การผลิตยูเรเนียมบริสุทธิ์โดยกระบวนการสกัดของเหลวด้วยของเหลว

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บทคัดย่อ

ได้ศึกษาการผลิตเค้กเหลืองที่บริสุทธิ์ทั้งระดับห้องทดลองและกึ่งโรงงาน กระบวนการประกอบด้วย การละลายและกรอง การสกัดของเหลวด้วยของเหลว และการตกตะกอนและกรอง ได้ศึกษาผลของอัตราส่วนการไหล (อัตราการไหลของชั้นสารอินทรีย์/อัตราการไหลของชั้นน้ำ) ต่อประสิทธิภาพการทำงานของกระบวนการสกัดของเหลวด้วยของเหลว การศึกษาอย่างละเอียดได้ทำทั้งการสกัด การล้างสิ่งเจือปน (scrubbing) และการล้างยูเรเนียม (stripping) ความบริสุทธิ์ของผลผลิตเค้กเหลืองที่ได้สูงถึง 90.32 % U_3O_8

Uranium Refining by Solvent Extraction

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ABSTRACT

The yellow cake refining was studied in both laboratory and semi-pilot scales. The process units mainly consist of dissolution and filtration, solvent extraction, and precipitation and filtration. Effect of flow ratio (organic flow rate / aqueous flow rate) on working efficiencies of solvent extraction process was studied. Detailed studies were carried out on extraction, scrubbing and stripping processes. Purity of yellow cake product obtained is high as 90.32 % U_3O_8.

1. Introduction

Uranium is the basis fuel material for reactors. Any reactor must contain one of the fissionable isotopes of either uranium or plutonium which is made from uranium.(1) The uranium demand projection for the period 1989-2005 based in reactor requirements is expected to increase from about 41,500 t U in 1989 to about 55,000 t U in 2005. The uranium supply for the same period, as judged from the projection of production capability based on existing and committed mines and mills producing from US $ 80 / kg U resources, does not seem to be able to fill the projected demand. Thereafter new uranium mines and mills will have to be constructed to produce from currently known resources. These mines will be located in the countries which currently host the established producers of low cost uranium.(2)

In Thailand, uranium was found in small amount in monazite ore. Most of the local deposits are in the southern part of the country where the mineral is produced as a by-product from tin-mining. The annual production capacity of monazite by the dressing of tin-tailing was estimated to be around 500 tons.(3) Monazite is broken with alkaline to give a mixture of thorium, uranium and rare earth hydroxides, which are dissolved in acid. Uranium and thorium are precipitated together as hydroxide and re-dissolved in nitric acid to become the feed solution for solvent extraction. Uranium is separated from feed solution and is precipitated as yellow cake. Then the yellow cake is refined by solvent extraction to achieve uranium of high purity.

In 1963, Cavendish J.H. (4) found that pulse velocity, operating temperature and type of plate used in column affected the capacity and/or efficiency of the column. The system tested was the re-extraction of uranium from tri-n-butyl phosphate-kerosene solvent. In 1964 V.I. Doronin and A.M. Nikolaev(4) studied the extraction of uranyl nitrate from HNO_3 solutions by TBP-kerosene in a pulsed column with alternating plates with oppositely directed orifices for inducing rotating flow. The results show that the efficiency is a simple power function of the pulsing intensity. In 1972, Franca, J.M.Jr.(6) reported uranium purification process in a pilot plant at the Chemical Engineering Department of the Atomic Energy Institute in S. Paulo, Brazil. Yellow cake was refined by solvent extraction. In 1974, Franca, J.M. Jr. and Messano, J.(7) made a detailed study on the parameters that are necessary in the measurement of three industrial pulsed columns set for a average/year production of 500 tons in high uranium purity for nuclear designs. In 1979, M. Yunus et al.(8) reported the pilot-plant studies made at the Pakistan Institute of Nuclear Science and Technology, Rawalpindi, on refining yellow cake.

This research was carried out to gain uranium of high purity. The optimum operating conditions were investigated and working efficiencies were calculated, These results are served as the operational experience and technical know-how on the refining of yellow cake by solvent extraction.

2. Materials and methods

2.1 Materials

- 100-litre stainlers steeltanks with stirring motors for yellow cake dissolution and purified yellow cake precipitation
- 6-stage laboratory mixer-settler with auxiliary equipments.
  mixer size 10x10x15 cm
  settler size 10x20x15 cm
  impeller speed : 860 rpm
  impeller type : two-blade paddle
- semi-pilotpulsed perforated-platecolumn with auxiliary equipments
  column diameter 7 cm
  column heigh 2 cm
  hole diameter 3 mm
  perforated plate free area 23 % /plate
  plate spacing 5 cm
  column material : glass
  plate material : teflon
- tank filter
  tank diameter 50 cm
  tank height 40 cm

2.2 Methods

A flow diagram of yellow cake refining is shown as Fig. 1 Approximate 6 kg yellow cake obtained from monazite processing was dissolved in nitric acid and its normality was adjusted to 4N. The solutionwas filtered by tank filter to get rid of some solid impurities. The feed compositionsare 18.9 g/l uranium and 23.6 g/l thorium. The feed solution obtained was then purified by solvent extraction. Becausethevolume of feed solution was low, only 90 l, the laboratory mixer settler was selected for extraction step to reduce uranium loss in pumps and piping during operation.

The extractant was 5 % tributyl phosphate in kerosene. The extractattained was scrubbed with 1 N HNO_3 to get rid of thorium and then was stripped with deionized water to recover uranium. The equipment used was semi-pilot pulsed perforated-plate column. Pulse velocity was 2 cm/s with 1 p/s frequency and 2 cm amplitude. The purified uranyl nitrate solution achieved was precipitated with NH_4OH to gain ammonium diuranate . Then theammonium diuranate slurrywasfiltered toachieve pure uranium in the form of ammonium diuranate precipitate or yellow cake. Uranium mass balance was also calculated to estimate % yield.

3. Results

3.1 Uranium extraction efficiency and % thorium extracted are plotted as a function of flow ratio in Fig. 2 and the data are listed in table 1

3.2 % U loss and % thorium scrubbed are plotted as a function of flow ratio in Fig. 3 and the data are also listed in table 2

3.3 % U stripped and % Th stripped are plotted as a function of flow ratio in Fig. 4 and the data are also listed in table 3

3.4 Mass flow of uranium is presented in fig. 5, % yield of uranium producedbasedon uranium in feed solution is 67.6%. % U_3O_8in yellow cake obtained from stripped solution is high as 90.32% and % U_3O_8 in yellow cake gained from scrubbed solution is 81.49%

4. Discussion and conclusion

4.1 Uranium extraction efficiency is as high as 99.9% at flow ratio (F_o/F_a) of 2.86 but % thorium extracted is high. The optimum condition should be flow ratio of 1.45 that % thorium extracted is only 3.8% buturanium extraction efficiency is as high as 98.9% . If pulsed perforated-plate column is used for extraction, % thorium extracted will be lower.(9)

4.2 % thorium scrubbed is higher than % uranium loss. The higher the flow ratio, the lower the scrubbing efficiency. the optimum condition should be run at flow ratio of 13.8 that % uranium loss is only 11.9 % . To reduce uranium loss from the organic phase, refined uranyl nitrate can be applied for scrubbing.(8)

4.3 Both stripping efficiencies for uranium and thorium are high but % uranium stripped is higher. The optimum condition should be flow ratio of 1 that %thorium stripped is lower than other conditions.

4.4 The purity of yellow cake product is satisfactory. % U_3O_8 is as high as 90.32% although % ThO_2 is 1.63 %. Yellow cake refining should be carried out again to eliminate thorium.

4.5 If the yellow cake refining is operated in commercial scale, the concentration of feed solution should be increased in order to reduce its volume and the plant area.

5. Acknowledgement

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Table 1 Uranium extraction efficiency and % thorium extracted as a function of flow ratio

organic flow rate / aqueous flow rate	uranium extraction efficiency, %	% thorium extracted
2.86	99.9	7.9
2.46	99.8	6.9
1.93	99.7	5.1
1.45	98.9	3.8
1.22	93.8	3.5

Table 2 Uranium loss and % thorium scrubbed as a function of flow ratio

organic flow rate / aqueous flow rate	% uranium loss	% thorium scrubbed
5	30.1	43.1
7.3	25.1	39.4
14	11.9	36.6

Table 3 Uranium stripped and % thorium stripped as a function of flow ratio

organic flow rate / aqueous flow rate	% uranium stripped	% thorium stripped
1	99.85	95.55
0.67	99.75	98.7
0.5	99.95	98.45

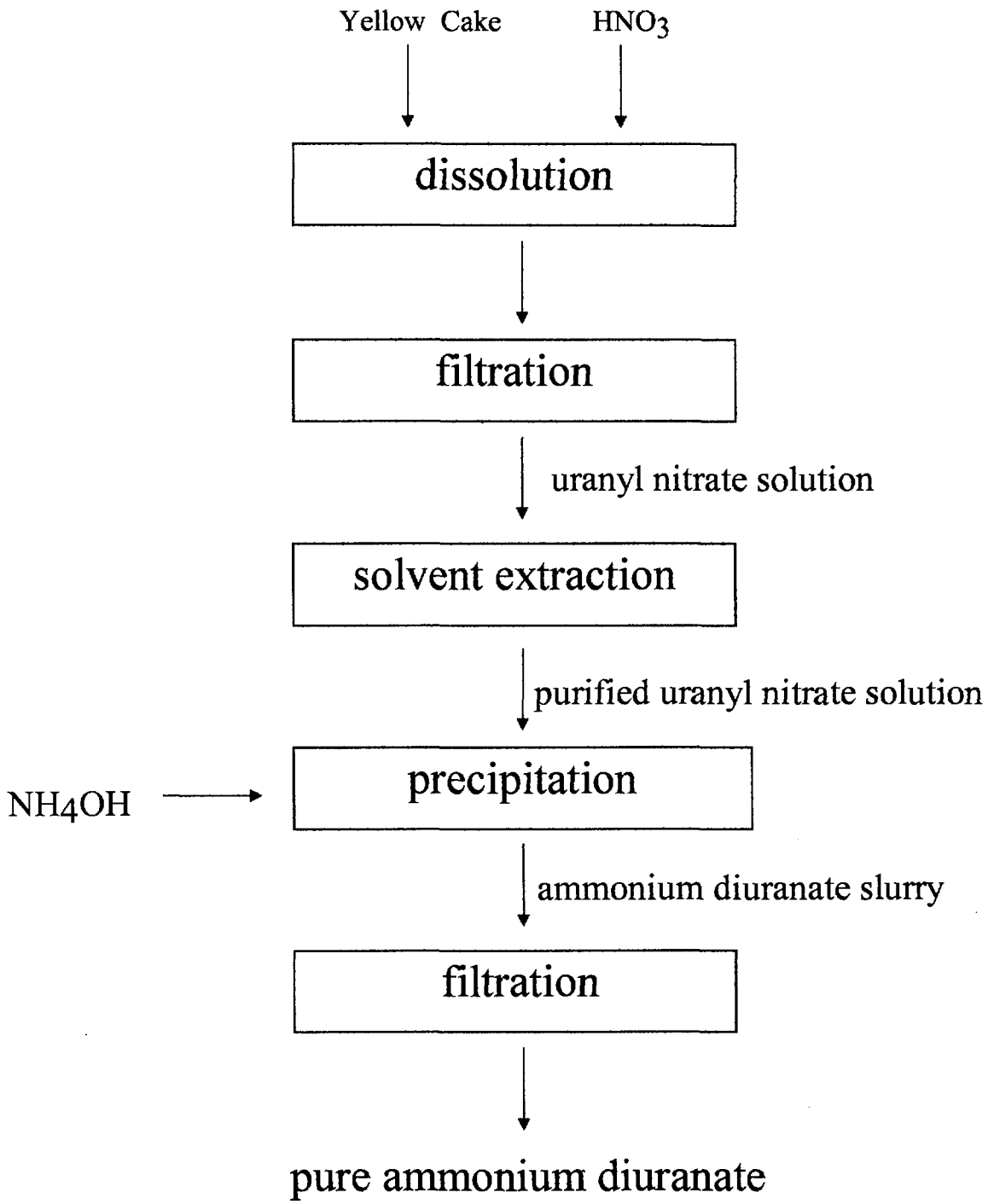


Fig. 1 flow diagram of yellow cake refining

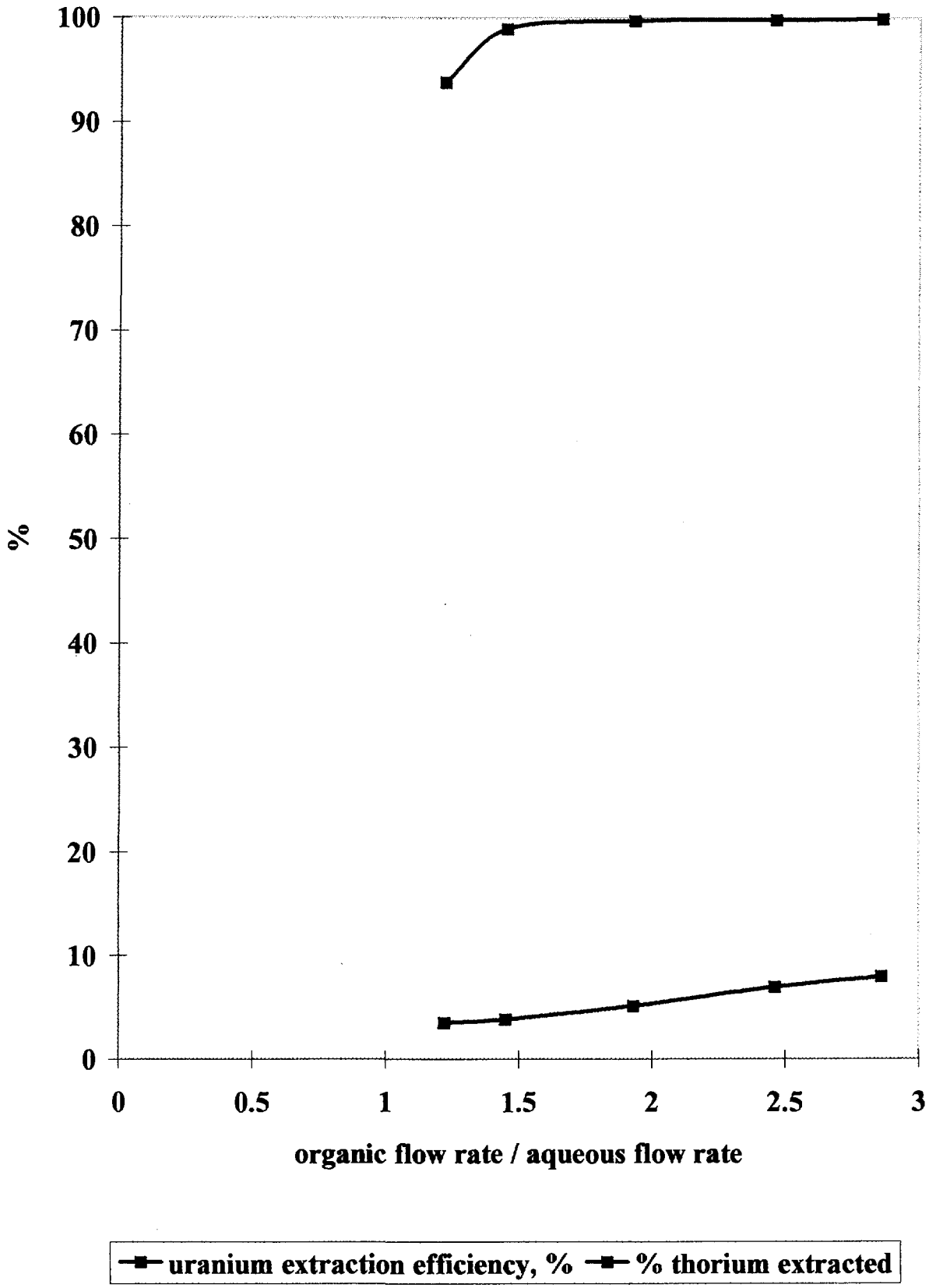


Fig. 2 Uranium extraction efficiency and % thorium extracted as a function of flow ratio

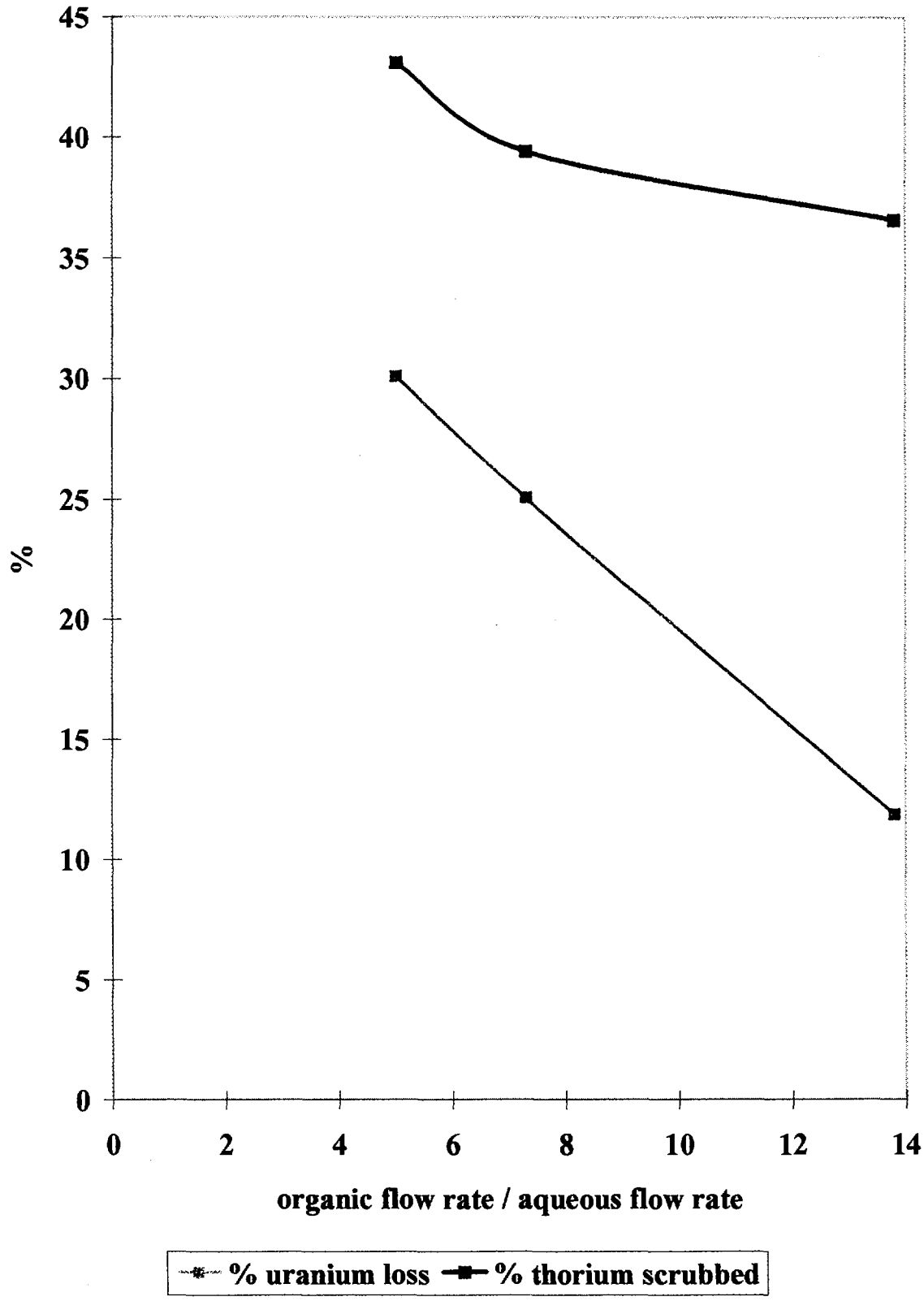


Fig. 3 % uranium loss and % thorium scrubbed as a function of flow ratio

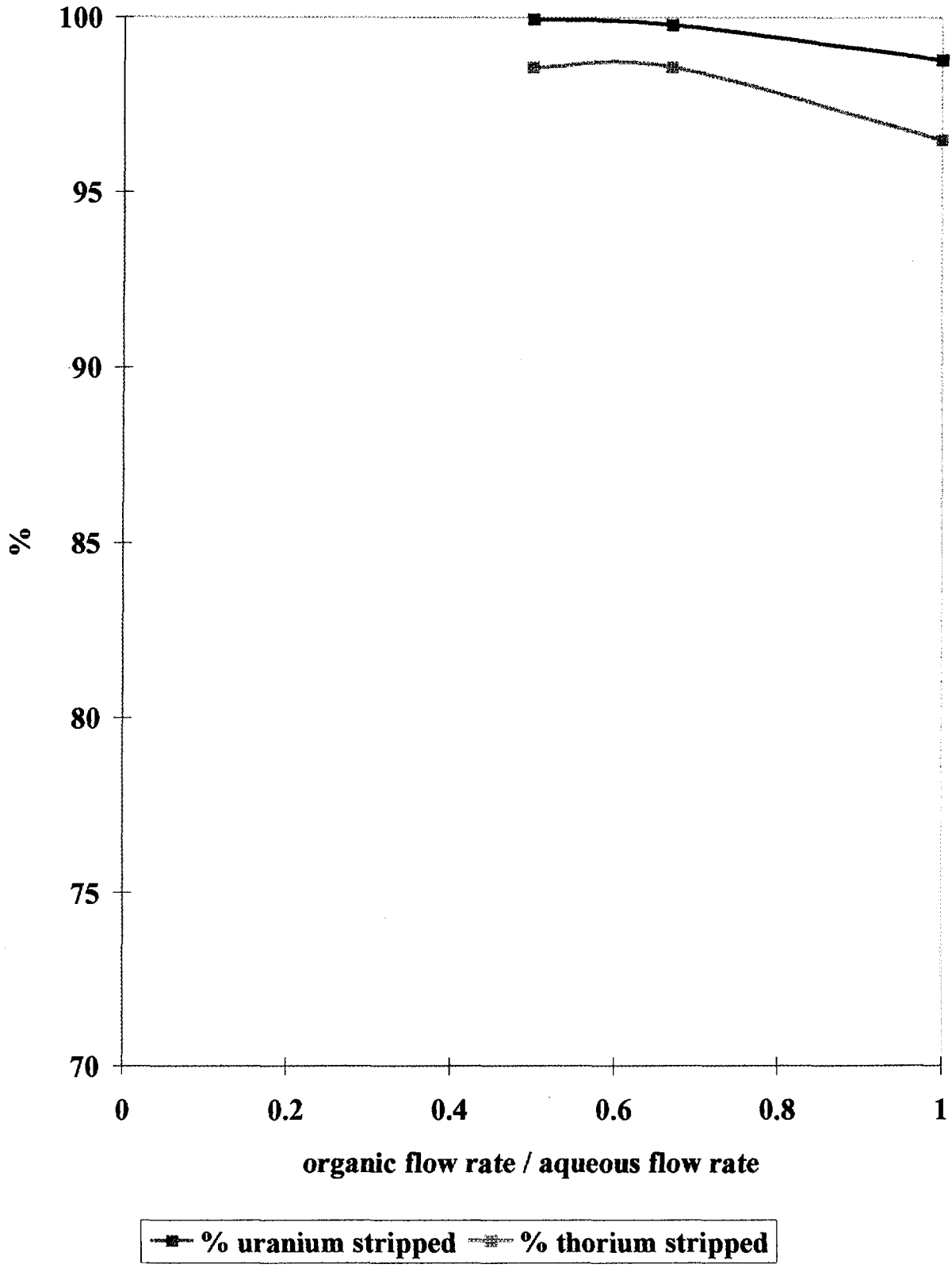
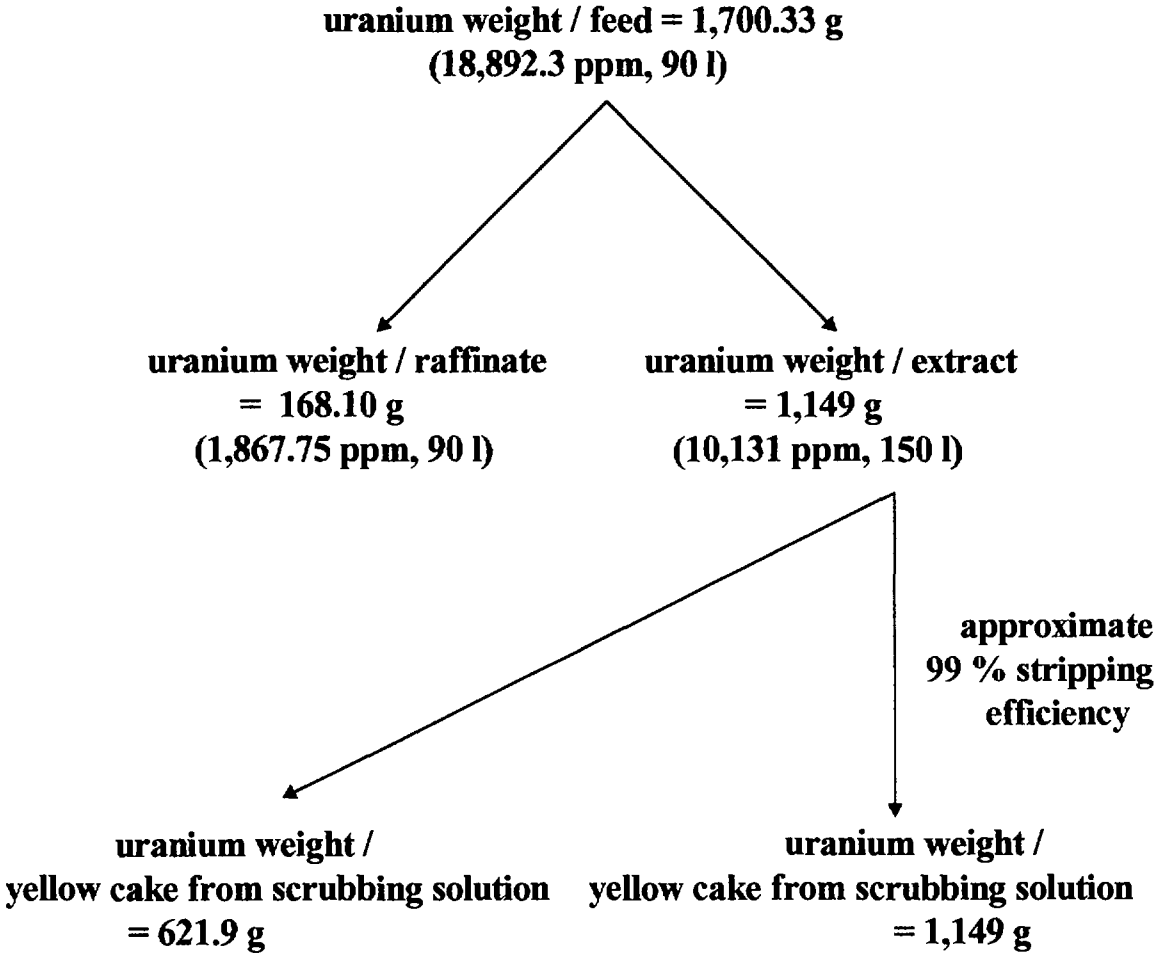


Fig. 4 % uranium stripped and % thorium stripped as a function of flow ratio



$$\% \text{ yield} = \frac{1{,}149}{1{,}700.33} \times 100 = 67.6\ \%$$

Fig. 5 Mass flow of uranium in slovent extraction process