أستخلاص تراكيز عالية من اليورانيوم السداسي المشعع وفصله عن نواتج الانشطار اللاعضوية

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الخلاصة

تم في هذا البحث دراسة استخلاص تراكيز عالية من اليورانيوم المشعع (سداسي التكافؤ) عن نواتج الانشطار(باعثات كاما عالية الشدة) باستخدام تقنية الجريان المتعاكس متعدد المراحل (منظومات الخلط والفصل) ، وقد أقتضت ضرورات العمل بهذه التقنية تصميم منهج تدفق عمليات مناسب يضمن استرداد كل كميات اليورانيوم الداخلة الى منظومة الفصل وتقليل الكميات المفقودة منها في مسالك النفايات النووية الى أدنى ما يمكن. ان كثرة المتغيرات الداخلة في بلوغ التصميم المناسب لهذا المنهج ، يستدعي استخدام البرامجيات الخاصة بالحسابات النظرية المعروفة في هذا المجال وتحديدا برنامج سفس SEPHIS code وقد اجريت العديد من التجارب النظرية التي تمخضت عن اختيار الظروف التشغيلية المثلى والتي طبقت لاحقا ميدانيا ، وكانت النتائج العملية المستحصلة قد عززت بالفعل أفضلية المنهج الذي اختير من الحسابات النظرية.

الكلمات المفتاحية :اليورانيوم السداسي المشعشع ،نواتج الأنشطار اللاعضوية

Recovery of High Concentration Hexavallent Irradiated Uranium From Inorganic Fission Products

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Abstract

In this study , extraction of irradiated high concentration hexavallent uranium from fission products (high gamma radiation) was carried out using multistages countercurrent continuous technique (mixer setller) , employing this technique requires a designing flow sheet that recover all the amounts of uranium and to minimize its losses in the nuclear waste streams. Due to the several parameters required to reach this design, SEPHIS program which is one of the famous code in this field were used to select the optimum conditions through many theoretical runs , finally the experimental results give a good assurance in SEPHIS results and its optimum conditions.

Introduction

Irradiation of uranium in nuclear reactor produces many inorganic short and long lived isotopes such as ^{131}I, ^{140}La, ^{141}Ce , ^{144}Pr , ^{95}Zr, ^{95}Nb , ^{137}Cs, ^{90}Sr and ^{91}Y in addition to other several isotopes .Uranium ions in aqueous solution can give very complex species because of its several oxidation states. The Latimer diagram for uranium in acidic medium is[1]:

$$UO_2^{2+} \xrightarrow{0.06\ V} UO_2^{+} \xrightarrow{0.58\ V} U^{4+} \xrightarrow{-0.63\ V} U^{3+} \xrightarrow{-1.70\ V} U$$

It shows that pentavalent state is unstable and should disproportionate to tetravalent and hexavalent . Uranium (IV) ions can easily be oxidized to the hexavalent state , which is the most stable oxidation state of uranium in acidic solution[2] , so reaction of uranium(IV) oxide with nitrate results in the formation of uranyl nitrates $UO_2(NO_3)_2$, in this formula , the nitrate groups are bidentate , binding this salt with TBP gives uranium with 8 coordinate , this important property lies in its high solubility in a range of organic solvents.[3,4,5]

The extraction of hexavalent uranium from some inorganic species in nitric acid media by tributyl phosphate (TBP)/kerosene has been studied previously, TBP is highly selective for hexavalent uranium, and provides excellent decontamination from most radioactive inorganic impurities .The equilibrium constant of the extraction reaction of uranium by TBP:

$$UO_2^{+2} + 2NO^{-3} + 2TBP \longleftrightarrow UO_2(NO_3)_2 \cdot 2TBP$$

Distribution ratio (Du) of uranium (which means $[U]_{org}/[U]_{aq}$)increases with the increase of both uranium and nitric acid concentration to reach the maximum at 5 M HNO3, The decrease of uranium concentration in the organic phase after this maximum can be explained by the fact that nitric acid will compete with $UO_2(NO_3)_2$, to form HNO_3•TBP, and HNO_3.2TBP. [6,7,8,9,10] .

In industry, separation and extraction of metals requires special technique called "multistage countercurrent continuous processes". In the multistage processes, the aqueous raffinate from one extraction unit is fed to the next unit as the aqueous feed, while the organic phase is moved in the opposite direction. Hence in this way even if the separation between two metals in each stage is small, the overall system can have a higher decontamination factor [8].

Due to several parameters influence the extraction process such as uranium concentration, nitric acid concentration, number of stage, TBP concentration and flow rates of organic and aqueous feed solutions , it is very important to design flow sheet of main process to reach the optimum conditions required for successful separation. To do that , it is necessary to start with computer aided process flowsheet calculations .One of the most important computer code in uranium reprocessing is SEPHIS (solvent extraction process having interacting solute) code developed at Oak Ridge National Laboratory. The SEPHIS code predicts the equilibrium distribution of uranium , plutonium (IV) , nitric acid and water between aqueous phase containing these components and an organic phase containing TBP at any concentration[9].

SEPHIS - guide flow sheet optimization studies and thus minimizes the amount of experimentation required to establish a particular set of operating conditions[10,11].

Decontamination of irradiated uranium from fission products is one of real optimization of flow sheet and this is carried out due to selection of suitable solvent/feed ratio , low ratio will lead to higher saturation of the solvent with uranium and possibly maximize decontamination of product streams[12,13].

Experimental

1- Reagents

*Nitric acid to prepare different concentration solutions (3.75 , 1.5 , 0.03 M).

*Organic solvent , Tributyl phosphate (TBP) , diluted in oderless kerosene (30%TBP/kerosene).

*Uranyl nitrate to prepare 170g/l uranium in 3.75M nitric acid.

2- Equipments:

*Two mixer settlers battery (16 stage for each), one for extraction and the second for stripping , hydraulic equilibrium have been carried out for both units with the same solutions flow rates and concentration of nitric acid as summarized in fig. 1

* four metering pumps for feeding solution through 4 streams (organic , feed , scrub , and strip).

*two glove boxes to prevent any contamination from uranium solution.

3- Mesurments.

a-Determination of uranium

Two methods were chosen for the determination of uranium namely spectrophotometric method and Davis & Gray method [14].

Spectrophotometric method was used for the determination of uranium at microgram/aliquot level .

This method is based on selective extraction of uranium as tetrapropylammonium –uranyl trinitrate complex and colour developing with dibenzoyl methane .The absorbance was measured at 415nm.

Davis & Gray method was used for the determination of uranium at gram/ aliquot level ,this method is based on the reduction of uranium (VI) to uranium (IV) in a concentrated phosphoric acid solution containing sulphamic acid.

The excess of ferrous is subsequently oxidized by nitric acid in the presence of Mo(VI) catalyst. After adding sulfamic acid and diluting the mixture with water, the determination to be completed by titration with standard potassium dichromate solution using Metrohm potentiometer by incremental addition.

b- **Determination of fission products**

Fission products activity were measured using GeLi detector of 97cm^3 active volume and 4096-multichannel analyser , Camac ADC-type 9060 linked with HP-computer (Princeton-Gamma Tech , Germany).

4- SEPHIS program model for theoretical study to select the optimum conditions flow sheet , using pc. computers to carry out this job.
Equipments have been supplied from chemistry research center in Tuwaitha.

Results and Discussion

Theoretically , 24 SEPHIS calculations run were carried out , the results (as summarized in table –1) indicate the following:

1-In the extraction unit ,the loss of uranium in aq.waste is so large (around 44.1g/l) when the ratio of org./feed flow rate equals 600/440 (run-1) , but when keeping all other input parameters intact , this amount should decrease gradually to (21g/l) when the ratio been 600/360 (run 1-5). It can be also concluded that the follow runs (6-10) consistence with this idea.

2- Run (11-19),reduces scrubbing solution (1.5M Nitric acid for all runs as shown in table-1) from 120 to 100 ml/hr results in a decreased the uranium in aq.waste , and this means that the ratio between org./scrub is also important to improve the extraction process .

3- In stripping unit (different acidity of nitric acid were used as summarized in table-1) , when org. /strip ratio equals 1 (run 1-16) , poor stripping of uranium was noticed , and unacceptable amount were lost in the organic waste , increasing this ratio (run 17-19) will improve recovery of uranium in the product and lowering its losses in the org. waste .

4- Reducing strip acidity (run 20-22) will improve the condition of org. waste and only trace amount of uranium will appear in this stream, while run 23 shows bad extraction due to increasing org./feed ratio relative to the previous run.

5- Finally , the goal of this theoretical study is to reach the optimum parameters , and the final run (24) clearly demonstrate that this run reflects the optimum conditions due to ultra trace amounts of uranium in org. and aq. waste which equals 10^{-12} g/l in both streams.

Experimentally , (fig -1) shows the application of optimum condition (results from theoretical calculations) in laboratory ,simulation solutions were prepared by adding different isotopes gamma radiation emitter to 170g/l uranium solution , the lost of uranium in the aq. and org. waste is so small and acceptable in such experiment and the difference between theoretical and experimental results is due to the fluctuation of solution pumps flow rate which altered the ratio of streams , so it is very necessary to obtain the best results from SEPHIS calculation and applied them in lab. to give reasonable and acceptable experimental results .

On the other hand , working near saturation of the solvent with uranium (below Saturation not over) will give good decontamination factor of uranium from fission products, and no gamma species were detectable , neither in product nor in org. waste and all of them (fission species) flow toward aq.waste

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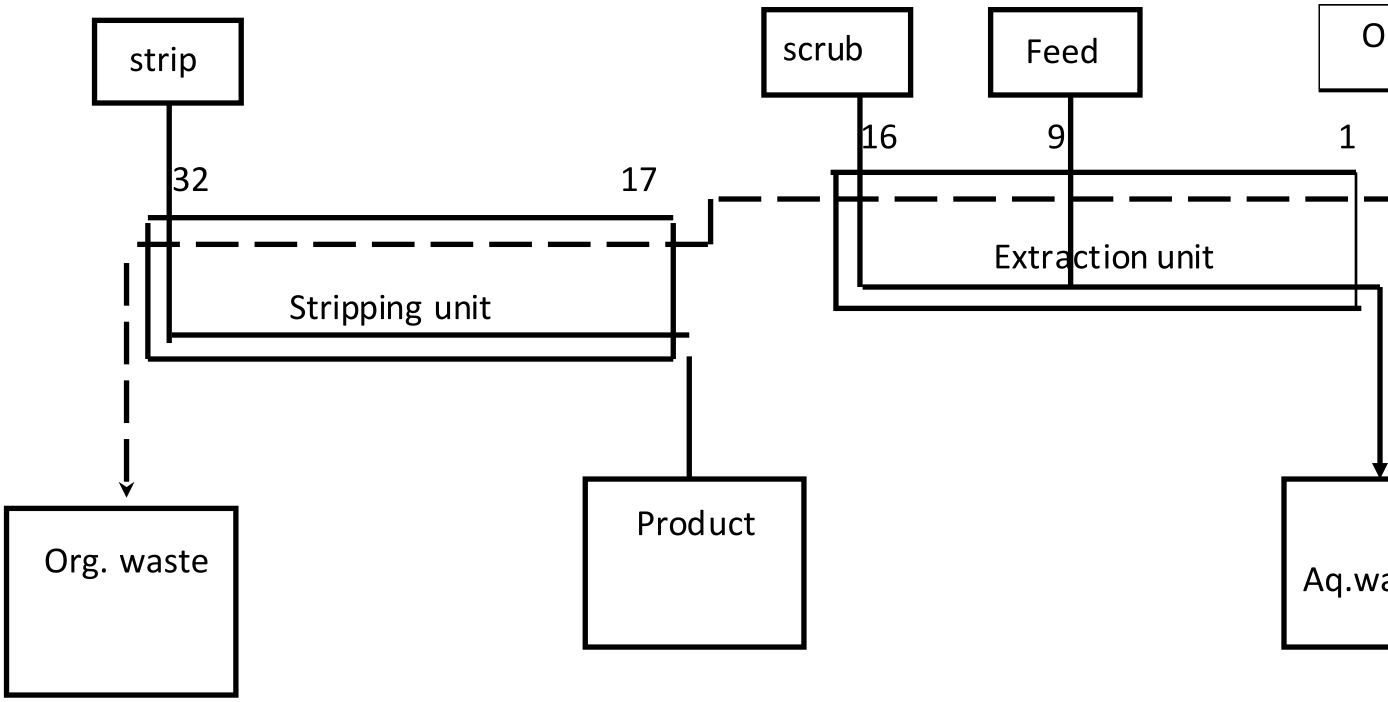
Table(1): SEPHIS Code Calculations

Run no.	$[H^+]$ strip	$[H^+]$ feed	$[H^+]$ scrub	Flow rate ml/hr				% U. Recovery	U. g/l AQ.waste	U. g/l Org.waste
				Feed strip	org.	scrub				
1	0.1	4	1.5	440	600	120	600	64.3	44.5	6.89
2	0.1	4	1.5	420	600	120	600	67.38	39	6.89
3	0.1	4	1.5	400	600	120	600	70.73	33.7	6.89
4	0.1	4	1.5	380	600	120	600	74.4	27.6	6.89
5	0.1	4	1.5	360	600	120	600	78.4	21.0	6.6
6	0.1	4	1.5	400	620	120	620	73.1	29.4	6.23
7	0.1	4	1.5	400	640	120	640	76.4	24.99	6.85
8	0.1	4	1.5	400	660	120	660	79.3	20.7	6.9
9	0.1	4	1.5	400	680	120	680	82	16	6.9
10	0.1	4	1.5	400	700	120	700	85.7	11.6	6.9
11	0.1	4	1.5	400	620	100	620	76	26	6.18
12	0.1	4	1.5	400	640	100	640	79	22.1	6.87
13	0.1	4	1.5	400	660	100	660	82	17.4	6.94
14	0.1	4	1.5	400	680	100	680	84.9	12.7	6.94
15	0.1	4	1.5	400	700	100	700	87.88	8	6.94
16	0.1	4	1.5	400	750	100	750	92.5	$2*10^{-11}$	6.42
17	0.1	4	1.5	400	750	100	775	94.7	$2*10^{-11}$	5.44
18	0.1	4	1.5	400	750	100	800	97.6	$2*10^{-11}$	3.33
19	0.1	4	1.5	400	750	100	825	97.6	$2*10^{-11}$	2.5
20	0.06	4	1.5	360	700	120	800	≥98.5	$2.4*10^{-11}$	$2.6*10^{-5}$
21	0.05	4	1.5	360	700	120	800	≥98.5	$2.4*10^{-11}$	$3*10^{-6}$
22	0.04	4	1.5	360	700	120	800	≥98.5	$2.4*10^{-11}$	$3*10^{-8}$
23	0.03	4	1.5	380	700	120	800	96.3	5.2	$1.6*10^{-10}$
24	0.03	4	1.5	360	750	120	850	≥98.5	$5.2*10^{-12}$	$6.2*10^{-12}$



	Feed	scrub	Strip	Org.	Product	Aq.waste	Org..waste
U g/l	170.47	-------------	-------------	--------------	70.54	0.011	0.011
%TBP-kerosene	--------------	-----------	-------------	30%	--------------	----------------	%30
HNO3-M	3.75	1.5	0.03	-----------	0.26	---------------	----------------
Gama dps	$2.8*10^6$	--------------	--------------	--------------	Nill	All Gama	Nill
Flow rate ml/hr	360	120	750	850	-----------	-----------	-------------

Fig.(1) : Experimental Run at Steady State Using Extraction and Stripping Units