Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Kyser, E. A.(2001) 'EXTRACTION OF PLUTONIUM INTO 30% TRIBUTYL PHOSPHATE FROM NITRIC ACID SOLUTIONS CONTAINING FLUORIDE, ALUMINUM, AND BORON', Separation Science and Technology, 36: 5, 729 — 741

To link to this Article: DOI: 10.1081/SS-100103617

URL: http://dx.doi.org/10.1081/SS-100103617

SEPARATION SCIENCE AND TECHNOLOGY, 36(5&6), 729–741 (2001)

EXTRACTION OF PLUTONIUM INTO 30% TRIBUTYL PHOSPHATE FROM NITRIC ACID SOLUTIONS CONTAINING FLUORIDE, ALUMINUM, AND BORON

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ABSTRACT

The processing of residues left over from the passing of the Cold War presents new challenges. Solvent extraction processing of high-fluoride-content plutonium residues requires some adjustments in order to prevent high losses of plutonium to the waste stream. Process solutions have a fluoride:plutonium ratio of up to 300:1 and contain up to 0.35 M total fluoride in nitric acid solution. Either complexing the fluoride with aluminum or increasing the total nitrate in the feed stream will increase the plutonium extraction into tributyl phosphate (TBP). The favored option was to perform minimal dilution of the dissolver solution to keep the concentrations of nitrate and plutonium high and to add sufficient aluminum nitrate to give acceptable plutonium extraction. This approach minimizes additional waste generation from aluminum salts. Determination of acceptable process chemistry conditions required a better understanding of the competition between fluoride and nitrate for the complexation of plutonium in a nitric acid solution. The actual solution matrix contained large amounts of Ca, F,

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H_3BO_3, Fe, Mg, and Al, with a small amount of plutonium, the extraction of which is a function of the aluminum and total nitrate concentrations. In this work, experimental batch data were obtained for the extraction of plutonium into 30 vol % TBP at ambient temperature from such a solution matrix and these data were modeled using complexation constants from the literature. Modeling shows the effects of the boric acid and aluminum on the free fluoride concentration and the resulting impact on the extraction of plutonium into TBP.

BACKGROUND

In earlier work, modifications to the flowsheet for the dissolution of sand, slag, and crucible (SSC) residue in a nitric acid/boric acid solution in a canyon dissolver were developed (1,2). SSC residue consists principally of CaF_2 and MgO, with lesser amounts of CaO, Ca metal, Pu metal, PuF_4, and PuO_2. Boric acid had been added to the dissolution flowsheet as a neutron poison to increase the mass of PuO_2 solids in the dissolver that would be safe for analyzed criticality scenarios. The flowsheet was modified after the recognition that the high levels of boric acid had a significant complexation effect on the free fluoride in the solution. This caused a reduction in the rate of PuO_2 dissolution as well as a dramatic increase in the rate of CaF_2 dissolution. The latter allowed elimination of the aluminum nitrate that had been necessary for the dissolution of slag (primarily composed of CaF_2). The corrosion rate of boric acid-calcium fluoride-nitric acid solution on stainless steel was found to be sufficiently low to eliminate the need for aluminum complexation in waste processing as long as nitric acid recovery was not performed. Due to the high F:Pu ratio in the dissolver solution and the removal of aluminum from the flowsheet, the potential exists for PuF_x complexes to interfere with the Pu extraction into TBP solvent. Investigation of these issues was the thrust of the work described in this paper.

Other SRS separations processing experiences are relevant to the current chemistry. The traditional processing of SSC involved HNO_3 dissolution with large amounts of aluminum nitrate to complex the fluoride. Boric acid was not needed because all of the steps were performed in geometrically favorable equipment. In this process problems were encountered with solid residues left in the dissolver due to solubility limitations. The solution was processed through anion exchange to recover the Pu from the large amounts of Al, Ca, and F present. At 8 M HNO_3 and with a minimum of 1.5 moles of Al per mole of F, Pu was recovered on anion exchange resin as an anionic nitrate complex. The combination of high HNO_3 and aluminum complexation of fluoride allowed the Pu to be separated from the fluoride. Both Pu-Al alloys (known as Scrub Alloy) and Pu metal have been recovered via canyon dissolution followed by solvent extraction and have some similarities to the current SSC recovery process. However, the relative amounts of Pu, F, Al, and B in the dissolver solution from those campaigns were quite different from the amounts in the SSC solutions currently under investigation.

EXPERIMENTAL METHODS

Distribution coefficients were determined in a batch extraction test. A solution was prepared by dissolving boric acid, ferric nitrate, calcium fluoride, concentrated HNO_3, deionized water, and/or 0.1M HNO_3 either by pipeting solutions or by weighing reagents on an analytical balance. After this solution was introduced into the glove box, a well-characterized solution of plutonium(IV) nitrate in nitric acid was pipeted into the solution matrix to obtain the desired plutonium and nitrate concentrations to simulate the dissolver solution. 3 milliliters of the dissolver solution was then pipeted into a previously prepared vial containing weighed amounts of aluminum nitrate nonahydrate (ANN) dissolved in 0.1 M HNO_3 to obtain the desired Pu, NO_3, and Al:F conditions. 2 milliliters of each vial was then pipeted into 2 milliliters of 30 % TBP solvent in a 15-milliliters glass or plastic centrifuge tube. These solutions were vortex-mixed for 1 min and centrifuged for 2 min and each phase was sampled for analyses by liquid scintillation counting (LSC), gamma-scan, and/or total acid/free acid methods. These analyses allowed the distribution coefficients ($D_{o/a}$) to be calculated for Pu, Am, and/or free acid between the phases. Gamma-scan results for ^{241}Am were used to correct the LSC alpha results. Often, the ^{241}Am was estimated from similar tests rather than measured because the activity of ^{241}Am was only a small fraction of the total alpha activity.

RESULTS AND DISCUSSION

Based on the low values for the Pu $D_{o/a}$ that were observed in the initial experiments, it was apparent that a chemical change was needed to significantly increase the Pu extraction. Three options were considered: dilution of the fluoride, aluminum complexation of the fluoride ion, or nitrate salting. Dilution was deemed undesirable, as the Pu concentration from the dissolution process was already undesirably low. Addition of Al as a solution of 60% ANN to an Al:F molar ratio of 3 to 4 would both dilute the solution and contribute to the generation of significant additional high-level waste. Since the dissolver solution was already at greater than 9 M HNO_3, operating the solvent extraction cycle at a higher-than-normal total nitrate had the potential to both keep the Pu concentration high and significantly improve the Pu extraction. A series of batch extraction tests was performed to investigate the effects of Al:F ratio and total nitrate on this extraction.

Generally the B concentration (from boric acid) was in the range of 0.1 to 0.15 M as that was the level expected during processing. Results from those tests are illustrated in Fig. 1. A more complete listing of the conditions and results is included in the appendix and in reference (3). The data show the effect of Al:F ratio and $[NO_3^-]_{total}$ on the Pu $D_{o/a}$ in nitric acid solutions with B, Ca, and Fe present in solution. As expected, Pu extraction is enhanced by the increase in Al:F ratio as well as the increase in $[NO_3^-]_{total}$. This is most likely due to shifts in the complexation of Pu-F and Pu-NO_3. Complexation of F^- by Al and B reduces the fluoride available to complex Pu; however, B is much less effective at complexing F^- than Al. Nitrate has a significant effect on the Pu $D_{o/a}$ as it is increased from 4 to 7 M where it appears to level off.

Based on complexation constants obtained in the literature (4,5,6), Pu is by far the best F^- complexant present ($\log K_1 = 6.77$) in these solutions. Aluminum is not as strong a complexant ($\log K_1 = 3.2$); however, with Al/Pu > 100 and having the capacity to complex three F^- ions in significant amounts, it effectively makes the F^- unavailable for Pu complexation. B is only a fair F^- complexation agent ($\log K_1 = 1.4$). Although B can complex up to four F^- ions, the presence of

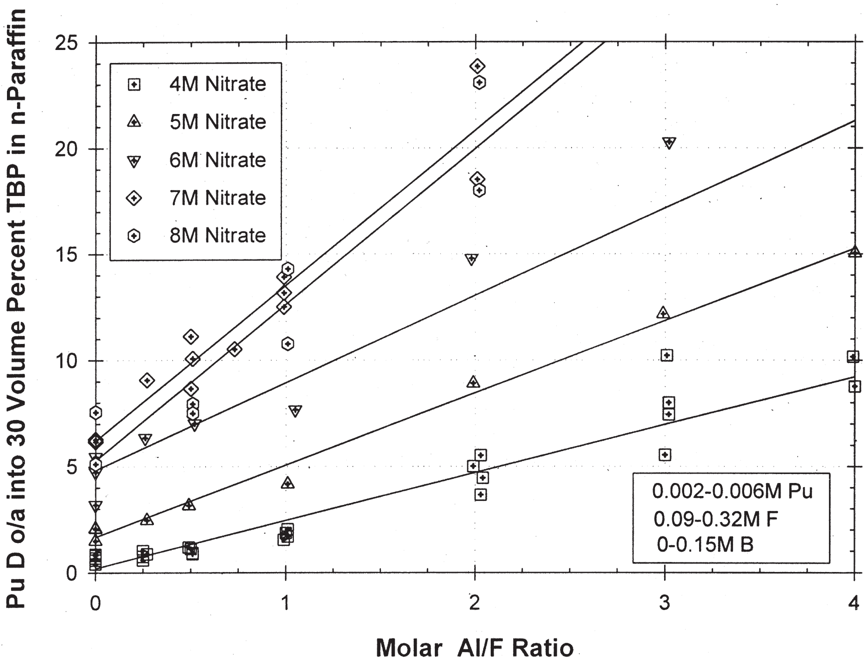

Figure 1. Effects of nitrate concentration and Al/F molar ratio on plutonium extraction.

Table 1. Complexation Equations and Equilibrium Constants

	Log K_n	Reference	Equation
$H^+ + F^- = HF$	log K_1=3.08	(4)	(1)
$HF + F^- = HF_2^-$	log K_2=0.65	(4)	(2)
$B(OH)_3 + nHF = H^+ + H_{3+n}BO_3F_{n;\ n=0,4}$	log K_1=1.38	(4)	(3)
	log K_2=2.41		
	log K_3=5.96		
	log K_4=8.11		
$Al^{3+} + nHF^- = AlF_n^{3-n} {}_+ nH^+;\ {}_{n=0,6}$	log K_1=3.21	(4)	(4)
	log K_2=5.37		
	log K_3=6.38		
	log K_4=6.09		
	log K_5=4.59		
	log K_6=1.81		
$Pu^{4+} + nF^- = Pu(F)_n^{4-n};\ {}_{n=0,2}$	log K_1=6.77	(5)	(5)
	log K_2=7		
$Pu^{4+} + nNO_3^- = Pu(NO_3)_n^{4-n};\ {}_{n=0,3}$	log K_1=0.97	(6)	(6)
	log K_2=0.46		
	log K_3=-1.82		

Al effectively limits it to only one. Plutonium nitrate complexes are not as strong as any of the F^- complexes mentioned (log K_1 = 0.97); however, with 4 to 6 M total nitrate present, mass action contributes to significant Pu nitrate complex formation. To better understand these competing effects, a model was developed based on complexation constants reported in the literature. The values used are shown in Table 1. Calculations of Pu, F, Al, and B in nitric acid solutions have been performed in an attempt to quantify these effects. They are summarized in Table 2. Increasing either the total nitrate concentration or the Al:F ratio will serve to shift Pu complexation in favor of nitrate complexes. This favors the extraction

Table 2. Relative Effects of NO_3, B, and Al on Pu-F and Pu-NO_3 Complexation

Species	Concentration (M)									
Pu, total	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
F, total	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Al, total	0	0	0.25	0.25	1.00	0	0	0.25	0.25	1.00
B, total	0.00	0.25	0	0.25	0.25	0	0.25	0	0.25	0.25
NO_3, total	4.00	4.00	4.00	4.00	4.00	6.00	6.00	6.00	6.00	6.00
PuF/ (Pu total)	0.839	0.580	0.120	0.095	0.014	0.730	0.412	0.082	0.062	0.009

of Pu into TBP. The only extractable species is believed to be $Pu(NO_3)_4$. Therefore the formation of multiple Pu-nitrate complexes favors extraction. The mechanism is the conversion of other complexes to the neutral species as the neutral species is consumed from the aqueous phase by extraction with TBP. These calculations show that Al is significantly more effective than B as a fluoride complexant based on its effect on the Pu $D_{o/a}$. By comparison, increasing the total nitrate concentration from 4 M to 6 M has less effect on the Pu $D_{o/a}$.

The effect of temperature on the complexation equilibria was briefly investigated by using the constants available for F, B, and Al complexation (8). No information was found concerning the effect of temperature on Pu complexation with F^- or NO_3^-. Calculations with F, B, and Al complexation showed a 10% increase in the free F^- as the temperature was increased from 25 to 55°C. The increase in free F^- is estimated to cause a corresponding increase in PuF_x^{4-x} complex formation and a resulting reduction in the Pu $D_{o/a}$. This may be offset by the general trend of $D_{o/a}$ for Pu to increase with temperature. A limited experimental investigation at 7 and 8 M total nitrate showed no significant effect of temperature on the Pu $D_{o/a}$ for Al:F ratios of 0 to 2. Those results are plotted in Fig. 2.

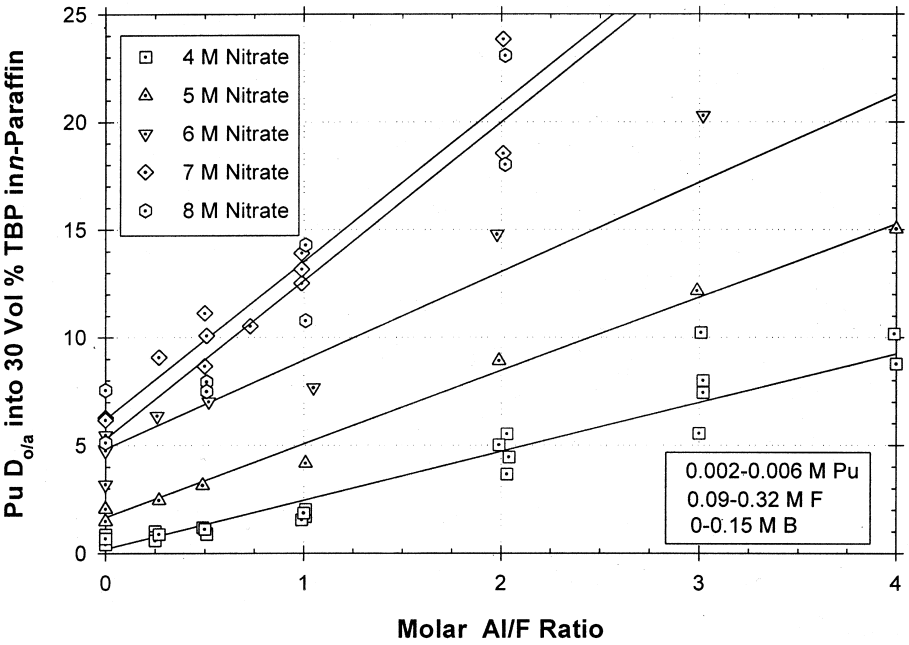

Figure 2. Effects of temperature, nitrate, and Al/F on plutonium extraction.

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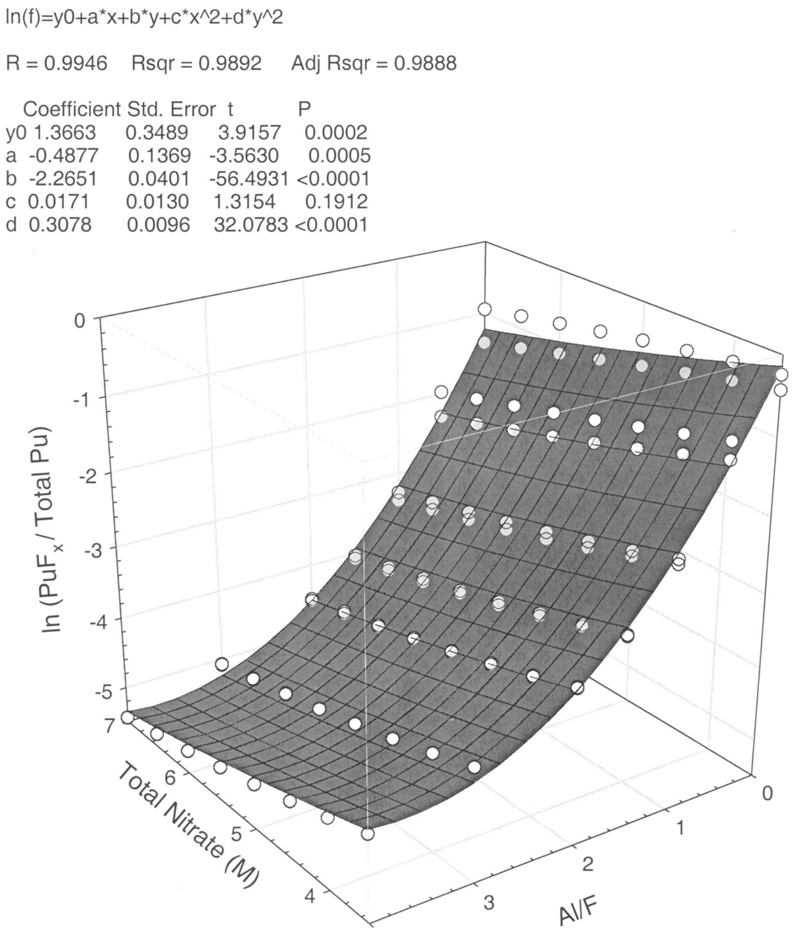

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ln(f)=y0+a*x+b*y+c*x^2+d*y^2

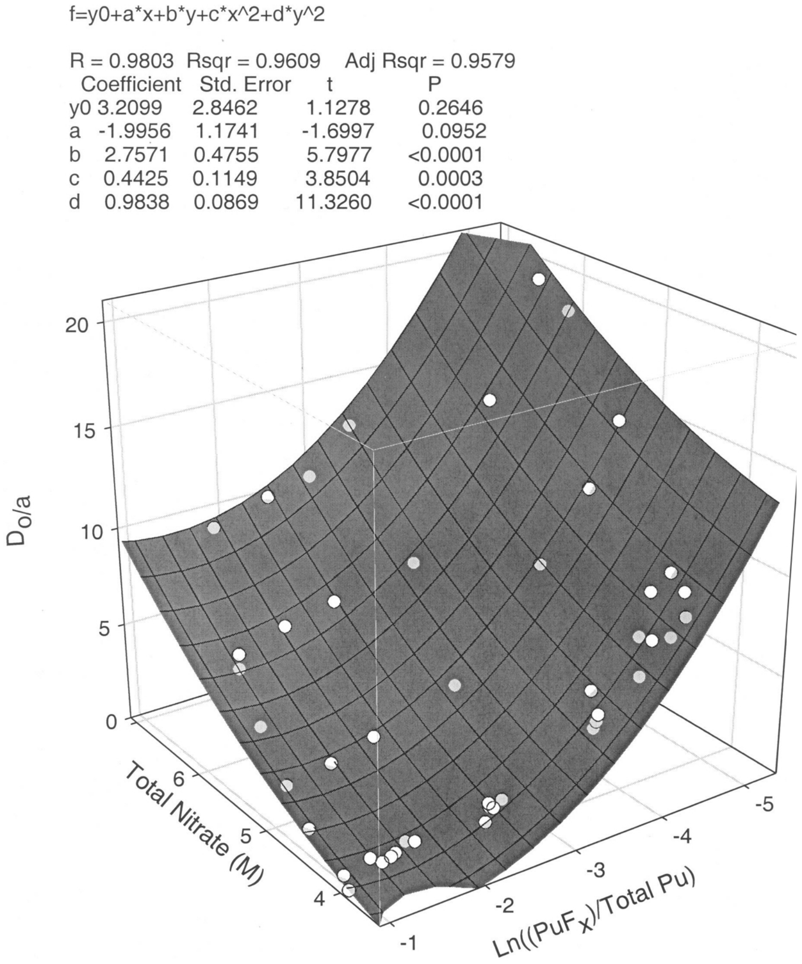
R = 0.9946    Rsqr = 0.9892    Adj Rsqr = 0.9888

   Coefficient Std. Error  t          P
y0 1.3663      0.3489      3.9157     0.0002
a  -0.4877     0.1369      -3.5630    0.0005
b  -2.2651     0.0401      -56.4931   <0.0001
c  0.0171      0.0130      1.3154     0.1912
d  0.3078      0.0096      32.0783    <0.0001
```

Figure 3. Fit of Ln(PuFx/Total Pu) ratio to nitrate concentration and Al/F ratio.

CORRELATION AND MODELING OF THE DATA

After examination of various alternatives, the choice was made to empirically correlate Pu $D_{o/a}$ as a function of $[NO_3]$ and $\ln\{[PuF^{3+}]/[Pu]_t\}$. This form has a variable to reflect salting effects and another that reflects fluoride complexation effects. The computation of the complexation becomes rather complicated in itself, making it convenient to curve-fit $\ln\{[PuF^{3+}]/[Pu]_t\}$as a function of $[NO_3]$ and $[[Al]/[F]$ for various values of [F]. Figure 3 shows the results of the calculation of Pu complexation for 0.1 and 0.2 M [F] plotted against $[NO_3]$ and [Al]/[F]. At low [Al]/[F] values, this calculation becomes a significant function of [F], making it necessary to provide a different fit for different levels of [F]. A 3D hyperbolic regression was performed in SigmaPlot 5.05™. A value for the Pu complexation variable was calculated for each measured $D_{o/a}$ datapoint of this study, taking into account the F, Al, B, NO_3, and Pu concentrations in the aqueous phase prior to extraction. Fig. 4 shows this data plotted against $[NO_3]$ and $\ln\{[PuF^{3+}]/[Pu]_t\}$ and another 3D hyperbolic surface fit through the data. This approach allows a relatively simple calculation of the Pu $D_{o/a}$. By appropriate rear-



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f=y0+a*x+b*y+c*x^2+d*y^2

R = 0.9803  Rsqr = 0.9609   Adj Rsqr = 0.9579
  Coefficient  Std. Error    t            P
y0 3.2099     2.8462       1.1278      0.2646
a   -1.9956   1.1741      -1.6997      0.0952
b   2.7571    0.4755       5.7977     <0.0001
c   0.4425    0.1149       3.8504      0.0003
d   0.9838    0.0869      11.3260     <0.0001
```

Figure 4. Fit of $D_{o/a}$ to $\ln(PuF_x/\text{Total Pu})$ and total nitrate.

rangement of the equations from these curve fits, an equation relating the minimum [Al] for a given range of [F] that will result in a minimum Pu $D_{o/a}$ can be written.

SOURCES OF ERROR AND UNCERTAINTY

Calculational and experimental uncertainties were constantly evaluated during the course of this work to minimize the effect on the most important results.

The literature values for complexation constants that were chosen for modeling the extraction behavior of Pu in this system were determined by variety of methods and are expected to be an imperfect representation of the chemical behavior of this multicomponent system. Insufficient data exist to perform a comprehensive evaluation of the effects of the uncertainties in these constants on the actual concentration of Pu species in the solutions of interest. Success of the modeling can be judged by the ability of the model to show the effect of chemical components in this complicated solution matrix on the Pu $D_{o/a}$.

A sample dilution error of less than 5 % would be expected due to the accuracy of the pipets. However, technician error on an individual dilution sometimes results in much larger discrepancies. (Such discrepancies probably occur more often with radioactive samples due to awkward working conditions.) Obviously inconsistent data points in the LSC analyses were routinely reanalyzed, and when necessary, the test was repeated until a Pu alpha value was obtained that appeared to be consistent with the other data points. Organic samples were found to be somewhat more difficult to pipet accurately, based on the number of samples where inconsistencies were observed. Counting errors were generally minor contributors to the total analytical uncertainty.

The wet-chemistry methods of free acid and fluoride by ion-selective electrode (ISE) were used only to a limited degree. The complex solution matrix had earlier been shown to cause a low bias in the fluoride by ISE method (2). The ability of the free acid method to handle the complex solution matrix was not validated and thus was not relied on heavily in this work. Most solutions were prepared gravimetrically based on estimated densities of the final solutions. The densities these solutions were determined primarily by the nitric acid and $Al(NO_3)_3$ concentrations, and the uncertainty in an estimated density was probably only about 1%.

All experimental work was performed at ambient conditions which ranged from 22 to 27°C, whereas the plant process will run at 40 to 50°C. Studies reported in the literature indicated that the free F^- should increase slightly (4) (which should reduce the Pu $D_{o/a}$), while the general trend would be for a small increase in the Pu $D_{o/a}$ (6). Overall, the temperature was found to have only a small influence on the Pu $D_{o/a}$ based on the limited data taken at high nitrate concentrations.

Table 3. Raw Data and Calculated Results

Sample ID	F (M)	B (M)	Al (M)	Pu (mM)	NO_3^- (M)	Fe (M)	Ca (M)	D O/A	ln(PuF/Pu(t))
Pu108A	0.1618	0.065	0.0000	2.7	3.92	0.01	0.08	0.22	−0.38
Pu108B	0.0809	0.065	0.0000	2.7	3.92	0.01	0.04	0.38	−0.72
Pu108C	0.0162	0.065	0.0000	2.7	3.92	0.01	0.01	1.26	−2.08
Pu108D	0.0173	0.000	0.0000	2.9	4.18	0.01	0.01	0.59	−1.36
Pu110A	0.1075	0.085	0.0000	3.8	4.01	0.02	0.05	0.80	−0.65
Pu110B	0.1060	0.084	0.0268	3.7	4.04	0.02	0.05	1.02	−1.01
Pu110C	0.1032	0.081	0.0504	3.6	4.01	0.02	0.05	1.19	−1.45
Pu110D	0.0991	0.078	0.1004	3.5	4.01	0.02	0.05	1.69	−2.39
Pu110E	0.0920	0.073	0.1863	3.2	4.01	0.01	0.05	3.66	−3.42
Pu110F	0.0858	0.068	0.2576	3.0	3.99	0.01	0.04	5.54	−3.94
Pu110G	0.0804	0.063	0.3227	2.8	3.99	0.01	0.04	7.00	−4.29
Pu111A	0.1478	0.068	0.0000	3.8	4.01	0.02	0.07	0.58	−0.43
Pu111B	0.1438	0.066	0.0365	3.7	4.02	0.02	0.07	0.75	−0.75
Pu111C	0.1399	0.064	0.0711	3.6	4.02	0.02	0.07	0.92	−1.26
Pu111D	0.1328	0.061	0.1316	3.4	4.01	0.02	0.07	1.54	−2.26
Pu111E	0.1206	0.055	0.2451	3.1	4.03	0.01	0.06	5.52	−3.41
Pu111F	0.1105	0.051	0.3339	2.8	4.03	0.01	0.06	7.43	−3.94
Pu111G	0.1019	0.047	0.4063	2.6	4.02	0.01	0.05	10.16	−4.28
Pu112A	0.1075	0.000	0.0000	3.8	4.01	0.02	0.05	0.40	−0.36
Pu112B	0.1056	0.000	0.0268	3.7	4.02	0.02	0.05	0.58	−0.61
Pu112C	0.1023	0.000	0.0526	3.6	3.98	0.02	0.05	0.87	−1.09
Pu112D	0.0975	0.000	0.0989	3.4	3.95	0.02	0.05	2.03	−2.20
Pu112E	0.0893	0.000	0.1821	3.1	3.89	0.01	0.04	4.45	−3.35
Pu112F	0.0823	0.000	0.2481	2.9	3.84	0.01	0.04	10.22	−3.87
Pu112G	0.0763	0.000	0.3111	2.7	3.81	0.01	0.04	9.79	−4.24
Pu113A	0.0661	0.052	0.0000	2.3	2.50	0.01	0.03	0.22	−0.40
Pu113B	0.0799	0.063	0.0000	2.8	2.99	0.01	0.04	0.34	−0.49
Pu113C	0.1080	0.085	0.0000	3.8	4.01	0.02	0.05	0.86	−0.65
Pu113D	0.1217	0.096	0.0000	4.2	4.51	0.02	0.06	1.48	−0.71
Pu113E	0.1345	0.106	0.0000	4.7	4.97	0.02	0.07	2.07	−0.77
Pu113F	0.1504	0.119	0.0000	5.2	5.55	0.02	0.08	3.19	−0.84
Pu113G	0.1632	0.129	0.0000	5.7	6.01	0.03	0.08	4.75	−0.88
Pu114A	0.1345	0.106	0.0000	4.7	4.97	0.02	0.07	2.05	−0.77
Pu114B	0.1315	0.104	0.0358	4.6	4.97	0.02	0.07	2.45	−1.21
Pu114C	0.1286	0.101	0.0635	4.5	4.95	0.02	0.06	3.15	−1.65
Pu114D	0.1252	0.099	0.1268	4.4	5.01	0.02	0.06	4.17	−2.63
Pu114E	0.1171	0.092	0.2333	4.1	5.04	0.02	0.06	8.91	−3.64
Pu114F	0.1084	0.085	0.3243	3.8	5.00	0.02	0.05	12.17	−4.17

Table 3. Continued

Sample ID	F (M)	B (M)	Al (M)	Pu (mM)	NO_3^- (M)	Fe (M)	Ca (M)	D O/A	ln(PuF/Pu(t))
Pu114G	0.1023	0.081	0.4094	3.6	5.03	0.02	0.05	15.03	−4.53
Pu115A	0.1632	0.129	0.0000	5.7	6.01	0.03	0.08	5.46	−0.88
Pu115B	0.1587	0.125	0.0420	5.5	5.97	0.03	0.08	6.35	−1.33
Pu115C	0.1545	0.122	0.0798	5.4	5.93	0.02	0.08	7.01	−1.86
Pu115D	0.1495	0.118	0.1563	5.2	5.98	0.02	0.07	7.66	−2.84
Pu115E	0.1408	0.111	0.2794	4.9	6.03	0.02	0.07	14.78	−3.80
Pu115F	0.1305	0.103	0.3944	4.5	6.01	0.02	0.07	20.28	−4.35
Pu115G	0.1217	0.096	0.4883	4.2	5.97	0.02	0.06	18.48	−4.69
Pu116A	0.2703	0.151	0.0000	6.7	7.05	0.03	0.14	0.98	−0.72
Pu116B	0.2608	0.145	0.0697	6.4	7.01	0.03	0.13	9.07	−1.16
Pu116C	0.2521	0.140	0.1294	6.2	6.96	0.03	0.13	10.07	−1.76
Pu116D	0.2470	0.138	0.1794	6.1	6.98	0.03	0.12	10.52	−2.26
Pu116E	0.2417	0.135	0.2399	6.0	7.03	0.03	0.12	12.51	−2.79
Pu118A	0.1623	0.065	0.0000	0.3	4.00	0.02	0.08	0.68	−0.38
Pu118B	0.1564	0.063	0.0416	0.3	3.98	0.02	0.08	0.87	−0.69
Pu118C	0.1509	0.061	0.0757	0.3	3.95	0.02	0.08	1.11	−1.17
Pu118D	0.1410	0.057	0.1411	0.3	3.91	0.02	0.07	1.86	−2.23
Pu118E	0.1247	0.050	0.2483	0.3	3.84	0.01	0.06	5.01	−3.32
Pu118F	0.1116	0.045	0.3367	0.2	3.79	0.01	0.06	7.99	−3.87
Pu118G	0.1011	0.041	0.4049	0.2	3.74	0.01	0.05	8.77	−4.21
Pu119A	0.2810	0.114	0.0000	2.9	7.00	0.03	0.1	6.27	−0.61
Pu119B	0.2647	0.107	0.1316	2.7	6.99	0.03	0.1	8.66	−1.58
Pu119C	0.2499	0.101	0.2486	2.6	6.98	0.03	0.1	13.17	−2.73
Pu119D	0.2256	0.091	0.4529	2.3	6.99	0.02	0.1	18.52	−3.89
Pu119AH	0.2810	0.114	0.0000	2.9	7.00	0.03	0.1	6.16	−0.70
Pu119BH	0.2647	0.107	0.1316	2.7	6.99	0.03	0.1	11.12	−1.56
Pu119CH	0.2499	0.101	0.2486	2.6	6.98	0.03	0.1	13.91	−2.79
Pu119DH	0.2256	0.091	0.4529	2.3	6.99	0.02	0.1	23.83	−4.01
Pu120A	0.3218	0.130	0.0000	3.3	8.00	0.03	0.0	7.55	−0.63
Pu120B	0.3031	0.123	0.1558	3.1	8.01	0.03	0.0	7.93	−1.69
Pu120C	0.2865	0.116	0.2888	2.9	8.00	0.03	0.0	14.29	−2.83
Pu120D	0.2585	0.105	0.5213	2.6	8.01	0.03	0.0	23.07	−3.96
Pu120AH	0.3218	0.130	0.0000	3.3	8.00	0.03	0.0	5.12	−0.73
Pu120BH	0.3031	0.123	0.1558	3.1	8.01	0.03	0.0	7.49	−1.64
Pu120CH	0.2865	0.116	0.2888	2.9	8.00	0.03	0.0	10.77	−2.88
Pu120DH	0.2585	0.105	0.5213	2.6	8.01	0.03	0.0	18.00	−4.09
Pu121A	0.0113	0	0	2.2	3.46	0.01	0.0	1.57	−1.42
Pu121B	0.0113	0	0	2.2	4.23	0.01	0.0	1.12	−1.70
Pu121C	0.0113	0	0	2.2	5.27	0.01	0.0	5.81	−2.01

(continued)

Table 3. Continued

Sample ID	F (M)	B (M)	Al (M)	Pu (mM)	NO_3^- (M)	Fe (M)	Ca (M)	D O/A	ln(PuF/Pu(t))
Pu121D	0.0113	0	0	2.2	6.30	0.01	0.0	10.41	−2.22
Pu121E	0.0113	0	0	2.2	7.33	0.01	0.0	16.19	−2.37
Pu122A	0.0113	0	0	2.2	3.46	0.01	0.0	1.58	−1.42
Pu122B	0.0113	0	0.0059	2.2	3.50	0.01	0.0	2.06	−2.00
Pu122C	0.0113	0	0.0110	2.2	3.51	0.01	0.0	2.58	−2.52
Pu122D	0.0113	0	0.0211	2.2	3.54	0.01	0.0	3.44	−3.28
Pu122E	0.0113	0	0.0425	2.2	3.59	0.01	0.0	5.94	−4.13
Pu123A	0.0000	0	0	2.3	3.49	0	0	15.41	−6.91
Pu123B	0.0006	0	0	2.3	3.49	0	0	7.04	−4.19
Pu123C	0.0011	0	0	2.3	3.49	0	0	5.08	−3.55
Pu123D	0.0032	0	0	2.3	3.49	0	0	2.78	−2.51
Pu123E	0.0053	0	0	2.3	3.48	0	0	2.03	−2.05
Pu123F	0.0106	0	0	2.3	3.48	0	0	0.81	−1.47
Pu124A	0.0005	0	0.0003	2.3	3.49	0	0	7.71	−4.37
Pu124B	0.0010	0	0.0005	2.3	3.49	0	0	7.22	−3.78
Pu124C	0.0031	0	0.0016	2.3	3.49	0	0	4.04	−2.90
Pu124D	0.0051	0	0.0026	2.3	3.50	0	0	2.81	−2.53
Pu124E	0.0102	0	0.0052	2.3	3.50	0	0	1.72	−2.07
Pu125A	0.0005	0	0.0005	2.3	3.50	0	0	6.39	−4.45
Pu125B	0.0011	0	0.0010	2.3	3.50	0	0	6.10	−3.90
Pu125C	0.0032	0	0.0031	2.3	3.51	0	0	3.92	−3.16
Pu125D	0.0053	0	0.0051	2.3	3.51	0	0	2.89	−2.88
Pu125E	0.0106	0	0.0103	2.3	3.52	0	0	2.43	−2.56

Cross-contamination of the samples was generally not believed to be a significant problem. This type of problem was most likely to affect results in cases where there was a large difference between the alpha activities of samples that were physically nearby and the lower concentration sample was contaminated. Such a problem would have had the greatest impact on samples with large $D_{o/a}$'s and would have decreased the measured Pu $D_{o/a}$. Modest inconsistencies (20 to 30%) were observed between some data values that could have been due to this or minor sample dilution errors. The number of data points taken reduces the impact of 20 to 30 % errors that may have occurred due to an isolated data point.

CONCLUSIONS

Batch distribution data with 30 vol % TBP have been obtained in complicated mixtures of F, Al, B, NO_3 and Pu that define conditions for acceptable solvent extraction operation. Correlation of these data by utilizing existing complexation data from the literature provides a means of estimating Pu extraction behavior in mixtures outside the range of conditions measured in this study.

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