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CERIUM OXALATE PRECIPITATION

T. P. CHANG

FEBRUARY 1987

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ABSTRACT

Cerium, a nonradioactive, common stand-in for plutonium in development work, has been used to simulate several plutonium precipitation processes at the Savannah River Laboratory. There are similarities between the plutonium trifluoride and the cerium oxalate precipitations in particle size and extent of plating, but not particle morphology. The equilibrium solubility, precipitation kinetics, particle size, extent of plating, and dissolution characteristics of cerium oxalate have been investigated. Interpretations of particle size and plating based on precipitation kinetics (i.e. nucleation and crystal growth) are presented.

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CERIUM OXALATE PRECIPITATION

INTRODUCTION

At the Savannah River Plant (SRP), plutonium is currently precipitated from dilute nitrate solution with hydrofluoric acid (HF) to form plutonium trifluoride (PuF_3). Cerium, a common surrogate for Pu, has been used often in the laboratory for scouting and development work, and in the plant for equipment functional testing. For instance, Ce was recently used for the "cold" functional testing of the new plant "C" and "D" precipitators.

Several factors are considered in selecting plutonium surrogates for use in precipitation studies, e.g. similar chemistry, product characteristics (particle size, distribution, and morphology), and extent of plating. Cerium trifluoride (CeF_3) was first considered for simulating PuF_3 because of the similar chemistry; e.g. one +3 cation reacts with three free fluoride (F^-) ions. Laboratory studies found however, that CeF_3 precipitations result in smaller particles due to their lower solubility and higher nucleation rates. In addition, the CeF_3 particles produced during functional testing of plant precipitators were even smaller than those produced in the lab. Consequently, very long filtration times were experienced. Besides the slow filtration, very light (if any) plating was observed, which differed from the noticeable plating usually associated with PuF_3 precipitation. Alternatives to the CeF_3 flowsheet were sought to provide meaningful tests and to keep the functional testing on schedule.

Tests conducted in the laboratory indicated that cerium oxalate (CeOX) could replace CeF_3 in simulating PuF_3 because of similar mean particle sizes and plating characteristics. Plant tests later demonstrated that similar-size CeOX particles and slightly heavier plating were produced in the new plant precipitators than would have been expected with PuF_3 .

In general, precipitator performance is measured by three parameters: filtration time, filtrate losses, and extent of plating. All these parameters can be related (only qualitatively at the present time) to the equilibrium solubility data. The task of optimizing precipitator performance could be a much easier one if the relationship between precipitation kinetics and supersaturation (or equilibrium solubility) is well understood and can be correlated quantitatively.

This report summarizes several fundamental properties of the cerium nitrate--oxalic acid--nitric acid system: solubility, nucleation rate, crystal growth rate, mean particle size, and plating characteristics. In addition, the rate of dissolution as a function of nitric acid concentration and temperature has been included. Our approach is to use this fundamental information to interpret phenomena observed during lab and full-scale experiments so that a better understanding of the precipitation mechanism can be achieved.

BACKGROUND

A two-stage precipitation system is currently used at the Savannah River Plant to precipitate PuF_3 , and a schematic diagram of this process is shown in Figure 1. Similar small-scale precipitators were set up in the laboratory for flowsheet optimization studies. Luerkens used both Pu and its surrogate, Ce, in his two-stage precipitation experiments.^{1,2} Figure 2 shows similar curves for the small-scale PuF_3 and CeF_3 mean particle size as a function of the first stage and "as mixed" hydrofluoric acid concentration ($[\text{HF}]_{\text{am}}$). However, factors such as the quality of mixing (i.e. scale of segregation and intensity of segregation defined by Danckwerts³), degrees of agitation at each stage, and the degree of supersaturation in the second stage were left out in Luerkens' correlation. A brief discussion of the mixing and shear stress effect on particle size distribution in a precipitator can be found in Chang's report.⁴

Particle Size & Precipitation Kinetics

Particle size distribution is of great importance to many precipitation processes. Generally, the particle size distribution in a mixed suspension, mixed product removal (MSMPR) precipitator can be correlated by using the population balance equation,^{5,6} which has two kinetics parameters: the nucleation rate (B), and the crystal growth rate (G). A simple population balance equation (Eq 1), proposed by Randolph and Larson,⁴ was adopted for evaluating the nucleation and crystal growth rates of CeOX .

$$dN/dx = n = (B/G) \cdot \exp(-x/(G \cdot t)) \quad (1)$$

where x = characteristics crystal size (micron)
 N = concentration of crystals smaller than x (#/vol)
 n = population density of crystals of size x (#/vol/micron)
 B = nucleation rate (#/vol/min)
 G = crystal growth rate (micron/min)
 t = average residence time (min)

FIGURE 1. Two-Stage PuF_3 Precipitation Process

FIGURE 2. Second-Stage Particle Size at Different First-Stage "As-Mixed" Hydrofluoric Acid Concentrations, $[HF]_{am}^{1,2}$

The nucleation rate is generally the dominating factor in influencing the precipitate's size distribution. Unfortunately, nucleation is the least understood, most difficult factor to describe by well-founded kinetic models. Because of the high supersaturation conditions for most precipitation processes, primary nucleation is expected to dominate. Walton⁷ proposed the following rate equation for primary nucleation.

$$B = C_1 \cdot \exp[-C_2 \cdot r^3 / (T^3 \cdot (\ln(S))^2)] \quad (2)$$

where C_1 & C_2 = characteristic constants
 r = activity coefficient (dimensionless)
 T = absolute temperature ($^{\circ}\text{K}$)
 S = supersaturation ration, $\text{conc}/\text{conc}_{\text{eq}}$ (dimensionless)

This highly nonlinear rate equation is extremely difficult to measure because the nucleation process is followed immediately by the growth of newly formed nuclei before crystals can be detected by most instruments. The growth kinetics has been studied rather extensively for several crystallization processes.^{8,9,10} The growth rate, G , depends usually on the degree of supersaturation as well as temperature and crystal morphology.¹¹ Semiempirical nucleation and growth rate equations are expressed by Eq 3 and 4.

$$B = C_b \cdot S^b \quad (3)$$

$$G = C_g \cdot S^g \quad (4)$$

where C_b & C_g = characteristic constants
 b & g = power law coefficients

Plating

Plating (or encrustation) is common in industrial crystallizers. Precipitates frequently deposit on the vessel surface, grow, and eventually flake off and block process lines. Plating is a serious problem for PuF_3 precipitation because the $\alpha\text{-N}$ reaction from plated materials releases neutrons, which contribute to personnel radiation exposure.

Several parameters have been identified that could affect the extent of plating in a precipitation process. Most important is the surface finishing (i.e. smoothness) of the process vessel.

Porter¹² reported that the extent of PuF_3 plating varied from 25mg/100cm² on a smooth platinum surface to 325mg/100cm² on a rough molybdenum surface. Other factors such as the degree of supersaturation in precipitators, the ability of mixing reactants, and the capability of suspending slurries can also affect the extent of plating. In most cases, higher supersaturation (either due to overall or localized supersaturation) leads to heavier plating. Typically, localized supersaturation occurs more often in small precipitators and may be the main source of plating. Settling of large particles and inability to remove very fine particles from vessel surfaces are likely to be the cause of plating in many full-scale precipitators. Varying flow pattern can sometimes reduce plating. This is especially true when the wetted vessel surface is not smooth.

EXPERIMENTAL PROGRAM

The experimental program consisted of three parts: (1) A study of cerium oxalate solubility in the cerium nitrate--nitric acid--oxalic acid system was conducted; (2) A series of single-stage precipitations was performed to examine the filtration rate, particle size, and extent of plating of the CeOX flowsheet; (3) the dissolution of CeOX in various nitric acid concentrations and at different temperatures was examined.

Solubility of Cerium Oxalate in Nitric Acid

Different portions of cerium nitrate solution, distilled water, and nitric acid were mixed at room temperature (22°C) in a 50 mL glass beaker agitated by a magnetic stirrer. Twenty-four runs were performed. Table 1 shows the amount of cerium nitrate, nitric acid, and oxalic acid added initially. Samples were left overnight then filtered. $[\text{Ce}^{+3}]$, $[\text{H}^+]$, and total oxalate $[\text{OX}]$ analyses were made on the filtrate samples.

Precipitation of Cerium Oxalate

The Pu-surrogate feed (0.12M cerium nitrate in 1.5M nitric acid) and the precipitant feed (0.8M oxalic acid) were added simultaneously to single-stage, lab-scale precipitators. A 3/4" marine propeller, rotated between 600 and 750 RPM, provided excellent mixing. Two polypropylene (PP) beakers from different vendors were used for evaluating the plating characteristics. One beaker, by Nalgene, had a smoother surface than the other one, by American Scientific Products (Figure 3). Constant liquid volume in the precipitator (75mL) was maintained by utilizing an overflow line. Experimental conditions such as the feed rates and concentrations are listed in Table 2. The particle population density and mean

TABLE 1**Test Conditions for Cerium Oxalate Equilibrium Experiment**

<u>Test</u>	<u>[Ce⁺³] (mL)</u>	<u>[HNO₃] (mL)</u>	<u>[H₂O] (mL)</u>	<u>[Oxalic Acid] (mL)</u>
E01	0.541	3.872	15.587	1.70
E02	0.541	3.872	15.587	2.36
E03	0.541	3.872	15.587	3.00
E04	0.541	3.872	15.587	4.20
E05	1.840	3.752	14.408	1.70
E06	1.840	3.752	14.408	3.00
E07	1.840	3.752	14.408	4.20
E08	1.840	3.752	14.408	5.20
E09	3.623	3.588	12.789	3.00
E10	3.623	3.588	12.789	4.20
E11	3.623	3.588	12.789	5.20
E12	3.623	3.588	12.789	6.20
E13	0.541	7.795	11.664	8.20
E14	0.541	7.795	11.664	10.40
E15	0.541	7.795	11.664	12.40
E16	0.541	7.795	11.664	15.60
E17	1.840	7.675	10.485	8.20
E18	1.840	7.675	10.485	12.40
E19	1.840	7.675	10.485	15.60
E20	1.840	7.675	10.485	18.40
E21	3.623	7.510	8.867	12.40
E22	3.623	7.510	8.867	15.60
E23	3.623	7.510	8.867	18.40
E24	3.623	7.510	8.867	20.00

Concentrations of Stock Solutions:

Cerium Nitrate: [Ce⁺³] = 0.462 m; [H⁺] = 0.471 M
Nitric Acid: [H⁺] = 5.099 M
Oxalic Acid [H⁺] = 2.02 M; [OX] = 1.07 m

(3a) New Nalgene Beaker

(3b) New ASP Beaker

(3c) Used Nalgene Beaker

(3d) Used ASP Beaker

FIGURE 3. Surfaces of Nalgene and American Scientific Product (ASP) Beakers: 3a & 3b Before Precipitation, 3c & 3d Rinsed with Hot Water after Precipitation

TABLE 2**Test Condition and Performance for Cerium Oxalate Precipitation**

Test	Feed Rates (mL/min)		Feed Conc. (M)		Beakers	Particle Man Size (microns)	Extent of Plating (mg/100 cm ²)	Relative Filtr. Rate*
	[Ce ⁺³]	[OX]	[Ce ⁺³]	[OX]				
P01	8.0	5.0	0.12	0.8	Nalgene	N/A	180	1.60
P02	8.0	4.0	0.12	0.8	Nalgene	21.1	150	1.97
P03	8.0	3.0	0.12	0.8	Nalgene	25.9	180	2.19
P04	8.0	1.0	0.12	0.8	Nalgene	20.2	270	1.74
P05	7.5	3.6	0.12	0.8	ASP	25.2	1110	1.77
P06	8.0	3.0	0.12	0.8	ASP	30.1	880	2.28
P07	8.0	2.0	0.12	0.8	ASP	22.6	790	1.64
P08	8.0	1.0	0.12	0.8	ASP	29.9	390	3.28
P09	8.0	0.5	0.12	0.8	ASP	26.4	260	2.31
P10	4.0	1.0	0.12	0.8	ASP	29.4	400	2.28
P11	8.0	5.0	0.12	0.7	ASP	N/A	770	1.89
P12	8.0	3.0	0.12	0.7	ASP	N/A	670	2.62

* The relative filtration rate is the ratio of times required to filter the same volume of cerium oxalate and distilled water, i.e. the higher the value the slower the filtration rate.

particle size were measured by a Coulter Counter®. The extent of plating was the weight gained by a precipitator during 60 minutes of precipitation. Particle morphology was examined by a scanning electron microscope (SEM).

Dissolution of Cerium Oxalate in Nitric Acid

The dissolution study of CeOX in nitric acid consisted of two parts. The first set of runs was conducted at room temperature (22°C), the second set at 50°C. Dissolution rates of CeOX in various nitric acid concentrations (3, 6, 8, 12, and 16M) were also investigated. Each sample (1.5 g of CeOX crystals) was mixed with 20 mL nitric acid of various concentrations with occasional agitation. The time needed to dissolve all solids was recorded.

RESULTS AND DISCUSSION

Solubility Data

Both kinetic parameters B and G are dependent variables of the equilibrium solubility as shown by Eq 1, 2, 3, and 4. As a result, the particle size and size distribution will be affected by the degree of supersaturation during precipitations. Solubility data for PuF_3 , Pu(III) oxalate , and CeF_3 can be found in the works of Burney and Tober,¹³ Burney and Porter,¹⁴ and Luerkens² respectively. CeOX solubility at room temperature was measured in this study. Table 3 shows the analytical results of $[\text{Ce}^{+3}]$, $[\text{H}^+]$, and $[\text{OX}]$ in the filtrate. As expected, cerium concentration in the filtrate increases as the nitric acid concentration increases, and decreases as the oxalate concentration decreases. The solubility relationship fitted by a nonlinear regression routine is expressed by Eq 5 and shown in Figure 4.

$$[\text{Ce}^{+3}] = 0.763 * [\text{H}^+]^{3.334} / [\text{OX}]^{1.717} \quad (5)$$

where $[\text{Ce}^{+3}]$ = cerium concentration in the filtrate (mg/liter)

$[\text{H}^+]$ = total acid in the filtrate (M)

$[\text{OX}]$ = total oxalate concentration in the filtrate (M)

We also can derive this solubility relationship from the solubility product constant¹⁵ (K_{sp}) and the dissociation constants of oxalic acid¹⁵ (K_1 , K_2). Assuming the filtrate solution is ideal (i.e. activity coefficient is equal to 1), the cerium concentration in the filtrate can be calculated from Eq 6.

$$[\text{Ce}^{+3}] = C_3 * [\text{H}^+]^{3.0} / [\text{OX}]^{1.5} \quad (6)$$

TABLE 3**Cerium Oxalate Equilibrium Solubility Data**

<u>Test</u>	<u>[Ce⁺³] (ppm)</u>	<u>[H⁺] (m)</u>	<u>[Total Oxalate] (M)</u>	
E01	112.0	1.050	5.57	E-02
E02	61.0	1.082	8.00	E-02
E03	37.6	1.097	1.074	E-01
E04	20.8	1.146	1.514	E-01
E05	757.6	1.039	1.98	E-02
E06	94.1	1.084	6.58	E-02
E07	41.8	1.143	1.091	E-01
E08	29.4	1.138	1.428	E-01
E09	1049.0	1.133	1.88	E-02
E10	194.0	1.129	5.19	E-02
E11	80.5	1.155	8.44	E-02
E12	46.9	1.188	1.195	E-01
E13	63.3	1.964	2.911	E-01
E14	43.1	1.964	3.434	E-01
E15	39.8	2.125	4.127	E-01
E16	28.3	1.964	4.501	E-01
E17	86.2	1.942	2.474	E-01
E18	40.4	1.931	3.557	E-01
E19	29.8	1.930	4.163	E-01
E20	24.9	1.911	4.635	E-01
E21	73.7	1.941	3.170	E-01
E22	50.7	1.984	3.790	E-01
E23	32.9	1.955	4.343	E-01
E24	34.0	1.937	4.624	E-01

FIGURE 4. Solubility of Cerium Oxalate in Nitric/Oxalic Acids

where $C_3 = M_{Ce} * 1000 \text{ mg/g} * (K_{sp}/(K_1 * K_2)^3)^{.5}$, 0.155
 M_{Ce} = molecular weight of cerium (g/mole), 140
 K_{sp} = solubility product constant of CeOX, $3.0 \text{ E-}29$
 K_1 = first dissociation constant of oxalic acid, $5.36 \text{ E-}2$
 K_2 = second dissociation constant of oxalic acid, $5.42 \text{ E-}5$

Equations 5 and 6 agree well. The constant term is 0.763 in Eq 5 and 0.155 in Eq 6. The deviation is probably due to nonideal solution behaviors.

Nucleation & Growth Rates, Particle Size

Because our precipitator was operated under the MSMPR mode, the nucleation and growth rates can be obtained by plotting the natural logarithm (ln) of the population density, n , versus the crystal size, x . According to Eq 1, a straight line should result. The growth rate is determined from the slope of the curve ($-1/(g*t)$) and the residence time (t). The nucleation rate is determined from the growth rate and the intercept (B/G).

Table 4 lists the population density data from one cerium oxalate precipitation (Run P02, Table 2) with as-mixed cerium and oxalic concentrations of 0.08M and 0.27M respectively in 1M nitric acid solution. The nucleation rate is $2.01\text{E}11$ nuclei/ m^3/minute and the growth rate is 2.6 microns/minute. The population density plot is shown in Figure 5 and it is not a straight line. (The growth rate of 2.6 microns/minute was determined by fitting data with a least-squares routine assuming constant G .) The smaller "absolute" slope (faster growth rate) for larger particles could mean that small crystals are being dissolved to provide nutrients for already-formed large crystals to grow further when the latter is thermodynamically favorable (the ripening effect¹⁶). This superficial faster growth rate for large crystals could also be the result of aggregation of small crystals. Size-dependent growth (e.g. 1 and 2.7 microns/min for crystals smaller and larger than 28.7 microns respectively) is another possibility. More extensive studies are needed to verify the relationships described by Eq 3 and 4 and to quantify the parameters.

The kinetic rates for PuF_3 and CeF_3 , as shown in Table 5, are derived from Luerkens' experimental results.^{1,2} CeF_3 exhibits the smallest mean size because of its higher supersaturation ratio, S , the fastest nucleation rate (B) and the slowest growth rate (G). Both B and G are related to S . PuF_3 and CeOX have very different B but similar S and more comparable mean particle size.

TABLE 4**Population Density Data of Run #P02**

<u>Particle Size</u> <u>(micron) x</u>	<u>Population Density</u> <u>(#/micron/M³) n</u>	<u>ln(n)</u>
11.4	1.179 E11	25.49
14.4	5.918 E10	24.80
18.1	3.005 E10	24.13
22.8	1.503 E10	23.43
28.7	7.353 E09	22.72
36.2	4.064 E09	22.13
45.5	2.443 E09	21.62
57.4	1.312 E09	21.00
7.23	6.764 E08	20.33
91.1	2.184 E08	19.20
114.8	5.852 E07	17.88
144.5	1.253 E07	16.34
182.0	8.689 E05	13.68

FIGURE 5. Population Density Plot of Cerium Oxalate from an MSMPR Precipitator

TABLE 5

**Kinetic Rates, Supersaturation Ratio, and Particle Size for
Laboratory PuF₃, CeF₃, and CeOX Precipitations**

	Nucleation Rate, B (#/M ³ /min)		Growth Rate, G (micron/min)	Supersaturation Ratio (c/c _{eq})		Mean Size (microns)
PuF ₃	1.72	E13	1.02	1.96	E3	13.1
CeF ₃	4.09	E13	0.41	3.71	E5	4.2
CeOX	2.01	E11	2.64	1.56	E3	21.1

Derived from Luerkens' PuF₃ data, DP-1680¹ Run #4,
Derived from Luerkens' CeF₃ data, DP-1684² Run #10,
CeOX data from this work Run #P02

As shown in Table 3, the mean particle size of CeOX precipitates ranges from 20 to 30 microns over a wide nitric acid/oxalic acid ration (R). Past experience with CeF₃ precipitation suggested that much smaller CeOX particles might be produced in a full-scale precipitator. One full-scale run was then performed in the laboratory. The CeOX mean particle size was around 13 microns, which was close to the size of PuF₃ particles produced in plant (10-15 microns). Subsequently, five plant runs in the new "D" precipitator produced mean size particles of 11.2, 13.6, 14.4, 14.7, and 13.2 microns, which agreed extremely well with the lab results.

Scanning electron microscope pictures were also obtained for routine morphology analyses. As shown in Figure 6, CeOX morphology is distinctly different from that of PuF₃ and similar to that of plutonium oxalate (PuOX). In this test work, we did not try to vary the flowsheet to examine its effect on the product morphology.

Plating

The extent of plating at various supersaturation levels is listed in Table 2. Results also show that different trends exist between precipitators with smooth and less-smooth surface finishes. This is illustrated in Figure 7. The extent of plating is very sensitive to the acid ratio R ($[\text{HNO}_3]_{\text{am}}/[\text{H}_2\text{C}_2\text{O}_4]_{\text{am}}$) in the rougher American Scientific Products beaker. However, the extent of plating in the smoother Nalgene beaker is not a strong function of R between the range of 3 to 30. Plating even decreases slightly in the smooth Nalgene beaker at small values of R.

It is likely that the plating on a less-smooth surface starts when newly formed nuclei are trapped on the rough surface (viewing from nuclei). More nuclei are formed at a smaller R, and more are trapped, hence more severe plating. On the other hand, it is difficult to trap nuclei and particles on a smooth surface. As excess oxalic acid increases (i.e. smaller R), the nucleation becomes the predominant step, which not only produces a large amount of fines, but also depleted cerium and oxalate rapidly. Because fewer particles are trapped on the smooth surface and because the supernatant condition no longer favors crystal growth, less plating is observed. At a larger R (i.e. lower supersaturation), nucleation rate reduces, fewer nuclei are produced, and a pro-growth environment is established because more nutrients are available. When the rate of deposition surpasses the rate of growth, more plated material will be seen. This probably explains why more plating is observed on a smooth surface at smaller values of R. In the plant large-scale precipitators, plating is sometimes caused by poor slurry suspension. Settling of large particles and inability to remove small particles from vessel surfaces have contributed significantly to the plating in large-scale slab precipitators.

PuF_3 (100X)

Pu Oxalate (100X)

CeF_3 (200X)

Ce Oxalate (100X)

FIGURE 6. SEM Pictures of Cerium, Plutonium Oxalates and Trifluoride

FIGURE 7. Extent of Cerium Oxalate Plating on Two Types Precipitator as a Function of $HNO_3/H_2C_2O_4$ Ratio (R)

Dissolution

Laboratory experiments showed that cerium oxalate dissolved easily in moderate (6-8M) and higher concentrations of nitric acid. Dissolution was much faster when the samples were heated to 50°C. Observations from this dissolution study are summarized in Table 6. Crystallization was observed in the 6M nitric acid solution after it was diluted with 10 mL distilled water and cooled overnight. Lower solubility at a lower temperature probably caused the recrystallization. The plant used 8M nitric acid during cleanout runs of new "C" and "D" precipitators and encountered no problems.

CONCLUSION

Switching from CeF_3 to cerium oxalate during the functional checkout of the new "D" precipitator proved to be very successful. Particle size and plating similar to the PuF_3 process were achieved. The filtration time was reduced to 15-25 minutes, which was far shorter than the 4-8 hours with CeF_3 . In addition, cerium oxalate in the system was flushed out easily and quickly with warm nitric acid. With CeF_3 , hot ANN ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 4M nitric acid was required and usually took more than 6 hours to dissolve the plated CeF_3 . A valid evaluation of the mixing and suspension capabilities of the new "D" precipitator was accomplished because of the similar particle size and settling velocity between PuF_3 and CeOX . Fast filtration and rapid removal of the CeOX also enabled the testing program to be kept on schedule. Overall, cerium oxalate was a better stand-in than the CeF_3 for the simulation of PuF_3 precipitation.

The measurement of fundamental properties of the cerium nitrate - nitric acid - oxalic acid system has allowed a better understanding of precipitation mechanisms and characteristics. A different approach, which utilizes kinetics data to optimize or predict precipitator performance (i.e. using simulation programs instead of performing full-scale experiments), is then possible.

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TABLE 6

**Dissolution of 1.5 grams Cerium Oxalate in 20 mL
Nitric Acid Solution**

Acid Conc.	Dissolution Time and Observation	
	22°C	50°C
3 M	solids remain after 30 min	solids remain after 30 min
6 M	solids remain after 30 min	90 seconds*
8 M	4 minutes	60 seconds**
12 M	3 minutes	30 seconds
16 M	2 minutes	10 seconds with large amount of NO _x gas evolved

* reprecipitation occurred after diluting (10 mL H₂O) and cooling

** no reprecipitation observed after diluting and cooling

NOMENCLATURE

- B = nucleation rate (#/vol/min)
 b = power law coefficient for nucleation rate equation
 C = solution concentration (M)
 C_{eq} = equilibrium concentration (M)
 C_1, C_2 = characteristic constants
 C_3 = constant
 G = crystal growth rate (micron/min)
 g = power law coefficient for growth rate equation
 K_1 = first dissociation constant of oxalic acid
 K_2 = second dissociation constant of oxalic acid
 K_b, K_g = characteristic parameter
 K_{sp} = solubility product constant of cerium oxalate
 M_{Ce} = molecular weight of cerium (g/mole)
 N = concentration of crystals smaller than x (#/vol)
 n = population density of crystals of size x (#/vol/micron)
 R = $HNO_3/H_2C_2O_4$ Ratio
 r = activity coefficient
 S = supersaturation ratio (C/C_{eq})
 T = absolute temperature ($^{\circ}K$)
 t = average residence time (min)
 x = characteristic crystal size (micron)
- $[Ce^{+3}]$ = cerium concentration in the filtrate (mg/liter)
 $[H^+]$ = total acid in the filtrate (M)
 $[OX]$ = total oxalate concentration in the filtrate (M)

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