

METHOD OF SEPARATING URANIUM FROM IRON AND THORIUM

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Acid leaching of uranium deposits is not a selective process. Sulfuric acid solubilizes iron(III) and half or more of the thorium depending on the mineralogy of this element. In uranium recovery by solvent extraction process, uranium is separated from iron by an organic phase consisting of 10 vol% tributylphosphate(TBP) in kerosine diluent. Provided that the aqueous phase is saturated with ammonium nitrate or made 4-5 M in nitric acid prior to extraction. Nitric acid or ammonium nitrate is added to the leach solution in order to obtain a uranyl nitrate product. Leach solutions containing thorium(IV) besides iron are treated in an analogous fashion. Uranium can be extracted away from thorium using 10 vol% TBP in kerosine diluent. The aqueous phase should be saturated with ammonium nitrate and the pH of the solution lowered to 0.5 with sufficient amount of sulfuric acid. In other words, the separation of uranium and thorium depends on the way the relative distributions of the two materials between aqueous solutions and TBP vary with sulfuric acid concentration. Thorium is later recovered from the waste leach liquor, after removal of sulfate ions. Uranium can be stripped from the organic phase by distilled water, and precipitated as ammonium diuranate.

Introduction

Tributyl phosphate is a solvent with very convenient properties. It is a commercial product and readily obtainable in large quantities. It is liquid over a wide range, from about -78 to 298 °C, and it is involatile at room temperature. It is very slightly miscible with water. It is chemically stable even to concentrated nitric acid. Indeed its main drawbacks are its rather high viscosity, and the fact that its density is similar to that of water. Both of these disadvantages can be overcome by diluting with a suitable inert material. The extracting power is so high that we can usually afford to do this.¹

Acid leaching of uranium deposits in which uranium mineralization is associated with major amounts of iron and thorium, usually yields solutions with concentrations of about 1g U/l and 6.0 g Fe/l.² The thorium content of the solution can be erratic, but its concentration may reach 1g Th/l.³ Table 1 shows a typical leach solution from Saagand deposits in Iran.

Table 1
Typical Saagand leach solution

	Free acid	U ₃ O ₈	Th	SO ₄	NO ₃
Leach liquor, g/dm ³	50	1.5	1.0	80	4.7

The high contamination of iron in commercial U₃O₈ is undesirable, because it interferes with the enrichment of uranium.^{4,5} As an intermediate material the yellow cake must conform to certain specifications, covering grade and impurities content. Penalty schedules reflect the increase in refinery costs due to impurities content in the mill product.²

Experimental

Extraction conditions of uranium with TBP were established from data obtained from synthetic solutions, and then extrapolated to the leach liquor. The procedure is to use different proportions of TBP in kerosine, keeping the aqueous phase constant in composition, and measure the percent extracted during this process. The concentration of nitric acid is adjusted to 6M which is taken from the calculated work by Goldberg et al.⁶ Then uranium extracted into 10 vol% TBP in kerosine from nitric acid solutions of varying acidity. The percent extracted first rises steeply with the acidity, then passes through a maximum and then falls again. Figures 1 and 2 illustrate the results.

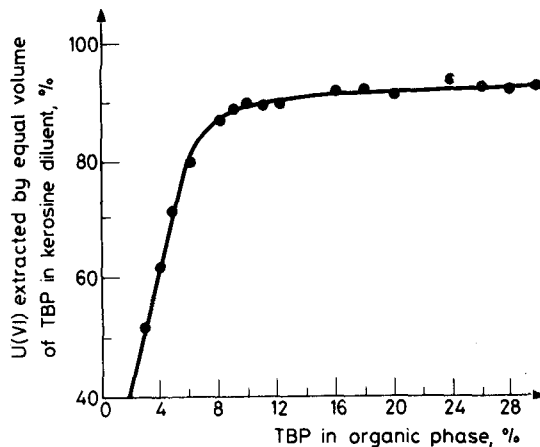


Fig. 1. Percent uranium in organic phase as a function of TBP in kerosine. Initial concentration of uranium and HNO₃ 1 g/dm³ and 6M, respectively, temperature 30 °C

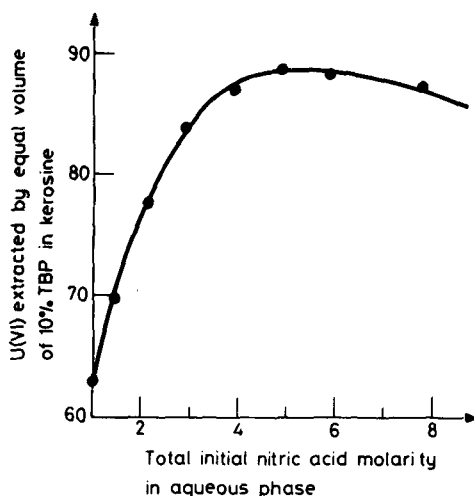


Fig. 2. Concentration of uranium in 10 vol% TBP as a function of aqueous molarities of nitric acid. Initial concentration of uranium 1 g/dm^3 , temperature 30°C

Table 2
The effect of sulfuric acid

Organic phase, $\mu\text{g/cm}^3$		pH of aqueous phase adjusted by sulfuric acid
U	Th	
657	8	0.5
702	18	0.9
731	174	1.3
774	260	1.6
798	394	2.0
830	456	3.2

Extraction conditions: aqueous phase; synthetic liquor containing 1.0 g U/l , 6.0 g Fe/l and 1.0 g Th/l ; ammonium nitrate 3M ; pH adjusted by sulfuric acid. Organic phase: 10 vol\% TBP ; temperature: 30°C ; phase ratio: 1; contact time: 5 min.

Uranium can be fractionated from iron into 10 vol\% TBP in kerosine, from an aqueous solution saturated with ammonium nitrate or made $4\text{--}5\text{M}$ in nitric acid. Much better separation can be obtained if nitric acid in the aqueous phase is replaced by ammonium nitrate. Uranium can be extracted away from thorium using 10 vol\% TBP in kerosine and salting out with ammonium nitrate. Provided that the pH of the solution is lowered to 0.5 by sulfuric acid. Table 2 shows the effect of

sulfuric acid. Uranium is stripped from the organic phase by distilled water and precipitated as ammonium diuranate. Thorium can be recovered from the waste leach liquor, after removal of sulfate ions by barium nitrate or lime and using 30 vol% TBP/diluent.

Results

The fractionation of uranium(VI) depends on the concentration of uncomplexed TBP in the organic phase. Thus one of the most important variables is the degree of solvent saturation with uranium, which is more strongly complexed by TBP than iron and thorium.

Thorium is found to be masked successfully by the addition of sulfuric acid. The extraction of thorium is reduced more drastically, thus permitting better separation from uranium.

Discussion

An enormous amount of work has gone into the development of extractive methods for uranium to solve the problems which have arisen in the extraction of uranium from ores, the purification of uranium, and the recovery of uranium from reprocessing stage.^{3,7} Solvent extraction by TBP has long been applied as a means of separating numerous elements from uranium in nitrate solutions.^{1,8}

Higher partition coefficient can be obtained for uranium if part of ammonium nitrate is replaced by nitric acid, but the corresponding increase is greater for thorium and iron. Separation of uranium from thorium, controlled ultimately by sulfuric acid is not equally effective when sulfuric acid is used along with nitric acid instead of ammonium nitrate.

For separation of uranium and thorium, most of the work has been done on the thorex process.⁷ A further report^{1,9} on extraction of uranium from thorium by 5 vol% TBP has been published. A comparison of this method carried out in the presence of sulfuric acid and salting out with ammonium nitrate reveals that the latter method seems equally favourable.

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