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THE CHELATE PROCESS I

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CHEMISTRY — SEPARATION PROCESSES FOR
PLUTONIUM AND URANIUM

University of California

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THE CHELATE PROCESS I

Price \$ 0.40

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Washington 25, D. C.

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THE CHELATE PROCESS I

ABSTRACT

The chelate process for the extraction and decontamination of plutonium has been investigated. The process is designed as an alternate process for the Hanford type operation.

The basic chemical factors have been studied and two flowsheets have been developed and tested for recovery of plutonium. An overall yield of plutonium in excess of 99% is reported for one flowsheet using benzene as the organic solvent and 98.5% when toluene was substituted for benzene. The general factors involved in establishing all details of the flowsheets are thoroughly discussed and decontamination studies are indicated to complete the study in the present equipment. (auth)

1. Introduction

Processes using fluorinated diketones as extracting or chelating agents^{1,2,3} appear to be very promising for obtaining plutonium from uranium irradiated in the pile. Such processes are in several important respects potentially superior to other solvent schemes.

1. Objectives and Present Status of the Method. The objectives of this process are much the same as for other solvent extraction schemes. They include the following: (1) recovery of plutonium in high yield, (2) decontamination of plutonium from fission products, (3) separation of plutonium from uranium, (4) concentration and isolation of uranium in a high degree of purity, (5) recovery and partial separation of biproducts, and (6) economical operation compared to existing processes. Of these objectives the recovery of plutonium has been adequately demonstrated. There is experimental evidence indicating that the decontamination will be sufficient. Recovery of Plutonium and its quantitative separation from uranium have been established. The cost of running the process is probably lower than that of any of the existing alternate processes. The other objectives have not been unequivocally proved; however, the present experimental evidence indicates that they may be attained. This report contains virtually all of the pertinent experimental data relating to the chelate process and summarizes the basic chemical factors involved.

2. Theory of the Process. Various substituted fluorinated 1-3 diketones are capable of forming unionized chelate compounds with metallic ions. Due to a high acid dependence of the extraction of these chelate compounds into non-polar solvents, great selectivity can be obtained for various ions. There are only a few aqueous ions which extract to an appreciable extent from 0.5 M nitric acid. Those now known are Pu(IV), Zr(IV), Np(IV)⁴, Ce(IV), U(IV), Fe(III), and Sn(IV). Among those ions showing very little tendency to extract with these diketones are the ions of the alkali elements, the alkaline earth elements, and the rare earth elements with the exception of Ce(IV). The following ions are also known to be included in the non-extracting group from 0.5M nitric acid: Pu(III), Pu(VI), Pu(V), UO₂⁺⁺, Sn(II), Ni(II), Co(II), Cr(III), Th(IV), Fe(II), Al(III), Bi(III), Np(V)⁴, and Cb(V)⁵.

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The chelate compounds are neutral molecules containing as many diketone groups as the metal ion has positive charges, each diketone having two bonds to the central metallic atom. The fraction of the metallic ions in solution forming the chelate compound is a direct function of the diketone concentration and an inverse function of the acid concentration. The compounds are soluble in non-polar solvents immiscible with water. Benzene has proved to be the most suitable solvent to use with toluene as the best alternate. Under the proper conditions the aqueous ions which chelate well can be quantitatively extracted into the non-polar solvent phase.

The essence of the chelate method for processing plutonium from dissolver solutions lies in the fact that under proper conditions all of the Pu(IV) together with the fission product elements having extraction coefficients greater than that of Pu(IV) may be extracted into the non-polar solvent phase. Then a reextraction, again under proper conditions, should return the Pu(IV) to the aqueous phase leaving the fission product elements having extraction coefficients greater than that of Pu(IV) in the non-polar solvent phase. If the extraction coefficient of Pu(IV) is different enough from that of the ions of the fission products and UO_2^{++} ion, very good isolation and decontamination of plutonium could be achieved simply by varying the acidity of ketone concentration in the proper manner while performing the extraction and reextraction steps.

An alternate reextraction step may be carried out by selectively reducing the Pu(IV) chelate from the non-polar solvent phase to Pu(III), which shows very little tendency to extract, leaving the extractable fission products behind in the non-polar solvent phase. This offers the added attraction that a better separation of plutonium from the extractable fission products may be achieved due to the fact that the ratio of diketone concentration to acid concentration, which directly determines the extraction level of the fission products, may be maintained much higher when Pu(III) is to be separated from the extractable fission products as compared to Pu(IV).

A number of diketones have been prepared and their names, formulas and properties are listed in Table 1. The structural modifications affect the suitability of use of the diketones in two major respects from the viewpoint of the process economics. First, differences in extracting power determine the relative amounts of the various diketones to achieve a given extraction level. The ratio of the molal concentration of the diketones necessary to obtain the same extraction into benzene of Pu(IV) compared to TFA is: 1 for FTA, $\frac{1}{3}$ for PTA, $\frac{1}{6}$ for ITA, $\frac{1}{7}$ for BTA, FBTA, PBTA and NTA, and $\frac{1}{15}$ for TTA. The methylated diketones MTFA and MPTA do not extract Pu(IV) to any appreciable extent. Secondly, differences in the distribution coefficient of the various diketones between benzene and nitric acid determine the amount of diketone that dissolves in the aqueous layer. This distribution shows no dependence on nitric acid concentration or diketone concentration at low ionic strength or low diketone concentration. Corrections due to activity coefficients become important only in solutions more concentrated than those used in this process. It would be expected the distribution coefficients of the diketones have no dependence on the volume ratio. The problem of diketone recovery is greatly simplified when the distribution of diketone is highly in favor of the benzene.

The ketone that was chosen for use in developing the chelate process was TTA. It has the advantages of being the most economical considering the cost per unit extracting power for Pu(IV) and has a favorable distribution between benzene and nitric acid which allows nearly quantitative recovery of the TTA and leaves very little TTA in the final aqueous phase which contains the product plutonium. In general, all of the ketones are quite stable in acid solution. The dependence of the extraction coefficient, i.e. the concentration of plutonium in benzene divided by the concentration of plutonium in the acid phase has the following form,

$$E \text{ Pu(IV)} = \frac{k(\text{TTA})^4}{(\text{H}^+)^4} = \frac{(\text{Pu(IV)})_{\text{benzene}}}{(\text{Pu(IV)})_{\text{aqueous}}}$$

Thus, the extraction coefficient can be varied between wide limits with relatively small changes in concentration of diketone and acid because of high power dependence. The extraction coefficient

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TABLE 1

Properties of Fluorinated Diketones of the General Formula

Name	R ₁	R ₂	Code Name	Density	D $\frac{\text{Benzene}^*}{0.5\text{N HNO}_3}$	Melting or Boiling Point	Relative Molar Concentration to give same extraction level as TFA (~20)†	Preliminary Estimate of Materials Cost per Mole	Preliminary Estimate of Materials Cost Per Lb.
Acetyltrifluoroacetone	CH ₃	H	TFA	1.27	1.0	b.107°	1	\$0.71	\$2.08
Propionyltrifluoroacetone	CH ₃ CH ₂	H	PTA	1.22	9.0	b.123°	1/3	0.71	1.93
Isovaleryltrifluoroacetone	(CH ₃) ₂ CHCH ₂	H	ITA	1.33	~100	b.84°	1/5	0.71	1.54
Benzoyltrifluoroacetone	C ₆ H ₅	H	BTA	-	~100	m.40°	1/7	1.11	2.33
Thionyltrifluoroacetone	$ \begin{array}{c} \text{HC}-\text{CH} \\ \parallel \quad \diagup \\ \text{HC} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{S} \end{array} $	H	TTA	-	42	m.43°	1/15	1.45	2.97
P-Fluorobenzoyltrifluoroacetone	PF ₆ C ₆ H ₅ (F)	H	FBTA	-	~100	-	1/7	Greater than BTA	-
P-Phenylbenzoyltrifluoroacetone		H	PBTA	-	~100	-	1/7	Greater than BTA	-
Naphthoyltrifluoroacetone		H	NTA	-	~100	-	1/7	Greater than BTA	-
2-Furoyltrifluoroacetone	$ \begin{array}{c} \text{HC}-\text{CH} \\ \parallel \quad \diagup \\ \text{HC} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} $	H	FTA	-	~100	-	1	Greater than BTA	-
Methylacetyltrifluoroacetone	CH ₃	CH ₃	MPTA	-	-	-	1	-	-
Methylpropionyltrifluoroacetone	CH ₃ CH ₂	CH ₃	MPTA	-	-	-	1	-	-

*D is the concentration of ketone in benzene divided by the concentration of ketone in 0.5N HNO₃.

† The compounds were compared under conditions where TFA gave an extraction coefficient of 20 for Pu(IV).

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cient of Pu(III) and Pu(VI) are of the order of 10^{-5} times that for Pu(IV) under conditions of interest although the dependence of their extraction coefficients on the concentration of diketone and acid is certainly different from fourth power.

Ions that complex Pu(IV) in dilute acid solution such as phosphate, sulfate, fluosilicate*, or nitrate ions affect the extraction coefficient in a very marked degree. Thus, 0.01M sodium fluosilicate or 0.01M sodium sulfate will cause the extraction coefficient to drop about one hundred fold. Large amounts of nitrate ion, i.e. 0.5M NO_3^- , cause a reduction of the extraction coefficient of Pu(IV) by a factor of twelve as compared to 0.5M perchlorate ion. However, it is possible to extract Pu(IV) from a solution as high as 0.5M sulfate or phosphate ion by adding an excess of uranium ions as uranyl nitrate. The uranyl ions complex sulfate or phosphate ions, thus effectively lowering the concentrations of these negative ions to the point where their tendency to complex Pu(IV) is unimportant.

The decontamination is based on the great selectivity of the chelation process. The ions of the fission products (as well as others) arranged roughly in decreasing order of extraction by a diketone solution in benzene are: Zr(IV), Pu(IV), Np(IV), Ce(IV), U(IV), Fe(III), Cb(V), Th(IV), Y(III), Sr(II), UO_2^{++} , Pu(III), Pu(VI), and Ce(III), the latter six ions being roughly the same. Under identical conditions where Zr(IV) and Pu(IV) are extracted to greater than 90%, Cb(V) is extracted about 3% and Y(III), Sr(II), UO_2^{++} , Pu(III), Pu(VI), and Ce(III) are extracted less than 0.1%^{5,6}.

The extraction and decontamination process is based on two main steps, one, extracting Pu(IV) and fission products having higher extractability than Pu(IV) away from those of low extractability, and two, extracting the fission products of high extractability away from plutonium by reducing Pu(IV) to Pu(III). The combination of these two steps, one following the other is one decontamination cycle. Either of the two steps may be performed on the initial UNH dissolver solution. By treating the dissolver solution with suitable reagents the plutonium may be placed in the (III) state and the extractable fission products removed by extracting with TTA in benzene. Following this Pu(III) may be oxidized to Pu(IV) and extracted away from the fission products that did not extract in the first step. The alternate introductory cycle consists of stabilizing Pu(IV) in the dissolver solution and extracting it along with the extractable fission products away from those of low extractability and uranyl ion. Following this the Pu(IV) is reduced to Pu(III) which goes into the aqueous phase leaving the fission products that extracted along with Pu(IV) in the initial step in the benzene. These cycles can be repeated until adequate decontamination is achieved. The latter type cycle has been the most extensively studied but the choice has been an arbitrary one. The chelate process has been studied as a countercurrent column operated process and as a batch type process. However, at the present time at least, the batch type process seems to be the most promising. The work on the use of the column will be reported elsewhere, consequently this report describes the data mainly from the point of view of a batch process.

2. Preliminary Process Studies

During the basic process research a preliminary test of a complete process consisting of three cycles was performed using the best information available at the time, primarily to see if the potential decontamination justified a more detailed investigation. Although attempts were made to achieve good product recovery, the experiment was designed more to gain an idea of the potentialities of the system than to obtain an accurate description of a final process. The general type process tested was to extract Pu(IV) directly from the dissolver solution and then to reduce the Pu(IV) chelate from the benzene-TTA solution to Pu(III) with hydroxylamine hydrochloride into nitric acid. The Pu(III) was then oxidized to Pu(IV) by nitrous acid and the cycle repeated twice more. Washes consisting of 0.05N nitric acid and 0.04M TTA in benzene were interposed after each extraction and reextraction respectively, to scrub fission products from the product containing solutions. The flowsheet is shown in Figure 1 and the results in Table 2.

*The action of fluosilicate may be due to complexing by fluoride ion liberated from the fluosilicate.

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FIGURE 1

TTA Process Flowsheet

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FIGURE 1 (Continued)

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TABLE 2

TTA Process		Tabular Results			
Step	Plutonium Loss % of Total	β Decontamination Factor		γ Decontamination Factor	
		Stepwise	Over-all	Stepwise	Over-all
Extraction A. - C†	-----*	15.5	15.5	3.6	3.6
0.05 N HNO ₃ Washes	0.23	1.0	15.5	1.0	3.6
Reduction C. - E.	1.6	56	870	42	151
TTA Washes	0.31	4.2	3700	1.8	274
Oxidation and extraction E. - F.	2.0	19	69,300	41	11,000
Reduction F. - I.	0.39	3.1	2.2×10^5	1.4	16,000
Oxidation and extraction I. - L.	1.8	5.2	1.1×10^6	15	2.5×10^5
Reduction L. - N.	0.79	1.5	1.7×10^6	1.6	3.7×10^5

*This loss was about 10%. Dissolver solution contained Pu(III) or Pu(VI).

Plutonium losses:

Reduction step losses 2.79%

Extraction losses 3.8%

Total losses 7.13%

†All capital letters refer to the solutions in the flowsheet shown in Figure 1.

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The over-all recovery in this process was about 93% not counting a 10% loss* in the extraction of the initial dissolver solution. This 10% loss was proven to be due to the presence of Pu(VI) in the dissolver solution. No attempt was made at this time to stabilize Pu(IV) in the dissolver solution. The other losses were spread fairly evenly throughout the process steps. The conditions of this experiment were changed by only a slight extent in subsequent work reported further on in this report where very good recovery was obtained, so the decontamination is a good approximation to that obtainable from this type process.

The over-all decontamination factors of 1.7×10^6 for beta and 3.7×10^5 for gamma radiation look promising. The stepwise decontamination in the washes was so low that they probably could have been eliminated with little over-all change. In the first cycle the best decontaminating step was the reduction which indicated that most of the fission product contamination present at that point was extractable by TTA in benzene. However, in the second and third cycles the decontamination in the reduction step virtually vanished while the decontamination of the extraction step became much better than in the first cycle. This would indicate that the contaminating species belonged to the non-extractible group of elements in those cycles. No positive identification of the activity limiting the decontamination was made.

3. Reduction of Pu(IV) Chelate to Pu(III)

In the first two sections of this report reference was made to the procedure of reducing Pu(IV) chelate in benzene by a suitable treatment to Pu(III) in the acid phase. In this section the experimental details of this step and the theories derived from the data are presented.

3.1 Reduction of Pu(IV) TFA chelate in Benzene to Pu(III) in the Aqueous Phase using Stannous Chloride. It was known that stannous ion would reduce Pu(IV) to Pu(III) in dilute hydrochloric acid medium, so it was studied as a reducing agent for Pu(IV) chelate in the two phase system. The experimental procedure was to equilibrate a 0.5N nitric acid solution containing Pu(IV) tracer with varying concentrations of TFA in benzene. The stannous chloride was added and the concentrations of plutonium in the two phases was followed as a function of time of shaking of the two layers.

If it is assumed that the rate law for the reduction is of the form $+ \frac{d(\text{Pu(III)})}{dt} (\text{Aq}) = k(\text{Sn(II)})_{(\text{Aq})} (\text{Pu(IV)})_{(\text{Aq})}$, and the Pu(IV) in the benzene is assumed to be in continual equilibrium with some form of Pu(IV) in the aqueous phase, substituting the material balance of total plutonium in the system leads to the following expression:

$$-\log(1 - \text{fraction reduced}) = \frac{k(\text{Sn(II)})t}{2.3(1 + RE)}$$

In this expression k is a specific rate constant of dimensions liters/mole/minute, (Sn(II)) the concentration of stannous ion in moles/liter, R the volume ratio benzene over water, E the equilibrium extraction coefficient for Pu(IV) and t the time in minutes. When the $\log(1 - \text{fraction reduced})$ is plotted against time, the value of k can be obtained from the slope of the straight line resulting. The calculated values of k with the experimental conditions are shown in Table 3.

*This loss was about 10%. Dissolver solution contained Pu(III) or Pu(VI).

Plutonium losses:

Reduction step losses	2.79%
Extraction losses	3.8%
Total losses	7.13%

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TABLE 3

Values of k for the Reduction of Pu(IV) TFA Chelate by Stannous

Chloride. R = 1.0 0.5M HNO ₃			
Exp't. No.	(Sn(II)) Moles/Liter	Equilibrium Extraction Coefficient of Pu(IV). ($\frac{\text{Benzene}}{\text{Water}}$)	k calculated from $-\log(1-\text{fraction reduced}) = \frac{k(\text{Sn(II)})t}{2.3(1 + RE)}$
1	0.1	2.5	12.9
2	0.1	8.4	16.7
3	0.1	13.8	18.6
4	0.1	8.4	17.3
5	0.1	13.8	19.3
6	0.05	2.5	17.8
7	0.05	8.4	17.8
8	0.05	13.8	13.4

The constancy of the value of k is in reasonable agreement with the hypothesized rate law, however, it is not certain from these data alone whether some other scheme can also be made to fit the data.

3.2 Reduction of Pu(IV) TTA Chelate in Benzene using Ferrous Chloride. In these experiments a solution of either hydrochloric acid or nitric acid containing Pu(IV) tracer was equilibrated with a benzene solution containing TTA by stirring vigorously. Ferrous chloride was then added and the distribution of plutonium between the two phases was measured as a function of time. The first set of experiments was performed with all conditions constant except for the concentration of ferrous chloride. These results appear in Table 4.

TABLE 4

Effect of the Concentration of Ferrous Chloride on the Reduction of Pu(IV) TTA Chelate

Constant conditions: 10 ml 0.5M HCl Equilibrium
5 ml 0.02M TTA in benzene - $E_{\text{Pu(IV)}} = 20$
Same apparent stirring

Time in Minutes	(FeII) moles/ liter	Percent Reduction				
		0.001M	0.004M	0.005M	0.010M	0.050M
2		20.2*	17.7	21.0*	14.5*	16.9
5		31.6	37.4†	36.5†	36.2†	31.6
10		59.9	60.2	60.1	66.3	66.0
20		80.9	87.4	88.1	92.8	87.8
30		96.2	97.4	96.8	99.1	97.8
45		99.1	99.97			
60		99.74				

*Measured at 2.5 minutes instead of 2.0 minutes.

†Measured at 5.3 minutes instead of 5.0 minutes.

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Next the dependence of the rate of reduction on the concentration of ketone, acid and Pu(IV) chelate in benzene was studied. The rate law may be expressed as

$$\frac{-d(\text{PuK}_4)_{(B)}}{dt} = \frac{k}{R} (\text{PuK}_4)_{(B)}^a (\text{HK})_{(B)}^c (\text{H}^+)_{(\text{Aq})}^d$$
$$-\log \frac{(\text{PuK}_4)_{(\text{B})}}{(\text{PuK}_4)_{(\text{B})}} = \frac{k_2}{2.3R} (\text{HK})_{(\text{B})}^c (\text{H}^+)_{(\text{Aq})}^d t.$$

From a series of experiments where alternately ketone or hydrogen ion concentrations are kept constant while the other is varied, the values of k_2 , c and d may be calculated. These experiments were performed and straight line plots resulted. The data are shown in Figure 2 and Figure 3. In Figure 2 the experiments in which the hydrogen ion concentration is held constant and the ketone concentration varied are shown. In Figure 3 the experiments in which the ketone concentration is held constant and the hydrogen ion varied are shown. In all these experiments the ionic strength was kept constant, potassium chloride being added when necessary.

$$\text{slope}_1 = \frac{k_2}{2.3R} (\text{HK})_{(\text{B})}^c (\text{H}^+)_{(\text{Aq})}^d$$
$$\log \text{slope}_1 = \log \frac{k_2 (\text{HK})_{(B)}^c (\text{H}^+)_{(Aq)}^d}{2.3R}$$

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The results shown in Figures 2, 3, 4, 5 and 6 along with previously demonstrated facts establish the form of the rate law of the reduction of Pu(IV) chelate in benzene by ferrous chloride in hydrochloric acid to be as follows:

$$\frac{-d(\text{PuK}_4)_{(B)}}{dt} = \frac{k_2 (\text{PuK}_4)_{(B)} (\text{H}^+)^2_{(Aq)}}{R (\text{HK})^2_{(B)}}$$

When the results of all of the experiments are combined the value of k_2 can be calculated independently in each experiment and the mean value obtained. This calculation is shown in tabular form in Table 5.

The procedure used to study the reduction step in the hydrochloric acid system was extended to the nitric acid system by repeating the same experiments in nitric acid. The salient calculation of k_2 in the nitric acid system is tabulated in Table 6. The curves obtained in the individual experiments were similar to those obtained in the hydrochloric acid system.

TABLE 5

Calculation of k_2 for the Reduction of Pu(IV) Chelate by Ferrous

Chloride in Hydrochloric Acid. $\sim 0.005\text{M Fe(II)}$

$$R = 1/2$$

Exp't. No.	(HK) moles/ liter	(H ⁺) moles/ liter	slope ₁	$\frac{k_2}{R}$
1	0.020	0.50	0.0351	1.29×10^{-4}
2	0.025	0.50	0.0221	1.27×10^{-4}
3	0.030	0.50	0.0141	1.17×10^{-4}
4	0.035	0.50	0.01115	1.25×10^{-4}
5	0.040	0.50	0.00796	1.17×10^{-4}
6	0.050	0.50	0.00489	1.12×10^{-4}
7	0.020	0.30	0.0124	1.27×10^{-4}

$$\text{Average } \frac{k_2}{R} = 1.22 \pm 0.06 \times 10^{-4}$$

$$k_2 = 6.1 \times 10^{-5} \text{ min}^{-1}$$

TABLE 6

Calculation of k_2 for the Reduction of Pu(IV) Chelate by Ferrous

Chloride in Nitric Acid. $\sim 0.005 \text{ M Fe(II)}$

Exp't. No.	R	(HK) moles/ liter	(H ⁺) moles/ liter	Slope	k_2
1	0.5	0.030	0.476	0.0307	1.39×10^{-4}
2	1.0	0.030	0.476	0.0137	1.25×10^{-4}
3	2.0	0.030	0.476	0.00645	1.18×10^{-4}
4	2.0	0.020	0.476	0.0156	1.26×10^{-4}
5	0.5	0.040	0.476	0.0156	1.26×10^{-4}
6	0.5	0.030	0.476	0.0303	1.38×10^{-4}
7	0.375	0.020	0.476	0.0755	1.12×10^{-4}

$$\text{Average } k_2 = 1.24 \pm 0.06 \times 10^{-4} \text{ Min}^{-1}$$

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The knowledge of the value of k_2 and the form of the rate law makes possible the calculation of the time required to achieve reduction to any desired degree of completion in a batch type process under all variations of the possible parameters. This calculated time will be valid strictly only within the range of experimentally verified conditions. Interpolation within that range will be valid, but extrapolation may or may not be valid depending upon where some other mechanism of the reduction may be more important. The formula for calculating the time required for reduction in the nitric acid system is as follows:

$$t = \frac{-2.3(HK)^2 R \log (\text{fraction not reduced})}{1.24 \times 10^{-4} (H^+)^2}$$

Values of t have been calculated at various equilibrium extraction levels for Pu(IV) in nitric acid. They are calculated for equal volumes of benzene and 0.5 M nitric acid, however, they can be converted to any volume ratio simply by multiplying t by the new R . All of these conditions lie in the experimentally verified range as long as the concentration of nitric acid is in the neighborhood of 0.4 M to 0.6 M. The results are shown in Table 7.

TABLE 7
Calculation of Time Required for Reduction of Pu(IV) Chelate by
Ferrous Chloride in Nitric Acid

R = 1		0.4M to 0.6M HNO ₃	0.001M to 0.05M FeCl ₂	
Equilibrium Ex- traction Coefficient				
of Pu(IV)	$\frac{(\text{Benzene})}{(\text{Water})}$	$\frac{(\text{HK})}{(\text{H}^+)}$	Time in minutes for 99.0% reduction	Time in minutes for 99.9% reduction
5.0	4.00×10^{-2}	59	89	
7.5	4.41×10^{-2}	72	108	
10.0	4.76×10^{-2}	84	125	
12.5	5.03×10^{-2}	94	141	
15.0	5.25×10^{-2}	102	153	
20.0	5.67×10^{-2}	119	179	
30.0	6.25×10^{-2}	145	218	
40.0	6.75×10^{-2}	168	252	
50.0	7.12×10^{-2}	187	281	
60.0	7.43×10^{-2}	204	306	
100.0	8.49×10^{-2}	267	401	

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A mechanism for the ferrous reduction procedure may be derived which will fit the observed rate law. The following steps may be formulated:

1. $\text{PuK}_4(\text{B}) = \text{PuK}_4(\text{W})$ rapid equilibrium, K_1^*
2. $\text{PuK}_4(\text{W}) + 2\text{H}^+ = \text{PuK}_2^{+2}(\text{W}) + 2\text{HK}(\text{B})$ rapid equilibrium, K_2^*
3. $\text{PuK}_2^{+2}(\text{W}) \xrightarrow{k'} \text{PuK}^{+3}(\text{W}) + \text{K}^-(\text{W})$ rate determining step
4. $\text{PuK}^{+3}(\text{W}) = \text{Pu(IV)}(\text{W}) + \text{K}^-(\text{W})$ rapid equilibrium
5. $\text{K}^-(\text{W}) + \text{H}^+(\text{W}) = \text{HK}(\text{B})$ rapid equilibrium
6. $\text{Pu(IV)}(\text{W}) + \text{Fe}^{++} = \text{Pu(III)}(\text{W}) + \text{Fe}^{+++}$ rapid and complete

From these the following derivation may be carried out:

$$\begin{aligned}
 1. \quad \frac{-d(\text{PuK}_4)(\text{B})}{dt} &= \frac{k'}{R} (\text{PuK}_2^{+2})(\text{W}) \\
 K_1 &= \frac{(\text{PuK}_4)(\text{W})}{(\text{PuK}_4)(\text{B})} \\
 K_2 &= \frac{(\text{PuK}_4)(\text{W}) (\text{H}^+)^2(\text{W})}{(\text{PuK}_2^{+2})(\text{W}) (\text{HK})^2(\text{B})} \\
 2. \quad \frac{-d(\text{PuK}_4)(\text{B})}{dt} &= \frac{k' k_1}{R K_2} \frac{(\text{PuK}_4)(\text{B}) (\text{H}^+)^2(\text{W})}{(\text{HK})^2(\text{B})} = \frac{k_2}{R} \frac{(\text{PuK}_4)(\text{B}) (\text{H}^+)^2(\text{W})}{(\text{HK})^2(\text{B})}
 \end{aligned}$$

This is identical with the experimentally verified rate law. The mechanism above is not the only one which will satisfy the correct rate law for various changes and permutations can be made. One thing all mechanisms have in common, however, is the rate determining step, reaction 3 above. It is quite possible that the slowest ketone to come off the plutonium atom may be different in a different acidity range. The reason that the third one should be lowest is rather obscure.

Since the best separation of plutonium from the extractable fission products is obtained when the Pu(IV) chelate is reduced to Pu(III) under conditions where the extracting power of the system is the highest practical value, two objections to the use of ferrous chloride as the reducing agent may be noted, first, the time required for 99.9% reduction of Pu(IV) in a system when the extraction coefficient for Pu(IV) is 100 is about 400 minutes or nearly seven hours. Second, the ferrous ion is not stable in the system for times much in excess of two hours. There appeared to be two methods of overcoming these objections. The first would be to stabilize the ferrous ion so that it would be possible to have it remain for seven hours in the system. The second would be to find a substance which would catalyze the rate of reduction of Pu(IV) chelate by ferrous ion.

As a first approach an attempt was made to stabilize the ferrous ion by adding small concentrations of urea.[†] It was shown that urea did not react with either Pu(IV) or TTA and did not complex with Pu(IV) . When the rate of reduction was measured it was found that urea not only stabilized the ion but seemed to increase the rate as well. The increase in rate was found to be dependent on the concentration of urea in the system. However, this effect was not wholly reproducible.

*The subscript of the K's refer to the step of the mechanism from which the corresponding expressions are derived.

† This was shown to be effective by Burgus and Leader⁷

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When 0.01M hydroxylamine hydrochloride was added to stabilize the ferrous ion it was found that the reduction could be carried out over at least a five hour period. These experiments were performed both in glass and stainless steel vessels.

It was hoped that a specific catalysis of the rate would be found by TFA because the transfer of the Pu(IV) chelate of TFA from one phase to the other was known to be much more rapid than that of TTA. This catalysis was observed experimentally. When the concentration of TFA was the same as that of TTA, 0.03M in the experiment, the rate of reduction was faster by a factor of two. The amount of TFA present was so low that its effect on the extraction equilibrium of Pu(IV) was insignificant. This catalysis was not considered to be practical because it would double the amount of the diketone required for the step and the diketone is still a rather expensive chemical. The mechanism of the catalytic action of TTA was not established.

When the reduction of plutonium chelate in benzene by ferrous ion was performed in 18-8 stainless steel vessels on a one and a half liter scale it was found that the rate of reduction was increased by a factor of two to three.* This was found to be quite reproducible within these limits.

The final procedure adopted for the reduction in the stainless steel vessels was to add 0.01M hydroxylamine hydrochloride to stabilize the ferrous ion. It was then possible to reduce plutonium (IV) chelate in benzene to an extent of greater than 99.8% with 0.002M ferrous chloride at an equilibrium extraction level of 100 for Pu(IV) in two to four hours. This may be compared with the theoretical time of seven hours based on experiments performed in all glass apparatus.

3.3 Reduction of Pu(IV) TTA Chelate in Benzene using Hydroxylamine Hydrochloride in nitric acid. It was well known that hydroxylamine hydrochloride would reduce Pu(IV) to Pu(III) in dilute nitric or hydrochloric acid medium, so it was studied as a reducing agent for Pu(IV) chelate in the same two-phase system. The experimental procedure was to equilibrate a 0.5N nitric acid solution containing Pu(IV) tracer with varying concentrations of TTA in benzene solution by shaking. The hydroxylamine hydrochloride was added and the concentrations of plutonium in the two phases were followed as a function of time of shaking of the two layers. It was established that there was no measurable reaction between 0.2M hydroxylamine in 0.5M nitric acid and ketone over a two hour period. The experimental results are shown in Table 8.

The rate of reduction of plutonium (IV) chelate in benzene by hydroxylamine hydrochloride was slower than the same reduction using ferrous chloride in all cases investigated.

TABLE 8

Reduction of Pu(IV) Chelate by Hydroxylamine Hydrochloride

(H ⁺) moles/ liter	(TTA) moles/ liter	(NH ₂ OH ⁺) moles/ liter	Volume Ratio R $\frac{\text{Benzene}}{\text{Water}}$	Time in Minutes	%Pu(IV) Reduced
0.5	0.02	0.1	$\frac{1}{2}$	10	74%
				20	96%
0.5	0.04	0.1	$\frac{1}{2}$	10	26%
				20	43%
				30	62%
				50	77%
0.5	0.06	0.1	$\frac{1}{2}$	10	14%
				20	21%
				30	29%
				50	42%

*See Figure 7.

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4. The Mechanism of the Extraction of Pu(IV) by TTA. In the preceding section a mechanism for the reduction of Pu(IV) chelate in benzene by ferrous chloride was presented. The rate law was shown to be $-\frac{d(\text{PuK}_4)_{(B)}}{dt} = \frac{k_2(\text{PuK}_4)_{(B)}(\text{H}^+)_{(Aq)}^2}{R(\text{HK})_{(B)}^2}$. The rate determining step was

shown to involve plutonium and diketone only. Therefore, it represents the rate of transfer of Pu(IV) from benzene to the aqueous phase. It is also known that the rate of approach to equilibrium extraction of Pu(IV) is relatively small compared to processes involving only diffusion equilibrium of a single species of size comparable to the Pu(IV) chelate. In order to explain this slow rate the following reasoning was employed.

The overall reaction for the extraction equilibrium has been shown elsewhere in this report to be

for which the equilibrium constant may be written,

$$K = \frac{(\text{PuK}_4)_{(B)}(\text{H}^+)_{(Aq)}^4}{(\text{Pu(IV)})_{(Aq)}(\text{HK})_{(B)}^4}$$

The equilibrium constant K is also equal to the ratio of the specific rate constants for the forward and reverse reactions, $\frac{k_1}{k_2}$.

At equilibrium the rate of the forward and reverse reactions are equal so the following can be written:

$$\frac{+d(\text{Pu(IV)})_{Aq}}{dt} = -k_1 f$$

where f is some function of $(\text{Pu(IV)})_{(Aq)}$, $(\text{H}^+)_{(Aq)}$ and $(\text{HK})_{(B)}$.

$$\text{Then, } \frac{k_2(\text{PuK}_4)_{(B)}(\text{H}^+)_{(Aq)}^2}{(\text{HK})_{(B)}^2} = R \frac{k_1}{f}$$

Solving for $\frac{k_1}{k_2}$ and equating to the known expression for K,

$$\frac{k_1}{k_2} = K = \frac{(\text{PuK}_4)_{(B)}(\text{H}^+)_{(Aq)}^4}{(\text{Pu(IV)})_{(Aq)}(\text{HK})_{(B)}^4} = \frac{(\text{PuK}_4)_{(B)}(\text{H}^+)_{(Aq)}^2}{R(\text{HK})_{(B)}^2 f}$$

$$\text{Therefore, } f = \frac{(\text{Pu(IV)})_{(Aq)}(\text{HK})_{(B)}^2}{R(\text{H}^+)_{(Aq)}^2} \text{ and, } \frac{-d(\text{Pu(IV)})_{(Aq)}}{dt} = \frac{k_1(\text{Pu(IV)})_{(Aq)}(\text{HK})_{(B)}^2}{R(\text{H}^+)_{(Aq)}^2}$$

The values of K and k_2 in both 0.5 M nitric and 0.5 M hydrochloric acid are known so the values of k_1 may be calculated. These values are shown in Table 9.

TABLE 9

Values of the Rate and Equilibrium Constants for the Chelating
System in 0.5 M HCl and 0.5 M HNO₃

Acid	K	k_2	k_1
HCl	7.80×10^6	6.10×10^{-5}	475
HNO ₃	1.39×10^6	1.24×10^{-4}	185

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These values are not the true thermodynamic values because the effect of ionic strength has not been considered, however, they are all valid in 0.3 to 0.5 M acid to $\pm 5\%$.*

It is difficult to experimentally verify the forward rate in the absence of the reverse rate, however, using both rates the rate of approach to equilibrium extraction can be measured and then calculated for comparison starting with all of the Pu(IV) in the acid phase. The calculations are presented first. From the foregoing rate expressions,

$$\frac{+d(\text{PuK}_4)_{(B)}}{dt} = \frac{k_1 (\text{Pu(IV)})_{(Aq)} (\text{HK})^2_{(B)}}{R (\text{H}^+)^2_{(Aq)}} - \frac{k_2 (\text{PuK}_4)_{(B)} (\text{H}^+)^2_{(Aq)}}{R (\text{HK})^2_{(B)}}$$

If C is the initial concentration of Pu(IV) in moles per liter, at all times,

$$C V_{(Aq)} = (\text{Pu(IV)})_{(Aq)} V_{(Aq)} + (\text{PuK}_4)_{(B)} V_B$$

$$C = (\text{Pu(IV)})_{(Aq)} + R (\text{PuK}_4)_{(B)} \text{ where } R = \frac{V_B}{V_w}$$

$$\text{Then, } \frac{+d(\text{PuK}_4)_{(B)}}{dt} = \frac{k_1 C (\text{HK})^2_{(B)}}{R (\text{H}^+)^2_{(Aq)}} - \frac{k_1 (\text{HK})^2_{(B)} (\text{PuK}_4)_{(B)}}{(\text{H}^+)^2_{(Aq)}} - \frac{k_2 (\text{PuK}_4)_{(B)} (\text{H}^+)^2_{(Aq)}}{R (\text{HK})^2_{(B)}}$$

$$\text{Let } A = \frac{k_1 (\text{HK})^2_{(B)}}{(\text{H}^+)^2_{(Aq)}} + \frac{k_2 (\text{H}^+)^2_{(Aq)}}{R (\text{HK})^2_{(B)}}$$

$$\text{Then } \frac{+d(\text{PuK}_4)_{(B)}}{dt} = \frac{k_1 C (\text{HK})^2_{(B)}}{R (\text{H}^+)^2_{(B)}} - A (\text{PuK}_4)_{(B)}$$

$$\text{When integrated the expression becomes, } (\text{PuK}_4)_{(B)} = \frac{k_1 C (\text{HK})^2_{(B)}}{R A (\text{H}^+)^2_{(Aq)}} (1 - e^{-At})$$

If f_{ext} is the fraction of the total Pu(IV) extracted at time t ,

$$f_{\text{ext}} = \frac{R (\text{PuK}_4)_{(B)}}{C} = \frac{k_1 (\text{HK})^2_{(B)}}{A (\text{H}^+)^2_{(Aq)}} (1 - e^{-At})$$

When t is infinite f_{ext} is equal to $f_{\text{ext}} \infty$ and,

$$f_{\text{ext}} \infty = \frac{k_1 (\text{HK})^2_{(B)}}{A (\text{H}^+)^2_{(Aq)}}$$

This latter expression is equivalent to the expression for the equilibrium constant on page 23.

*Some inconsistencies have arisen when later more highly purified preparations of TTA were used which may make these figures impossible to reproduce exactly. However, since these figures were all obtained with the same preparation of TTA they are selfconsistent.

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Then,

$$\frac{f_{\text{ext}}}{f_{\text{ext}}} = (1 - e^{-At}) = 1 - e^{-\left(\frac{K_1 (\text{HK})^2_{(\text{B})} + k_2 (\text{H}^+)^2_{(\text{Aq})}}{R (\text{HK})^2_{(\text{B})}}\right)t}$$

It is interesting to note that the half time for equilibrium extraction appears as the well known form, $T_{1/2} = \frac{0.693}{A}$

An examination of the form of the term A yields further information.

$$\text{If } y = \frac{(\text{HK})_{(\text{B})}}{(\text{H}^+)_{(\text{Aq})}},$$

$$A = k_1 y^2 + \frac{k_2}{R} y^{-2}$$

Since A consists of two terms the first of which increases with increase in y and the second of which decreases, there will evidently be a minimum value of A when the two terms are equal. Upon differentiation and equating the resulting derivative to zero, the position of the minimum may be shown to correspond to the following:

$$y^4 = \frac{(\text{HK})^4_{(\text{B})}}{(\text{H}^+)^4_{(\text{Aq})}} = \frac{k_2}{k_1 R}$$

The function, A, is plotted against the equilibrium extraction coefficient for Pu(IV) which is determined by the ratio $\frac{(\text{HK})_{(\text{B})}}{(\text{H}^+)_{(\text{Aq})}}$ for both 0.5M hydrochloric acid and 0.5M nitric acid in Figure 8.

To realize the physical significance of the plot in Figure 5 the formula derived for the half time of equilibrium extraction must be referred to, namely $T_{1/2} = \frac{0.693}{A}$. The conditions corresponding to the minimum value of A will be the conditions where the slowest rate of extraction occurs. It may be noted that in both 0.5M hydrochloric acid and 0.5M nitric acid the minimum lies around an equilibrium extraction coefficient for Pu(IV) of two to three and that the curves are relatively flat in the region of one to ten. This is of an important disadvantage in the use of the chelate process in a countercurrent column. The principal advantage of column operation is to achieve complete extraction of Pu(IV) by working under batch equilibrium extraction coefficients in the range of one to ten, where in this system the transfer rate will be the slowest. More will be said about this below.

Using the expression for $\frac{f_{\text{ext}}}{f_{\text{ext}}}$ as derived previously, curves may be calculated for the approach to extraction equilibrium at different equilibrium extraction coefficients. These may be directly confirmed by experiment. The results both calculated and experimental are shown in Figures 9 and 10.

The experimental values obtained are in excellent agreement with the calculated values. Other experiments, not shown, have indicated that the calculations at higher extraction coefficients are qualitatively correct except that at extraction coefficients of around 10,000 to 20,000 the observed rate is slower than that calculated. The actual diffusion process may become important in that region.

Some further conclusions with respect to counter-current column operation of the chelate process may be obtained. The contact time in the range of one to ten of equilibrium extraction coefficient for Pu(IV) must be of the order of ten minutes per plate. This puts a rather severe limit on the amount of throughput and size of columns required. This contact time may be shortened considerably providing some catalyst may be found for the extraction. As was noted in the previous section the rate of reduction of plutonium chelate in benzene was increased a factor of two to three by operating in stainless steel vessels. Any catalytic effect could be profitably applied to the use of counter-current columns in this system.

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The fact that the rate of approach to extraction equilibrium agrees so well with the calculated rate which is based primarily on the rate law for the reverse reaction as determined from the ferrous reduction experiments constitutes one of the most powerful arguments for the validity of the theory of the reduction procedure. Based on the rate law for the extraction reaction a mechanism may be devised. It is as follows:

- (1) $\text{Pu(IV)} + \text{HK} = \text{PuK}^{+3} + \text{H}^+$ rapid equilibrium
- (2) $\text{PuK}_1^{+3} + \text{HK} = \text{PuK}_2^{+2} + \text{H}$ rate determining step
- (3) $\text{PuK}_2^{+2} + 2\text{HK} = \text{PuK}_{4(\text{B})} + 2\text{H}^+$ rapid equilibrium

As was true in the mechanism of the reextraction this mechanism has possible variations and permutations all of which have the same rate determining step. Also in a different acidity range the slowest ketone to go on the plutonium ion may be different. It must be remembered that all of this theory is based on experiments in the acidity range of 0.3M to 0.6M and the conclusions strictly apply only in that acidity range. However, that range covers the region of interest in the actual process, hence from a practical point of view the process steps where the theory applies are on a rather firm theoretical basis.

5. Stabilization of Pu(IV) in Process Solutions

Since the extraction of plutonium from an aqueous phase into a benzene phase as the TTA chelate is extremely specific for Pu(IV) it is necessary to have available a method for quantitatively oxidizing Pu(III) to Pu(IV) in order to perform the extraction following each reduction. In view of the small differences of potential between the various oxidation states of plutonium it is necessary to either critically adjust the potential of the oxidizing solution or to utilize differences in the kinetics of oxidation of the various states in order to achieve quantitative oxidation of Pu(III) to Pu(IV). The following sections will deal with work done on this problem.

5.1 The Use of Dichromate and Permanganate to Oxidize Pu(III) to Pu(IV). The oxidation of Pu(III) to Pu(IV) by dichromate^{8,9} or permanganate⁹ proceeds very rapidly, however, the oxidation of Pu(IV) to Pu(VI) by both dichromate^{10,11} and permanganate is known to be slow.¹² It was hoped that the concentration of dichromate or permanganate and the other variables available could be adjusted so that Pu(III) could be oxidized to Pu(IV) which could be extracted by TTA in benzene before a measurable amount of Pu(VI) was formed. Permanganate or dichromate in 1 M nitric acid oxidized TTA at a measurable rate so the oxidation had to be performed in 0.25 M to 0.5 M acid and a low concentration of either oxidizing agent. Using dichromate concentrations as low as 10⁻⁵ M and permanganate concentrations as low as 10⁻⁴ M, a measurable amount of non-extractable plutonium, probably Pu(VI), was found within the time required to perform the extraction.

In order to quench the oxidizing power of the dichromate or permanganate, experiments were performed in which sodium arsenite was added immediately after the dichromate or permanganate. Arsenious acid does not rapidly reduce Pu(IV) in acid solution.¹³ In these experiments either the arsenic acid formed in the destruction of dichromate or permanganate ions complexed the Pu(IV) or the arsenious acid reduced the Pu(IV) more rapidly than expected, so that the extraction coefficient of Pu(IV) was lowered by a large amount. Therefore, although no thorough test of the possibilities of this method was made, the first results seemed to offer no advantage whatever over the possible use of nitrous acid. This work is discussed in Sec. 5.3.

5.2 Stabilization of Pu(IV) using Permanganate Ion and Arsenious Acid. It has been reported that arsenious acid rapidly reduces Pu(VI) to Pu(IV)^{13,14} and no further.¹³ If this were true a possible scheme for stabilizing the Pu(IV) state would be to oxidize Pu(III) to a mixture of Pu(IV) and Pu(VI) and then add arsenious acid to destroy the permanganate and reduce the Pu(VI) to Pu(IV). The oxidation of Pu(III) to Pu(IV) by permanganate is known to be quite rapid⁹ but further oxidation to Pu(VI) is moderately slow.¹² Using trace concentrations of Pu(VI) and

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concentrations of arsenious acid from 0.01 to 0.10 M in 0.5M nitric acid no formation of Pu(IV) was detectable over a twelve-hour period. The detection of Pu(IV) was made by trying to extract plutonium from the solution with a TTA benzene phase. Other workers^{15,16} have also found this reduction of Pu(VI) by arsenious acid to be quite slow. Therefore, this method was discarded as impractical.

5.3 Oxidation of Pu(III) to Pu(IV) by Nitrous Acid. In the chelate extraction decontamination work previously reported; one of the most serious losses of plutonium occurred in the extraction steps of the redox cycles.* In those experiments 0.1 M–0.2 M hydroxylamine hydrochloride was used to reextract the plutonium from the benzene phase to the aqueous phase by reducing the Pu(IV) chelate to Pu(III). The oxidation back to Pu(IV) was then carried out by adding from 0.1 to 0.2 M excess of nitrous acid over the amount of hydroxylamine and warming for about twenty minutes at 80°C. It was desirable to eliminate both the unnecessarily large losses of plutonium in the extraction steps and the cumbersome heating period required by the above procedure.

Since it is possible that the various oxidation states of plutonium might be involved in either an equilibrium or a steady state with a nitrous acid system, it is desirable to consider the behavior of such systems with respect to their equilibria and kinetics in attaining those equilibria. Most of the available data on nitrous acid and its reactions due to E. Abel have been summarized by Yost and Russell.¹⁷

The principal equilibrium involving nitrous acid and its decomposition products in acid solution is $3\text{HNO}_2 = \text{H}^+ + \text{NO}_3^- + 2\text{NO} + \text{H}_2\text{O}$. At 25°C. the equilibrium constant, $K = (\text{H}^+) (\text{NO}_3^-) \text{P}^2\text{NO}/(\text{HNO}_2)^3$, is given by the above authors to be 28.7, where concentrations are in moles/liter, pressure in atmospheres and time in minutes. The rate expressions for the forward and reverse reactions are given as,

$$\frac{d(\text{HNO}_2)}{dt} = \frac{k_1 (\text{HNO}_2)^4}{\text{P}^2\text{NO}} \quad k_1 = 46 \text{ at } 25^\circ\text{C}, \text{ concentrations in moles/liter, pressure in atmospheres, and time in min.}$$

$$\frac{d(\text{HNO}_2)}{dt} = k_2 (\text{HNO}_2) (\text{H}^+) (\text{NO}_3^-) \quad k_2 = 1.6 \text{ at } 25^\circ\text{C}.$$

Under most conditions the nitrous acid systems should rapidly reach equilibrium and the potential of the solutions should maintain a constant value. If all conditions of equilibrium are actually reached in experiments involving plutonium a steady state is impossible and the various oxidation states of plutonium would be in true equilibrium with the nitrous acid system.

In a given acidic solution containing nitrous acid and its decomposition products at equilibrium, the potential of the solution will be determined by the ratio of $\text{PNO}/(\text{HNO}_2)$ at constant acidity. The smaller this ratio the more negative will be the potential. Since the reaction $\text{NO} + 1/2 \text{O}_2 = \text{NO}_2$ is known to be quite rapid and complete in the gaseous phase at room temperature it is to be expected that the amount of oxygen present in the reaction vessel would affect the observed potential. Measurements of the potentials of nitrous acid systems using a gold electrode and a hydrogen reference cell have been made and some of the results are shown in Figure 11. The measurements were made in a closed vessel in which the solution could be stirred if desired. The air volume and liquid volume were about the same. Inasmuch as sufficient data concerning the solubilities of the various gases present and the kinetics of all the reactions taking place are not available no quantitative explanations of the curves shown can be given. The qualitative explanations however, are obvious. In order to attain the most negative potential possible from a nitrous acid system it is necessary that the oxygen present be in excess over the nitrous acid initially added. This can most easily be accomplished by using nitrous acid concentrations less than 0.01 M in a vessel containing roughly equal volumes of air and solution. The nitrous acid concentration of 0.01 M is given because oxygen in air is also approximately 0.01 M (moles/liter).

*See Fig. 1 and Table 2, this report.

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In the attempt to show that Pu(III) and Pu(IV) are involved in equilibrium with the nitrous acid systems two types of experiments were carried out. The methods, together with the data obtained, are given in the following paragraphs.

One type of experiment consisted of measuring the rate of extraction of plutonium into a TTA benzene phase from an aqueous phase initially containing Pu(III) tracer and nitrous acid under conditions of constant potential. To maintain constant potential at high nitrous acid concentrations it was necessary to fill the reaction vessel with nitrogen and have it so arranged that aliquots could be withdrawn by opening the vessel to an atmosphere of nitrogen. In this manner the potential of the solution could be maintained quite constant.

To develop a general expression relating the fraction of plutonium not extracted into the benzene phase from a solution containing nitrous acid to the time of reaction, the following assumptions are made. First it is assumed that the expressions for the rate of oxidation, reduction, and extraction of plutonium are all first order with respect to the plutonium concentration. Secondly, it is assumed that under the conditions used the rate of reextraction of Pu(IV) Chelate in benzene to Pu(IV) in the water need not be considered. This was justified by making the equilibrium extraction coefficient of Pu(IV) extremely high ($\sim 20,000$).

With these assumptions in mind the critical differential equations governing the situation are,

$$\begin{aligned} 1) \frac{d(\text{Pu(IV)})_{(Aq)}}{dt} &= k_1(\text{Pu(III)})_{(Aq)} - k_2(\text{Pu(IV)})_{(Aq)} - k_3(\text{Pu(IV)})_{(Aq)} \\ 2) \frac{Rd(\text{PuK}_4)_{(B)}}{dt} &= k_3 (\text{Pu(IV)})_{(Aq)} \end{aligned}$$

where,

k_1 = constant in term for rate of oxidation of Pu(III) to Pu(IV).

k_2 = constant in term for rate of reduction of Pu(IV) to Pu(III).

k_3 = constant in term for rate of extraction of Pu(IV) from water into benzene.

R = benzene volume/water volume

All of the k 's contain specific reaction rate constants and functions of concentrations of reactants whose forms are not known. The constant k_3 was determined by extracting trace concentrations of Pu(IV) from solutions of various compositions because at these high extraction levels the law governing the rate of extraction derived in the preceding section of this report was shown not to apply. Utilizing the above equations, the plutonium material balance relationship, and using obvious limits of integration the general relationship relating the fraction of plutonium not extracted into the benzene and time of reaction is,

$$\text{F.N.E.} = \frac{m_1 m_2}{m_1 - m_2} \left(\frac{e^{m_1 t}}{m_1} - \frac{e^{m_2 t}}{m_2} \right)$$

where,

$$m_1 = \frac{-(k_1 + k_2 + k_3) + \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}}{2}$$

$$m_2 = \frac{-(k_1 + k_2 + k_3) - \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}}{2}$$

t = time in minutes.

This equation will apply to any situation where a trace concentration of Pu is undergoing oxidation and reduction between the (III) and (IV) states and the (IV) state is being extracted at a specific rate from water into benzene. It is for the purpose of interpreting experiments done under these conditions that the equation is considered.

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Three specific situations are of interest in that they might lead to an understanding of the reaction taking place. These are,

$$(1) k_1 \approx k_2 < k_3$$

If this were true then, $F.N.E. = e^{-k_1 t}$, and a plot of $-\ln F.N.E.$ versus time would give a straight line of slope k_1 . By varying the concentrations of reactants the form of the rate law for the oxidation of Pu(III) to Pu(IV) could be determined and the specific reaction rate constant evaluated.

$$(2) k_1 \approx k_2 \gg k_3$$

In this case $F.N.E. = e^{-\frac{k_3 t}{K+1}}$, when $K = \frac{[Pu(III)]}{[Pu(IV)]}$ in the aqueous phase. K would also equal k_2/k_1 . Again a plot of $-\ln F.N.E.$ versus time would give a straight line whose slope would be $\frac{k_3}{K+1}$. As mentioned above k_3 can be determined in separate experiments. With k_3 known the value of K is easily obtained. By assuming that Pu(III) and Pu(IV) are involved in a true equilibrium with the nitrous acid system, the value of K could be calculated from a measurement of the solution potential and the E° of the Pu(III-IV) couple. If the experimental K and the calculated K agreed, the equilibrium mechanism would be proved and an idea as to the rates involved in attaining the equilibrium could be obtained.

$$(3) k_1 \approx k_2 \approx k_3$$

In this case the general expression would apply, i.e.

$$F.N.E. = \frac{-k_1 k_3}{m_1 - m_2} \left(\frac{e^{m_1 t}}{m_1} - \frac{e^{m_2 t}}{m_2} \right)$$

A plot of $-\ln F.N.E.$ versus time might give either a straight line or a curved line depending upon the exact values of the k 's. By assuming an equilibrium mechanism the ratio of k_2/k_1 could be calculated from potential measurements. Then by empirically selecting values of k_2 and using the ratio of k_2/k_1 to determine k_1 , $F.N.E.$ versus time curves could be calculated and compared with experimental curves. Of course this is the least desirable situation and is the one which would yield the least amount of information.

Typical experimental curves of $F.N.E.$ versus time are given in Figure 12.* Table 10 summarizes the pertinent data applying to those experiments.

Column 2 gives the measured potential of the solution during the experiments. Column 3 gives the E° potential of the Pu(III)-(IV) couple. When nitric acid solutions were used the E° was estimated from known potential measurements and a consideration of nitrate complexing constants of Pu(IV).^{18,19,20,21} It was assumed that there was no nitrite complexing of Pu(IV). The E° value for 1 M HCl was used for all HCl solutions studied. Column 7 gives the values of k obtained from the measured slopes of the curves shown in Figure 12 and the values of k_3 listed in Column 6 assuming that case (2) above is applicable. Column 8 gives the values of K calculated from potential measurements.

*See Figure 12 on page 13.

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TABLE 10

Data on the Time Dependence of the Extraction of Plutonium from Nitrous Acid Solutions. (Pu initially present as Pu(III). See Figure 13 for experimental curves.)

1	2	3	4	5	6	7	8
Exp.	E meas. (volts)	E° Pu(III-IV) (volts)	(HNO ₂) moles/ liter	Conditions	k ₃ (min ⁻¹) (experi- mental)	K* meas.	K* calc.
I	-0.920	-0.966	0.001M	0.25M HCl	8.7	265	5
II	-0.892	-0.966	0.10M	0.25M HCl	8.7	190	20
III	-0.965	-0.945	0.005M	0.50M HNO ₃	2.5	22	0.5
IV	-1.05	-0.9	0.005M	2M UNH 0.25M HNO ₃	-	-	10 ⁻³

*K = (Pu(III)) / (Pu(IV)) in aqueous phase.

The large discrepancy between K_{meas.} and K_{calc.} indicates that the assumption involved in case (2) is not applicable. It is thought that the discrepancy is larger than that due to experimental errors and errors in selecting constants. Probably case (1) is applicable to some of the conditions and case (3) is applicable to others although it is impossible to draw definite conclusions.

Figure 13 shows the plots of two experiments similar to those shown in Figure 12 with the exception that Pu(IV) was added initially instead of Pu(III). For that situation the relationship between the fraction of Pu not extracted as a function of time of reaction is,

$$F.N.E. = k_3 \left\{ \frac{(k_2 + k_3 + m_2)}{m_1 - m_2} \left(\frac{e^{m_1 t}}{m_1} - \frac{e^{m_2 t}}{m_2} \right) - \frac{e^{m_2 t}}{m_2} \right\}$$

where the k's and m's have the same definition as before. The two experiments of Figure 13 are identical with the exception that in experiment I the Pu(IV) was added to the system one half to two minutes before the extraction was started. The difference in the final slopes of the two is probably due to the error in determining the final small concentrations of experiment II. They had to be obtained by measuring the large fraction and subtracting from the total and can not be very accurate. The dotted curves are those calculated assuming different values of k₂ and assuming the ratio k₁/k₂ to be defined by the potential measurements and the value of k₃ obtained from experiment. The agreement is fair when k₂ = 1 and k₁ = 1/5 and the assumption is made that k₁ ≈ k₂ ≈ k₃.

Although conclusions from this work cannot be definite, it seems possible to explain the observed behavior on the premise that Pu(III) and Pu(IV) are involved in a true equilibrium with the nitrous acid system rather than in a steady state. Probably the constants for the rates of oxidation and reduction, under the conditions of these experiments, are of the order of magnitude indicated.

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The other type of experiment carried out in the attempt to show that Pu(III) and Pu(IV) are involved in equilibrium with the nitrous acid system consisted of measuring the distribution of trace concentration of plutonium between a TTA benzene phase and an acid phase containing nitrous acid when the true distribution of Pu(IV) between the phases was known. From this known distribution and the material balance the ratio of (Pu(III)) / (Pu(IV)) in the aqueous phase may be determined. Then, from a measurement of the solution potential and the E° for the Pu(III)-(IV) couple the same ratio may be calculated. Unfortunately there is a slow reaction between nitrous acid and TTA which makes it difficult to get good equilibrium results when high nitrous acid concentrations and low TTA concentrations are used. Only one such experiment was done. The results are given in Table 11. The assumption was made that the first measurements taken constituted the equilibrium condition. These measurements gave the same results from two to six minutes, after which the extraction coefficient fell off slowly to zero.

TABLE 11

Data on Equilibrium Determination of $\frac{(\text{Pu(III)})}{(\text{Pu(IV)})}$ Ratio in Aqueous Phase at High Nitrous Acid Concentration

(HCl)	(HNO ₂)	(TTA)	Known Equilibrium E_w^B Pu(IV)	Meas. E_w^B of Tot. Pu	E meas. (volts)	E° Pu(III)- IV	$\frac{(\text{Pu(III)})}{(\text{Pu(IV)})}$ in aqueous phase
mol/l.	mol/l.	mol/l.					
0.25M	0.10M	0.01M	20	1.16	0.888	-0.966*	Calc. 21 Meas. 16

*Complexing of Pu by NO_2^- or NO_3^- formed from HNO_2 was assumed negligible as was the relatively small effect of lower chloride ion concentration.

The experiments presented in this section were all exploratory in nature. Their purpose was to put the oxidation steps of the redox cycles on a footing which was a little more firm than just the empirical fact that some conditions worked satisfactorily while others did not. A complete and definite understanding of the behavior of plutonium in nitrous acid systems would require a large number of well planned and carefully carried out experiments.

5.4 Oxidation of Pu(III) to Pu(IV) for Extraction Following Reduction by Ferrous Iron.

Assuming the existence of a moderately rapid equilibrium between Pu(III), Pu(IV), nitrous acid and its decomposition products, the ratio $K = \frac{(\text{Pu(III)})}{(\text{Pu(IV)})}$ in the aqueous phase will be deter-

mined by a consideration of the appropriate E° potential for the Pu(III-IV) couple and the potential of the system under consideration. In an extraction if R is the volume ratio of benzene/water and E is the equilibrium extraction coefficient for Pu(IV), the fraction of Pu extracted at equilibrium will be $RE/1+RE+K$. When $E = 100$ and $R=K=1$ the fraction extracted will be 0.98 instead of 0.99 in the absence of Pu(III), i.e. when $K=0$. Consequently the extraction efficiency will not be seriously lowered if K can be kept equal to or less than unity. As previously indicated the most convenient way to get a favorable value of K is to have the oxidizing power of the nitrous acid system a maximum which is done by using low concentrations of nitrous acid in an atmosphere of air or oxygen. The formation of any appreciable amount of Pu(VI) in these solutions is not likely because the equilibrium in most nitrous acid systems favors Pu(III) or Pu(IV) rather than Pu(VI), and also the rate of oxidation of Pu(IV) to Pu(VI) is known to be quite small.*

*See Sec. 5.5 of this report

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In Table 12 are summarized the data of several experiments in which the Pu(IV) chelate was reduced out of the benzene to Pu(III) with ferrous iron and then oxidized with nitrous acid and reextracted. Figure 14 shows the approach to equilibrium versus time in one instance. It would be desirable to understand the kinetics of this step well enough to be able to calculate accurately the time of extraction necessary to reach the practical equilibrium. Unfortunately ferrous iron is oxidized rather slowly by nitrous acid²² and the rate of oxidation of Pu(IV) does not follow any simple expression in these solutions. Consequently the time of extraction necessary to attain equilibrium must be experimentally determined for each new condition. It is evident that when 99% over-all product recovery is being attempted in the extraction decontamination process such details must be carefully considered. The equilibrium results given in Table 12 agree quite well with the expected values when the ratio of (Pu(III)) aque- (Pu(IV))

ous is calculated from potential data.

TABLE 12

Extraction of Pu which has been reduced by Ferrous Iron
to Pu(III) and Reoxidized to Pu(IV) by Nitrous Acids

(Fe ⁺⁺) mol/l.	(HNO ₂) mol/l.	E _{meas.} (volts)	E° (Pu(III-IV)) (volts)	R	Equi- librium E _w ^B Pu(IV)	Meas. % Ex- tracted	Calc. % Extract- ed
0.0018	0.0035	-0.984	-0.945*	1	22.8	96	95.5
0.002	0.004	-0.980	-0.945	0.5	72	97	96.8
0.004	0.008	-0.972	-0.945	0.375	4.5	51†	60

*All experiments were done in 0.5 M HNO₃.

†The E Pu(IV) was probably reduced here due to the relatively large amount of ferric iron present after oxidation. Ferric extracts moderately well and will thus reduce the concentration of TTA somewhat.

5.5 Reduction of Pu(VI) by Nitrous Acid and by Ferrous Iron. The composition of the dissolver solutions to be used in the TTA chelate process in 2 M uranyl nitrate and about 0.25 M nitric acid. Since no specific complexer for Pu(IV) can be added to stabilize that state because the complexing would lower the extraction efficiency, there will always be the possibility of having appreciable amounts of Pu(VI) or Pu(III) formed in the dissolver solution. It is, therefore, necessary to have available a method for quantitatively stabilizing plutonium as Pu(IV), thus rendering all the plutonium in a dissolver solution extractable.

Most reducing agents are thought to reduce Pu(VI) to oxidation states lower than (V) by the following mechanism:

- (1) Pu(VI) + reducing agent → Pu(V), moderately rapid
- (2) Pu(V) + Pu(III) → Pu(IV), moderately slow in microconcentrations of Pu, very slow in trace concentrations.
- (3) Pu(V) + reducing agent → lower oxidation states of Pu, extremely slow (except for Fe⁺⁺ as the reducing agent.)

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Several experiments were done to determine the rate at which nitrous acid reduced Pu(VI) present in trace concentrations. The reduction was followed by continuously extracting the solution containing the Pu(VI) and nitrous acid with a TTA benzene phase. The results of those experiments are given in Table 13.

TABLE 13

Reduction of Pu(VI) by Nitrous Acid

Exp.	Concentrations (mol/l)			Results
	(UNH)	(HNO ₃)	(HNO ₂)	
1	0	0.5M	0.01 M	No reduction detectable over a 12 hr. period
2	2.0 M	0.25 M	0.001M	50% reduced in 1 hour
3	2.0 M	0.25 M	0.003M	50% reduced in 1 hour
4	2.0 M	0.25 M	0.01 M	50% reduced in 2/3 hour

In order to check upon the validity of the reductions obtained in the uranyl nitrate solutions which were being continuously extracted by a TTA benzene phase, a one phase system of uranyl nitrate, nitric acid, nitrous acid and trace Pu(VI) in one case, Pu(IV) in another, were allowed to stand for two hours. The solutions were then briefly extracted with a TTA benzene phase. In neither the system containing Pu(VI) nor the one containing Pu(IV) was there any appreciable change in oxidation state in the two hour period. It is possible that in 2 M UNH a product of the nitrous acid - TTA reaction acts as a moderately fast reducing agent. Weight is lent to this belief by the observation that the fraction of plutonium extracted versus time curves exhibited induction periods of ten to twenty minutes for the 2 M uranyl nitrate solutions containing nitrous acid when these solutions were being continuously extracted by a TTA benzene phase. In most systems, however, it seems certain that nitrous acid does not reduce Pu(VI) to oxidation states lower than Pu(V) at an appreciable rate.

Ferrous iron has been reported elsewhere^{23,24,25} to reduce Pu(VI) to Pu(III) rapidly. This presumably is due to the fact that the Fe(II)-Pu(V) reaction is quite rapid. The action of ferrous iron in reducing trace Pu(VI) in 2 M uranyl nitrate, 0.25 M nitric acid solutions was studied by the following method. The uranyl nitrate solutions containing trace concentration of Pu(VI) was made 0.002 M in ferrous chloride and 0.002 M in urea. Urea was added to stabilize the ferrous iron. The exact concentration required in actual process work will have to be determined by work on true dissolver solutions. The system was then allowed to stand for fifteen minutes. The solution was then made 0.01 M in nitrous acid and immediately extracted with a TTA benzene phase. Within twenty minutes the systems reached equilibrium and the equilibrium extraction coefficients corresponded to those obtained by extracting Pu(IV) from

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uranyl nitrate solutions of the above concentrations and acidity. (Note: in 2 M uranyl nitrate, 0.25 M nitric acid solutions containing low concentrations of nitrous acid the equilibrium ratio of $\text{Pu(III)} / \text{Pu(IV)}$ aq. is the order of magnitude of 10^{-3} .) Using this method it seems likely that quantitative extraction of plutonium from dissolver solutions is easily accomplished regardless of what oxidation states of plutonium are initially available.

6. Process Studies in Glass Equipment

Utilizing the results given in the preceding sections several preliminary plutonium recovery experiments from synthetic dissolver solutions were carried out. The first two experiments were done in glass on a thirty milliliter scale, the rest were done in number 304 18-8 stainless steel on a liter and a half scale. Certain extrapolations of the data of the previous sections were made to recover plutonium successfully. The effect of these extrapolations is mentioned in the discussion of the results of the experiments. The flow sheets and results of the experiments in glass are given respectively in Figure 15 and Table 16.

As may be seen from Table 14 the recoveries of plutonium were in general quite close to the expected values. The recovery in the extraction of the dissolver solution in Experiment I was thought to be low due either to incomplete reduction of Pu(VI) by the ferrous iron or to non-attainment of equilibrium in the extractions. In Experiment II Table 14, changes were made to correct these two possible factors and the recovery was as expected. However, the work done in stainless steel equipment indicates that the rate of reduction is increased due either to the stainless steel, to the increase in volume used, or to the use of commercial grade chemicals. A discussion of this effect will be presented in Sec. 7 of this report. From Figure 15 it will be noted that in step III a deficiency of nitrous acid was added with respect to the urea and iron (one mole of urea reacts with two moles of nitrous acid to give nitrogen and carbon dioxide.) This was done because it was thought that some of the urea might have been destroyed in the long period of stirring required to get complete reduction. In the work done on the liter and a half scale in stainless steel equipment hydroxylamine hydrochloride was used in place of urea. It is emphasized again that the final excess of nitrous acid present in these extractions must be small for best recovery of plutonium.

Figure 16 shows a generalized flowsheet of the TTA batch extraction decontamination process. It outlines the steps necessary to recover plutonium successfully in such a process and gives the details which must be considered in designing the actual process for use. The flexibility of the process is obvious from the number of permutations of steps and conditions which may be used to achieve whatever results are desired. It seems likely that the exact conditions which give the best results with our present equipment and scale will not necessarily give the best results in other equipment and on a larger scale. The changes necessary to fit the process to different equipment and larger scale should however be only in the adjustment of details well within the flexibility of the flowsheet. The generalized flowsheet in Figure 16 is but one of the two possible. Depending on unknown decontamination factors it may prove advantageous to use the steps in inverted orders. The theory of the flowsheet for process will be very similar to that in Figure 16.

7. Semi-works Process Studies

A laboratory has been equipped to study the chelate process on a liter and a half scale. The apparatus essentially consists of mixers and transfer equipment constructed of number 304, 18-8 stainless steel. The equipment is designed to test a process consisting of three cycles and will handle enough activity to make possible the measurement of gamma decontamination factor or 10^6 with ease and safety.

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FIGURE 15 Flowsheets for Pu Recovery Experiments using the

Batch TTA Chelate Process in Glass Equipment

Exp. I

vol = 30 ml

Extraction of dissolver Solution

(1) Solution made 0.002M in FeCl_2
and 0.002 in $\text{CO}(\text{NH}_2)_2$

(2) Solution stood for 15 minutes || (2)' Solution stood for 25 minutes

(3) Made solution 0.01 M in HNO_2

(4) Extracted twice with 10 ml. of 0.09M TTA in benzene ($\text{Pu(IV)}=63$)

(a) Stir extraction for 20 minutes || (a)' Stir extractions for 30 minutes

Discard
water
residue

Combine two benzene phases and dilute to 40 ml with benzene

Exp. II

vol = 30 ml

Discard
Water
residue

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Fig. 15-c

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FIGURE 16

Generalized Flowsheet of TTA Batch Extraction Decontamination Process

I. Extraction of Plutonium from the dissolver solution

Dissolver Sol.
2 M $\text{UO}_2(\text{NO}_3)_2$

0.25 M HNO_3
Pu(Any oxid.
state)

- A. Reduction of plutonium in the dissolver solution to Pu(III)
All oxidation states of Pu are reduced quantitatively to Pu(III)
by dilute concentrations of Fe(II) and $\text{CO(NH}_2)_2$

1. The $\text{CO(NH}_2)_2$ is added to stabilize the Fe(II) , the exact concentration will depend upon the dissolver solution in use.
2. Concentration of Fe(II) must be kept small so that very little TTA will be used up in extracting Fe(III) following oxidation of Pu(III) and Fe(II) by HNO_2 .
3. Concentration of both Fe(II) and $\text{CO(NH}_2)_2$ must be small enough so that a small excess of HNO_2 may be conveniently added.

B. First Extraction of Pu(IV)

A small excess of HNO_2 over Fe(II) and $\text{CO(NH}_2)_2$ is added to oxidize Pu(III) to Pu(IV) and the Pu(IV) is extracted with a TTA benzene phase. In general it is believed that two extractions here will give the most efficient plutonium recovery and best decontamination.

1. The concentration of TTA and the volume of extracting phase used will be determined by the recovery of Pu desired, the volume reduction desired, and a consideration of the dilution of the TTA benzene phase necessary to get a suitable rate of reduction in the next step. A consideration of the decontamination obtained by the various permutations of R and E is also necessary (this is unknown at present).
2. The fraction of the total plutonium extracted is given by $F = \frac{RE}{1 + RE + K}$ where R is the volume ratio benzene/water, K is the ratio $\text{Pu(III)}/\text{Pu(IV)}$ in the aqueous layer and E is the equilibrium extraction coefficient for Pu(IV).
3. The extraction time must be long enough to reach equilibrium.
4. The aqueous residue contains greater than 99.5% of the $\text{UO}_2(\text{NO}_3)_2$ in all cases thus far investigated. The exact amount will vary depending on the acidity and ketone concentration used.
5. The aqueous residue is discarded or saved for subsequent uranium recovery and the benzene extracts are combined if two extractions are done.

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II. First Reduction of Pu(IV) chelate.

The benzene phase from the first extraction containing Pu(IV) chelate, fission products and TTA is diluted with benzene. A nitric acid phase containing Fe(II) and $\text{CO}(\text{NH}_2)_2$ or $\text{NH}_3\text{O HCl}$ is added and the plutonium reextracted from the benzene by reducing Pu(IV) chelate to Pu(III).

- A. The concentration ratio $(\text{TTA})/(\text{HNO}_3)$ used must be adjusted so that the equilibrium E of Pu(IV) is high enough to result in good decontamination but not so high that an undue loss of Pu due to Pu(III) extraction will result or that an excessive amount of time is required for quantitative reduction of Pu(IV).
- B. The volume ratio will be determined by the aqueous volume reduction desired, rate of reduction of Pu(IV) chelate, and decontamination considerations as yet unknown.
- C. The concentrations of Fe(II) and $\text{CO}(\text{NH}_2)_2$ will be determined by the same conditions as in I. The use of NH_3OHCl in place of $\text{CO}(\text{NH}_2)_2$ is preferred because of its superior stabilizing action toward ferrous ion.
- D. The time required for essentially quantitative reduction will be determined by a consideration of volume ratio, E of Pu(IV) and any specific catalytic effects due to equipment or chemicals. The ferrous ion is known to be stable for at least five hours.
- E. The benzene residue is discarded or saved for recovery of active zirconium which constitutes at least 90% of all fission activity present.

III. Second extraction of Pu(IV)

The oxidation and extraction conditions will be determined by the same considerations as Step II, although the exact conditions will be different due to the changed acidity and absence of UNH. Steps I and II, constituting a cycle, are repeated as many times as necessary to achieve the decontamination required.

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TABLE 14

Results of Pu Recovery Experiments Using Batch TTA Chelate Process

STEP	%Pu Recovery		
	Experiment I	Experiment II	Calculated
I. Extraction of dissolver solution			
a. Over-all	99.2	99.8	99.75*
b. First extraction	94.0	94.1	95.0
c. Second extraction	5.2	5.7	4.75
II. First reduction	99.55	99.2	99.9 [†]
III. Second Extraction			
a. Over-all	99.8	99.73	99.9
b. First extraction	97.3	97.0	97.0
c. Second extraction	2.5	2.73	2.9
IV. Second Reduction		99.63	99.9 [†]

*The calculated recoveries on the extraction steps correspond to the formula:

$$\% \text{ extracted in each extraction} = \frac{R}{1+RE+K} E$$

where $R = \frac{\text{Benzene volume}}{\text{Water volume.}}$

$E = \text{Equilibrium extraction coefficient of Pu(IV) and } K = (\text{Pu(III)}) / (\text{Pu(IV)}) \text{ aq.}$

[†]The calculated recoveries on the reduction steps are those which it is possible to get if the reduction is carried out for a long time.

In Figure 17 the schematic drawing of one cycle of the hot laboratory equipment for the semi-works study is shown. The actual equipment which contained the active material was behind a lead wall four inches thick and six feet in height. The lines for the addition of reagents, oxygen inlets and aliquot removal were brought over the top of the wall. All valves on lines that contained active solution were stainless steel needle valves manually operated through the wall. All valves on service lines (individual water aspirators, air, oxygen and emergency showers) were solenoid type valves if inside the walled off area and ordinary manual valves if located outside the wall. A double bank of mirrors gave a normal horizontal view as well as a vertical view. The photographs in Figure 18 show the actual arrangement of the equipment.

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FIG. 17

SCHEMATIC DRAWING OF THE HOT LABORATORY EQUIPMENT FOR
SEMI-WORKS STUDY OF THE CHELATE PROCESS

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FIGURE 18

Photographs of the Hot Laboratory Equipment for Semi-Works
of the Chelate Process

View looking at front of wall

1. Handles of manual valves
2. Aliquot tubes
3. House vacuum line
4. Oxygen manifold
5. Reagent addition funnels
6. Emergency showers
7. Air line inlet
8. Service line solenoid valves

View looking down the row of
mixers

1. Calibrated transfer bottles
2. Cans covering solenoid valves to protect from emergency showers
3. Air motors
4. Mixers
5. Air exhaust manifold
6. Emergency showers
7. Reagent addition lines
8. Aliquot removal lines

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The procedure of performing a cycle consisted first of draining an aqueous solution from a bottle into an extracting mixer. The benzene phase and other reagents necessary for the extraction were added through the reagent addition tubes which were connected to funnels outside of the wall. Then the extraction was performed by mixing the two phases using the air stirrer and the two phases allowed to settle while still in the mixer. After removing small portions of each phase through their respective aliquot tubes over the wall for analysis, the benzene phase was sucked into the next bottle in the line from left to right. When the volume was read and color of solution noted it was drained into the reducing or reextraction mixer where the appropriate aqueous phase was previously added. This was then stirred, allowed to settle, and aliquots removed and the aqueous phase sucked into the next bottle. This cycle was repeated three times going through six mixers and seven bottles. No attempt was made to perfect the system of phase separation for the chemical yields and decontamination were the figures most desired.

At the time of this writing, a thorough test of the decontamination attainable in the process has not been made in this equipment. The delay in carrying out such work has been due to difficulties which have arisen in preparing the initial dissolver solutions. However, one decontamination and recovery experiment has been done which will be discussed below. As it was not a strictly representative test no unqualified statements about decontamination factors can be made at this time.

The recovery of plutonium has been satisfactorily tested in the semi-works equipment using both benzene and toluene as solvents for TTA. It was found as has been previously mentioned that conditions chosen from experiments done in glass vessels on a small scale using C. P. reagents had to be modified somewhat when stainless steel equipment, larger volumes, and technical grade reagents were used. The process conditions which have been chosen as most suitable in the present semi-works equipment are given in the detailed flowsheets of Figure 19 (using benzene as the solvent) and Figure 20 (using toluene as the solvent). The tabulated data in Table 15 indicate the detailed recovery performance of the process in individual runs using benzene (in Column 1) and toluene (in column 2) following the flowsheets of Figures 19 and 20. These results have been duplicated numerous times in individual tests of the separate steps and in other complete process runs. It should be emphasized that the process is capable of giving a plutonium recovery of virtually any desired figure by making simple changes in the conditions of acidity or ketone concentrations in the various steps. The decontamination factors will of course change as the requirement on plutonium recovery changes. We shall in our future work investigate the decontamination attainable in a process consisting of three cycles yielding a 99% recovery of plutonium.

The use of toluene as the organic solvent will be thoroughly investigated since the industrial health hazard is much less than for benzene.

From the work done so far it has been found that the extraction coefficient (organic/aqueous) using toluene as the solvent is about one half that obtained when using benzene. The Pu(III) extraction coefficient, however, is about the same using toluene and benzene. The distribution coefficient of TTA between the organic phase and the aqueous phase seems to be unchanged when using toluene in place of benzene. These facts indicate that the process using toluene will require roughly 20% more TTA to achieve the same plutonium recovery as compared to the process using benzene. Moreover, the separation coefficient of Pu(IV) and Pu(III) using toluene is about one half that obtained when using benzene. This may or may not result in a lowering of decontamination factors depending upon the manner in which the distribution coefficients of the fission product elements are changed. Since the TTA distribution coefficient between the organic phase and the aqueous phase is about the same for toluene and benzene the problem of TTA recovery will be the same in both cases.

As previously mentioned one decontamination and recovery run has been carried out in the semi-works equipments. This was not a representative test of the process for several reasons. First, the dissolver solution contained a high concentration of ferric iron (~0.04M) which was introduced into the solution from the 18-8 stainless steel equipment during the process of dissolving the uranium slug in concentrated nitric acid. Since ferric iron has an appreciable extraction coefficient, large amounts of ketone will be used up in forming the ferric chelate if a large concentration of iron is present in the initial dissolver solution.

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FIGURE 19

TTA PROCESS FLOWSHEET USING BENZENE AS THE ORGANIC SOLVENT IN

SEMI-WORKS EQUIPMENT

CYCLE I

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Fig. 19-b

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FIGURE 20

TTA PROCESS FLOWSHEET USING TOLUENE AS THE ORGANIC SOLVENT IN THE
SEMI-WORKS

CYCLE I

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Fig. 20-b

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CYCLE III. Repeat Cycle II in every detail

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give a plutonium recovery of 99%. In one experiment on the liter and a half scale in stainless steel equipment a three cycle process has given decontamination factors for beta and gamma radiation of the order of magnitude of 10^7 and 10^5 - 10^6 respectively. Although the plutonium recovery in this experiment was not altogether suitable, it has shown that only a few minor changes in the flowsheet are necessary to make the recovery of plutonium 99%. It is felt that these changes will not noticeably affect the decontamination obtained.

In its present form, the process is definitely known to fill the following requirements:

1. Recovery and concentration of plutonium. The recovery of plutonium can be made 99% complete in a three cycle process using benzene as the solvent. When toluene is used, the recovery can be made 98.5% complete or greater. Theoretically, plutonium may be concentrated by as much as 40 fold in the chelate process, when processing 2M UNH solution containing plutonium. This limit is placed on the volume reduction attainable by the solubility of plutonium chelate in benzene which has been determined by W. H. Reas in unpublished results to be 0.012M. As yet the solubility of plutonium chelate in toluene has not been determined.

2. Recovery of Uranium. No effort has been directed toward the recovery of uranium. However, it is known that greater than 99.5% of the uranium remains in the aqueous residue from the initial extraction of plutonium from the dissolver solution along with all fission products except zirconium. It seems likely that a satisfactory batch solvent extraction method can be developed to recover and decontaminate the uranium.

3. The cost of chemicals exclusive of dissolving the uranium slugs has been calculated to be less than \$300.00 per ton of uranium metal processed through three cycles of the chelate process. This assumes that the TTA is recovered to an extent of at least 80%. This requires nothing more elaborate than precipitation and a simple distillation. This cost compares favorably with any existing process now known.

4. Recovery and Partial Separation of By-products. The fission products are partially separated in the initial extraction of Pu(IV) from the dissolver solution. The first benzene or toluene extract consists of over 95% zirconium.

5. The process is extremely flexible. Conditions can be selected to make the chelate process work within a wide range of requirements.

At the present time the following factors are unknown or at best partially worked out:

1. Decontamination. No complete decontamination studies have been possible as yet because of difficulties in reproducing the conditions of Hanford dissolving operations. In all cases the rate of corrosion of the equipment has been excessive and has introduced too great an amount of iron in the solution of the slug to permit the initial extraction to be a true representation of the flowsheet conditions. The process is designed to handle the iron that is present in the Hanford dissolver solution. Every indication from the studies performed on the remainder of the process is that in a three cycle process, the decontamination will be close to 10^6 and 10^7 for gamma and beta radiation respectively when the Clinton slugs are used as starting materials.

2. Choice of Solvent. The choice of solvent for the TTA is still open. Benzene seems to be somewhat better chemically than toluene. Octane, chlorobenzene, carbon tetrachloride and chloroform are vastly inferior to the first two. Other solvents not yet investigated may prove to be superior to both benzene and toluene.

3. Recovery of Uranium. The problem of the recovery and decontamination of uranium has received virtually no attention to date. Although it is definite that the TTA method cannot be used for this purpose, it is felt that a suitable batch extraction method using similar equipment to the chelate process could be developed.

4. Applications of the chelate process to column operation. This problem has received but little study to date. The time necessary for extraction of the Pu(IV) chelate in glass equipment indicates that the residence time per plate would be of the order of ten minutes or more, however, the reverse of the rate of chelation was increased considerable when the experiments were performed in stainless steel. This may indicate that the rate of chelation may be subject to catalysis. It would seem desirable to further consider the possibility of some type of continuous operation of the chelate process.

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5. Separations based on rates of extraction. There are indications from unpublished experiments that the rate of extraction of some of the fission products is as much as ten or more times slower than that of Pu(IV). Therefore, it may be possible to increase the decontamination in the chelate process by stirring the two phases for just the time required for equilibrium extraction of Pu(IV) at which time some of the fission products would be only partially extracted. It would be desirable to have accurate rate data on the extraction of the various fission product species and plutonium in the equipment designed for ultimate use. Since it was not possible to reproduce the rate measurements when the process was performed in stainless steel as compared to glass apparatus, it will probably be necessary to measure all of the rates concerned in the equipment ultimately used.

Despite the uncertainties outlined in the preceding paragraphs, the theoretical studies performed on the individual and combined steps fundamental to the process indicate that with one or two minor exceptions the chemical theory underlying the operation of the chelate process is rather well understood.

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