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Kinetic Study and Process Optimization of Plutonium Barrier Units for Enhanced Plutonium Stripping in the PUREX Process

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Abstract: In the PUREX (the plutonium uranium reduction extraction) process, a plutonium barrier unit (1BXX) is used to achieve deep plutonium stripping. According to the operating experience of the French reprocessing plant, after the separation of uranium and plutonium in the first cycle (1B + 1BXX), the plutonium barrier unit has excellent stripping effect, such that the removal of plutonium from uranium can already be achieved in the first cycle, and the second cycle only needs to focus on the removal of neptunium from uranium in order to obtain a qualified uranium product. In recent decades, China has also been actively conducting research on the plutonium barrier unit process to reduce the plutonium concentration in the primary uranium product in the first cycle to avoid the need to remove neptunium and plutonium at the same time in the second cycle, and to improve the efficiency and feasibility of reprocessing. Due to the lack of design basis for plutonium barriers to achieve deep plutonium stripping at present, this study conducts a basic study on the plutonium barrier unit, aiming to provide data for the optimization of plutonium barriers in the actual reprocessing process at a later date. In this work, a kinetic study on the reduction and stripping of trace plutonium from dibutyl phosphate-containing organic phases was carried out first, and the kinetic equations for the reduction and stripping of Pu(IV) by U(IV) under flow process conditions were obtained. The effects of U(IV) addition on the extraction loss of U(IV) and the concentration distribution of U(IV) at various stages were investigated by process simulation. Additionally, the oxidation of U(IV) under process conditions was investigated to clarify the process chemistry of U(IV) oxidation and to provide a reference for the oxidation consumption of U(IV). Finally, the process parameters of the plutonium barrier unit were preliminarily designed based on the above research.

Keywords: plutonium barrier; HDBP; plutonium stripping; U(IV)

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1. Introduction

Energy is an important material basis for various human activities [1]. The development of nuclear power has been ongoing in recent decades, and with it has come the issue of storing and disposing of large quantities of spent fuel [2]. Spent fuel contains uranium (U), plutonium (Pu) and a large number of fission product (FP) elements, which are extremely radioactive [3]. In order to improve the utilization rate of U and Pu resources and maintain the sustainable development of nuclear energy, the treatment of spent fuel is required to recover the U and Pu contained and lower their radioactivity [4]. A reprocessing process may efficiently increase the pace at which uranium resources are utilized, decrease the quantity of radioactive waste produced, and assure the long-term viability of nuclear energy [5].

Operational experience of reprocessing plants has shown that the PUREX process is a more economical, safe and reliable process compared to other reprocessing processes [6]. The process uses tributyl phosphate (TBP) as the extractant, and n-dodecane, kerosene or hydrocarbon mixtures as the diluent. The separation and recovery of U, Np, Pu and FPs are

achieved by adjusting the valence state [7], taking advantage of the chemical properties of TBP, which readily extracts U(VI), Pu(IV), Np(IV) and Np(VI) but not Pu(III), Np(V) and FPs [8,9].

Briefly, the PUREX process consists of a uranium and plutonium co-extraction unit (1A), a uranium and plutonium separation unit (1B) and a uranium stripping unit (1C) [10,11]. Because the uranium-containing organic phase product stream resulting from the 1B unit still contains Pu (about 0.1 per cent of the total plutonium), a plutonium barrier unit (1BXX) is occasionally set up after the 1BX column to further increase the separation factor of Pu and U ($SF_{U/Pu}$) and to prevent these traces of plutonium from entering the uranium purification cycle (1C unit). Uranium-plutonium separation at the UK THORP plant in 1B unit (1BX, 1BS and 1BXX) proved satisfactory, with a $SF_{U/Pu}$ range from 1.4×10^4 to 6.5×10^4, which is an order of magnitude higher than the design value of the process (3.3×10^3) [12].

At present, the most widely used reductant in the separation of U and Pu is U(IV) [13–15]. U(IV) associated with hydrazine (N_2H_4) as holding reductant is commonly used in reprocessing plants [16,17], which has a mature process, does not introduce impurities, and yields a relatively pure plutonium nitrate solution with high reduction efficiency [18].

However, in the U and Pu separation process, there are still several insoluble problems: Firstly, in order to ensure the effective reduction of Pu(IV), it is necessary to add a large amount of U(IV), which is many times larger than the stoichiometric amount [19,20]; and secondly, although U(IV) can theoretically reduce Pu(IV) in depth, the $SF_{U/Pu}$ is not as high as in the multi-stage reverse extraction process. In addition, domestic and foreign reprocessing plant operation experiences show that organic solvent irradiation products have a certain negative impact on plutonium stripping and that irradiation products can be strongly coordinated with Pu(IV), making it difficult for Pu(IV) to be completely stripped. Although some studies have shown that irradiation products such as dibutyl phosphate (HDBP) have a small thermodynamic effect on U(IV) as a reductant [21,22], it has little effect on the reduction and stripping of U(IV) [23,24]. However, the exact extent of its influence on the kinetics of the U(IV) reduction–recovery reaction is not fully understood.

Compared with column 1B, the 1BXX unit has a higher flow ratio and longer residence time. In order to achieve complete stripping of trace plutonium in the plutonium barrier unit, it is necessary to provide sufficient reaction time for the reduction of Pu(IV) by U(IV), especially in the presence of irradiation products. The longer reaction time requires special attention to the reoxidation of U(IV), and the consumption of U(IV) caused by high-flow organic phase extraction of U(IV) should not be neglected. Reasonable process parameters such as the addition point, the flow ratio and the number of stages should be designed to ensure a reasonable distribution of U(IV) in the plutonium barrier so that there is enough U(IV) at all stages to reduce the trace Pu(IV).

In this work, the kinetics of reductive stripping of trace Pu(IV) by U(IV) in the presence of HDBP were investigated. Process parameters such as U(IV) addition model and flow ratio were also designed by investigating the reoxidation of U(IV) in the presence of HDBP and combining these with process simulation calculations. A stability study of U(IV) was also conducted to elucidate the process chemistry of U(IV) oxidation by spectrophotometry. All these provide some experimental basis for investigating the process design of the plutonium barriers unit during reprocessing.

2. Experimental Setup

2.1. Reagents and Instruments

The HDBP used was produced by the Sinopharm Group, with a purity >98%. The rest of the reagents are produced by Sinopharm Group (Shanghai, China) and are analytically pure. A UV-visible spectrophotometer by PerkinElmer Lambda, USA was used.

2.2. Extraction and Stripping Experiments

Kinetic research: At 15 °C, an aqueous solution of HNO_3 containing U(IV) and Pu(IV) was mixed with an equal volume of a 30% TBP/n-dodecane solution containing HDBP,

shaken for various periods and divided into phases. Then, 25 µL of the aqueous and organic phases were used to prepare 3–5 samples in parallel for the measurement of Pu concentration.

The kinetic rate equation can be expressed as follows:

$$r = -d[Pu(IV)]/dt = k[Pu(IV)]_{(o)}{}^{m} [U(IV)]_{(a)}{}^{n} [HNO_3]_{(a)}{}^{x} [HDBP]_{(o)}{}^{y} \quad (1)$$

m, n, x and y are the number of reaction steps for the HDBP concentration in the organic phase, respectively.

***U(IV) stability studies*:** For stability experiments of U(IV) in the aqueous phase: Prepare a 0.01 mol/L U(IV) and 0.1 mol/L hydrazine solution in HNO_3, stir sufficiently, take samples in the cuvette every half hour, and measure the spectral changes with time. For stability experiments of U(IV) in the organic phase: A 0.01 mol/L U(IV) and 0.1 mol/L hydrazine solution in HNO_3 was prepared and extracted into a 30% TBP-n-dodecane solution. With thorough stirring, samples were taken every half-hour and placed in a cuvette, and the spectra were measured as a function of time.

2.3. Methods of Analysis

Trace Pu concentration in the aqueous phase containing U: Take 1 mL of the aqueous phase sample, adjust the acid to 2 mol/L, and let it stand for 5 min; add 0.1 mL 1 mol/L $NaNO_2$, then add 0.1 mL 1 mol/L N_2H_4; after that add 1 mL 0.5 mol/L TTA-xylene solution, and extract for 15 min, then separate the two phases. Wash the organic phase twice with equal volume 1 mol/L nitric acid. Take 0.5 mL of the washed organic phase, dilute it to 2.5 mL with isopropanol, and measure the Pu-238 concentration using α-energy spectrometry after the preparation of the source. Calculate the total Pu concentration in accordance with the abundance of Pu isotopes.

Trace Pu concentration in the organic phase containing U: Take 1 mL of TBP organic phase sample, stripping four times with equal volume 0.1 mol/L nitric acid. For the aqueous phase, analyze the Pu concentration according to the above aqueous phase analysis method. For the organic phase, take 0.5 mL and dilute it to 2.5 mL with isopropanol, and then use α-energy spectrometry to measure the Pu concentration after the preparation of the source. The Pu concentration is the sum of the measured concentrations of the two phases.

U(IV) concentration: Take 3 mL of sample, add 0.5 mol/L H_2SO_4 - 1 mol/L HNO_3 - 0.1 mol/L NH_2SO_3H mixed acid solution to 20 mL, add 2.0 mL titanium trichloride solution, wait until the color fades to colorless, then add two drops of ferric sulphate, with sodium diphenylamine sulfonate as indicator, and titrate with 0.5 mol/L potassium dichromate. The end point is reached by titration when the solution is bright purple.

2.4. Analyses of Simulation Software

The simulation carried out using the plutonium barrier process simulation program named 1NA Mixer-Settler Simulation Software, which is developed by the China Institute of Atomic Energy (CIAE) [25–29]. The plutonium barrier is designed with 6 stages, with the 1BU unit added from the first stage, and 1BXXX can be added to all 6 stages. 1BU has a 70 g/L U(VI) addition and 0.035 mol/L HNO_3. The 1BXXX unit has a total 15 g/L U(IV) addition, 1 mol/L HNO_3, and 0.1 mol/L hydrazine. (Figures 1 and S1)

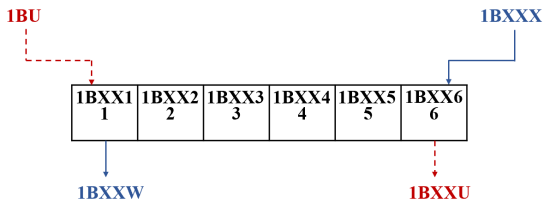

Figure 1. Flow chart of the 1BXX unit.

3. Results

3.1. Kinetic Study of U(IV) Reduction and Stripping of Pu(IV)

3.1.1. Reaction Equilibrium Time

U(IV) is widely used as a reductant in the PUREX process, but in the plutonium barrier unit, Pu extraction remains challenging, which may be caused by the strong coordination between HDBP and Pu(IV). According to the literature, hydroxylamine nitrate (HAN) and weak acid cannot effectively strip HDBP-coordinated Pu(IV). However, U(IV) is less affected by HDBP, even when the concentration of HDBP reaches 1×10^{-3} mol/L, U(IV) could effectively reduce and strip Pu(IV) [30–32]. Previous studies have found that using U(IV) as the reductant, the presence of HDBP also leads to a decrease in the rate of Pu(IV) reduction and stripping. Therefore, investigating the kinetic effect of HDBP on Pu(IV) reduction and stripping is necessary.

As seen in Figure 2a, the reduction and stripping equilibrium could be reached in 120 s, with the reduction and stripping rate of Pu(IV) in the organic phase reaching up to 99%. When 0.02% HDBP was added to the organic phase, the reduction and stripping rates were noticeably reduced, with the stripping equilibrium extended to 300 s. It was evident that HDBP had kinetic effects on the Pu(IV) reduction and stripping reaction. Based on the effect of the complete reaction, the Pu extraction rate in the presence of 0.02% HDBP was not significantly different from that in the absence of HDBP. As shown in Figure 2b, the reaction rate accelerated at low Pu(IV) concentrations, and the reaction equilibrium could be always reached in 60 s regardless of the presence or absence of HDBP, with no difference in the stripping rate at equilibrium. HDBP had the most significant effect on the reaction rate in the first 50 s of the reaction.

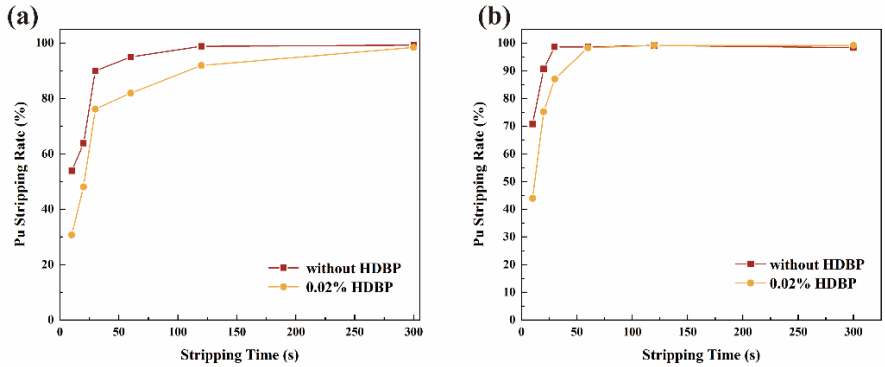

Figure 2. Equilibrium time of (**a**) 0.015 g/L Pu(IV); (**b**) 0.0015 g/L Pu(IV). ([HNO_3]: 1 mol/L, [U(IV)]: 0.5 g/L).

3.1.2. Reaction Kinetics Equation

As shown in Figure 3a, the higher the Pu(IV) concentration added to the organic phase, the faster the Pu(IV) concentration decreases, and the reaction reaches equilibrium at 120 s. Since the HNO_3 concentration ($[HNO_3]_{(a)}$), U(IV) concentration ($[U(IV)]_{(a)}$), and HDBP concentration ($[HDBP]_{(o)}$) are constant in the reaction, Equation (1) can be assuming as follows:

$$k1 = k\,[U(IV)]_{(a)}{}^{n}\,[HNO_3]_{(a)}{}^{x}\,[HDBP]_{(o)}{}^{y} \quad (2)$$

Equation (1) can be rewritten as follows:

$$r = -d[Pu(IV)]/dt = k_1\,[Pu(IV)]_{(o)}{}^{m} \quad (3)$$

where k is the reaction rate constant, and k_1 is the apparent reaction rate constant. Supposing m = 1, a straight line should result from plotting $\ln[Pu(IV)]_{(o)}$ versus *t* by indefinite integration of Equation (3). The data obtained at different Pu(IV) concentrations were processed, and the results are shown in Figure 3b. It can be seen that $\ln[Pu(IV)]_{(o)}$ is linear

with time, confirming that the reaction to $[Pu(IV)]_{(o)}$ is level 1, with m = 1, and the slope value of the straight line is $-k_1$.

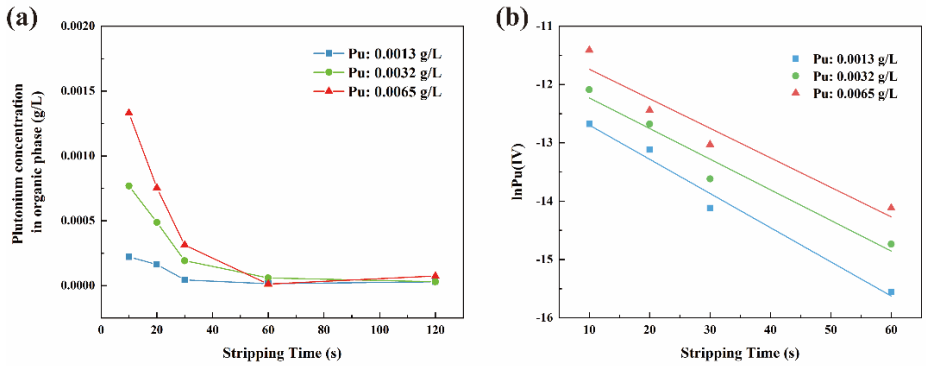

Figure 3. Relation between stripping time and (**a**) Pu(IV) and (**b**) ln[Pu(IV)](o). ([HNO_3]: 1 mol/L, [U(IV)]: 0.5 g/L, [HDBP]: 0.02%).

Under different U(IV) concentrations (0.5~2.0 g/L), the changes in Pu(IV) concentration in the organic phase with stripping time are shown in Figure 4a. With higher U(IV) concentrations, the Pu(IV) concentration in the organic phase decreases more quickly, with the reaction reaching the equilibrium in 120 s when U(IV) was 2.0 g/L, while the other reactions reached equilibrium in 30~60 s. Figure 4b shows $\ln[Pu(IV)]_{(o)}$ versus stripping time at various U(IV) concentrations. The slope of the straight line varies with different U(IV) concentrations. With the increase of U(IV) concentration, the $-k_1$ value decreases, which indicates that the reaction rate of U(IV) reduction and stripping of Pu(IV) increases with the increase of U(IV) concentration.

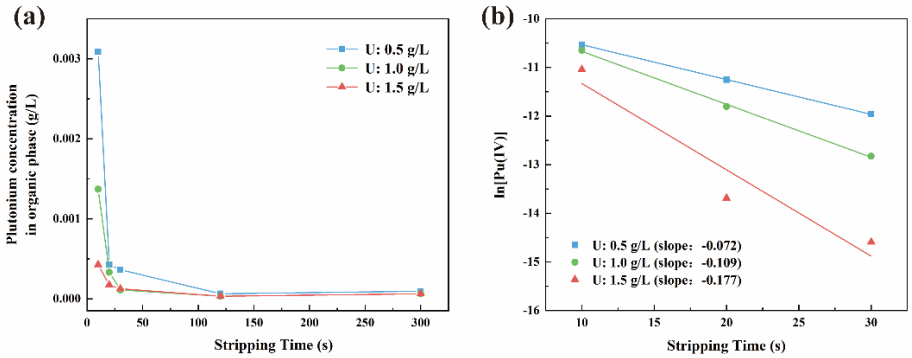

Figure 4. Relation between stripping time and (**a**) Pu(IV) and (**b**) ln[Pu(IV)](o) at different U(IV) concentrations. ([HNO_3]: 1 mol/L, [Pu(IV)]: 0.013 g/L, [HDBP]: 0.02%).

Equation (2) can be written as follows:

$$\ln k_1 = \ln k + n \ln[U(IV)]_{(a)} + x\ln[HNO_3]_{(a)} + y \ln[HDBP]_{(o)} \quad (4)$$

Figure 5 shows the relationship between $\ln k_1$ and $\ln[U(IV)]_{(a)}$, fitted to obtain a straight line slope of 0.80, R_2 = 0.9618; that is, the reaction to U(IV) concentration is a 0.8 order reaction. The reaction is not a first order reaction, which may be due to the complex interaction between U(IV) and Pu(IV). The reaction involves both redox reactions, mass transfer, and the distribution of U(IV) between the two phases.

The changes in Pu(IV) concentration in the organic phase with stripping time for different HNO_3 concentrations (0.3~2.0 mol/L) are shown in Figure 6a. At higher HNO_3 concentrations (ranging from 0.3 to 2.0 mol/L), the decrease in Pu(IV) concentration in the organic phase slows with increasing time. Under 2.0 mol/L HNO_3, the reaction approached equilibrium in only 120 s. At high HNO_3 concentrations, the reaction took longer to reach equilibrium due to the reoxidation of Pu(III). At the same time, the salting-out effect of

HNO_3 gradually increased. At 2.0 mol/L HNO_3, the Pu(IV) distribution ratio (D_{Pu}) reached 8.8, which is twice as large as the D_{Pu} in 1 mol/L HNO_3. Longer reaction times are required under increased acidity. Due to the increase in D_{Pu}, the plutonium retention in the organic phase becomes more severe. At 2.0 mol/L HNO_3, even after 120 s stripping, there was still 10^{-4} g/L Pu(IV) in the organic phase, and the plutonium retention reached up to 4.01%. Therefore, the acidity in the process should be controlled and not too high to ensure sufficient reductive stripping of Pu(IV).

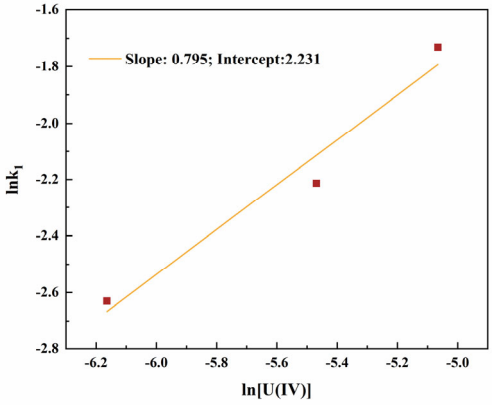

Figure 5. Relation between lnk_1 and $ln[U(IV)]_{(a)}$. ([Pu(IV)]: 0.013 g/L, [HNO_3]: 1 mol/L, [HDBP]: 0.02%).

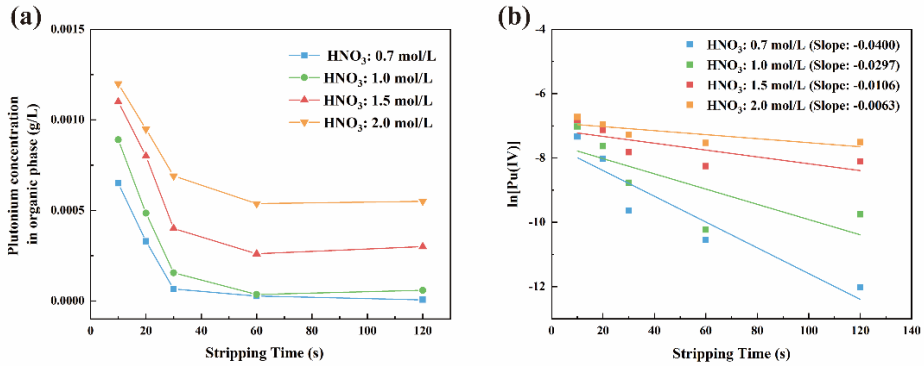

Figure 6. Relation between stripping time and (**a**) Pu(IV); (**b**) $ln[Pu(IV)]_{(o)}$ at different HNO_3 concentrations. ([Pu(IV)]: 0.0025 g/L, [U(IV)]: 0.5 g/L, [HDBP]: 0.02%).

Figure 6b shows the variation of $ln[Pu(IV)]_{(o)}$ with stripping time at different initial HNO_3 concentrations. The slope of the straight line increases gradually with the increase in HNO_3 concentration, which indicates that the reaction rate of U(IV) reductive stripping of Pu(IV) decreases with the increase in HNO_3 concentration.

Similarly, from Equation (4), keeping $[HDBP]_{(o)}$, $[U(IV)]_{(a)}$, and $[Pu(IV)]_{(o)}$ constant, lnk_1 is linearly related to $ln[HNO_3]$, as shown in Figure 7, which yields a straight line with a slope of -2.00 and $R_2 = 0.85$. The reaction with respect to HNO_3 concentration is a reversed second-order reaction. HNO_3 is not only involved in the oxidation of Pu(III) and U(IV) in the reaction but also in the coordination of U and Pu. The acidity also has an important effect on the D of U(IV) and Pu(IV). Under the experimental conditions, the HNO_3 concentration has a relatively large effect on the kinetics of the reaction. Therefore, the acidity should be included as a major consideration in the design of the process parameters. Although a lower acidity will be favorable for Pu stripping, it will also increase the stripping amount of U(VI). At the same time, the hydrolysis of plutonium should be taken into consideration when the acidity of the aqueous phase is lower than 0.3 mol/L. Therefore, the determination of the acidity requires a combination of factors to be considered.

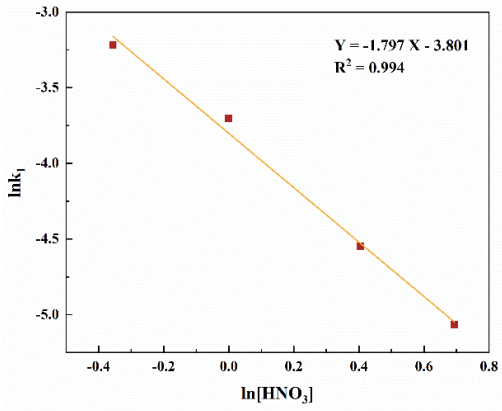

Figure 7. Relationship between $\ln k_1$ and $\ln[HNO_3]_{(a)}$. ([Pu(IV)]: 0.0025 g/L, [U(IV)]: 0.5 g/L, [HDBP]: 0.02%).

The time-dependent changes of Pu(IV) concentration in the organic phase at different HDBP concentrations (0.5–2.5 mmol/L; 0.5 mmol = 0.01%) are shown in Figure 8a. With the increase in HDBP concentration, the decrease in Pu(IV) concentration in the organic phase became slower. At 2.5 mmol/L HDBP, the equilibrium stripping time reached 120 s, while at 0.5 mmol/L HDBP, the reaction reached equilibrium in only 30 s. This indicates that HDBP has a greater influence on the kinetics of Pu(IV) reduction and stripping. Figure 8b shows the variation of ln[Pu(IV)] with time under different initial HDBP concentrations. The increasing $-k_1$ value with increasing HDBP concentration indicates that the reaction rate of U(IV) reductive stripping of Pu(IV) decreases with increasing HDBP concentration.

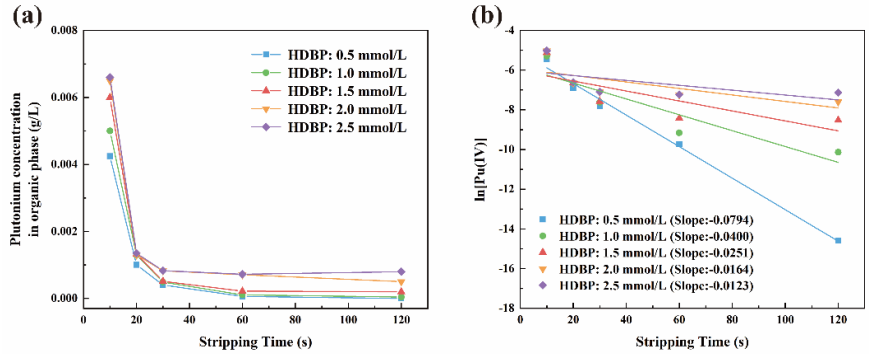

Figure 8. Relation between stripping time and (**a**) Pu(IV) and (**b**) $\ln[Pu(IV)]_{(o)}$ at different HDBP concentrations. ([Pu(IV)]: 0.003 g/L, [U(IV)]: 0.5 g/L, $[HNO_3]$: 1 mol/L).

From Equation (4), keeping $[HNO_3]$, [U(IV)], and [Pu(IV)] constant, $\ln k_1$ versus ln[HDBP] is shown in Figure 9, yielding a straight line slope of −1.18, R_2 = 0.95. The reaction to HDBP concentration is a −1.2 order reaction. The coordination between HDBP and Pu(IV) is affected by various factors such as U(IV) concentration and acidity, and there is also a competitive relationship with TBP and NO_3^-. HDBP has a greater kinetic effect on the reaction than U(IV) under experimental conditions.

Based on the experimental results, the kinetic equation for the reductive stripping of trace Pu(IV) by U(IV) in the presence of HDBP was calculated as follows:

$$r = -d[Pu(IV)]/dt = k\,[Pu(IV)]_{(o)}{}^{1.0}\,[U(IV)]_{(a)}{}^{0.8}\,[HNO_3]_{(a)}{}^{-2.0}\,[HDBP]_{(o)}{}^{-1.2} \quad (5)$$

$\ln[Pu(IV)]_{(o)}$ is linear with time, and the slope is k_1. According to different HNO_3, HDBP, and U(IV) concentrations and k_1 values, the reaction rate constant k can be calculated according to Equation (2), and the results are shown in Table 1. The kinetic rate constant for the reductive stripping of trace Pu(IV) by U(IV) in the presence of HDBP was 0.0025 ± 0.0006 $(mol/L)^{2.4}s^{-1}$.

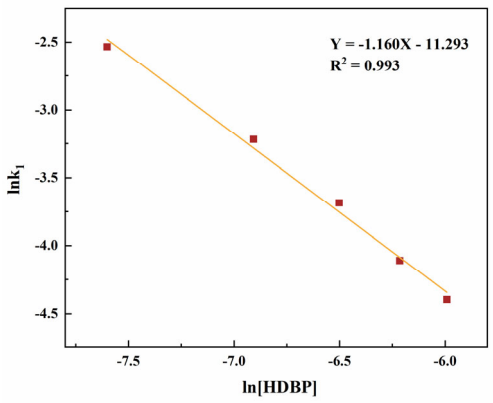

Figure 9. Relation between $\ln k_1$ and $\ln[HDBP]_{(o)}$. ([Pu(IV)]: 0.003 g/L, $[HNO_3]$: 1 mol/L, [U(IV)]: 0.5 g/L).

Table 1. Kinetic constants (k) of reduction stripping of Pu(IV) with U(IV).

U(IV) mol/L	HDBP mol/L	HNO_3 mol/L	k_1 s^{-1}	k $(mol/L)^{2.4}s^{-1}$
0.0021	0.0010	1.0	0.0720	0.0029
0.0042	0.0010	1.0	0.1090	0.0025
0.0063	0.0010	1.0	0.1775	0.0029
0.0021	0.0005	1.0	0.1325	0.0023
0.0021	0.0010	1.0	0.0704	0.0028
0.0021	0.0020	1.0	0.0243	0.0022
0.0021	0.0025	1.0	0.0205	0.0024
0.0021	0.0010	0.7	0.1099	0.0019
0.0021	0.0010	2.0	0.0189	0.0026
	Average of rate constants		0.0025 ± 0.0006	

Based on the kinetic equation, the initial Pu(IV) concentration was designed to be 10^{-3} g/L with the residence time as 2 min, and the HDBP content was 0.02%. The U(IV) concentration required for the complete reaction could be calculated from Equation (5). The presence of 0.034 g/L U(IV) in the organic phase can achieve the deep reduction of Pu(IV). However, for the design of U(IV) addition in the actual process, the loss of U(IV) and oxidation loss should be considered.

3.1.3. The Effect of Phase Ratio on the Reaction

Since the design of the 1BXX unit requires a large flow ratio in order to reduce the total amount of U(VI) stripping into 1BXXW. The effect of different phase ratios on the reduced stripping of trace Pu(IV) from U(IV) was investigated. Using 0.012 g/L Pu(IV), 0.5 g/L U(IV), and 0.02% HDBP as the organic phase, 1 mol/L HNO_3 as the aqueous phase, take the phase ratios (organic phase/aqueous phase) of 1:1, 2:1, 5:1, and 10:1, respectively. When Pu(IV) was reduced and stripped to equilibrium, the Pu retention and stripping rate were obtained as shown in Table 2. As the phase ratio increased, the stripping rate decreased, and the Pu retention in the organic phase increased by an order of magnitude.

Table 2. Relationship between phase ratio and reduction stripping of Pu(IV) with U(IV).

Phase Ratio	Plutonium Retention in the Organic Phase, g/L	Stripping Rate, %
1:1	0.0001	99.24
2:1	0.0002	99.31
5:1	0.0006	98.67
10:1	0.0015	98.22

3.2. U(IV) Extraction Losses Study

According to the experience of foreign reprocessing plants, the multi-point U(IV) addition model in the plutonium barrier unit was used (Figure S2). Compared with single-point addition, U(IV) was more evenly distributed at all stages, which ensured that there was enough U(IV) to reduce and strip Pu(IV). In the case of single-point addition, there is a possibility that a large amount of U(IV) will be extracted into the organic phase and lost to the 1C unit at the addition stage. Thus, it is necessary to study the U(IV) distribution at various stages and the U(IV) loss in the plutonium barrier unit under the multi-point addition model.

The process simulation was conducted without Pu, and the flow ratio was set to 10:1 (organic/aqueous). Firstly, a single-point addition at the sixth stage in the 1BXX unit was simulated. The results are shown in Figure 10. The U(IV) concentration was not uniformly distributed at all stages under the single-point addition, and the U(IV) concentration in the organic phase was about five times different between the first stage and the sixth stage. This is not conducive to the reductive stripping of trace Pu(IV) from 1BU. It was also observed that about 56.42% of U(IV) was lost into the organic phase at the addition stage. Therefore, in the following simulation, it is necessary to focus on the $D_{U(IV)}$ at all stages, and the loss of U(IV) also needs to be taken into account in order to reduce the loss of U in actual process applications.

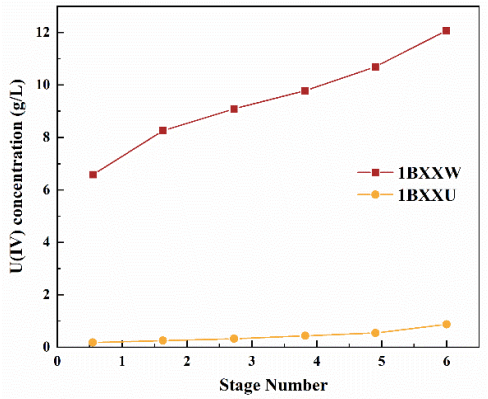

Figure 10. The distribution of U(IV) at each stage during single point addition at the sixth stage.

Multi-point addition simulations were then performed (Table S1). The first addition model: The aqueous phase of HNO_3 containing U(IV)-hydrazine was added equally in the first four stages (1BXX1–1BXX4), and the aqueous phase of HNO_3 containing hydrazine was added equally to the fifth and sixth stages (1BXX5–1BXX6). The distribution of U(IV) concentrations in the aqueous and organic phases at different stages in the 1BXX unit is shown in Figure 11.

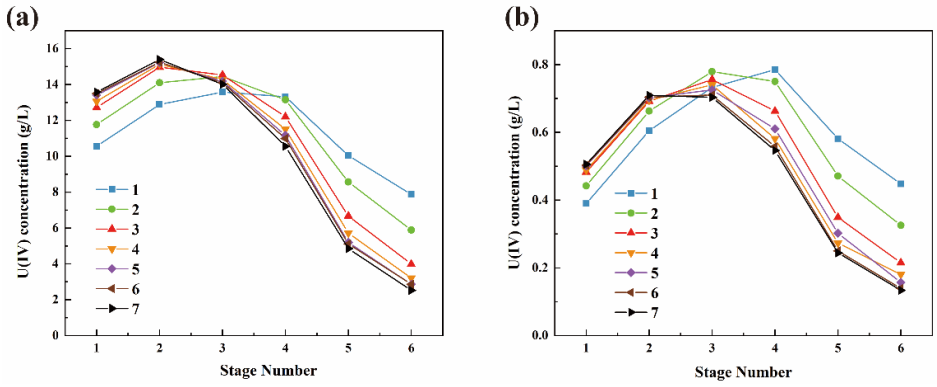

Figure 11. The U(IV) concentration at the first addition model in (**a**) the aqueous phase and (**b**) the organic phase.

Compared to the single-point addition, the U(IV) concentration in the multi-point addition was more evenly distributed across all stages. With the increase of the flow rate of the fifth and sixth stages, the U(IV) concentration in the organic phase effluent of the sixth stage decreased gradually, and when the ratio of the fifth and sixth stage flow rate to the total flow rate increased to more than 0.25, the concentration of U(IV) in the organic phase effluent was lower and remained nearly constant. At the same time, the distribution of U(IV) at all stages became more uneven with the increase of the flow rate of the last two stages. A large amount of U(IV) was carried into the first few stages with an increasing trend of U(IV) concentrations, while that in the last few stages showed a decreasing trend. It is worth noting that although the loss of U(IV) in the last stage was less, the U(IV) in the organic phase of the fifth stage was also reduced, which may be difficult to ensure the reduction and stripping of Pu(IV).

Therefore, the second addition model is set (Table S2): The first five stages (1BXX1–1BXX5) were averaged and added with HNO_3-U(IV)-hydrazine, and the sixth stage (1BXX6) was added with HNO_3-hydrazine. The distribution of U(IV) in the aqueous and organic phases are shown in Figure 12. Compared with the first addition model, the distribution of U(IV) in the organic phase this time was more uniform at all stages, although the U(IV) extracted into the organic phase in the sixth stage increased, the total amount was relatively small. As the reduction and stripping effect of Pu(IV) is the first index, the stripping effect should be ensured first, and then the loss of U(IV) should be controlled. Therefore, the second addition model is more optimized compared to the first model.

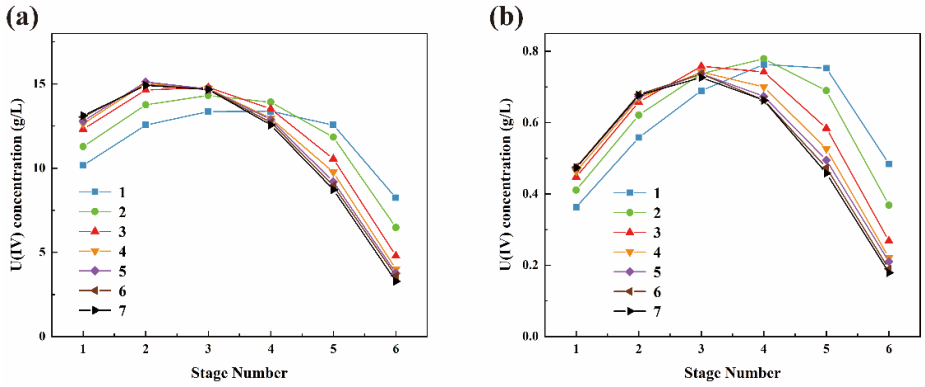

Figure 12. The U(IV) concentration at the second addition model: (**a**) aqueous phase; (**b**) organic phase.

The U(IV) loss for the second addition model was simulated, and the results are shown in Table 3. The U(IV) loss reached a low level when the liquid flow in sixth stage was 0.75 of the total 1BXXX flow. The distribution of U(IV) at each stage should also be taken into account when selecting an addition model to ensure the stripping rate of Pu(IV).

Table 3. Wastage loss of U(IV) at the second addition model.

Stage Number	1	2	3	4	5	6	7
U(IV) concentration in organic phase of 6th stage, g/L	0.48	0.36	0.26	0.22	0.20	0.19	0.18
Wastage loss of U(IV), %	31.89	24.33	17.55	14.75	13.32	12.38	11.83

Multi-point addition resulted in a more homogeneous distribution of U(IV) at all stages, and U(IV) extraction losses were greatly reduced. Thus, the addition model was further optimized by changing the first five flow ratios based on the second addition model where the eighth optimization model has the lowest extraction loss, noted as the third addition model, in which the first five stages of aqueous phase flow rate 1BXX1:1BXX2:1BXX3:1BXX4:1BXX5 = 3:3:2:1:1, and the aqueous phase flow in the sixth stage rate accounted for the total flow rate to be 0.5, and the loss of U(IV) was 15.94%, which was at a desirable low level (Table 4).

Table 4. Optimization of the first five flow ratios in the second addition model.

Number	1st	2nd	3rd	4th	5th	6th	Wastage Loss of U(IV), %
1	0.2	0.2	0.2	0.2	0.2	0.1	24.33
2	0.3	0.25	0.2	0.15	0.1	0.1	19.22
3	0.1	0.15	0.2	0.25	0.3	0.1	29.19
4	0.2	0.2	0.1	0.2	0.3	0.1	26.08
5	0.3	0.2	0.1	0.2	0.2	0.1	22.16
6	0.3	0.2	0.1	0.1	0.3	0.1	20.83
7	0.3	0.1	0.1	0.2	0.3	0.1	24.97
8	0.3	0.3	0.2	0.1	0.1	0.1	15.94
9	0.2	0.1	0.1	0.3	0.3	0.1	27.97

From the results, it can be seen that the third addition model had a more uniform distribution of U(IV) concentration in the first five stages compared to the second addition model. However, the loss of U(IV) in the sixth stage was more serious, which needs to be explained in future research after more detailed consideration of various aspects.

3.3. Study on Oxidative Loss of U(IV)

The oxidative loss of U(IV) in the process reduces the U(IV) concentration in the organic phase and may result in inadequate reductive stripping of Pu(IV). In order to optimize the process conditions of the plutonium barrier, it is necessary to understand the oxidation loss of U(IV) in the process to ensure that there is sufficient U(IV) entering into the organic phase for the reduction of Pu(IV), and then to determine the concentration of U(IV) added to the process in combination with the kinetics of the U(IV) reduction stripping and the loss of flow. It can also explore the oxidation mechanism of U(IV) and provide data for preventing U(IV) oxidation in the process.

3.3.1. Stability Studies of U(IV) in Aqueous Phases

As can be seen in Figure S3, under the combined action of oxygen and HNO_3, even with the protection of hydrazine, the oxidation of U(IV) occurred at 3.5 h. After stirring for 5 h, the U(IV) in the HNO_3 solution was oxidized by 10.11%. The presence of hydrazine consumed the HNO_2 in solution and protected U(IV). After 3.5 h, the hydrazine was consumed, which in turn oxidized U(IV).

Since it could not be determined whether the oxidation was a direct reaction by O_2 or if O_2 was only involved in the generation of nitrogen oxides in solution, thus facilitating the oxidation, further experiments were conducted in the perchloric acid solution system (Figure S4). It was observed that there was no significant oxidation of U(IV) within 5 h. This indicates that the direct oxidation of U(IV) by O_2 was not significant for several hours, and the rate of direct oxidation of U(IV) by O_2 was slow. Therefore, in the HNO_3 system, the oxidation of U(IV) by O_2 was mainly due to the participation of O_2 in the generation of nitrogen oxides in solution. O_2 can react with NO generated from the oxidation of U(IV) by HNO_2, and then generate HNO_2 to participate in the oxidation process.

3.3.2. Stability Studies of U(IV) in Organic Phases

From Figure S5, it can be seen that in 30% TBP-n-dodecane, the oxidation rate of U(IV) was faster, with obvious oxidation appearing after stirring for 0.5 h, due to the almost absence of hydrazine in the organic phase. At this time, the oxidation of U(IV) by HNO_3 was more effective. The reaction mechanism in the organic phase was similar to that in the aqueous phase, with a slower rate of direct oxidation of U(IV) by O_2 in the organic phase. Due to the limited extraction of HNO_2 into the organic phase, the overall oxidation of U(IV) in the organic phase is not significant.

3.3.3. Oxidative Loss of U(IV) in Process

The oxidation in the aqueous phase under process conditions was negligible due to the presence of hydrazine in the aqueous phase. The oxidation loss of U(IV) occurred mainly in the organic phase. According to the kinetic equation for the oxidation of U(IV) in 30% TBP, the oxidation of U(IV) at all stages of the organic phase was calculated at the single-point addition model and the third addition model. The HNO_2 concentration in the organic phase was 10^{-5} mol/L. The results of the calculations are shown in Tables S3 and S4.

Although the theoretical oxidation effect of the multi-point addition model is not much different from that of the single-point addition model, in the actual reprocessing process, it is necessary to combine the extraction loss and oxidation loss of U(IV) to consider the distribution of U(IV) at each stage, and the difference in the actual oxidation effect will be more obvious.

4. Conclusions

In this work, the process design of the 1BXX unit was centered around the kinetics of reductive stripping of trace Pu(IV), the U(IV) addition model, and the study of the oxidation mechanism of U(IV) in the process. The effects of Pu(IV) concentration, U(IV) concentration, HNO_3 concentration, and HDBP concentration on the kinetics of U(IV) reductive stripping of trace Pu(IV) in the HNO_3-30% TBP/n-dodecane system were investigated, and the kinetic equations for the reductive reaction in the presence of HDBP were determined. The reaction rate constants, k, were obtained by calculation. Through the process simulation, considering the plutonium stripping effect of the plutonium barrier unit and the difficulty of achieving the flow control, the multi-point addition of U(IV) was preliminarily optimized. The final plutonium barrier parameters were set as follows: flow rate 10:1, residence time 2 min, acidity 1 mol/L, U(IV)-hydrazine-HNO_3 addition in the first five stages, and hydrazine-HNO_3 addition in the sixth stage. The flow rate was determined as 1BU:1BXX1:1BXX2:1BXX3:1BXX4:1BXX5:1BXX6 = 200:3:2:1:1:1:3:10. U(IV)-extraction loss was about 15.94% under this condition. The stability of U(IV) in organic and aqueous phases were investigated by spectrophotometry. The process chemistry of O_2 oxidation of U(IV) in two phases were similar. The rate of direct oxidation of U(IV) by O_2 was slower, and the O_2 was mainly involved in the oxidation of U(IV) by oxidizing NO to NO_2, which was then involved in the oxidation process of U(IV). This study provides fundamental data for the future parameter design of plutonium barriers and provides a basis for plutonium barrier unit optimization.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations11090278/s1. Figure S1. The graphic interface for I/O of parameter, Figure S2. Various addition model and parameter diagram, Figure S3. Spectrogram of U(IV) in nitric acid., Figure S4. Spectrogram of U(IV) in perchloric acid., Figure S5. Spectrogram of U(IV) in 30%TBP., Table S1. Flow radio of the first addition model, Table S2. Flow radio of the first addition model, Table S3. The oxidation of U(IV) in organic phase at single point addition, Table S4. The oxidation of U(IV) in organic phase with the third addition model.

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