of varying first stage residence time is shown in Figure 9. As the first stage residence time is increased, the first stage conversion is increased. However, if the solubility conditions are "growth" conditions, the standard deviation of the particle size distributions will decrease as the residence time is increased. This is shown in Figure 10. The current FB-Line first stage residence time is approximatley 2.5 minutes. The new FB-Line design has incorporated a longer first stage residence time of about 8.0 minutes.

Long residence time can be used to suppress hydrogen ion effects on the first stage conversion as shown by equation 5. As the ratio of hydrogen ion concentration to first stage residence time becomes small relative to the precipitation rate constant, the overall effect of hydrogen ion concentration on conversion diminishes.

Filtrate Losses

Table 4 shows filtrate losses for each precipitation test. All filtrate losses were in the range expected from equilibrium solubility considerations. Total precipitation and digestion times were held constant throughout the series of precipitation tests. Total precipitation time was one hour with 5 minutes digestion at the end of each run.

Conclusions

The overall performance of the plutonium trifluoride precipitation process is controlled by the "as mixed" total fluoride. All measures of precipitation performance have been experimentally linked to the "as mixed" total fluoride.

The validity of a mathematical model of the precipitation system was experimentally verified. The mathematical model predicts a steady-state first stage conversion which relates, in a single equation, all of the major process variables. This equation was used to calculate the precipitation rate constant for the plutonium trifluoride precipitation process.

The recommended conditions for optimum plutonium trifluoride precipitation using a two stage precipitation system are summarized below:

$\underline{[Pu]_t = 25\text{-}35\ g/L\ ,\ [H^+] = 2\text{-}3\ M}$

1. The "as mixed" total fluoride in the first stage precipitator should be in the range of 0.10 to 0.15 M to minimize plating and maximize second stage particle sizes.

2. The "as mixed" total fluoride in the second stage precipitator should be in the range of 0.7 to 1.0 M to minimize losses from precipitation and complexation.

3. The residence time in the second stage precipitator should be at least 10-15 minutes to insure maximum precipitation.

These conditions can be accomplished, without changing the current concentration of the plutonium feed stream or the hydrofluoric acid precipitant streams, by decreasing the hydrofluoric acid flow rate to the first stage precipitator from 185 ml/minute to 25 ml/minute. The hydrofluoric acid to the second stage precipitator would then have to be increased from 185 ml/minute to 345 ml/minute to meet condition 2.

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TABLE 1

Plutonium Trifluoride Experimental Design

Test #	$[Pu]_f$,M	$[HNO_3]_f$,M	$[HF]_{am}$, M
1	0.120	2.4	0.10
2	0.120	2.4	0.20
3	0.120	2.4	0.40
4	0.120	2.4	0.80
5	0.120	2.4	1.00
6	0.120	2.4	2.00
7	0.030	6.5	0.40
8	0.030	6.5	0.80
9	0.030	6.5	1.00
10	0.030	6.5	1.50
11	0.030	6.5	2.00
12	0.030	6.5	2.50

---

* Note The subscript "f" denotes feed concentrations.

TABLE 2

Plutonium Trifluoride Equilibrium Solubility Data

[Pu] ,g/l	$[HNO_3]$,M	$[HF]_{am}$, M	$[F^-]$ x10^5, M
0.332	0.43	0.050	8.37
0.044	0.43	0.100	16.74
0.071	0.43	0.252	42.19
0.177	0.43	0.440	73.67
0.678	0.20	0.0252	9.07
0.039	0.20	0.0504	18.14
0.024	0.20	0.1260	45.36
0.063	0.20	0.220	79.20
0.832	1.96	0.226	8.30
0.225	1.96	0.452	16.60
0.194	1.96	1.130	41.51
0.228	1.96	2.260	83.02

TABLE 3

Plutonium Trifluoride Rapid Nucleation Data

[Pu] ,g/1	$[HNO_3]_T$,M	$[HF]_{am}$, M
12.87	2.09	0.1815
12.87	2.09	0.1815
2.38	1.80	0.3036
2.37	1.79	0.308
0.873	1.57	0.413
0.873	1.56	0.413
12.00	2.94	0.275
11.95	2.93	0.280
2.18	2.83	0.435
2.20	2.86	0.417
0.744	2.36	0.674
0.748	2.37	0.664
13.65	1.09	0.108
13.65	1.09	0.108
2.67	1.18	0.149
2.67	1.12	0.147
1.03	0.962	0.188
1.03	0.968	0.179

TABLE 4

Actual Precipitation Conditions

	Flow Rates (mL/min)			"As Mixed" Concs., M		
Run #	Plutonium	HF	Adjustment	Plutonium	HF	H^+
1	2.4	0.07	0.7	0.111	0.153	1.96
2	2.5	0.08	1.0	0.112	0.167	1.95
3	2.4	0.05	0.8	0.125	0.110	1.97
4	2.1	0.13	0.8	0.107	0.314	1.89
5	2.3	0.22	0.6	0.104	0.471	1.84
6	2.3	0.44	0.3	0.096	0.867	1.69
7	5.6	1.20	0.8	0.095	0.952	1.66
8	6.3	1.00	1.0	0.099	0.744	1.74
9	7.3	0.90	1.0	0.102	0.616	1.78
10	7.2	1.00	1.2	0.101	0.641	1.78
11	7.3	1.00	1.0	0.102	0.621	1.78
12	7.3	1.00	1.0	0.101	0.604	1.78
13	7.3	1.00	1.0	0.101	0.650	1.78
14	1.9	0.40	1.0	0.025	0.939	4.11
15	2.9	0.24	1.2	0.029	0.412	4.60
16	2.1	0.28	1.1	0.029	0.635	4.39
17	2.1	0.40	0.8	0.026	0.864	4.18
18	2.1	0.67	0.6	0.024	1.306	3.78
19	1.7	1.01	0.2	0.019	2.012	3.12

TABLE 5

Plutonium Trifluoride Experimental Design

RUN #	Conversion	Grams Plated	Filtrate Losses , mg/L
1	0.0	0.08	9.0
	0.0	0.075	
2	0.03	0.16	15.0
	0.01	0.14	
3	0.00	0.00	21.0
	0.00	0.00	
4	0.428	0.43	13.0
	0.321	0.42	
5	0.572	0.88	49.0
	0.558	0.91	
	0.660	-	
	0.600	-	
6	0.974	0.68	40.0
	0.973	0.68	
	0.969	-	
	0.969	-	
7	0.963	*	16
	0.961		
8	0.967	*	< 25
	0.968		
9	0.886	*	< 25
	0.926		
10	0.838	*	< 25
	0.882		
11	0.837	*	29.0
	0.887		
12	0.818	*	11.0
	0.872		
13	0.887	*	32.0
	0.863		
14	0.762	0.64	55.0
	0.774	-	
15	0.183	0.069	9.0
	0.154	-	
16	0.449	0.043	85.0
	0.413	-	
17	0.723	0.67	53.0
	0.701	-	
18	0.93	0.49	12.0
	0.916	-	
19	0.987	0.12	33.0
	0.985	-	

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* Note The grams of plated material were not measured on these runs.

** Note Multiple analytical measurements were included where applicable.

TABLE 6

Particle Size Distribution Data for Plutonium Trifluoride Second Stage Precipitator

Run #	Mean (um)	Median (um)	STD. DEV. (um)	% < 5.0 um (%)
1	11.7	11.2	6.0	5
	11.6	11.2	5.0	6
	11.5	11.2	4.3	6
2	10.4	9.7	5.7	13
	10.4	9.0	7.1	14
	11.3	10.0	7.7	12
3	11.1	10.2	5.6	13
	10.8	9.8	5.5	13
	10.5	9.7	5.1	14
4	13.4	11.2	8.9	13
	12.9	11.1	7.9	12
	13.0	11.2	8.0	12
5	13.0	11.4	7.7	11
	13.4	11.4	8.6	11
	11.8	9.7	8.6	14
6	10.6	9.7	5.8	16
	10.0	9.4	4.9	18
	10.4	9.5	5.5	17
7	9.1	7.2	6.3	25
	9.5	7.1	7.1	27
	10.0	7.1	8.0	30
8	8.1	6.6	4.9	27
	8.7	6.4	6.2	33
	9.5	6.7	7.9	31
9	13.6	9.9	12.2	21
	9.2	6.3	7.9	37
	9.6	7.9	7.0	25
10	10.5	7.6	8.6	27
	11.6	7.9	10.9	26
	10.7	8.1	8.0	23
11	7.7	6.2	5.0	34
	8.1	6.5	5.6	30
	9.5	7.7	6.2	23
12	9.5	6.1	9.6	35
	8.5	7.1	5.0	27
	8.6	6.3	6.5	33
13	7.9	6.3	5.2	35
	8.4	6.6	6.5	31
	9.6	7.7	8.2	24

TABLE 6 (cont)

Particle Size Distribution Data For Plutonium Trifluoride Second Stage Precipitator

RUN #	Mean (um)	Median (um)	STD. DEV. (um)	%< 5.0 um (%)
14	9.9	8.9	5.2	14
	9.9	8.7	5.5	16
	10.0	9.0	5.1	15
15	10.1	9.1	5.4	11
	9.5	8.9	4.3	11
	9.8	9.0	5.0	11
16	10.1	9.2	5.1	12
	10.1	9.3	4.8	12
	10.1	9.3	4.8	12
17	8.3	7.6	4.4	15
	8.3	7.6	4.2	16
	7.8	7.3	3.4	19
18	10.8	9.6	6.1	19
	11.1	9.5	6.8	20
	11.5	9.8	7.3	19
19	15.8	13.3	10.7	10
	14.8	13.2	8.6	11
	19.5	16.6	12.6	8

TABLE 7

Statistical Parameters for Precipitation Model
"As Mixed" Total Fluoride

Least-square Coefficient	Total Plutonium , Total Hydrogen ion, M	
	0.120 M Pu, 2.0 M H^+	0.03 M Pu, 5.2 M H^+
a_0	-0.25 ±0.01	-0.306 ± 0.007
a_1	1.79 ±0.05	1.16 ±0.03
Correlation Coefficient	0.99	0.99
Standard Deviation of Y(x)	±0.05	±0.03

TWO STAGE ACTINIDE PRECIPITATION SYSTEM

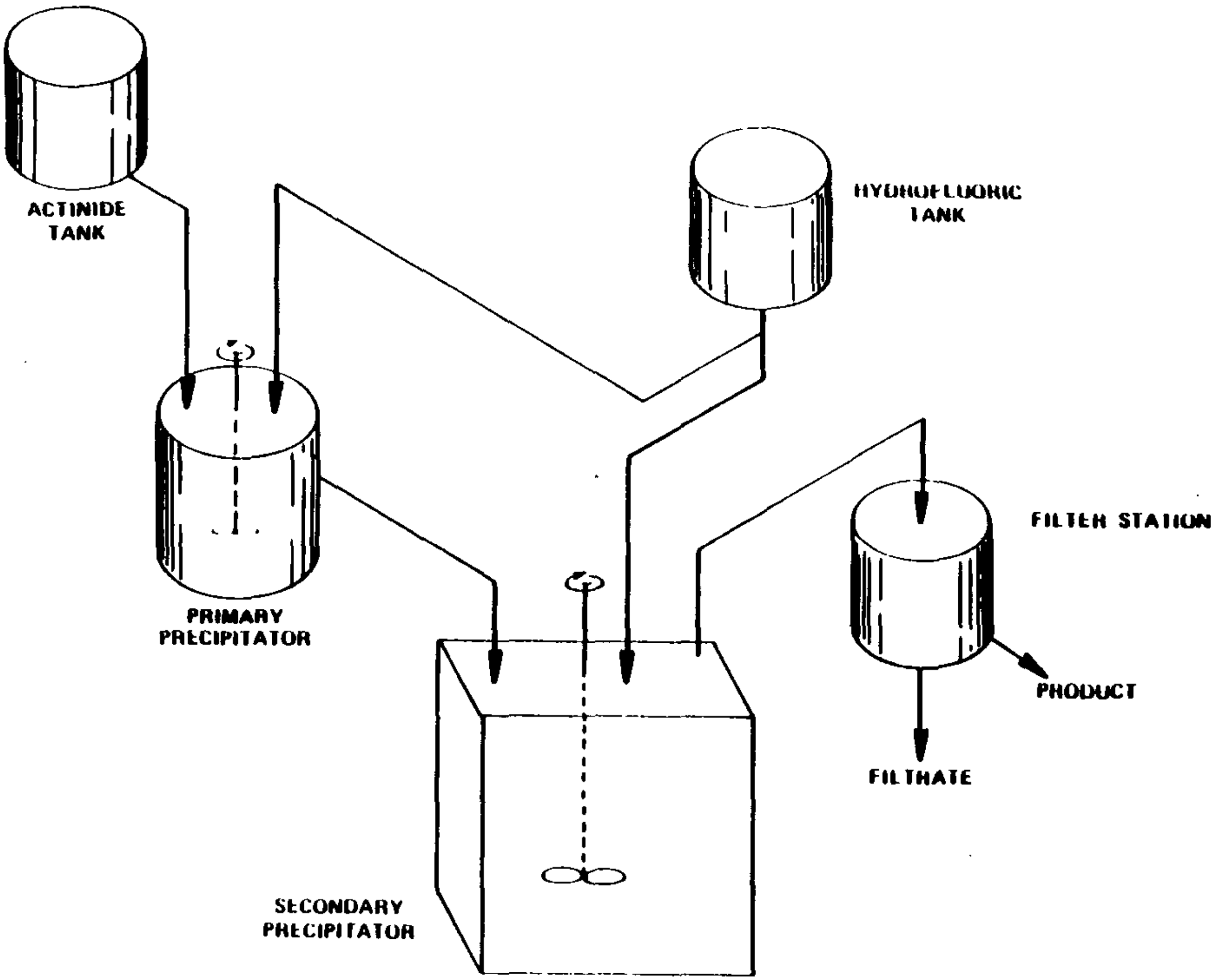

Figure 1. A Two Stage Precipitation System

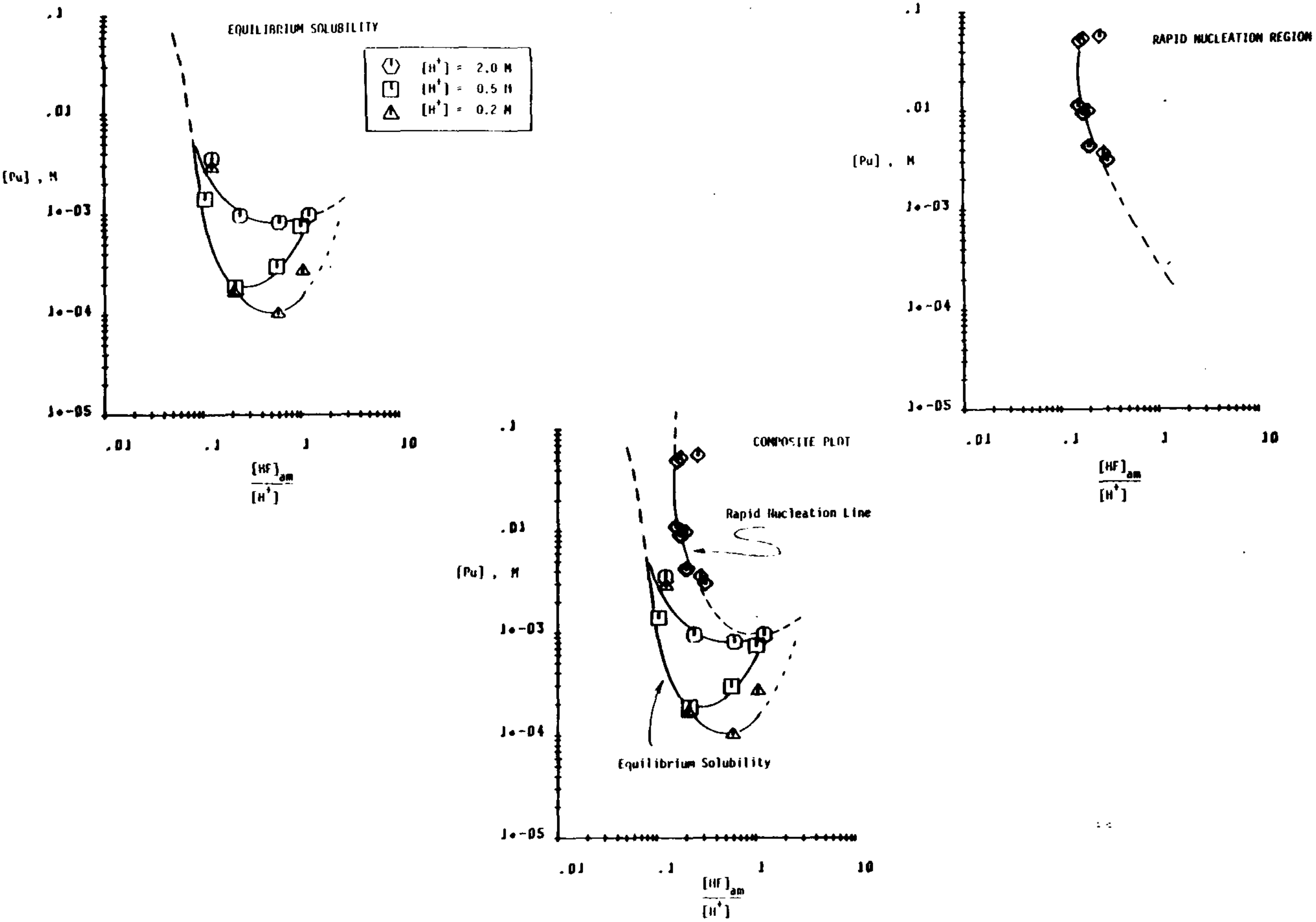

Figure 2. Plutonium Trifluoride Equilibrium Solubility and Rapid Nucleation Regions.

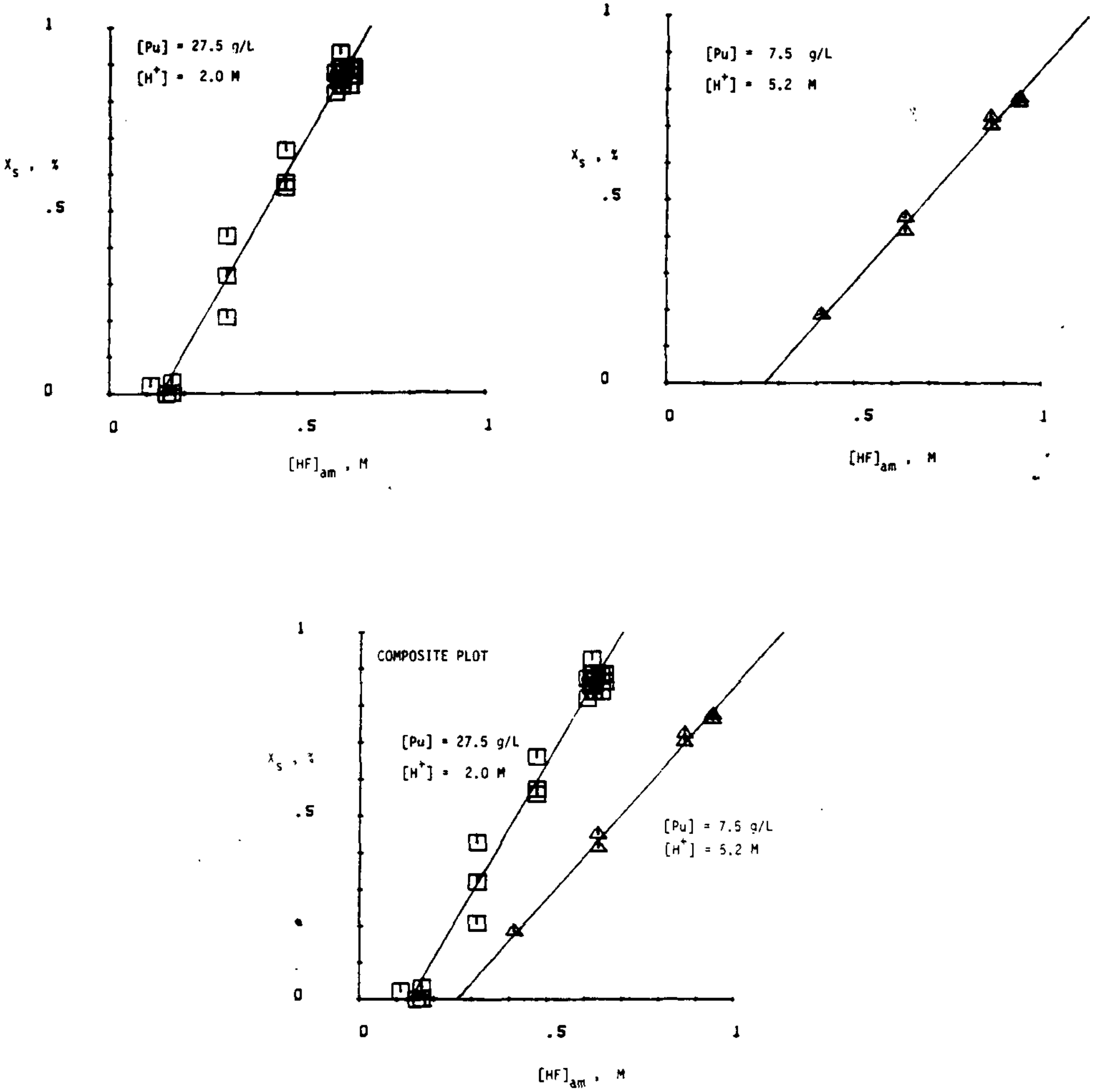

Figure 3. First Stage Conversion as a Function of "as mixed" Total Fluoride.

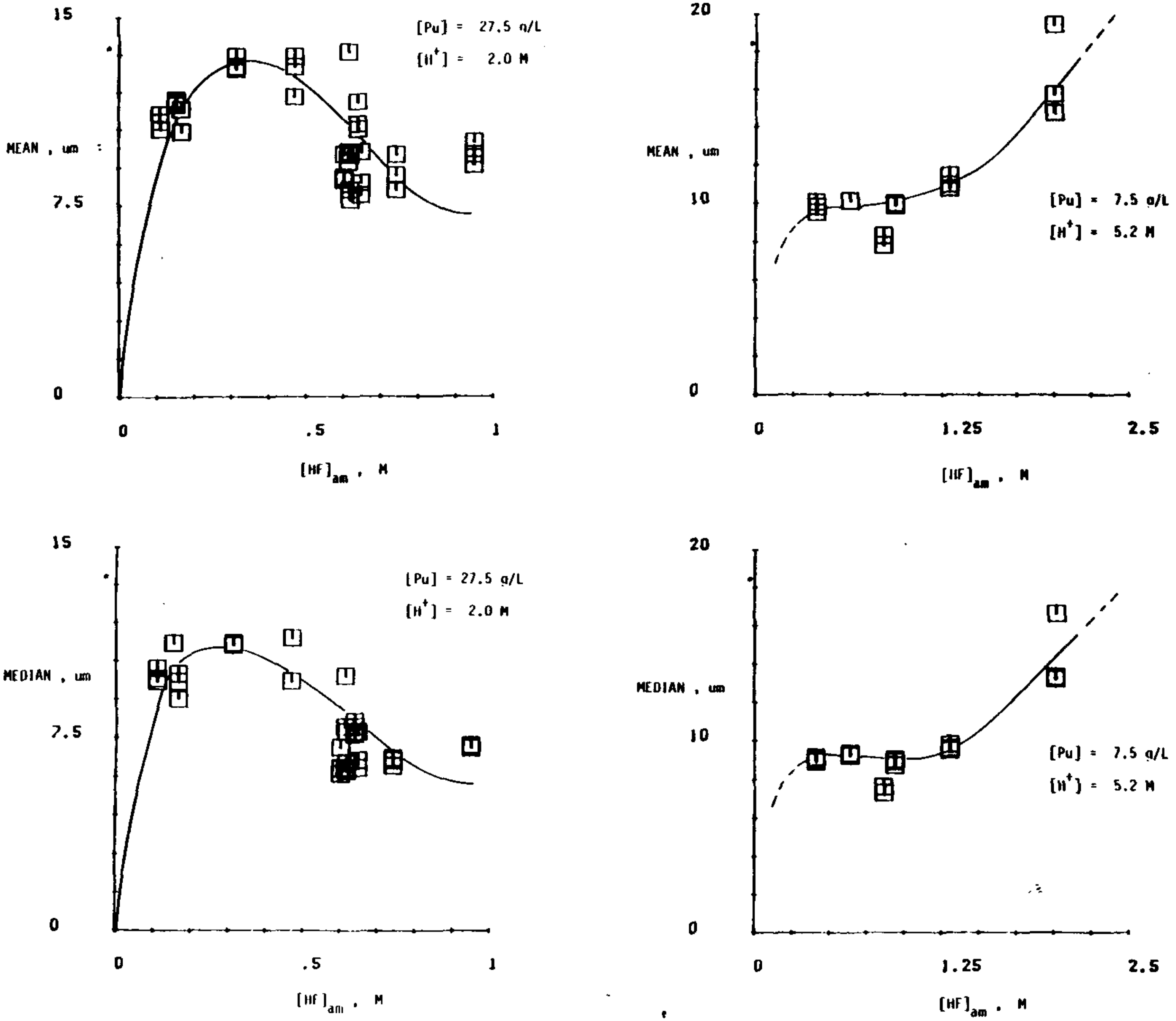

Figure 4. Second Stage Particle Size at Different Plutonium and Hydrogen ion Concentrations.

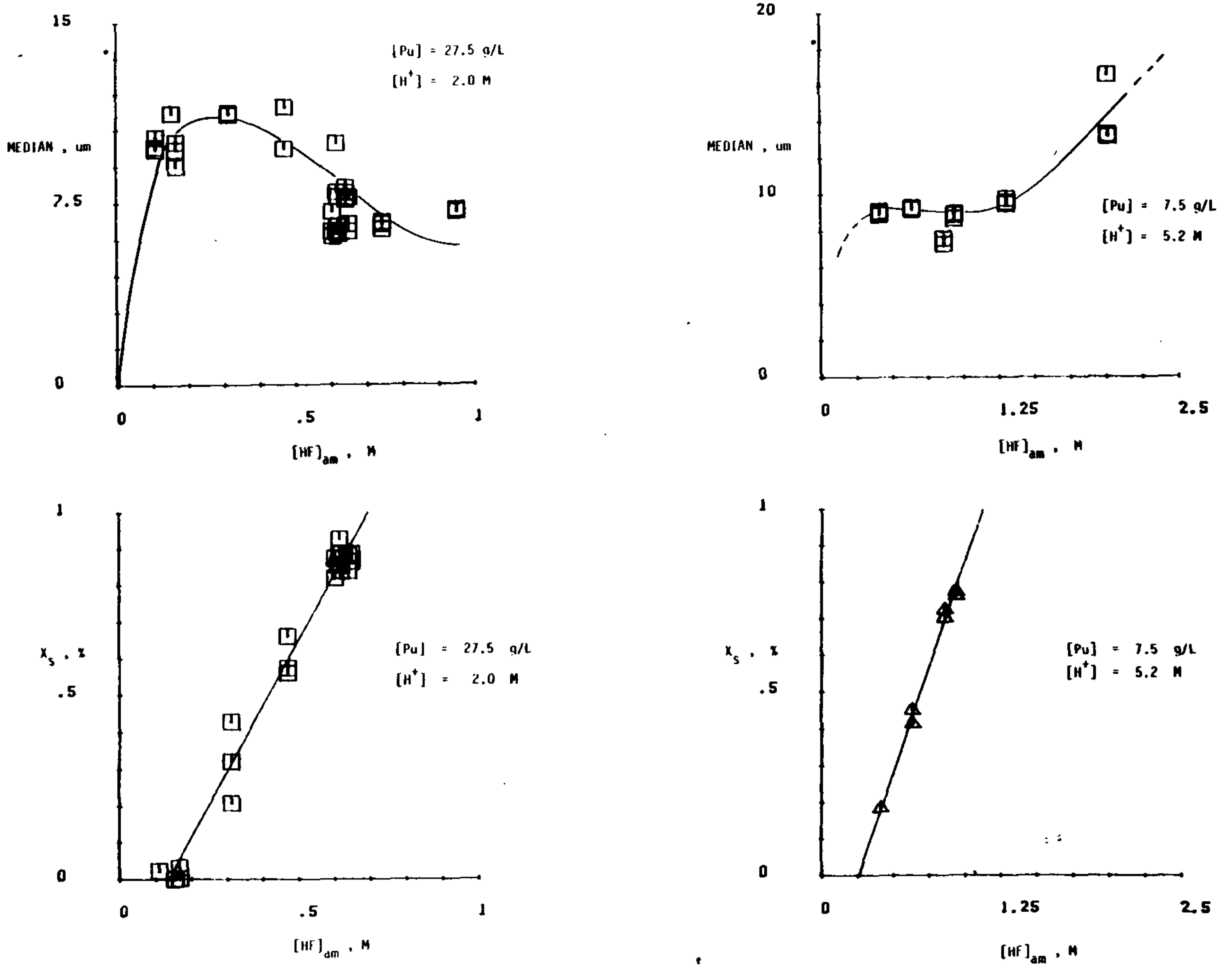

Figure 5. Second Stage Particle Size as a Function of First Stage Conversion.

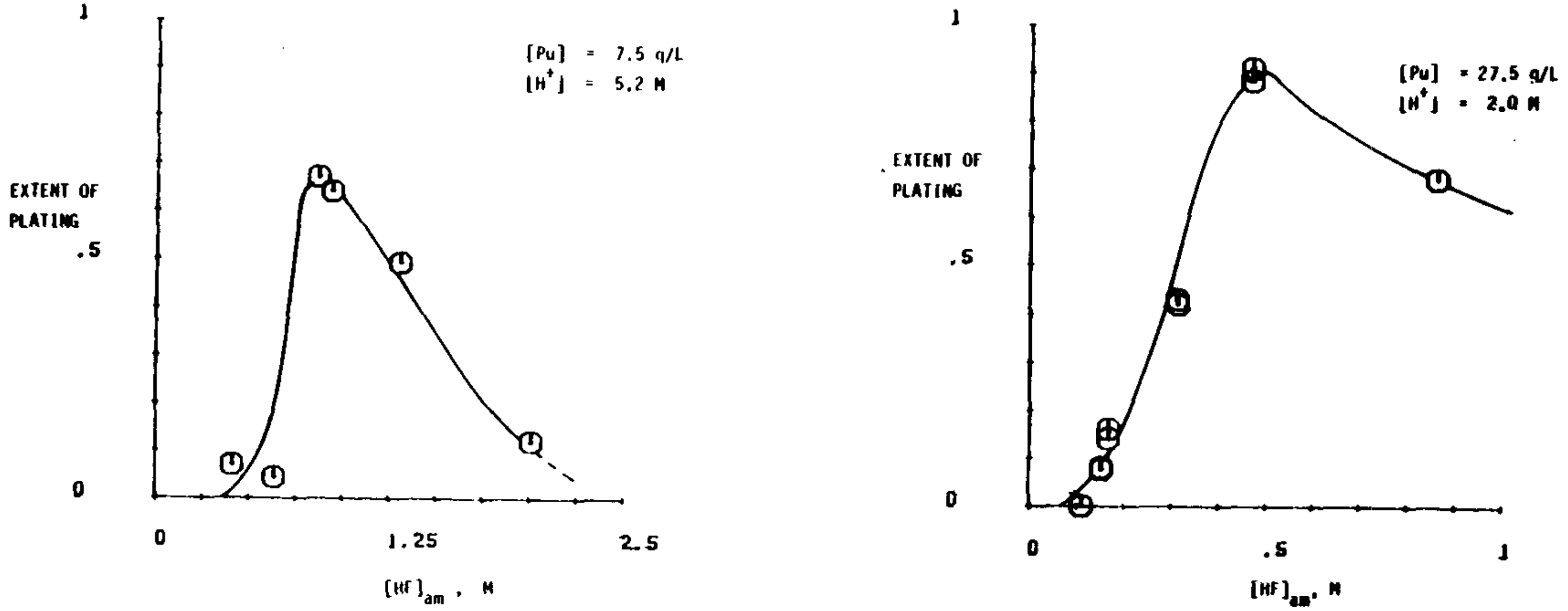

Figure 6. "Plating" in the First Stage Precipitator at Different Plutonium and Hydrogen Ion Concentrations.

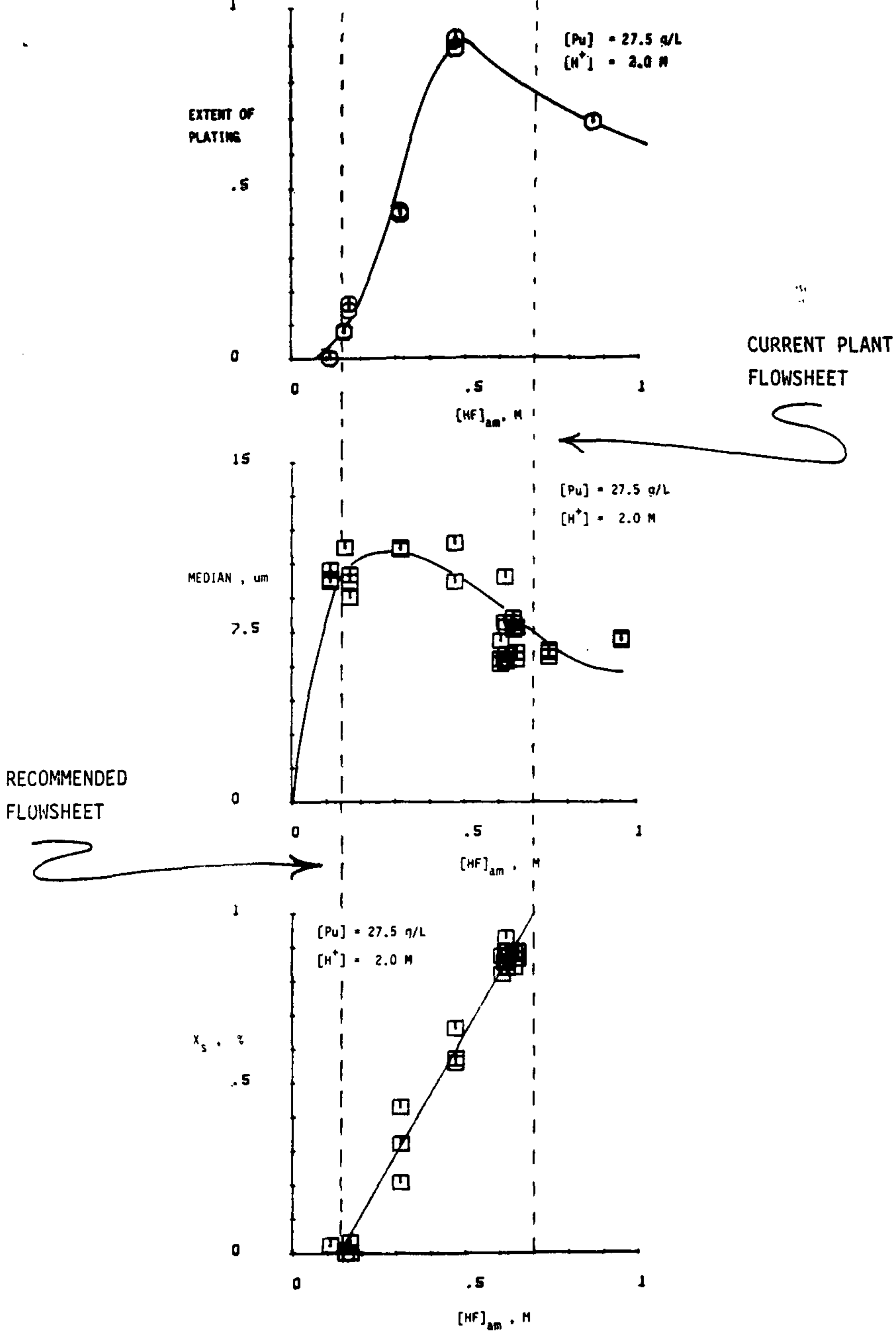

Figure 7. Optimum Precipitation Conditions for Plutonium Trifluoride.

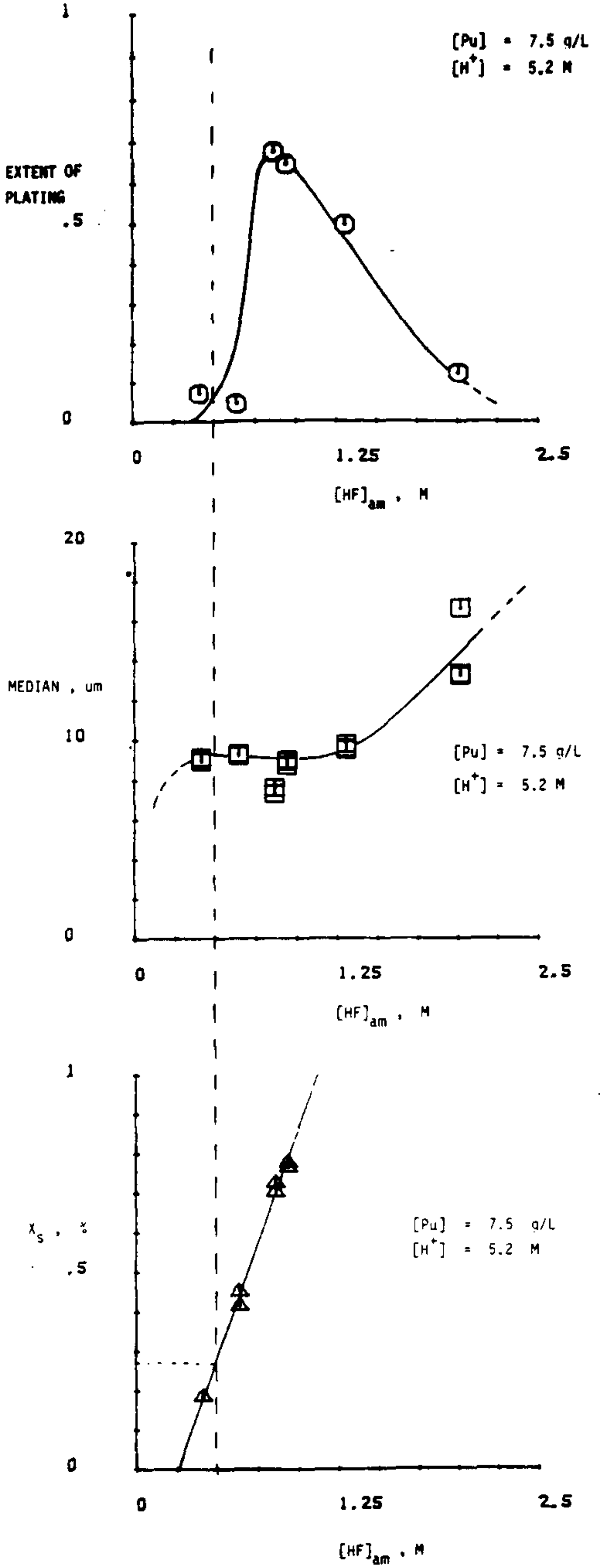

Figure 8. Optimum Precipitation Conditions for Plutonium Trifluoride.

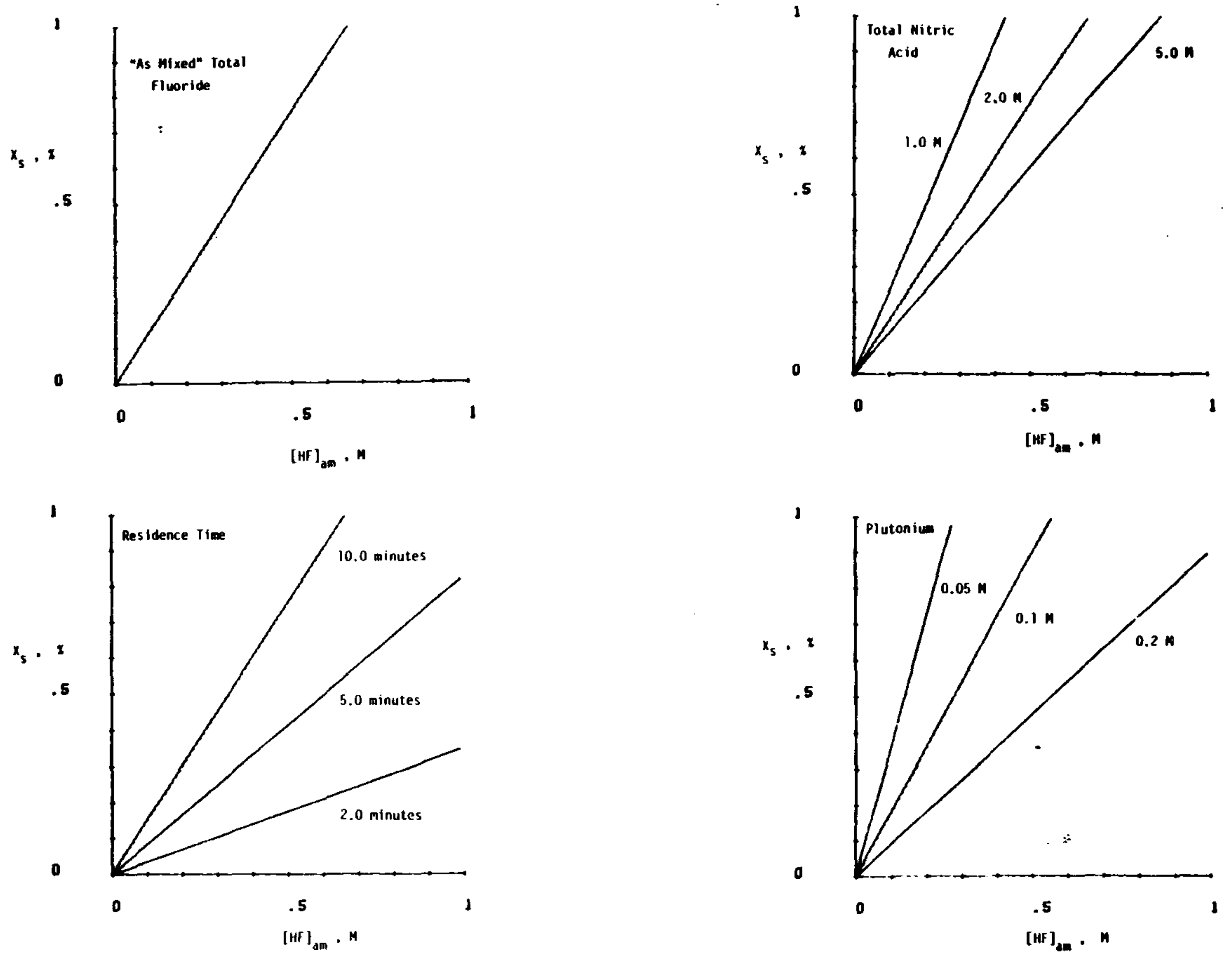

Figure 9. The Effect Of Process Variables on Conversion.

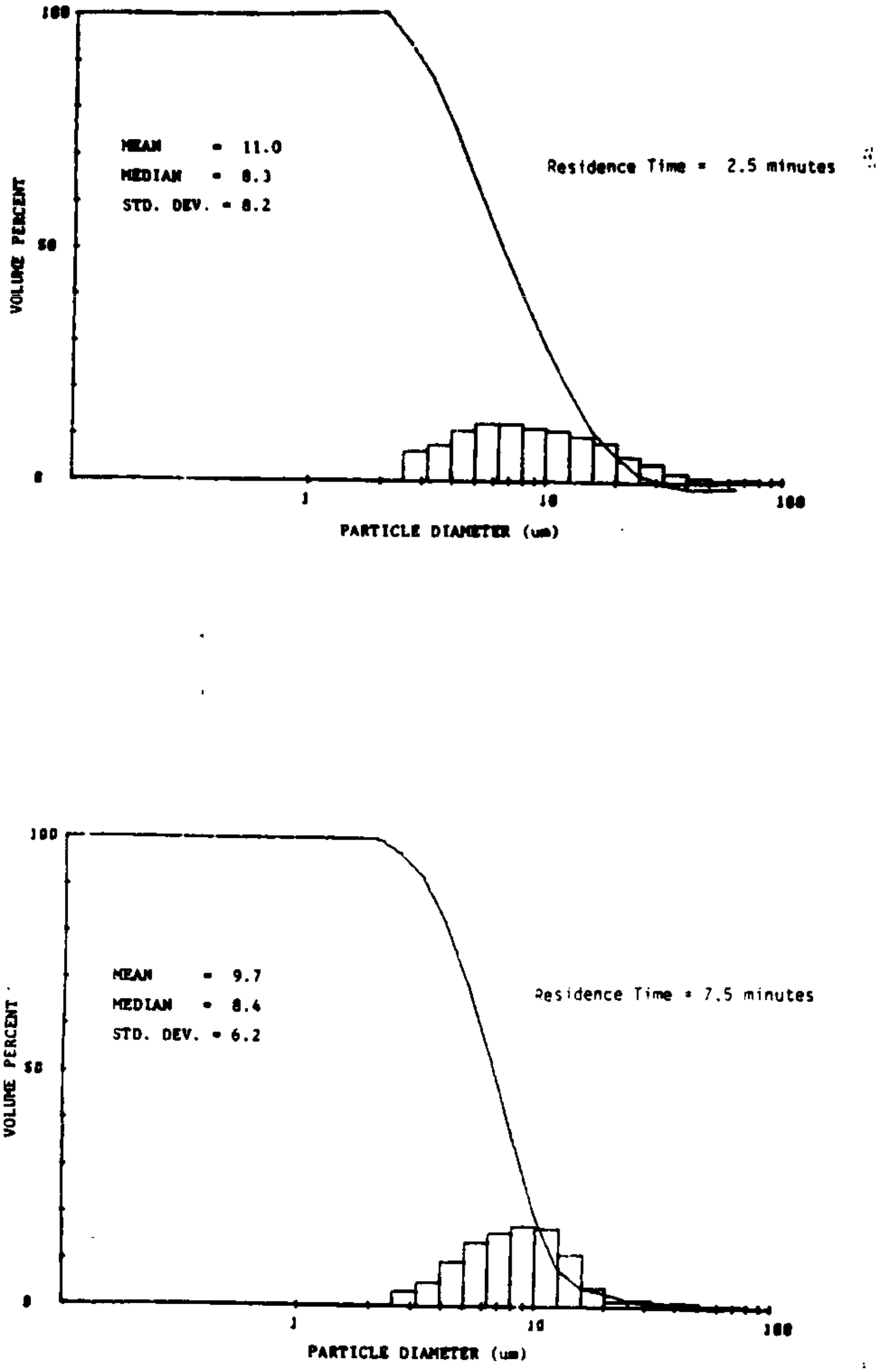

Figure 10. Effect of Residence Time on Particle Size Distributions.