An improvement in APOR process I-uranium/plutonium separation process (Postprint)

Authors: XIAO Song-Tao, LI Li, YE Guo-An, LUO Fang-Xiang, LIU Xie-Chun, YANG He, LAN Tian

Date: 2023-06-18T00:00:00+00:00

Abstract

The reduction stripping behavior of Pu(IV) from 30%TBP/OK with hydroxysemicarbazide (HSC) was investigated, and the separation efficiency of HSC and DMHAN-MMH for U/Pu partitioning in Purex process was compared. The results show that HSC can effectively realize the separation of Pu from U; using mixer-settlers to simulate U/Pu separation in 1B bank of PUREX, from 16-stage counter current extraction experiment (in which 6 stages for supplemental extraction, 10 stages for stripping) with flow rate ratio (1BF:1BX:1BS) =4:1:1 in 1B contactor, good result was achieved that the yields are both more than 99.99% for uranium and Pu, the separation factor of plutonium from uranium (SFPu/U) is 2.8104, and separation factor of uranium from plutonium (SFU/Pu) is 5.9104. As a stripping reductant, HSC can effectively achieve the separation of Pu from U and the separation effect is nearly the same with DMHAN-MMH, which contributed to replace enough the latter with HSC in the U/Pu separation in Advanced Purex Process Based on Organic Reagent (APOR) process.

Full Text

Preamble

An Improvement in the APOR Process: I—Uranium/Plutonium Separation Process

XIAO Song-Tao, LI Li, YE Guo-An, LUO Fang-Xiang, LIU Xie-Chun, YANG He, and LAN Tian
China Institute of Atomic Energy, P.O. Box 275 (26), Beijing 102413, China

(Received June 27, 2014; accepted in revised form September 20, 2014; published online August 20, 2015)

Abstract: The reduction stripping behavior of Pu(IV) from 30% TBP/OK with hydroxysemicarbazide (HSC) was investigated, and the separation efficiency of HSC and DMHAN-MMH for U/Pu partitioning in the Purex process was compared. The results show that HSC can effectively achieve the separation of Pu from U. Using mixer-settlers to simulate U/Pu separation in the 1B bank of PUREX, a 16-stage counter-current extraction experiment (with 6 stages for supplemental extraction and 10 stages for stripping) was conducted with a flow rate ratio (1BF : 1BX : 1BS) = 4 : 1 : 1 in the 1B contactor. Excellent results were achieved: the yields for both uranium and plutonium exceeded 99.99%, the separation factor of plutonium from uranium (SFPu/U) was 2.8×10^4, and the separation factor of uranium from plutonium (SFU/Pu) was 5.9×10^4. As a stripping reductant, HSC can effectively achieve the separation of Pu from U, with separation performance nearly identical to DMHAN-MMH, demonstrating its potential to replace DMHAN-MMH in U/Pu separation in the Advanced Purex Process Based on Organic Reagent (APOR) process.

Keywords: APOR process, Hydroxysemicarbazide, Reduction stripping, Separation of Pu from U, Pu(IV)
DOI: 10.13538/j.1001-8042/nst.26.040605

Introduction

The Purex (Plutonium and Uranium Recovery by Extraction) process has been employed worldwide for spent fuel reprocessing. The typical Purex process includes three extraction cycles: U/Pu co-decontamination and separation, uranium purification, and plutonium purification. First developed in the USA in the 1940s, the Purex process has since been refined by researchers in many countries, including France, the UK, Russia, Japan, and China [1].

In the U/Pu co-decontamination and separation cycle of the Purex process, Pu is separated from U through the stripping of Pu(IV) from the organic phase using an aqueous reductant solution, based on the reduction of Pu(IV) to Pu(III). Consequently, the development of improved reductants represents a principal research focus in the Purex process. Since the 1960s, U(IV)-N_2H_4 has been studied as a reductant in the 1B unit of the Purex process and applied at the French Marcoule nuclear fuel reprocessing plant [2]; it has since been successfully implemented in commercial reprocessing plants such as UP-2, UP-3, and THORP.

An important trend in developing future reprocessing extraction processes is the use of high-efficiency, salt-free reductants in U/Pu separation and purification, including hydrazine [3], hydroxylamine [4, 5], and their derivatives [6–9]. N,N-dimethylhydroxylamine (DMHAN), a hydroxylamine derivative in which two hydrogen atoms are substituted by methyl groups, was investigated as a Pu(IV) reductant by Koltunov et al. [6] in Russia. Their results demonstrated that DMHAN can reduce Pu(IV) at a very rapid rate in nitric acid solution.

The APOR process, developed by ZHANG Xian-Ye et al. at the China Institute of Atomic Energy, utilizes two organic reagents—N,N-dimethylhydroxylamine (DMHAN) and monomethyl hydrazine (MMH)—to create a two-cycle aqueous reprocessing process [10]. Compared with U(IV) and hydrazine reductants, DMHAN and MMH offer three evident advantages: (1) elimination of U and Pu interference from Tc, thereby simplifying the first cycle and reducing hot-region facilities by 2/5; (2) a 20-fold increase in separation factors, improving the quality of U and Pu products; and (3) removal of the security risk associated with hydrazoic acid explosion. However, the APOR process still requires improvement in several areas: (1) DMHAN and MMH, as modified liquid rocket propellants, have high heats of combustion, posing certain security risks in large-scale nuclear fuel reprocessing plants [11]; (2) DMHAN synthesis involves a vacuum pyrolysis process that is unsuitable for preparation near nuclear facilities [12]; and (3) the oxidation and radiolysis products are complex [13].

For these reasons, we developed a new organic reductant, hydroxysemicarbazide (HSC) [14, 15], to replace DMHAN and MMH for U/Pu separation. HSC offers several benefits: (1) good hydrophilicity (molecular formula $HONHCONHNH_2$); (2) rapid reduction of Pu(IV) to Pu(III) [14]; (3) minimal HNO_3 requirement to neutralize its alkalinity (pH = 8.0), thereby reducing the salting-out effect on the extraction distribution of Pu(III); and (4) decreased solid waste and reduced environmental impact.

This paper investigates the application of HSC in U/Pu separation and compares it with DMHAN-MMH. The effects of HSC concentration, HNO_3 concentration in the stripping solution, NO_3^- in the organic phase, phase-contacting time, phase ratio, and temperature on the Pu(IV) reaction rate were examined. To evaluate the feasibility of applying HSC in uranium and plutonium partitioning in the Purex process, HSC was compared with DMHAN-MMH using a 16-stage counter-current extraction in the 1B contactor.

Experimental

Reagents and Apparatus

All chemicals used were of analytical-reagent grade. HSC and DMHAN were synthesized as described in Refs. [12, 16] with purity exceeding 99%. MMH was provided by China Aerospace Science & Industry Corp. with purity exceeding 99%. Pu(IV) stock solutions in nitric acid were prepared through reduction by Fe(II), oxidation by HNO_2, and purification with 2606 anion-exchange resin (poly(4-vinyl-N-methylpyridinum nitrate)).

Macro-scale uranium concentration in the aqueous phase was measured by redox titration; for organic phase measurements, U(VI) was back-extracted with mixed acid before titration. Micro-scale uranium in the aqueous phase was measured by TOPO extraction-Br-PADAP colorimetry (at 575 nm); for organic phase measurements, U(VI) was back-extracted with saturated Na_2CO_3 before TOPO extraction [17]. Plutonium concentration in stock solutions was measured by K-edge and alpha counting, while process samples were analyzed by scintillation counting [18] (LS-6000L, Beckman Corp.). Nitric acid concentration was measured by titration with NaOH after complexing U(VI) and Pu(IV) with $(NH_4)_2C_2O_4$; for organic phase measurements, nitric acid was back-extracted by deionization before pH titration (PHS-3C, Shanghai Precision Instrument Co., Ltd., China).

A DC-1020 low-temperature thermostatic water bath (Ningbo Xinzhi Biological Technology Co., Ltd., China) maintained constant temperature during reduction stripping experiments, and a mixer-settler extractor was used for bench-scale experiments.

Procedures

Single-stage back-extraction tests in centrifugal extraction tubes involved: maintaining the solution at constant temperature for 0.5 h, introducing it into centrifugal extraction tubes according to the designed phase ratio, stirring for several minutes, and allowing phase separation before analysis.

Multi-stage counter-current tests were conducted using miniature mixer-settlers, with the flowsheet shown in Fig. 1 [Figure 1: see original paper]. The flow streams to the mini-banks were specified to simulate U/Pu separation in the 1B bank of PUREX. The mini-banks had a phase ratio of 1.5:1, with 16 total stages (10 for reduction stripping and 6 for supplemental extraction). The mixing and settling chamber volumes were 3 mL and 5 mL, respectively, with a 60 s residence time in each mixing chamber. The flow rate ratio of feed solution (1BF), uranium supplement extraction stream (1BS), and aqueous stripping stream (1BX) was 4:1:1.

Results and Discussion

Single-Stage Tests of Pu(IV) Stripping by HSC

The effects of phase-contacting time, phase ratio, and concentrations of H^+, NO_3^-, HSC, and U in the organic phase, as well as temperature, on the Pu(IV) stripping rate were investigated.

Influence of Phase-Contacting Time At 21 °C, with phase ratios varying from 1:1 to 6:1, the stripping rates of Pu(IV) as a function of phase-contacting time were measured at HSC, H^+, NO_3^-, and Pu(IV) concentrations in the organic phase of 0.05 mol/L, 0.4 mol/L, 0.4 mol/L, and 0.8 g/L, respectively. The results are shown in Fig. 2 [Figure 2: see original paper]. The stripping rates increased with phase-contacting time at all phase ratios. At a given contact time, the stripping rate decreased with increasing phase ratio. At a phase ratio of 1:1 and contact time of 5 s, the stripping rate was 92.8%; at a phase ratio of 4:1, the stripping rates were 58.7% and 84.5% at contact times of 5 s and 20 s, respectively. Notably, the reduction stripping of Pu(IV) approached equilibrium at a 4:1 phase ratio and 30 s contact time, achieving a stripping rate of 91.9%. Therefore, at large phase ratios, appropriately increasing contact time can significantly improve the Pu(IV) stripping rate.

Influence of H^+ Concentration At 21 °C, with a phase-contacting time of 30 s and phase ratios of 1:1 and 4:1, the influence of H^+ concentration on the stripping rate was investigated at HSC, NO_3^-, and Pu(IV) concentrations in the organic phase of 0.05 mol/L, 0.4 mol/L, and 0.8 g/L, respectively. The results are shown as solid symbols in Fig. 3 [Figure 3: see original paper]. The stripping rate decreased with increasing H^+ concentration because the reaction rate between HSC and Pu(IV) is inversely proportional to H^+ concentration (to the power of 0.43) [4]. Increased H^+ concentration reduces the amount of Pu(III) formed from Pu(IV) reduction. Additionally, rapid extraction/back-extraction equilibrium of Pu(IV) exists between the aqueous and organic (30% TBP/kerosene) phases, while Pu(III) is poorly extracted by 30% TBP/kerosene, resulting in decreased Pu(IV) stripping into the aqueous phase. When H^+ concentration increased from 0.3 to 1.0 mol/L, the Pu(IV) stripping rate decreased from 89.2% to 70.7%. Thus, lower H^+ concentration is preferred for Pu(IV) back-extraction by HSC. When the stripping time was extended to 90 s with other parameters unchanged (shown as blank symbols in Fig. 3), the results indicate that properly extending stripping time can increase the stripping rate if higher H^+ concentration is required by the process.

Influence of NO_3^- Concentration At 21 °C, with a phase-contacting time of 30 s and phase ratios of 1:1 and 4:1, the influence of NO_3^- concentration on the stripping rate was investigated at HSC, H^+, and Pu(IV) concentrations in the organic phase of 0.05 mol/L, 0.4 mol/L, and 0.8 g/L, respectively. The results are shown in Fig. 4 [Figure 4: see original paper]. The Pu(IV) stripping rate decreased with increasing NO_3^- concentration because the reaction rate between HSC and Pu(IV) is inversely proportional to NO_3^- concentration (to the power of 0.58), so increased NO_3^- concentration reduces the amount of Pu(III) formed. Another reason is the salting-out and synergistic extraction effects, which increase the distribution ratio of Pu(IV) between TBP/kerosene and nitric acid aqueous solutions with NO_3^- concentration, thereby decreasing the amount of Pu(IV) back-extracted and the stripping rate. As shown in Fig. 4, at a phase ratio of 4:1, when NO_3^- concentration increased from 0.4 to 1.0 mol/L, the Pu(IV) stripping rate decreased from 85.3% to 77.6%. Thus, lower NO_3^- concentration is beneficial for Pu(IV) back-extraction by HSC.

Influence of HSC Concentration At 21 °C, with a phase-contacting time of 30 s and phase ratios of 1:1 and 4:1, the influence of HSC concentration on the stripping rate was investigated at NO_3^-, H^+, and Pu(IV) concentrations in the organic phase of 0.4 mol/L, 0.4 mol/L, and 0.8 g/L, respectively. As shown in Fig. 5 [Figure 5: see original paper], the Pu(IV) stripping rate increases with HSC concentration. Below 0.05 mol/L, increasing HSC concentration significantly increases the stripping rate, while above 0.05 mol/L, HSC concentration has only a minor effect. Therefore, 0.01 mol/L is the optimal concentration when using HSC as a reductant for U/Pu separation.

Influence of U(VI) Concentration At 21 °C, with a phase-contacting time of 30 s and phase ratios of 1:1 and 4:1, the influence of U(VI) concentration on the stripping rate was investigated at NO_3^-, HSC, H^+, and Pu(IV) concentrations in the organic phase of 0.4 mol/L, 0.05 mol/L, 0.4 mol/L, and 0.8 g/L, respectively. As shown in Fig. 6 [Figure 6: see original paper], the Pu(IV) stripping rate increases with U(VI) concentration. At a phase ratio of 4:1, the stripping rate increased by 7.5% at a U(VI) concentration of 5.0 g/L.

Influence of Temperature At a phase-contacting time of 30 s and phase ratios of 1:1 and 4:1, the influence of temperature on the stripping rate was investigated at NO_3^-, HSC, H^+, and Pu(IV) concentrations in the organic phase of 0.4 mol/L, 0.05 mol/L, 0.4 mol/L, and 0.8 g/L, respectively. As shown in Fig. 7 [Figure 7: see original paper], the Pu(IV) stripping rate increased with temperature because the Pu(IV) distribution ratio decreases with increasing temperature, thereby increasing Pu concentration in the aqueous phase. Additionally, temperature increase accelerates the reaction rate between HSC and Pu(IV): a 10 °C increase accelerates the reaction rate by approximately 10 times. Thus, appropriately high temperature increases the Pu(IV) stripping rate in the U/Pu separation process.

Multi-Stage Counter-Current Tests of Pu(IV) Stripping

Under identical experimental conditions, comparative experiments were conducted using either DMHAN-MMH or HSC as the Pu(IV) reductant in mixer-settlers to evaluate the feasibility of HSC for uranium and plutonium partitioning. The flowsheet is shown in Fig. 1 [Figure 1: see original paper]. The 1BF solution contained 90.97 g/L U, 0.79 g/L Pu, and 0.18 mol/L HNO_3 in 30% TBP/kerosene. The 1BS stream was 30% TBP/kerosene with 0.50 mol/L HNO_3, and the 1BX stream was an aqueous solution containing either 0.10 mol/L DMHAN, 0.15 mol/L MMH, and 0.30 mol/L HNO_3, or 0.30 mol/L HSC and 0.30 mol/L HNO_3.

Initially, the mixer-settler was fed with a uranium-free solution. After two hours, the 1BF solution containing uranium and plutonium was introduced. Two hours later, instantaneous samples were taken and analyzed every 30 minutes for 6 hours.

DMHAN-MMH as the Pu(IV) Reductant The experiment achieved steady state after 2.5 hours. The concentration profiles of uranium, nitric acid, and plutonium are shown in Fig. 8 [Figure 8: see original paper]. At the stripping step, both organic and aqueous phases had higher uranium concentrations, while the organic phase had lower nitric acid concentration (approximately 0.02 mol/L). At the supplemental extraction step, the higher nitric acid concentration in 1BS facilitated uranium extraction, achieving a satisfactory result with U concentration of only 5×10^{-3} g/L in the 1BP outlet. The Pu concentration in 1BU was 25 µg/L. Calculations showed U and Pu yields of 99.99% and 99.96%, respectively; material balances of 99.9% for U and 98.5% for HNO_3; and separation factors of 2.5×10^4 for Pu from U (SFPu/U) and 6.0×10^4 for U from Pu (SFU/Pu).

In Fig. 8, uranium concentration declined to 30 mg/L when the supplemental extraction stage reached stage 4, providing a higher uranium yield of 99.99%. A plutonium concentration peak appeared at stage 7, indicating plutonium accumulation in the aqueous phase, which we attribute to the oxidation product of DMHAN—formaldehyde. At the stripping step, uranium concentration did not change significantly, and the lower concentration in the organic phase outlet agreed with theoretical calculations. In the aqueous phase, uranium concentration increased significantly in stages 7-11 and remained essentially constant in stages 11-16. In the organic phase, plutonium concentration decreased significantly in stages 7-11 but remained nearly constant in stages 12-16; in the aqueous phase, plutonium concentration was orders of magnitude lower in stages 7-11 but remained almost constant in stages 11-16. The nitric acid concentration in the organic phase decreased significantly in stages 7-13 but remained almost constant in stages 14-16, while the nitric acid concentration in the aqueous phase decreased obviously in stages 7-12 but remained almost constant in stages 13-16.

HSC as the Pu(IV) Reductant The experiment achieved steady state after 2.0 hours. The concentration profiles of uranium, nitric acid, and plutonium are shown in Fig. 9 [Figure 9: see original paper]. At the stripping step, both organic and aqueous phases had higher uranium concentrations, while the organic phase had a lower HNO_3 concentration of approximately 0.02 mol/L. At the supplemental extraction step, the higher HNO_3 concentration in 1BS facilitated uranium extraction, achieving a satisfactory result with uranium concentration of only 6.11×10^{-3} g/L in the 1BP outlet. In the experiment containing no plutonium, the uranium yield was 99.998%, and the material balances for U and HNO_3 were 99.92% and 97.5%, respectively.

At the supplemental extraction step, uranium concentration in the aqueous phase declined to 50 mg/L at stage 2, providing a yield exceeding 99.99%. At higher stage numbers, it decreased only slightly. The plutonium distribution ratio remained almost constant in stages 1-6, without a plutonium peak, unlike the result using DMHAN-MMH as reductant, suggesting no uncertainties in the U/Pu separation process. Plutonium concentrations in the aqueous and organic phases were approximately 3.2 g/L and 0.2 g/L, respectively, with small differences between stages. The nitric acid distribution in the supplemental extraction step was similar to that of plutonium.

Calculation results show the separation factor of plutonium from uranium (SFPu/U) is 2.8×10^4, and the separation factor of uranium from plutonium (SFU/Pu) is 5.9×10^4. Comparing the results of experiments using DMHAN-MMH or HSC as reductant for Pu/U separation, the separation factors SFPu/U and SFU/Pu are nearly identical. From this perspective, HSC can replace DMHAN-MMH for separating Pu from U in the APOR process.

Conclusion

As a new organic reductant, HSC can effectively achieve the separation of Pu from U, with excellent results: the separation factor of plutonium from uranium (SFPu/U) is 2.8×10^4, and the separation factor of uranium from plutonium (SFU/Pu) is 5.9×10^4. The separation performance using HSC as reductant is nearly identical to DMHAN-MMH, and furthermore, no plutonium peak exists compared to the result using DMHAN-MMH as reductant. Therefore, HSC has good application prospects in the Purex process and represents a promising alternative reductant for Pu/U separation in the APOR process.

References

[1] Suzuki A. Handbook on process and chemistry of nuclear fuel reprocessing (Version 2). Japan Atomic Energy Agency, Tokyo, 2008.

[2] Schlea C S, Caverly M R, Henry H E, et al. Uranium(IV) nitrate as a reducing agent for plutonium(IV) in the Purex process. Technical report, DP-808, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC, 1963. DOI: 10.2172/4651247

[3] Koltunov V S and Baranov S M. Organic derivatives of hydrazine and hydroxylamine in future technology of spent nuclear fuel reprocessing. Global' 95, Versailles, France, 1995.

[4] Yarbro S L, Schreiber S B, Ortiz E M, et al. Reducing Pu(IV) to Pu(III) with hydroxylamine in nitric acid solutions. J Radioanal Nucl Ch, 1998, 235: 21–25. DOI: 10.1007/bf02385931

[5] Scott Barney G. A kinetic study of the reaction of plutonium(IV) with hydroxylamine. J Inorg Nucl Chem, 1976, 38: 1677–1681. DOI: 10.1016/0022-1902(76)80660-4

[6] Koltunov V S and Baranov S M. Organic derivative of hydrazine and hydroxylamine in future technology of spent fuel reprocessing. Radiokhimiya, 1993, 35: 67–71.

[7] Yan T H, Zhen W F, Ye G A, et al. Synthesis of dihydroxyurea and its application to the U/Pu split in the PUREX process. J Radioanal Nucl Ch, 2009, 279: 293–299. DOI: 10.1007/s10967-007-7289-1

[8] Zhang A Y, Hu J X, Zhang X Y, et al. Hydroxylamine derivative in Purex process. J Radioanal Nucl Ch, 2002, 252, 565–571. DOI: 10.1023/A:1015867107219

[9] Li G L and He H. Study on mechanism for oxidation of N,N-dimethylhydroxylamine by nitrous acid. J Radioanal Nucl Ch, 2011, 287, 673-678. DOI: 10.1007/s10967-010-0912-y

[10] He H, Ye G A, Tang H B, et al. An advanced Purex process based on salt-free reductants. Radiochim Acta, 2014, 102: 127–133. DOI: 10.1515/ract-4-2120

[11] Liu Z J and Guo B. Review of gas test technology of hydrazine rocket propellant. Low Temp Special Gases, 2007, 25: 37–42. (in Chinese) DOI: 10.3969/j.issn.1007-7804.2007.02.009

[12] Li G L, He H, Hu J X, et al. The synthesis and characterization of N,N-dimethylhydroxylamine. Chemical Reagents. 2006, 28: 202–204. (in Chinese) DOI: 10.3969/j.issn.0258-3283.2006.04.008

[13] Chen H, He H, Li G L, et al. Pulse radiolysis of aqueous N,N-Dimethylhydroxylamine solutions. J Radiat Res Radiat Process, 2010, 28: 138–143. (in Chinese)

[14] Xiao S T, Ye G A, Liu X C, et al. Kinetics of reaction between Pu and Hydroxysemicarbazide in nitric acid solution. Atom Energy Sci Technol. 2011, 45: 277-281. (in Chinese) DOI: 10.7538/yzk.2011.45.03.0277

[15] Xiao S T, Ye G A, Liu X C, et al. Study on kinetics of reaction between Hydroxysemicarbazide and HNO_2 in perchloric acid solution. Atom Energy Sci Technol. 2011, 45: 403-407. (in Chinese) DOI: 10.7538/yzk.2011.45.04.0402

[16] Ren S J, Wang R B, Komatsu K, et al. Synthesis, biological evaluation, and quantitative structure activity relationship analysis of new schiff bases of hydroxysemicarbazide as potential antitumor agents. J Med Chem, 2002, 45: 410–419. DOI: 10.1021/jm010252q

[17] Johnson D A and Florence T M. Spectrophotometric determination of uranium(VI) with 2-(5-bromo-2-pyridylazo)-5-diethyl-aminophenol. Anal Chim Acta, 1971, 53: 73–79. DOI: 10.1016/S0003-2670(01)80072-6

[18] Yu E J, Huang H A, Zhou X Q, et al. Plutonium portioning in the third plutonium cycle of the Purex process with hydrazine stabilized hydroxylamine nitrate. Atom Energy Sci Technol. 1993, 27: 80–88. (in Chinese)

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.