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Methyl-hydrazine deoxidize Tc(VII) in nitric acid in presence of U(VI) and behavior of technetium in the U/Pu splitting stage of APOR process

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Abstract

The reaction between methyl-hydrazine and Tc(VII) in nitric acid in present of U(VI) was studied in this paper, the influence of acidity, methyl-hydrazine concentration, and temperature on the reaction was investigated meanwhile. Results showed that U(VI) can accelerate this reaction distinctly. When U(VI) concentration is 80 g/l, Tc(VII) can be deoxidized in 1.5 hours, on the contrary, the reaction will last 6 hours if there is no U(VI) in the system. The behavior of technetium in the U/Pu splitting stage was investigated using a multistage mixer-setter. In this experiment about 90% Tc(VII) was deoxidized within 3 stages when contacting with the reducing reagent and uranium. Finally nearly 99.9% of technetium went to plutonium stream.

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Keywords: Technetium, methyl-hydrazine, uranium, salt-free, PUREX

1. Introduction

A advanced salt-free PUREX process based on organic reductant (abbreviated as APOR process) was explored by China Institute of Atomic Energy, which adopt N,N-dimethylhydroxylamine(DMHAN) as reducing agent and methyl-hydrazine(MMH) as stabilizer in U/Pu splitting stage and plutonium

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purification stage. DMHAN can rapidly reduce Pu(IV) to Pu(III), and MMH acts as HNO₂ scavenger. Pu(III) unloaded from organic phase and separated from uranium[1].

In the U/Pu splitting stage of PUREX process the behavior of technetium is controlled by both its redox characteristics and the partitioning coefficient of Tc(VII). Tc(VII) has a moderate partitioning coefficient in TBP/kerosene-HNO₃ system [2-5], but the low valence technetium basically not be extracted, therefore the reaction between technetium and reducing agent has an crucial influence on technetium distribution. The deoxidization of Tc(VII) by MMH in nitric acid is very slow [6]. When $c_0(\text{HNO}_3) = 1.5 \text{ mol/l}$, $c_0(\text{Tc(VII)}) = 75 \text{ mg/l}$ and $c_0(\text{MMH}) = 0.15 \text{ mol/l}$, it need 6 hours to deoxidize 90% of Tc(VII) to lower valence at 40°C. Especially in the former 2 hours less than 15% of Tc(VII) was deoxidized. But in the spent nuclear fuel reprocessing process, there is high concentration of uranium and plutonium in the system. The influence of uranium on the reaction has rarely been reported. In this paper, the reaction between technetium and MMH in presence of uranium in nitric acid was detailed studied, further more, the behavior of technetium in the U/Pu splitting stage was investigated using a multistage mixer-setter in order to have a better understanding of the behavior of technetium in this system.

2. Experiment details

2.1. Instruments and reagents

Tri-n-butyl phosphate was obtained from Sinopharm chemical reagent Ltd., and purified by contacting it with 5% solution of sodium carbonate for the removal of acidic impurities. It was then washed with distilled water until pH = 7. Stock solution of uranium was prepared by dissolving UO₂ pellets with concentrated nitric acid and filtrated before use. Plutonium nitrate solution and neptunium nitrate solution were purified by anion exchange. NH₄TcO₄ was bought from Oak Ridge National Laboratory and dissolved with distilled water. 2,4,6-Trimethylpyridine was bought from Fluca chemical reagent company. All other chemicals used were of analytical grade.

Liquid scintillation spectrometer manufactured by Beckman was used for technetium measurement.

2.2. Analysis Method

The concentration of uranium was determined by a potassium dichromate titration method after uranium was reduced to a tetravalent state. Alpha-ray spectrometer was used to determine the concentrations of plutonium. The estimation of free acidity was carried out by titrating suitable aliquot of the sample against standard alkali after complexing the uranium and other hydrolysable ions by potassium oxalate solution using a glass electrode. Liquid scintillation spectrometer was used to detect technetium concentration after technetium was extracted from alkaline solution.

2.3. Experimental Methods

The reaction between Tc(VII) and MMH was carried out in a water bath equipment.

Bench experiment was done employing a multistage mixer-setter. Flowsheet is shown in Figure 1, process parameters are described in table 1.

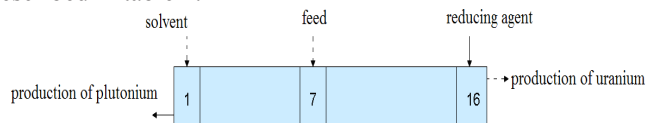


Fig.1 Flowsheet of U/Pu splitting stage in Bench experiment

Tab.1 The process parameters of the Bench experiment

stream	Content	feed stage	Flux ml/min
feed	91.8 g/l U, 0.92 g/l Pu, 0.18 M HNO ₃ , Tc, Zr, Ru, 30%TBP/kerosene	7	3.16
Reducing agent	0.1 M C ₂ H ₆ NOH·HNO ₃ , 0.15 M N ₂ H ₄ ·HNO ₃ , 1 M HNO ₃	1	0.79
solvent	0.5 M HNO ₃ , 30%TBP/kerosene	16	0.79

3. Experiment details

3.1. Influence of uranium on the reaction

The reaction between MMH and Tc(VII) in nitric acid with different uranium concentration was studied first. The concentration of heptavalent technetium vs time was showed in Figure 2:

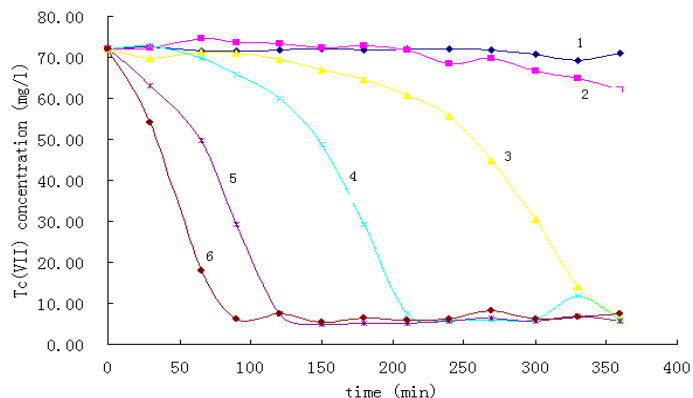


Fig.2 The influence of U(VI) on reaction of Tc(VII) and MMH in nitric acid
 30°C, $c_0(\text{Tc(VII)})=72 \text{ mg/l}$, $c_0(\text{MMH})=0.15 \text{ mol/l}$, $c_0(\text{HNO}_3)=0.25 \text{ mol/l}$
 U(VI): 1—0 g/l, 2—5 g/l, 3—10 g/l, 4—20 g/l, 5—40 g/l, 6—80 g/l

It is obviously that, U(VI) acts a significant role in promoting reaction between the Tc(VII) and MMH, When Tc(VII) concentration is of 80 g/l, the reaction reach equilibrium in 1.5 hours, the Tc(VII) concentration reserve less than 10% of the initial concentration, but in the absence of U(VI), Tc(VII) concentration remained almost unchanged in 6 hours.

The deoxidization of heptavalent technetium by MMH went through a similar course as described in literature [7]. The reaction is relatively slow at first which is called induction period, followed by relatively rapid reaction stage called the fast reaction period. It may be a very complicated course [7-9], and the mechanism will not be discussed in this paper.

U(VI) promoting the reaction is mainly in shortening the length of the induction period. A higher uranium concentration get a shorter induction period, when U(VI) concentration is 5 g/l, The reaction is not yet entered the fast reaction period within 6 hours; and when the U(VI) concentration is 40 g/l or 80 g/l, there is almost no induction period observed. In contrast, U(VI) has little effect on the fast reaction

period, when U(VI) concentration increase from 10 g/l to 80 g/l, the velocity of fast reaction period increased slightly.

3.2. The influence of MMH and acidity

The influence of MMH concentration and acidity on the reaction was shown in Figure 3 and 4. The reaction rate accelerated while MMH concentration increasing.

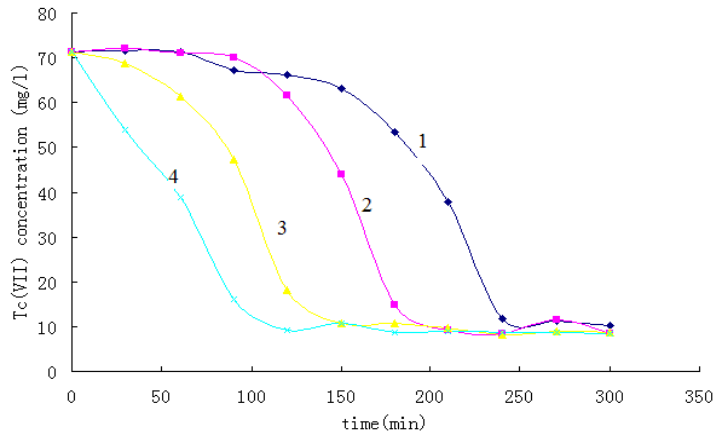


Fig.3 The influence of MMH concentration on the reaction
 $c_0(\text{Tc(VII)})=72 \text{ mg/l}$, $c_0(\text{U(VI)}) = 40 \text{ g/l}$, $c_0(\text{HNO}_3) = 0.25 \text{ mol/l}$
 $c_0(\text{MMH}): 1-0.05 \text{ mol/l}$, $2-0.1 \text{ mol/l}$, $3-0.2 \text{ mol/l}$, $4-0.3 \text{ mol/l}$

In a certain acidity range, a smaller nitric acid concentration will get a faster reaction rate, but need to ensure an "appropriate" acidity. When the concentration of nitric acid is only 0.05 mol/l, the reaction rate slows down, even lower than the acidity of 1.65 mol/l. The acidity of 0.25 mol/l is an "appropriate" acidity in the experiment we did, it may relative with concentration of MMH or other conditions.

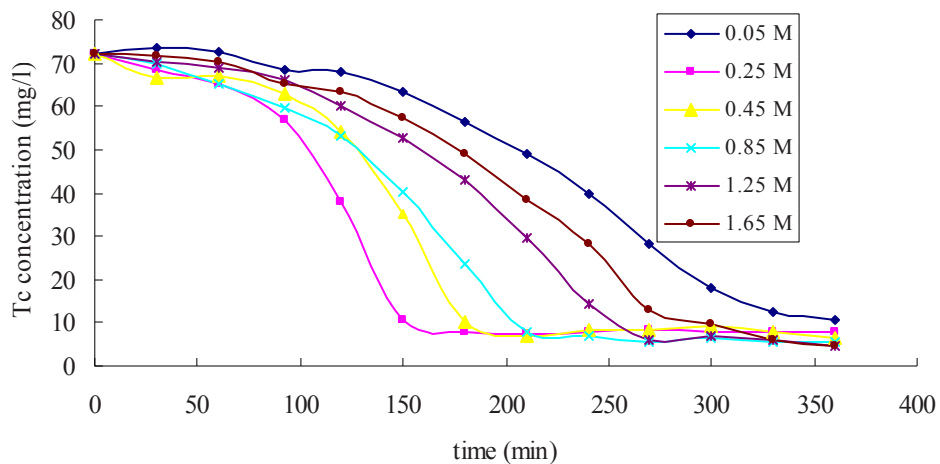


Fig.4 Reaction of Tc(VII) and MMH by different HNO_3 concentration
 $c_0(\text{Tc(VII)})=72 \text{ mg/l}$, $c_0(\text{U(VI)})=40 \text{ g/l}$, $c_0(\text{MMH})=0.15 \text{ mol/l}$

3.3. The influence of temperature

Reactions in 25, 30, 38, 45 Degrees Celsius were investigated, the data was shown in Figure 5. It can be seen that the temperature has a significant influence, when temperature rising, reaction accelerated remarkably.

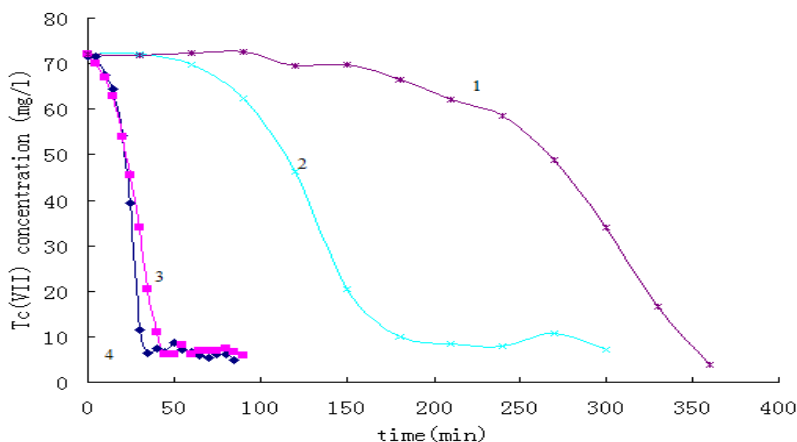


Fig.5 The influence of temperature on the reaction $c_0(\text{Tc(VII)})=72 \text{ mg/l}$, $c_0(\text{U(VI)})=40 \text{ g/l}$, $c_0(\text{MMH}) = 0.15 \text{ mol/l}$, $c_0(\text{HNO}_3) = 0.25 \text{ mol/l}$ temperature: 1—25 °C, 2—30 °C, 3—38 °C, 4—45 °C

3.4. The behavior of technetium in U/Pu splitting stage

Figure 6 showed the distribution of technetium in each stage of bench experiment when the experiment run for 96 hours. The concentration of technetium in the production of uranium stream which was sampled discontinuously is described in table 2.

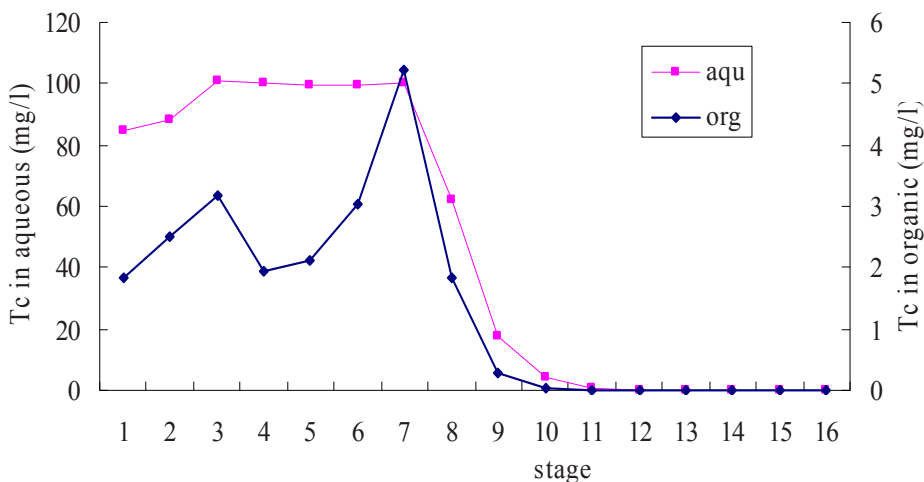


Fig.6 Technetium concentration in each stage of bench experiment

Tab.2 Technetium concentration in the production of uranium stream

sample	Run time, h	Concentration of Tc(VII) g/l
production of uranium 1	6	2E-6
production of uranium 3	18	6E-7
production of uranium 5	30	3E-6
production of uranium 7	42	2E-6
production of uranium 9	54	5E-7
production of uranium 11	66	3E-7
production of uranium 13	78	2E-6
production of uranium 15	90	2E-6

Seen from figure 6, technetium was reduced to lower valent within 4 stages in the experiment then goes into the aqueous phase. Finally only trace amount technetium goes into the production of uranium stream. More than 99% technetium goes into aqueous phase. The profile of figure 6 was got after the experiment run for 96 hours. It can be supposed that the technetium distribution profile when the experiment just started is very different with figure 5. It may need a long time for each stage accumulating a certain amount of low valent technetium to get a balance state. Though the technetium concentration in the mixer-setter is unstable at the beginning, but we can see that technetium hardly can pass through the back-extract segment of the mixer-setter, the concentration of technetium in production of uranium which was sampled in 6th hour is very low.

Technetium concentration in production of plutonium is changed from 0.08 mg/l to 0.19 mg/l, as table 3. It may associate with the running state of the mixer-setter.

Tab.3 Technetium concentration in the production of plutonium stream

sample	Run time, h	Concentration of Tc(VII) g/l
production of plutonium 1	6	0.168
production of plutonium 3	18	0.187
production of plutonium 5	30	0.101
production of plutonium 7	42	0.160
production of plutonium 9	54	0.086
production of plutonium 11	66	0.079
production of plutonium 13	78	0.174
production of plutonium 15	90	0.144

Tab.4 Concentration of uranium and acidity in each stage

stage	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
H ⁺ , M	1.4	1.2	1.2	1.1	1.1	1.1	1.0	0.6	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.4
U, g/l	0.003	0.007	0.03	4	6	24	54	82	77	59	91	90	94	100	91	93

Behavior of technetium in the experiment can be explained as follow:

The mixer-setter provides a suitable condition for reducing of technetium. The concentration of uranium and acidity in each stage is expressed as table 4. Contrasting with the kinetics of MMH deoxidize Tc(VII) in nitric acid in presence of U(VI), the system of back-extract segment is very favorable for

reducing of technetium, so technetium can be reduced very quickly. And with the accumulating of low valent technetium in each stage, the reaction between Tc(VII) and MMH will start from fast reaction period. About 90% of technetium was reduced within 3 stages.

The residual MMH in production of plutonium was determined in the experiment. Result showed less than 50% of MMH was consumed in the mixer-setter.

Tab.5 Concentration of MMH in production of plutonium

sample	MMH, M	
Reducing agent	0.148	
production of plutonium1	0.073	Analyze after sampling 32 hours
production of plutonium3	0.079	Analyze after sampling 32 hours
production of plutonium4	0.073	Analyze after sampling 8 hours
production of plutonium6	0.082	Analyze after sampling 8 hours

4. Conclusion

U(VI) can significantly promote the reaction between Tc(VII) and MMH, the reaction get faster when there is a higher uranium concentration. Similarly, increasing MMH concentration, reaction rate is also accelerated. Acidity on the reaction is more complex, there is a suitable acid in the reaction, the acidity is greater than or less than the "appropriate" acidity the reaction will get show.

In bench experiment of U/Pu splitting stage about 99.9% of technetium goes into aqueous phase with plutonium. Technetium is reduced very fast within 4 stages. which is due to the suitable acidity and uranium concentration in the U/Pu splitting tank.

MMH is consumed less than 50% in the bench experiment. Though MMH is over-consumed than chemometrics, the amount of MMH is sufficient in this experiment.

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