Selective Separation of Uranium, Vanadium, and Rhenium from Sulfuric-Acid Oil-Shale-Ash Leachates by Integrated Ion Exchange and Solvent Extraction

Shamshiddin K. Kurbanov

Military Institute of Information and Communication Technologies and Communications, University of Military Security and Defense of the Republic of Uzbekistan, Uzbekistan

ABSTRACT

An integrated ion-exchange and solvent-extraction route was evaluated for the selective recovery of uranium, vanadium, and rhenium from sulfuric-acid leach liquors produced during processing of metalliferous oil-shale ash. Three commercial anion exchangers (PFA-460, A-600, and AMP) were compared under static and dynamic conditions. The most favorable operating region for selective uranium loading was approximately pH 1. In column tests, PFA-460 exhibited the latest 10% uranium breakthrough (about 150 bed volumes) and the highest dynamic uranium capacity (76.85 g L^{-1} of resin), whereas A-600 and AMP reached 10% breakthrough after about 40 bed volumes. The corresponding resin-phase U:V ratios after 300 bed volumes were 2.7:1, 4.0:1, and 5.3:1, respectively, demonstrating a capacity–selectivity trade-off. Uranium desorption with 0.1–0.2 M HNO_3 in 1 M NH_4NO_3 followed by ammonium-diuranate precipitation produced a concentrate containing >40% U and ≤0.2–0.3% V. Subsequent amine extraction transferred 97.3–97.9% of rhenium to the organic phase, but molybdenum co-extraction remained significant (19.4–22.8%). Organic-phase washing improved the Re:Mo ratio in the strip solution to approximately 14–21:1. The results define a technically coherent sequence for separating U, Re, and a vanadium-rich Fe–V residue from complex sulfate liquors, while identifying Re/Mo separation as the principal remaining purification challenge.

Keywords: Oil shale ash; uranium; vanadium; rhenium; ion exchange; solvent extraction

Highlights

- PFA-460 reached the highest dynamic uranium capacity of 76.85 g L^{-1}.
- AMP provided the highest U/V selectivity, with a resin-phase ratio of 5.3:1.
- Near pH 1, uranium sorption was favored without strong vanadium co-removal.
- Amine extraction transferred 97.3–97.9% of rhenium to the organic phase.
- An integrated flowsheet yields uranium, rhenium, and Fe–V product streams.

1. Introduction

Leach liquors generated from metalliferous shale and black-shale feeds are chemically complex because uranium, vanadium, molybdenum, rhenium, iron, and other elements can coexist in strongly acidic sulfate media. For dilute uranium-bearing liquors, ion exchange is widely used to concentrate and

purify uranium because anionic uranyl-sulfate complexes can be selectively loaded on strong-base anion exchangers [1,2]. The chemistry is strongly dependent on free acidity, sulfate activity, competing anions, oxidation state, and the concentration of impurity metals, making resin selection and pH control central to process performance.

Black-shale processing also requires effective management of vanadium and associated critical metals. Recent reviews emphasize that vanadium recovery from shale-type resources is governed by mineral occurrence, oxidation state, and the ability of pretreatment and leaching operations to release refractory vanadium-bearing phases [3]. For uranium–vanadium ores of the Kyzylkum region, combined hydrometallurgical routes have demonstrated that both metals can be recovered, but the downstream separation of multi-element liquors remains a key process-design problem [4].

Rhenium introduces an additional separation challenge because perrhenate is readily extracted by tertiary amines, whereas molybdenum may co-extract under similar conditions. Tertiary-amine systems have been used for rhenium recovery from sulfate media and industrial leach streams [5–7], but high Re recovery does not automatically guarantee high Re/Mo selectivity. Therefore, an integrated flowsheet must balance uranium loading capacity, U/V discrimination, rhenium extraction, impurity rejection, and the disposition of the residual vanadium-rich stream.

The objective of this study was to evaluate an integrated sequence comprising (i) selective uranium/vanadium sorption from sulfuric-acid oil-shale-ash leach liquors, (ii) uranium desorption and ammonium-diuranate precipitation, (iii) rhenium desorption and amine solvent extraction, and (iv) precipitation of a Fe–V product from the remaining vanadium-bearing liquor. Particular attention was paid to the capacity–selectivity trade-off among PFA-460, A-600, and AMP resins and to the effect of iron-associated precipitation on the interpretation of vanadium removal at elevated pH.

2. Materials and methods

2.1 Leach liquors and ion exchangers

Two process liquors were examined: a uranium–vanadium liquor from the first leaching stage, with an initial concentration ratio U:V of approximately 1:3, and a vanadium-rich liquor from the second (sulfation-assisted) stage. Both liquors contained excess sulfuric acid (30–40 g L^{-1}) and iron in the approximate range 0.7–7 g L^{-1}. The anion exchangers were PFA-460 and A-600(U) (Purolite) and AMP resin.

2.2 Static and dynamic sorption tests

Static experiments were conducted for 24 h at solution-to-resin volume ratios of 100:1 to 200:1. The pH range investigated was 0.5–3, with adjustment using sodium carbonate; hydrogen peroxide and ammonium sulfite were used in redox-modification tests. Dynamic experiments were carried out in columns containing 20 mL of resin at a feed rate of five bed volumes per hour. Uranium breakthrough and metal loading were used to compare kinetic performance and selectivity.

2.3 Desorption, precipitation, and rhenium extraction

Loaded uranium was desorbed with 0.1–0.2 M HNO_3 containing 1 M NH_4NO_3, followed by precipitation of ammonium diuranate using 25% NH_3. Rhenium was selectively desorbed using an acidic nitrate solution containing 4.0% HNO_3 and 80–90 g L^{-1} nitrate. Solvent extraction was then performed with an organic phase containing 32% trialkylamine, 58% kerosene, and 10% fatty alcohols at an organic-to-aqueous phase ratio of 1:1.

2.4 Data interpretation and figure reconstruction

The original dataset reports point values for resin capacities, breakthrough thresholds, U/V ratios, rhenium extraction, molybdenum co-extraction, and washing performance. Where the source manuscript presented only schematic curves rather than complete numerical series, the corresponding figures in this manuscript remain explicitly labelled as schematic reconstructions. No additional experimental measurements were inferred from curve shape.

3. Results and discussion

3.1 Dynamic uranium breakthrough and resin capacity

In column operation, PFA-460 showed substantially delayed uranium breakthrough relative to A-600 and AMP. The 10% uranium breakthrough criterion was reached after approximately 150 bed volumes for PFA-460, compared with about 40 bed volumes for A-600 and AMP (Fig. 1). The corresponding dynamic uranium capacities were 76.85, 53.18, and 68.14 g L^{-1} of resin, respectively. Thus, PFA-460 provided the highest loading capacity and the most favorable breakthrough behavior among the three resins.

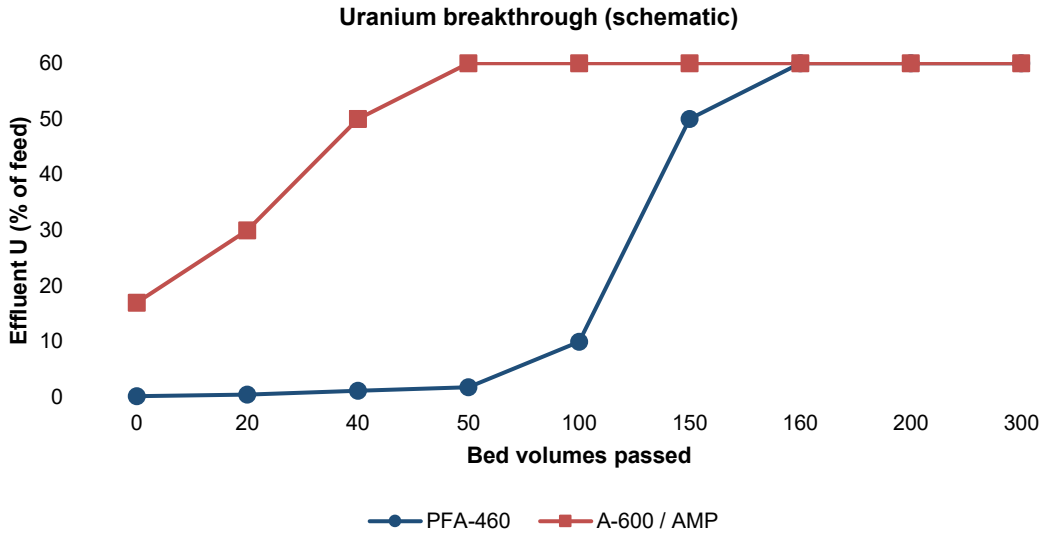

Figure 1. Schematic uranium breakthrough behavior for the tested anion exchangers. The source manuscript reported the 10% breakthrough points (~150 bed volumes for PFA-460 and ~40 bed volumes for A-600/AMP); the connecting curves are schematic and do not represent independently measured intermediate points.

3.2 Capacity–selectivity trade-off in U/V separation

The superiority of PFA-460 in dynamic uranium capacity did not translate into the best uranium/vanadium separation. After 300 bed volumes, the U:V ratio in the resin phase was 2.7:1 for PFA-460, 4.0:1 for A-600, and 5.3:1 for AMP, compared with an initial solution ratio of approximately 1:3. AMP therefore provided the strongest discrimination in favor of uranium, whereas PFA-460 prioritized throughput and loading capacity (Fig. 2). This inverse relationship between capacity and selectivity is a practical design constraint: resin choice depends on whether the process is limited primarily by column productivity or by downstream purification burden.

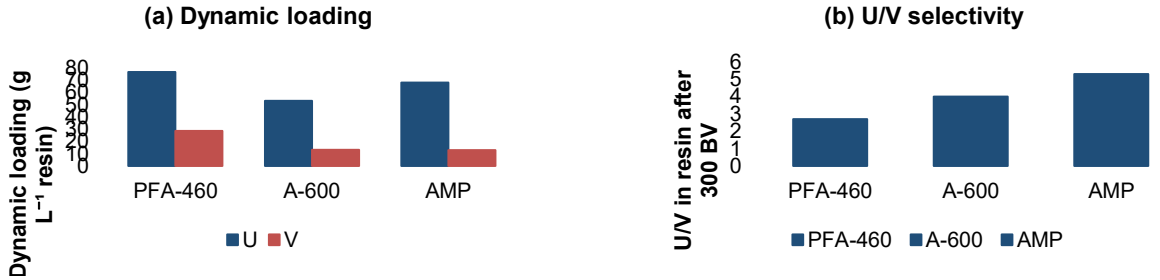

Figure 2. Comparison of PFA-460, A-600, and AMP: (a) dynamic U and V loading; (b) U/V ratio in the resin phase after 300 bed volumes. The initial U:V ratio in the feed solution was approximately 1:3.

Table 1. Comparative sorption characteristics of the three anion exchangers.

Parameter	PFA-460	A-600	AMP
U capacity, static at pH≈1 (g L^{-1})	57.4	44.0	45.4
V capacity, static at pH≈1 (g L^{-1})	12.7	9.36	8.58
U capacity, dynamic (g L^{-1})	76.85	53.18	68.14
10% U breakthrough (bed volumes)	~150	~40	~40
Resin-phase U:V after 300 bed volumes	2.7:1	4.0:1	5.3:1

3.3 Effect of pH and the role of iron co-precipitation

Within the low-pH region, uranium loading changed only modestly and reached a reported maximum near pH 1. The source data give static uranium capacities at pH≈1 of 57.4, 44.0, and 45.4 g L^{-1} for PFA-460, A-600, and AMP, respectively. Vanadium loading at the same condition was markedly lower (12.7, 9.36, and 8.58 g L^{-1}), supporting pH≈1 as a useful operating window for preferential uranium sorption.

At the upper end of the pH range, the apparent vanadium removal increased sharply. Parallel redox measurements and analysis of precipitated solids in the source study attributed much of this increase to vanadium co-precipitation with Fe(III) hydroxide rather than to true ion-exchange loading. Consequently, apparent resin capacity derived solely from solution depletion becomes misleading once iron hydrolysis and co-precipitation are significant. This distinction is important for process scale-up because precipitation changes both solid–liquid handling and the metal balance.

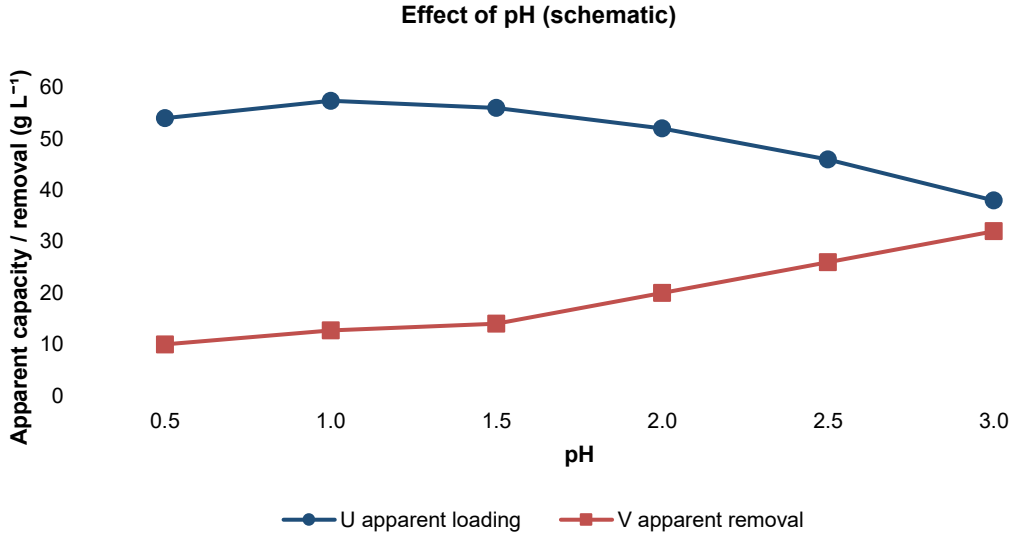

Figure 3. Schematic influence of pH on apparent U and V loading. Only the pH≈1 values are directly reported numerical sorption data; the remaining trend is reconstructed from the source figure. The higher-pH vanadium increase includes co-precipitation with $Fe(OH)_3$ and should not be interpreted as pure resin uptake.

3.4 Uranium desorption and ammonium-diuranate precipitation

Uranium desorption reached 87.7–90% in the first cycle with 0.1 M HNO_3 in nitrate medium and approached complete recovery in a second cycle when the acid concentration was increased to 0.2 M. Subsequent precipitation with ammonia yielded an ammonium-diuranate product containing more than 40% U with residual vanadium not exceeding approximately 0.2–0.3%. These results demonstrate that the sorption stage can be coupled to a conventional uranium concentration step while maintaining a low vanadium content in the uranium product.

3.5 Rhenium extraction and Re/Mo separation

Selective rhenium desorption from the uranium-depleted anion exchanger reached approximately 98%. In the subsequent amine solvent-extraction step, 97.3–97.9% of rhenium transferred to the organic phase. Molybdenum co-extraction, however, remained substantial at 19.4–22.8%, confirming that rhenium recovery efficiency and Re/Mo selectivity must be considered separately. Similar behavior is well established for tertiary-amine extraction systems, in which perrhenate is strongly extracted but chemically related oxyanions can also load depending on acidity and anion speciation [5–8].

Washing of the loaded organic phase removed 61.9–75.0% of the co-extracted molybdenum while causing rhenium losses of 20.5–23.0%. The resulting strip solutions had Re:Mo ratios of approximately 14–21:1. The wash therefore improved purity but at a measurable rhenium penalty, indicating that future optimization should target a higher Mo-removal/Re-retention ratio through acidity control, alternative modifiers, or staged scrubbing. Recent work on tertiary-amine systems has shown that large increases in Re/Mo separation factors are possible when solution speciation and competing anions are deliberately controlled [8].

Table 2. Rhenium extraction and organic-phase washing performance.

Stage	Re (%)	Mo impurity (%)
Extraction, series 1	97.9	22.8
Extraction, series 2	97.3	19.4
Organic wash, phase ratio 2:1	−23.0 (loss)	−75.0 (removed)
Organic wash, phase ratio 5:1	−20.5 (loss)	−61.9 (removed)

3.6 Integrated flowsheet and vanadium-rich product

The individual separation operations can be assembled into a single process sequence in which uranium is first selectively loaded and recovered as ammonium diuranate, rhenium is subsequently recovered through nitrate desorption and amine extraction, and the residual vanadium-bearing liquors are combined for Fe–V precipitation. Neutralization of the second-stage vanadium liquor with sodium carbonate to pH 3–5, after preliminary removal of residual uranium near pH 0.5, produced an Fe–V cake containing approximately 30–35% Fe and up to 15% V. The source study identifies this material as compositionally comparable with vanadium-bearing metallurgical feedstocks and therefore potentially suitable for further ferrovanadium processing.

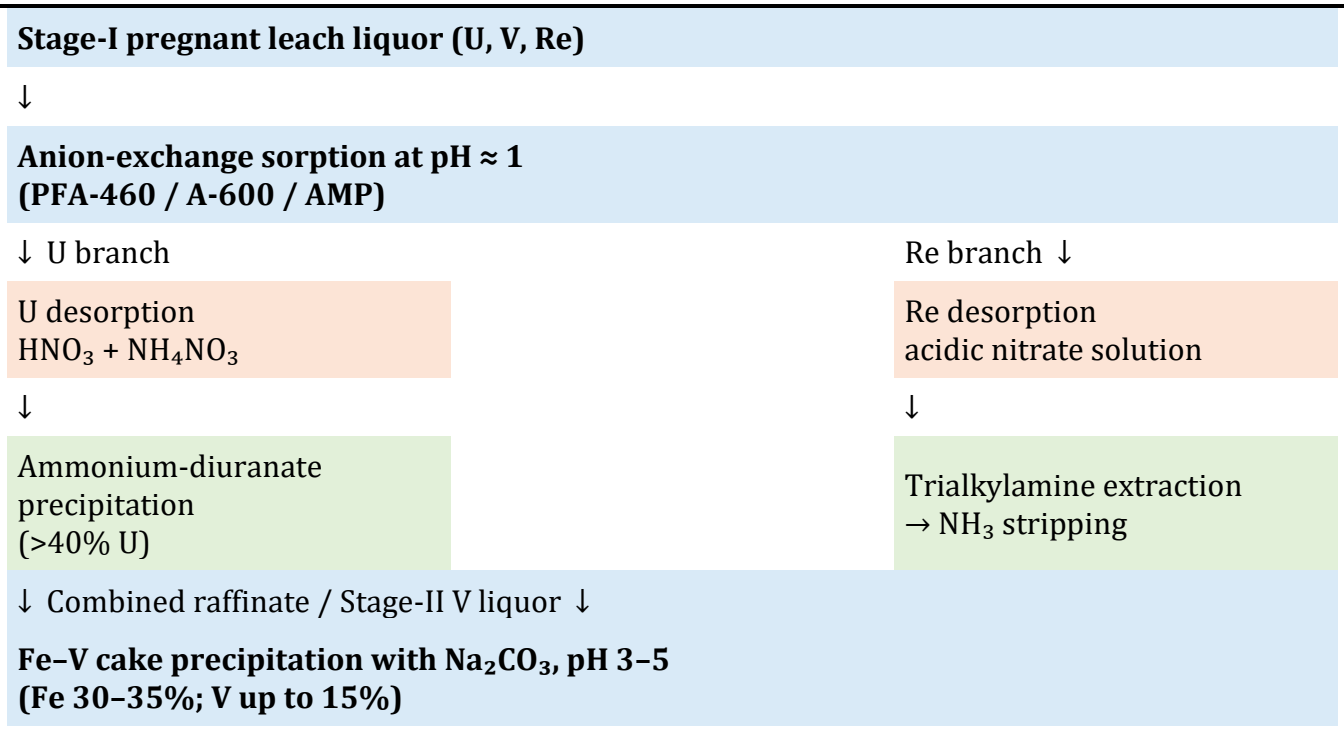

Figure 4. Editable process flowsheet for selective recovery of U, Re, and a vanadium-rich Fe–V product from sulfuric-acid oil-shale-ash leach liquors. All boxes and text are editable directly in Word.

3.7 Process implications and remaining limitations

The results support a sequential rather than simultaneous separation strategy. PFA-460 is attractive where uranium throughput and column loading dominate, whereas AMP is preferable where U/V discrimination is the principal objective. The rhenium stage achieves high recovery but still requires improved molybdenum rejection. In addition, the source manuscript does not report replicate variability, analytical detection limits, detailed resin conditioning procedures, or a complete mass balance across all unit operations. These items should be documented before final journal submission because they are required to assess reproducibility and scale-up uncertainty.

4. Conclusions

1. PFA-460 provided the highest dynamic uranium capacity (76.85 g L^{-1}) and the latest 10% breakthrough (~150 bed volumes), but the lowest U/V selectivity among the three tested resins.
2. AMP achieved the strongest U/V discrimination, with a resin-phase U:V ratio of 5.3:1 after 300 bed volumes, compared with 4.0:1 for A-600 and 2.7:1 for PFA-460.
3. An operating region near pH 1 favored selective uranium sorption; at higher pH, vanadium removal is increasingly affected by Fe(III)-hydroxide co-precipitation and cannot be treated as pure ion-exchange loading.
4. Uranium desorption and ammonium-diuranate precipitation yielded a product containing >40% U and ≤0.2–0.3% V.
5. Amine extraction recovered 97.3–97.9% of rhenium, but Mo co-extraction of 19.4–22.8% remained the main purification limitation; washing improved the final Re:Mo ratio to approximately 14–21:1.

Declarations

Funding: [Please insert funding information or state that no specific funding was received.]

Conflict of interest: [Please confirm the final conflict-of-interest statement before submission.]

Data availability: [Please specify availability of the underlying experimental dataset.]

Author contributions: S.K. Kurbanov: conceptualization, methodology, investigation, data interpretation, and manuscript preparation. [Please confirm or revise the CRediT roles.]

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Submission note: This manuscript is structured in an international hydrometallurgy-journal style. Before submission, complete the bracketed declarations and replace schematic figure reconstructions with raw experimental series if available.