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The Use of Tri-*n*-octylamine for the Separation of Vanadium(V) from Acidic Sulfate Uranium Leach Liquors

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NOTE

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Abstract

Extraction of vanadium(V) from acidic sulfate solutions by a mixture of tri-*n*-octylamine and tributylphosphate (used as modifier) dissolved in kerosene has been studied. The distribution coefficient of vanadium(V) increases with an increase in pH and vanadium(V) concentration. The presence of iron(III) in aqueous solution does not have any appreciable effect, while large amounts of sulfate ion depress the distribution coefficient. Uranium(VI) has a distribution different from vanadium(V). Based upon these results, a scheme for the separation of vanadium(V) from uranium leach liquors has been made and checked experimentally.

INTRODUCTION

Sulfuric acid leaching of uranium ores containing the minerals carnotite and tyuyamunite yields solutions which contain uranium(VI) as well as vanadium which is present mostly in the pentavalent state because an oxidant is added during leaching. Vanadium, if recovered from such solutions, may be a useful by-product of uranium.

Extraction of uranium from sulfuric acid leach liquors by different types of amines has been exhaustively studied in separation schemes where other elements, including vanadium, are briefly mentioned (*1–5*). These schemes are based on either of two concepts: (a) coextraction of all the elements in the organic phase followed by their selective stripping or (b) reduction of the leach liquors to convert vanadium into unextractable

tetravalent form. Selective stripping of the elements from the organic phase requires very selective stripping agents while reduction of vanadium requires addition of foreign elements, usually iron(II), which when present in large quantities causes precipitation when working at pH's near 2.0. In the present work vanadium(V) has been separated from uranium(VI) by extracting at different pH's with a solvent consisting of 0.1 *M* tri-*n*-octylamine dissolved in kerosene in which 3% tributylphosphate has been added as modifier to prevent third phase formation (*6*). In the flow diagram that has been evolved, both the elements are obtained separately in the organic phase without the addition of any foreign element.

EXPERIMENTAL

Reagents

Vanadium(V) solutions were prepared by dissolving ammonium vanadate, NH_4VO_3 (May and Baker), in warm water; uranium(VI) solutions were prepared from uranyl sulfate, $UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ (BDH); while ferric ammonium nitrate (J. T. Baker) was the source of iron(III) solutions.

The extractant tri-*n*-octylamine, TOA (Eastman Kodak), was used as supplied. The concentration of the organic solutions of this reagent was checked by nonaqueous titration with perchloric acid using crystal violet as indicator.

Tri-*n*-butylphosphate, TBP (Fisher), was purified according to the method of Flanary et al. (*7*).

These and all the other reagents used were of chemically pure or analytical grade quality.

Equilibration

Known volumes of organic and aqueous phases were shaken together in well-stoppered bottles by a wrist action mechanical shaker at room temperature for a sufficient time to reach equilibrium. After shaking, the phases were centrifuged, and aliquots from each were drawn out by a pipet for analysis. The aliquots of organic phase were first stripped by 0.5 *M* sodium carbonate in the cases of vanadium(V) and uranium(VI). All the experiments were carried out in duplicate to check the reproducibility. The distribution coefficient *D* of a metal was calculated by

$$D = \frac{\text{concentration of metal in the organic phase}}{\text{concentration of metal in the aqueous phase}} \times \frac{\text{volume of the aqueous phase}}{\text{volume of the organic phase}}$$

Methods of Analysis

All the elements were analyzed spectrophotometrically using a Beckmann DU-2 spectrophotometer according to known methods (*8*, *9*). Vanadium(V) and uranium(VI) were analyzed by the peroxide method. Iron(III) was determined by measuring the optical density due to Fe^{3+} ions in dilute sulfuric acid at 305 mμ. Simultaneous analysis of the three elements in the synthetic leach liquor was carried out by removing the interferences of each element. Color due to Fe(III) was masked by adding small amount of orthophosphoric acid to the solution. The interference of vanadium(V) in measuring the uranium(VI) concentration was removed by heating the solution near boiling and then cooling to room temperature before taking the optical density. Uranium(VI) did not interfere in the vanadium(V) analysis. The removal of interferences was checked by making calibration curves with solutions having all three elements present in approximately the same amount as expected in the extracted layers.

RESULTS AND DISCUSSION

Extraction of Vanadium(V)

Extraction of vanadium(V) from acidic sulfate solutions by a solvent consisting of 0.1 *M* tri-*n*-octylamine and 3% tributylphosphate was studied as a function of pH, vanadium(V) concentration, iron(III) concentration, and sulfate ion concentration in the aqueous phase. It was observed that tributylphosphate alone does not extract any vanadium(V) under these conditions.

The extraction isotherms of vanadium(V) at pH values of 1.0, 1.65, and 2.0 are shown in Fig. 1. The slope of the isotherm of pH 1.0 varies from 0.85 to 1.3, signifying an average value of the distribution coefficient equal to 1.0. At higher pH's the extraction isotherms have a very steep rise. The increase in distribution coefficient with increasing pH may be attributed to the formation of polymeric anionic species of vanadium(V) (*10*). This is also evident by an increase of distribution coefficient with an increase in vanadium(V) concentration at a certain pH. Maximum loading of the organic phase could not be studied because the solutions having a total vanadium(V) concentration of 3.5 g/l were found to precipitate during shaking.

There is little effect of Fe(III) on the extraction of vanadium(V) when it is present up to a concentration of 3 g/l in the aqueous solution (Fig. 2); large amounts of sulfate ions depress the distribution coefficient (Fig. 3). The extraction of an anion of vanadium(V), denoted by X^{n-}, by a tertiary

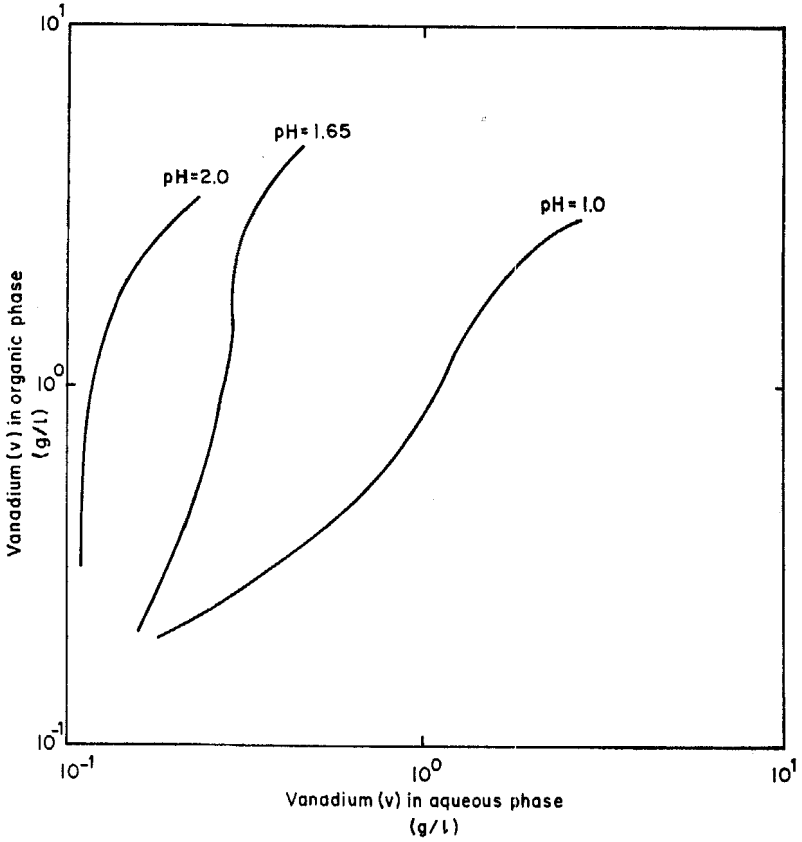

FIG. 1. Extraction of vanadium(V) from aqueous solution at different pH's by 0.1 *M* TOA + 3% TBP dissolved in kerosene, pre-equilibrated with 0.1 *M* H_2SO_4.

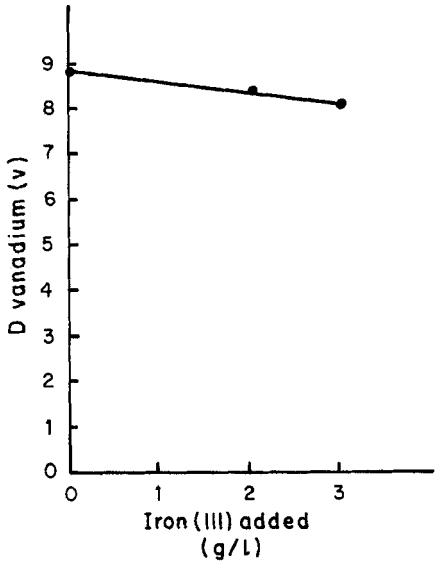

FIG. 2. Effect of the addition of iron(III) on the distribution coefficient of vanadium(V). Aqueous phase, 1 g/liter vanadium(V) at pH 2.0 containing varying amounts of iron(III); organic phase, 0.1 *M* TOA + 3% TBP dissolved in kerosene pre-equilibrated with 0.1 *M* H_2SO_4.

amine bisulfate or sulfate may be expressed in the following manner, which shows that the increase of sulfate or bisulfate ions should decrease the extraction of vanadium(V) in the organic phase:

$$n[(R_3NHHSO_4)]_o + [X^{n-}]_a \rightleftarrows [(R_3NH)_nX]_o + n[HSO_4^-]_a$$

$$n[(R_3NH)_2SO_4]_o + 2[X^{n-}]_a \rightleftarrows 2[(R_3NH)_nX]_o + n[SO_4^{2-}]_a$$

Extraction of Uranium(VI)

The extraction isotherms for uranium(VI) at pH 1.0 and 2.0 (Fig. 4) show that the extraction is much higher at pH 1.0 compared to that of vanadium(V), and thus it could be a basis for the separation of the two elements.

Separation Scheme

The scheme for the separation of vanadium(V) from uranium leach

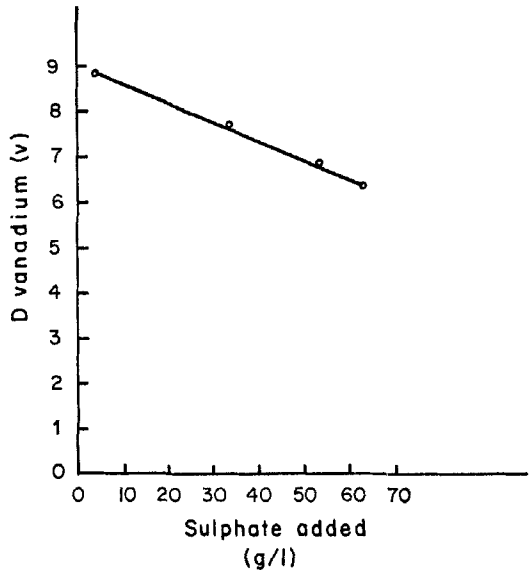

FIG. 3. Effect of the addition of sulfate ions on the distribution coefficient of vanadium(V). Aqueous phase, 1 g/liter vanadium(V) containing varying amounts of sulfate ions at pH 2.0; organic phase, 0.1 *M* TOA + 3% TBP dissolved in kerosene pre-equilibrated with 0.1 *M* H_2SO_4.

liquors thus evolved is shown in Fig. 5. This was checked by carrying out experiments with a synthetic leach liquor of the following composition:

Uranium(VI) = 1 g/l
Vanadium(V) = 0.5 g/l
Iron(III) = 3 g/l
Sulfate = 60 g/l

Table 1 gives the analysis of the uranium and vanadium products obtained. Ninety-two percent of the uranium was recovered in the first extraction column as a result of single batchwise extraction and two successive scrubbings with 0.5 *N* sulfuric acid. The feed of the second extraction column consists mainly of vanadium(V) and iron(III), and after two successive extractions vanadium(V) was found mainly in the organic phase (65%) while 93% of iron(III) remained in the raffinate.

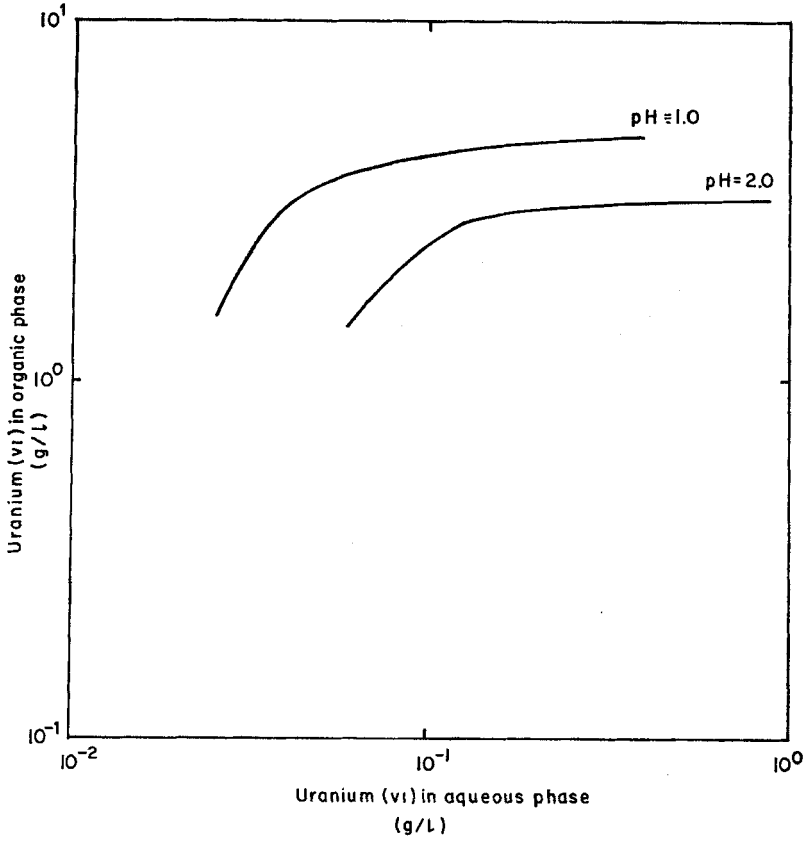

FIG 4. Extraction of uranium(VI) from aqueous solutions at pH's 1.0 and 2.0, by 0.1 *M* TOA + 3% TBP dissolved in kerosene, pre-equilibrated with 0.1 *M* H_2SO_4.

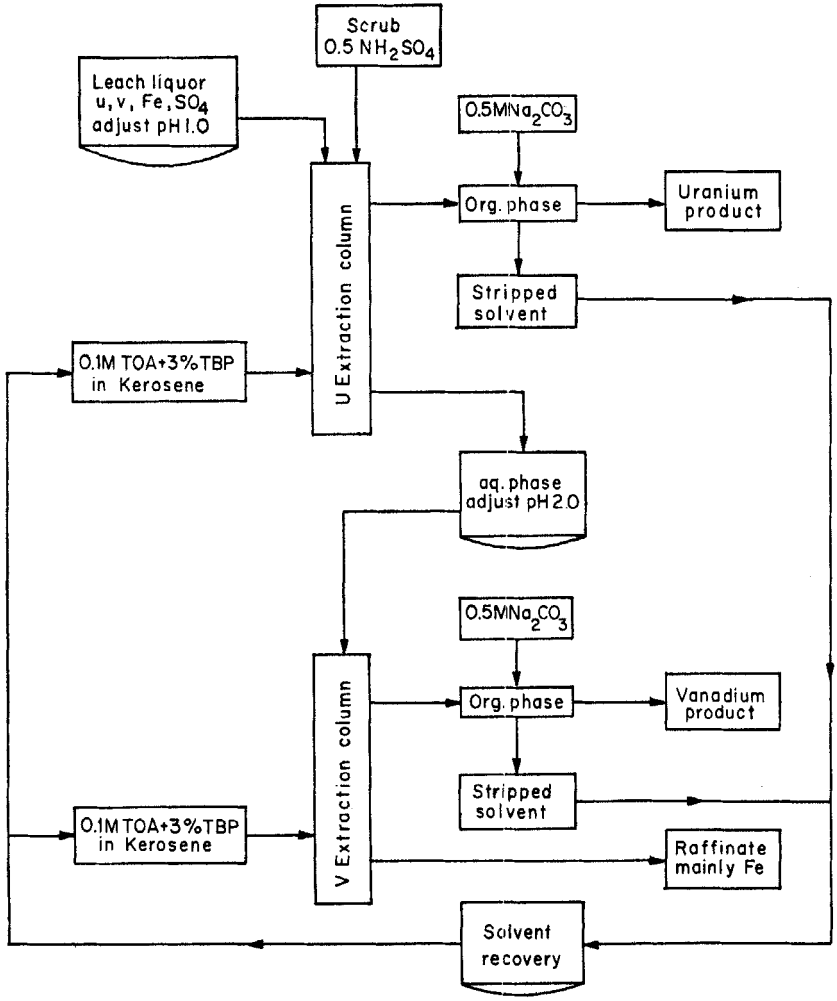

FIG. 5. A scheme for the separation of vanadium from uranium leach liquor.

TABLE 1

Separation of Vanadium(V) from Synthetic Uranium Leach Liquor[a]

	Uranium(VI) (mg)	Vanadium(V) (mg)	Iron(III) (mg)	% Recovery		
				U(VI)	V(V)	Fe(III)
Uranium product	9.2	0.43	0.00	92.0	8.6	—
Vanadium product	1.05	3.29	5.29	10.5	65.8	8.4
Raffinate	—	1.37	27.9	—	27.5	93.1

[a]Organic phase (solvent): 0.1 *M* Trioctylamine + 3% TBP in kerosene. Aqueous phase (feed): Synthetic leach liquor containing uranium(VI) = 10 mg; vanadium(V) = 5 mg; Fe(III) = 30 mg, sulfate = 600 mg. Equilibrations: Equal volumes of organic and aqueous phases were mixed and the experiment was carried out according to scheme in Fig. 5.

CONCLUSION

This study shows that the separation of vanadium(V) from uranium(VI) can be successfully achieved without using any reducing agent. Multistage contact can improve the recovery of vanadium(V).

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