

# SEPARATION AND PURIFICATION OF ULTRAMICROGRAM URANIUM FROM SATURATED NaCl SOLUTION

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## ABSTRACT

This paper summarizes the results of the coprecipitation of ultramicrogram uranium with  $\text{Fe}(\text{OH})_3$  from saturated NaCl solution and separation of uranium from  $\text{Fe}(\text{III})$  by solvent extraction with TBP as extractant. In the first step, the coprecipitation efficiency of uranium is more than 95 %; in the second step, extraction percentage of uranium is more than 98 %, and stripping efficiency of uranium is nearly 100 % (twice stripping) and separation factor (separation of  $\text{Fe}(\text{III})$  from uranium) is more than  $10^3$ .

**Keywords:** TBP extraction  $\text{Fe}(\text{OH})_3$  coprecipitation Trace amount uranium

## 1 INTRODUCTION

Since concentration of uranium in real waste leachates (such as spent fuel leached by saturated NaCl solution) is very low, and chemical constitution of real waste leachates is complex, in order to determine the concentration of uranium, pre-concentration and purification of uranium are necessary. Until now, it was found that uranium can be absorbed by  $\text{Fe}(\text{III})$  hydroxide from natural water<sup>[1,2]</sup>. In author's work<sup>[3]</sup>, the results showed that  $\text{Fe}(\text{OH})_3$  can effectively sorb  $\text{UO}_2^{2+}$  in saturated NaCl solution ( $\text{pH} \approx 8$ ). The solubility of  $\text{Fe}(\text{OH})_3$  is very low. Although the selectivity of coprecipitation process is not so good, however, its efficiency is higher. Therefore, in this work, coprecipitation of  $\text{UO}_2^{2+}$  with  $\text{Fe}(\text{OH})_3$  for concentration, and separation and then purification of uranium from  $\text{Fe}(\text{III})$  with TBP/DOD- $\text{HNO}_3$  system<sup>[4-6]</sup> were studied.

## 2 EXPERIMENTAL

### 2.1 Materials and instruments

Tributyl phosphate (TBP) (a reagent for extraction analysis), n-Dodecane (DOD) (a reagent for synthesis);  $\text{FeCl}_3$ ,  $\text{HNO}_3$ ,  $\text{NaOH}$  and other reagents are analytical reagents; U-232, Fe-59 used for tracers. LSC and Ge(Li) counter were used for  $\alpha$  and  $\gamma$  measurements, respectively. pH meter for measuring pH value of the solutions.

## 2.2 Coprecipitation

10 ml saturated NaCl solution containing  $\text{UO}_2^{2+}$  (U-232 as tracer) and enough Fe(III) were added into a plastic vessel (15ml) and then adjusted pH value with NaOH solution, after that, filtered with a filter (450 nm). Activities of the filtrate were measured and coprecipitation efficiency can be calculated.

## 2.3 Solvent extraction

Two ml of aqueous and organic portions were contacted by shaking (5 min) and then separated by centrifugation. The organic solution was pre-equilibrated with an appropriate acid solution containing no uranium and Fe(III), such that no change in nitric acid concentration in aqueous phase would occur in the final equilibration. The final aqueous and organic phases were sampled and measured to calculate the extraction percentage or the distribution ratio,  $D$ , the ratio of concentrations of element in organic and aqueous phases, and separation factor, SF,

$$D = C_{\text{org}} / C_{\text{aq}} \quad (1)$$

where  $C_{\text{org}}$ ,  $C_{\text{aq}}$  are metallic ion concentration in organic and aqueous phases respectively,

$$\text{SF} = (C'_{\text{Fe}} / C'_{\text{U}}) / (C''_{\text{Fe}} / C''_{\text{U}}) \quad (2)$$

where  $C'_{\text{Fe}}$ ,  $C'_{\text{U}}$  are concentration of Fe(III) and  $\text{UO}_2^{2+}$  in the sample before separation respectively;  $C''_{\text{Fe}}$ ,  $C''_{\text{U}}$  are concentration of Fe(III) and  $\text{UO}_2^{2+}$  after separation in the product respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 Titration of Fe(III) in saturated NaCl solution with NaOH solution

From Fig.1a, it can be seen that the amount of NaOH used increases with increasing the amount of Fe(III), and pH value of the system changes from 2 to 12, while adding NaOH solution into the system.

### 3.2 Coprecipitation

a. Influence of pH, from Fig.1b it can be seen that at pH =8-10, the coprecipitation efficiency  $\approx 99\%$ .

b. Influence of amount of Fe(III), in 50 ml saturated NaCl solution adding 20-30 mg Fe(III), which is enough to coprecipitate  $\text{UO}_2^{2+}$  (Fig.1c).

c. Influence of  $\text{UO}_2^{2+}$  concentration. The experimental results showed that at pH=8, 0.4 mg/ml Fe(III) for any concentration of  $\text{UO}_2^{2+}$  (trace—  $10^{-6}$  mol/l), coprecipitation efficiency  $> 95\%$  (Table 1).

### 3.3 Solvent extraction

a. Influence of TBP / DOD on activity measurement, the experimental results showed that adding 0.5 ml 30 % TBP / DOD organic into the aqueous sample does not

Table 1

Influence of concentration of  $\text{UO}_2^{2+}$  on coprecipitation efficiency, 0.4 mg/ml Fe(III)

$\text{UO}_2^{2+}/\text{molL}^{-1}$	Trace	$10^{-8}$	$10^{-7}$	$10^{-6}$
Efficiency/%	97	96	95	100

Table 2

Influence of  $\text{HNO}_3$  concentration on extraction of  $\text{UO}_2^{2+}$  with 30 % TBP / DOD

Content of $\text{UO}_2^{2+}$	Trace			
$\text{HNO}_3/\text{molL}^{-1}$	4	6	8	4*
Extraction percentage	97	100	105	102
Content of $\text{UO}_2^{2+}$	$1 \times 10^{-6}$ mol/L			
$\text{HNO}_3/\text{molL}^{-1}$	3.5	5	7	
Extraction percentage	92	98	97	

\* Aqueous phase containing Fe(III) 10 mg/ml

Aq. phase  $\text{HNO}_3$ , U-232 tracer, 5 mg/ml Fe(III),  $V_o / V_a = 1$

Table 3

Stripping efficiency with water as stripping reagent  $V_o / V_a = 0.5$

* $\text{HNO}_3/\text{molL}^{-1}$	3.5	5	7
** Total efficiency / %	99.5	98.7	97.9

\* Before extraction the concentration of  $\text{HNO}_3$  in aq. phase  $\text{UO}_2^{2+} 1 \times 10^{-6}$  mol/l

\*\* Fe(III), 5 mg/ml, after twice stripping

Table 4

Stripping efficiency with water as stripping reagent

$\text{HNO}_3/\text{molL}^{-1}$	4* <sup>1</sup>	6* <sup>1</sup>	8* <sup>1</sup>	4* <sup>2</sup>
The first stripping efficiency/%	60	52	51	59
The second stripping efficiency/%	46	51	52	46
Total efficiency/%	~100	~100	~100	~100

\* The concentration of  $\text{HNO}_3$  in aq. phase containing U-232 tracer and \*<sup>1</sup> 5 mg/ml Fe(III), \*<sup>2</sup> 10 mg/ml Fe(III) before extraction,  $V_o / V_a = 0.5$

Table 5

Influence of  $\text{HNO}_3$  on extraction of Fe(III) and separation factor of Fe(III) from uranium by 30 % TBP / DOD Aq. phase Fe(III) 2.5 or 5 mg/ml, Fe-59 as tracer,  $\text{HNO}_3$ ,  $V_o / V_a = 1$  contact time, 5 min

$\text{HNO}_3/\text{molL}^{-1}$	4	6	8
$D^{*1}$	$1.2 \times 10^{-4}$	$0.9 \times 10^{-3}$	$3.3 \times 10^{-3}$
$SF^{*1}$	$8.3 \times 10^3$	$1.1 \times 10^3$	$3.0 \times 10^2$
$D^{*2}$	$3.5 \times 10^{-4}$	$6.8 \times 10^{-4}$	$5.3 \times 10^{-3}$
$SF^{*2}$	$2.9 \times 10^3$	$1.5 \times 10^3$	$1.9 \times 10^2$

D, distribution ratio of Fe(III)

SF, separation factor of Fe(III) from uranium

\*<sup>1</sup> Fe(III) 2.5 mg/ml \*<sup>2</sup> Fe(III) 5 mg/ml

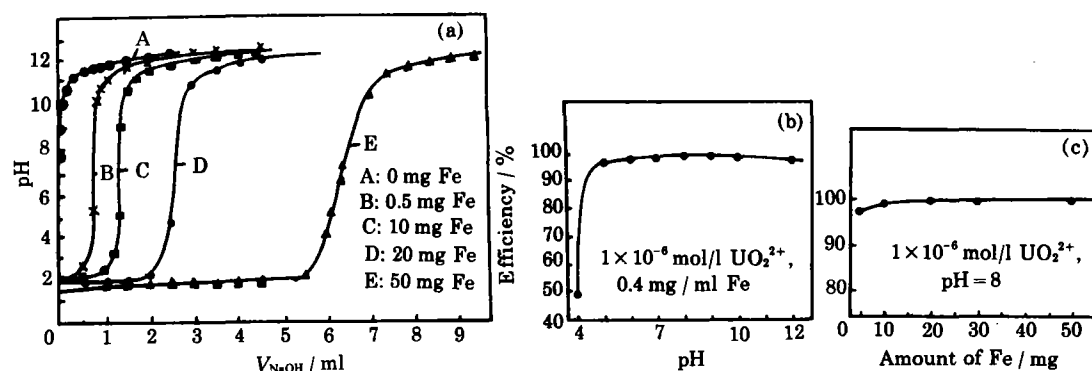


Fig.1 Titration of Fe(III) in 50 ml saturated NaCl solution with 0.45 mol/l NaOH (a), influence of pH (b) and of amount of Fe(III) (c) on coprecipitation efficiency of uranium

change counts of the sample (measured by LSC).

b. Influence of  $\text{HNO}_3$  concentration, from Table 2, it can be seen that in 2 ml solution (5–6 mol/l  $\text{HNO}_3$ ) containing  $\text{UO}_2^{2+}$  (trace or  $10^{-6}$  mol/l) and  $\text{Fe(III)}$  (10 or 20 mg), the extraction percentage of  $\text{UO}_2^{2+} \approx 100\%$ . From the published data<sup>[7]</sup>, extraction of  $\text{UO}_2^{2+}$  by TBP from 4–6 mol / L  $\text{HNO}_3$  solution, the distribution ratio of  $\text{UO}_2^{2+}$  reaches a maximum value.

c. Stripping efficiency, for avoiding other ions brought into the system, bidistilled water was used as stripping reagent for stripping  $\text{UO}_2^{2+}$  from organic phase. From Table 3 and 4, it can be seen that after twice stripping, the stripping efficiency for uranium is about 100 %.

d. Separation factor, in order to estimate a separation factor (separation of  $\text{Fe(III)}$  from uranium), the experiments on extraction of  $\text{Fe(III)}$  from  $\text{HNO}_3$  solution by 30 % TBP / DOD have been carried out. The results are shown in Table 5. From Table 5 it can be seen that for extraction of  $\text{UO}_2^{2+}$  from 4–5 mol/l  $\text{HNO}_3$  containing  $\text{Fe(III)}$  by 30 % TBP / DOD, SF is more than  $10^3$ .

#### 4 CONCLUSION

The results show that it is possible to use  $\text{Fe(III)}$  as carrier for complete coprecipitation of  $\text{UO}_2^{2+}$  and to use 30 % TBP / DOD– $\text{HNO}_3$  system for separation of  $\text{UO}_2^{2+}$  from  $\text{Fe(III)}$ . The coprecipitation condition: pH 8–9;  $\text{Fe(III)}$  20–30 mg/50 ml saturated NaCl solution;  $\text{UO}_2^{2+}$ , trace –  $10^{-6}$  mol/l. Extraction condition: 5–6 mol/l  $\text{HNO}_3$ ; 30 % TBP / DOD; phase ratio=1; contact time 5 min. Stripping condition: stripping reagent, bidistilled water; twice stripping operation; phase ratio  $V_{\text{org}} / V_{\text{aq}} = 1/2$ ; contact time 5 min. The coprecipitation efficiency > 95 %, the extraction percentage > 98 %, stripping efficiency of  $\text{UO}_2^{2+} \approx 100\%$  and  $\text{SF} > 10^3$ .

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#### REFERENCES

- 1 Laskorin B N, Metalnikov S S, Terentiev A S. Proceeding of the second united nations international conference on the peaceful uses of atomic energy. Geneva: United Nations Publication, 1958: Vol.3, 211
- 2 Dai Minhai, Wu Shawchii. *Separ Sci*, 1975; 10(5):633
- 3 Ye Yuxing, Marx G, Keiling C H. *J Nucl Radiochem* (in Chinese), to be published
- 4 Petrich G, Kolarik Z. The 1981 Purex distribution data index, KFK 3080. Kernforschungszentrum Karlsruhe BRD, 1981:1–103
- 5 Wallach K S, Tributyl phosphate (TBP) and its application in solvent extraction, Ls-70(pt.1). Jerusalem: Israel Atomic Energy Commission, Tel Aviv, 1963:1–259
- 6 Tarnero Maurice. Study of the physicochemical agents influencing uranium and plutonium extraction by Tributyl phosphate in nitric media, CEA-R-3206. Fontenay-aus-Roses, France: Commissariat a L'energie Atomique, 1967, 1–84
- 7 Розен А М, Хорхорина Л П, Карпачев С М. и гд *Радиохимия*, 1962; Том 4(5):591