



3 4456 0361417 7

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

ORNL-2820
Technology-Raw Materials

SOLVENT EXTRACTION RECOVERY OF
VANADIUM (AND URANIUM) FROM
ACID LIQUORS WITH DI(2-ETHYLHEXYL)
PHOSPHORIC ACID

D. J. Crouse
K. B. Brown

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this
document, send in name with document
and the library will arrange a loan.



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price \$2.25. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-2820

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section C

SOLVENT EXTRACTION RECOVERY OF VANADIUM (AND URANIUM) FROM
ACID LIQUORS WITH DI(2-ETHYLHEXYL) PHOSPHORIC ACID

D. J. Crouse and K. B. Brown

Work done by: F. G. Seeley
A. D. Kelmers
J. M. Schmitt
W. D. Arnold

DATE ISSUED

NOV 11 1959

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION



3 4456 0361417 7

ABSTRACT

Bench-scale studies were made on use of di(2-ethylhexyl)-phosphoric acid in an organic diluent (Dapex process) for solvent extraction recovery of vanadium from acid leach liquors. Vanadium may be stripped from the solvent by either acidic or alkaline reagents, the former having been studied in considerably greater detail. A process for single-cycle recovery and separation of uranium and vanadium from sulfate leach liquors was shown to be attractive both from the standpoint of operation and chemical costs. Process schemes for recovery of vanadium from uranium-barren liquors are also described. On the basis of the encouraging laboratory results, pilot scale tests for specific applications are recommended.

CONTENTS

	Page
1.0 Summary	4
2.0 Introduction	6
3.0 Experimental Materials and Techniques	7
4.0 Extraction of Vanadium from Acidic Sulfate Solutions	8
4.1 Rate of Extraction	9
4.2 Effect of pH	10
4.3 Effect of Sulfate Concentration	10
4.4 Extraction Isotherms	10
4.5 Effect of Diluent Modifiers	13
4.6 Effect of Temperature on Extraction of Vanadium and Other Metals	15
5.0 Extraction of Vanadium from Acidic Leach Liquors	17
5.1 Extractions from Sulfate-Chloride Liquors	17
5.2 Simultaneous Vanadium-Uranium Extractions from Sulfate Liquors	17
6.0 Vanadium Stripping	21
6.1 Stripping with Sulfuric Acid	21
6.2 Stripping with Alkaline Solutions	28
7.0 Recovery of Vanadium from Strip Solutions	30
7.1 Recovery from Acid Strip Solutions	30
7.2 Recovery from Alkaline Strip Solutions	38
8.0 Phosphate Content of Vanadium Products	39
8.1 Sources of Phosphate Contamination	40
8.2 Separation of Inorganic Phosphate from Vanadium	43
9.0 Process for Simultaneous Recovery of Uranium and Vanadium from Leach Liquors	53
9.1 Continuous Runs	55
9.2 Estimated Process Reagent Costs	75
10.0 Processes for Recovery of Vanadium from Uranium-Barren Leach Liquors	77
10.1 Acid Stripping Process	77
10.2 Sodium Carbonate Stripping Process	78
10.3 Combination Acid-Basic Stripping Process	78
11.0 References	79
12.0 Appendix. Comparison of Vanadium Extraction Ability of Several Dialkylphosphoric Acids	80

1.0 SUMMARY

A solvent extraction process for extracting vanadium from acidic ore leach liquors with di(2-ethylhexyl)phosphoric acid (D2EHPA) was developed through laboratory scale. In initial batch tests the effect of numerous variables on the extraction and stripping processes were evaluated and methods for recovering vanadium from the pregnant strip solutions were explored. Subsequent continuous runs in bench-scale equipment successfully demonstrated a single-cycle process for recovery and separation of uranium and vanadium from sulfate liquors of the type obtained by the "acid cure" vanadium leach process.

Batch Test Results for Vanadium

Extraction. Vanadium(IV) was extracted much more strongly than vanadium(V). The vanadium(IV) extraction coefficients from sulfate solutions, although much lower than those for uranium(VI), were sufficiently high for process use when the liquor pH was 1.5-2.0 and when extractant concentrations were as high as 0.2-0.4 M. A postulated reaction mechanism indicated the vanadium coefficient to be proportional to the aqueous vanadium concentration and the square of the free reagent concentration, and inversely proportional to the fourth power of the hydrogen ion concentration. The vanadium extraction coefficient decreased somewhat when the sulfate concentration was increased from 0.2 to 1.0 M.

Extraction isotherms with vanadyl sulfate solutions indicated a maximum vanadium loading of 0.5 mole per mole of D2EHPA.

Diluent modifiers, added to prevent separation of the extractant from the diluent during alkaline stripping, depressed vanadium extractions, the effect being relatively large for alcohol additive but minor for TBP.

The vanadium extraction coefficient increased 60-70% with increase in the extraction temperature from 15 to 50°C.

Stripping. Stripping with dilute sulfuric acid was efficient, producing strip solutions highly concentrated in vanadium. The efficiency of acid utilization increased slightly with increase in stripping acid concentration in the range 0.75-1.5 M.

Vanadium was precipitated directly from the solvent on contact with a basic solution, e.g., ammonia or sodium carbonate. The vanadium precipitate was colloidal and could not be separated by filtration.

Recovery from Strip Solutions. Vanadium was quantitatively recovered, as hydrated vanadyl oxide, by neutralizing the acid strip solution with ammonia. In an alternative method vanadium was recovered by oxidation of the strip solution with sodium chlorate to precipitate "red cake." Recoveries in the latter case were considerably improved by adjusting the strip solution pH to 1-2 either prior to or following the oxidation step, but, even under the most favorable conditions, it appeared that appreciable vanadium recycle (5-10%) would be required with this method.

Oxidation with air of vanadium(IV) precipitates, dispersed in carbonate strip solutions, to soluble pentavalent vanadium was partially successful. The rate of oxidation was impractically low unless the solution was maintained fairly alkaline (pH ~10) during the oxidation step.

Phosphate Content of Products. Preparation of products meeting phosphorus specifications was a major problem when the vanadium was recovered from the strip solution by hydrolytic precipitation with ammonia. Both organic phosphate from the extraction reagents and inorganic phosphate extracted from the liquor as a metal-phosphate complex contribute phosphate to the product, the latter usually being the more important contributor. Removal of the inorganic phosphate from the strip solution, prior to vanadium precipitation by adsorption on a column of activated zirconium oxide, appeared to be an economical method for eliminating phosphorus contamination.

Continuous Test Results for Uranium and Vanadium

Continuous testing was confined to demonstration of a process for uranium-vanadium recovery in which the two elements were extracted together and separated by selective stripping. Iron in the feed liquor was reduced to ferrous to minimize iron extraction. Vanadium was stripped with 0.75-1 M H_2SO_4 and uranium with 0.94 M Na_2CO_3 solution. Seven continuous runs were made with synthetic leach liquors and a leach liquor obtained from a Western mill. A drop in pH during extraction severely depressed the extraction efficiency, particularly in the lower extraction stages, making high vanadium recoveries difficult. Vanadium recoveries were 82-93% for the seven runs, recoveries for five of the runs falling in the range of 90-91%. Results suggested that vanadium recoveries could be increased by continuous adjustment of pH in the extraction system. Uranium recoveries were 99.0 to >99.8%. Recoveries >99.8% appeared to be typical of the process when using the recommended circuit arrangement. Vanadium products prepared by the ammonia precipitation method analyzed 93-99% V_2O_5 ; uranium products analyzed 76-88% U_3O_8 . Chemical reagent costs for recovery of vanadium by this flowsheet were estimated to be ~13¢ per pound of V_2O_5 recovered.

Only a single-cycle process was demonstrated, but two-cycle processes for uranium and vanadium recovery are possible and may be preferable for treating liquors with a relatively high uranium/vanadium ratio. Three potential process arrangements are described for recovering vanadium from the uranium-barren liquors.

2.0 INTRODUCTION

The intent of the studies reported here was to define process flowsheets for recovery of vanadium (and uranium) from acidic ore leach liquors and to determine, as far as is possible from small-scale tests, the reagent costs that might be realized in practice. Considerable information on uranium recovery by dialkylphosphoric acid extraction (Dapex process) has been reported previously.¹⁻³ Over a period of years, concurrently to development of the uranium recovery process, adaptation of this system to vanadium recovery has also been investigated^{1,3-6} on a relatively low priority basis. This report summarizes data obtained during the course of this work, including data previously reported.

Two general process possibilities were considered: (1) simultaneous extraction of uranium and vanadium from the leach liquor, with separation of the two elements by selective stripping, and (2) extraction of vanadium from the liquor after uranium has been removed in a prior extraction cycle. The studies were primarily directed toward treatment of leach liquors of the type obtained by the "acid cure"⁷ or the direct hot acid leaching treatment,⁸ although extractions from liquors similar to those derived from the salt roast--acid leach process⁹ were also briefly examined. Experimental work included both batch and continuous extraction tests. The latter have been restricted thus far to the two-product process, but, owing to similarity in chemistry, many of the data can also be used in considerations of the process for recovery of vanadium alone.

Since the outset of the studies at ORNL, extensive independent development work on vanadium recovery using D2EHPA has been conducted by the Kerr-McGee Oil Industries, Union Carbide Nuclear Company, and the Climax Uranium Company.¹⁰ A large-scale installation¹¹ has been operated by Kerr-McGee at their Shiprock mill and a full-scale installation was recently put in operation at the Rifle mill of Union Carbide Nuclear.

Discussions of several topics of general importance to the use of dialkylphosphoric acids as extraction agents are not included or are treated only briefly in this report, e.g., reagent availability, reagent stability, losses of reagents to aqueous solutions, synergistic reagent combinations, diluent

additives for prevention of third-phase formation during alkaline stripping, and extraction selectivities with regard to other metals. These topics have been considered previously in reports covering use of the Dapex process for uranium recovery, particularly ORNL-1903 and ORNL-2172.

3.0 EXPERIMENTAL MATERIALS AND TECHNIQUES

Except for experiments shown in the appendix, all tests were made with di(2-ethylhexyl)phosphoric acid (D2EHPA) as the extractant and kerosene was used exclusively as a diluent. As in previous work with uranium, this particular dialkylphosphoric acid was chosen since it is commercially available and is generally above the average for reagents of this class with regard to performance desired.

Tributylphosphate (TBP) or a long-chain alcohol was ordinarily added as a diluent modifier since these materials will prevent third-phase formation when the solvent is stripped with sodium carbonate.¹⁻³ The presence of TBP also furnishes a synergistic reagent combination to give much higher uranium extraction power than is possible with D2EHPA alone. This factor is of importance in the process described for simultaneous recovery of uranium and vanadium.

The D2EHPA reagent used was from a 50-lb shipment (batch I) from Union Carbide Chemicals Company, South Charleston, West Virginia. The reagent contained small amounts of impurities, which were removed by scrubbing several times with either 6 M HCl or Na₂CO₃ solution. The hydrochloric acid was used on solvents containing D2EHPA alone, and the sodium carbonate solutions on solvents that also contained alcohol or TBP.

The aqueous solutions studied in the extraction tests were synthetic sulfate leach liquors, actual leach liquors obtained from operating mills, and "pure" solutions of individual metals. Compositions of the solutions used in each set of experiments are given with the experimental data.

Batch extraction tests were made by contacting the organic and aqueous phases in separatory funnels, agitation being supplied by a Burrell wrist-action shaker at a maximum setting of 10. Continuous countercurrent extraction tests were made in bench-scale mixer-settlers of the type described in ORNL-2172, Appendix A.

4.0 EXTRACTION OF VANADIUM FROM SULFATE SOLUTIONS

Extraction of vanadium(IV) with 0.2 M D2EHPA from 0.5 M sulfate solutions in the pH range 1.0-3.0 was much stronger than that of vanadium(V) (Table 4.1). The coefficients for vanadium(IV), although low at pH 1.0, were useably high at pH 1.5-3. Subsequent studies were therefore confined to extraction of tetravalent vanadium.

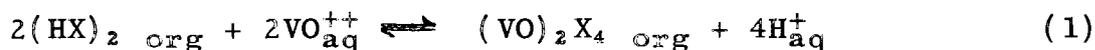
Table 4.1. Extraction of Vanadium(IV) and Vanadium(V) from Sulfate Solutions

Aqueous: 3.6 g V₂O₅/liter, 0.5 M sulfate
 Organic: 0.2 M D2EHPA in kerosene
 Phase ratio, a/o: 2/1
 Contact time: 2 min

Initial pH	Extraction Coefficient (E _a)	
	V(V)	V(IV)
1.0	0.2	1.1
1.5	-	4.3 ^a
2.0	0.7	7.5 ^a
3.0	0.2	16 ^a

^aCoefficients appreciably affected by vanadium loading of the organic phase.

Assuming that D2EHPA exists in hydrocarbon solutions as a dimer, as appears to be the case,¹² the extraction reaction can be expressed as



where X⁻ represents the di(2-ethylhexyl)phosphate anion. On the basis of eq. 1, the extraction coefficient,

$$E_a^o = \frac{(\text{V})_{\text{org}}}{(\text{V})_{\text{aq}}} = \frac{K(\text{VO}^{++})_{\text{aq}}[(\text{HX})_2]^2}{(\text{H}^+)^4} \quad (2)$$

would be expected to vary directly with the aqueous vanadium concentration and the square of the free reagent concentration, and inversely with the fourth power of the hydrogen ion concentration as long as other conditions remain the same. It would be decreased by aqueous complexing agents that decrease the effective concentration of the vanadyl cation.

4.1 Rate of Extraction

Of the metal ions previously studied (ref. 1, pp. 19, 22, 31), extraction of uranium is reasonably rapid, while extraction of aluminum and iron is slow. In batch tests, where the phases were contacted by vigorous shaking in a separatory funnel, the extraction of vanadium(IV) at ambient temperatures was also rapid (Table 4.2). In these tests, vanadium was extracted with 0.3 M D2EHPA in kerosene or kerosene-TBP diluent from vanadyl sulfate—sodium sulfate solutions at final pH's of 1.3-1.6. Equilibration was more than 95% complete in 1 min and complete in less than 5 min. The presence of TBP in the diluent appeared to decrease the extraction rate, although not seriously, and depressed the extraction coefficient somewhat.

Table 4.2 Vanadium(IV) Extraction Rate

Head aqueous: 0.35 M sulfate

A: 5.2 g V₂O₅ per liter, pH 1.5

B: 5.2 g V₂O₅ per liter, pH 2.0

C: 4.8 g V₂O₅ per liter, pH 2.0

Organic: 0.3 M D2EHPA in indicated diluent

Phase ratio, a/o: 1/1

Procedure: phases contacted by vigorous shaking in a separatory funnel for the indicated time and allowed to separate for ~1 min

Diluent	Head Aqueous	Temp., °C	Final pH	Contact Time, min	g V ₂ O ₅ /liter		Vanadium Extr. Coeff. (Eq)
					Aqueous	Organic	
Kerosene	A	28	1.3	1	1.09	4.1	3.8
				5	1.05	4.2	4.0
				10	1.04	4.3	4.1
				20	1.04	4.2	4.0
				40	1.04	4.2	4.0
	B	26	1.5	1	0.59	4.5	7.6
				5	0.55	4.7	8.5
				10	0.57	4.7	8.2
				20	0.55	4.7	8.6
				40	0.48	4.7	9.8
Kerosene + 0.2 M TBP	C	26	1.6	0.5	1.3	3.4	2.6
				1	0.89	3.7	4.2
				5	0.77	3.9	5.1
				10	0.77	3.9	5.1
				20	0.77	3.9	5.1
				40	0.77	3.9	5.1

Interpretation of data from batch-mixer (6 and 12 in. dia) studies⁵ of the vanadium(IV) extraction rate in terms of continuous flow shows that, with a power input of 80 hp/1000 gal and an o/a ratio of 1/1, the residence time of the dispersion in the mixer should be 3.5 min for 90% and 1.6 min for 80% stage efficiency. With 30 hp/1000 gal, the residence requirements for these efficiencies were 5 and 2 min, respectively. All the tests were made with 0.25 M D2EHPA in kerosene + 0.2 M TBP at ambient temperatures. Faster vanadium transfer would be expected at higher temperatures, e.g., 40°C, but this has not been confirmed experimentally.

4.2 Effect of pH

The vanadium extraction coefficient increased exponentially with increasing pH from 1.0 to 2.2 (Fig. 4.1) in tests in which vanadium was extracted by 0.3 M D2EHPA in kerosene-TBP diluent from 0.47 M sulfate solutions. At pH 1.8 the coefficient was ~8.5 for extraction from solution A (4.6 g V₂O₅/liter) and ~6 for extraction from solution B (0.9 g V₂O₅/liter). The increase (rather than the usual decrease) of extraction coefficient with increase in vanadium loading (curve A vs curve B) is confirmatory evidence that extraction is dependent on the vanadium concentration and is consistent, at least qualitatively, with eq. 2.

4.3 Effect of Sulfate Concentration

Compared to the effect of pH, the effect of varying the sulfate concentration in the range 0.2-1.1 M was minor (Fig. 4.2). In tests with a vanadium solution containing ~1 g of V₂O₅ per liter, the extraction coefficient decreased from ~3 at 0.2 M to 2.3 at 0.6 M and to 2.0 at 1.1 M sulfate. With a more concentrated vanadium solution, the coefficient actually increased slightly in the 0.6-1.1 M sulfate range, but this increase was probably due to small variations in pH. Comparison of the curves for the two head solutions again shows the increase in extraction coefficient with increase in vanadium concentration noted in Sec. 4.2.

4.4 Extraction Isotherms

Isotherms (Fig. 4.3) for extraction of vanadium with 0.3 M D2EHPA from three different vanadyl sulfate solutions varying in pH from 1.0 to 3.0 again showed the strong dependence of extraction on the acidity of the aqueous phase. With the solution of highest pH, the organic loading appeared to be approaching a maximum vanadium concentration of about 14 g of V₂O₅ per liter, equivalent to approximately 0.5 mole of vanadium per mole of D2EHPA. An isotherm (Fig. 4.3) was also obtained for extraction of vanadium from one of the solutions (pH 1.5) with 0.2 M D2EHPA in kerosene. In the

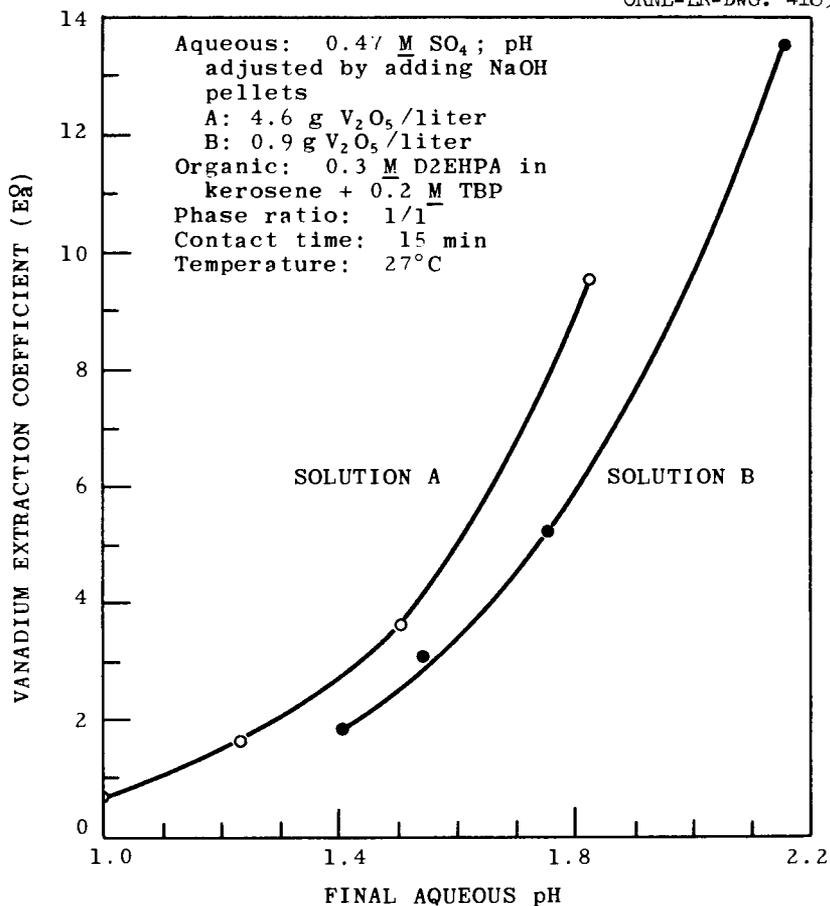


Fig. 4.1. Effect of pH on vanadium(IV) extraction.

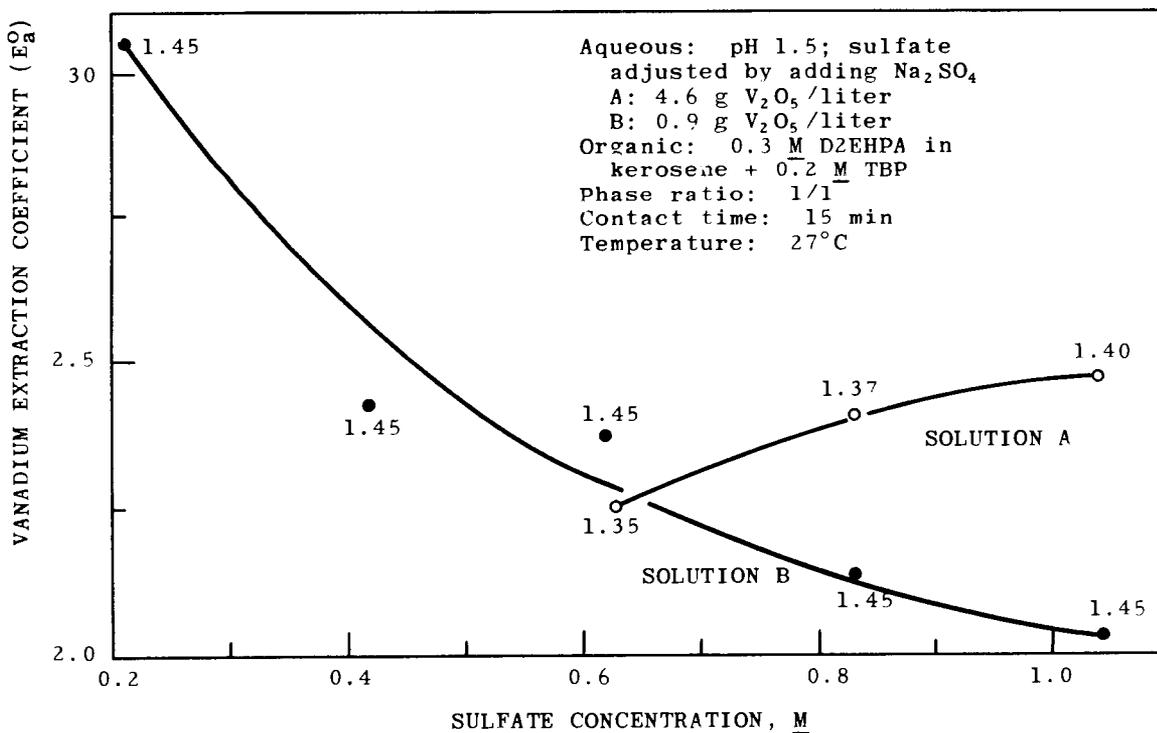


Fig. 4.2. Effect of sulfate concentration on vanadium(IV) extraction. Final aqueous pH is shown for each point.

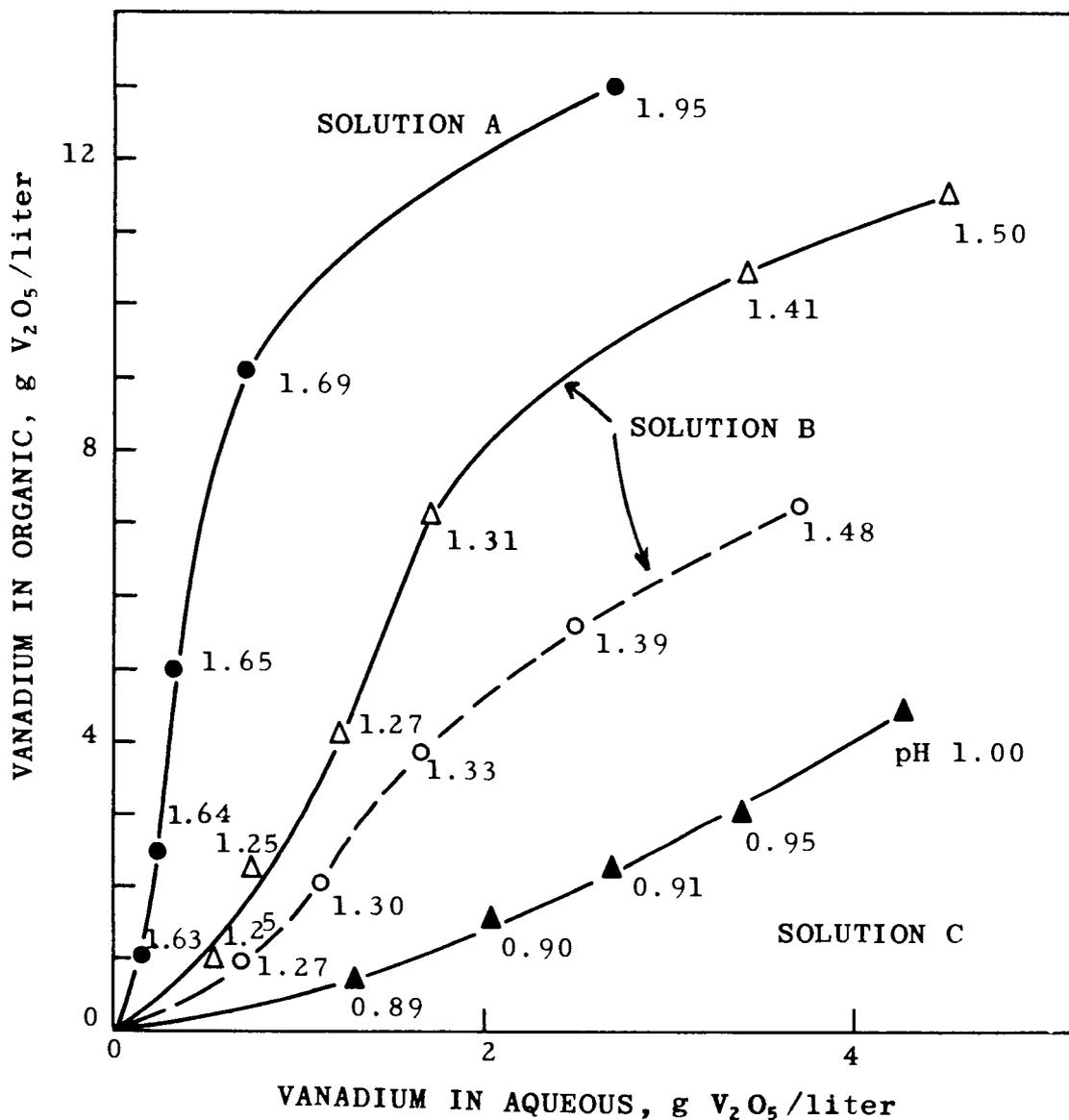


Fig. 4.3. Isotherms for extraction of vanadium(IV) with — 0.3 M D2EHPA at 28-30°C and ---- 0.2 M D2EHPA in kerosene at 27°C. Head aqueous: 5.2 g V₂O₅/liter, A-0.37 M sulfate, pH 3.0; B-0.37 M sulfate, pH 1.5; C-0.48 M sulfate, pH 1.0. Isotherms were obtained by varying the extraction phase ratio, 10 min contact. Final pH is shown for each point.

regions of relatively low loading, other conditions being the same, the vanadium extraction coefficient was decreased by a factor of ~2 by decreasing the reagent concentration from 0.3 to 0.2 M.

It should be noted that the final pH of the aqueous phase is not the same for each point on a given isotherm because of differences in the extent of the vanadyl—hydrogen ion exchange (eq. 1). Because of the fourth-power dependence of extraction on the aqueous acidity (eq. 2), the decrease in pH that occurs during extraction severely depresses the slope of the isotherm, particularly in the dilute vanadium region where the resultant pH is lowest. It also tends to give the isotherms a concave curvature, rather than the conventional straight line or slightly convex curvature, in the dilute region. The dependence of the vanadium coefficient on the aqueous vanadium concentration (eq. 2), however, appears to be a much stronger factor contributing to this concave curvature.

It is obvious that the pH drop during extraction is of considerable process importance. Thus, although the feed liquor pH can be adjusted to a high value, e.g., pH 2, where extractions are favorable, this pH is not maintained in the extraction system, but in the lower stages falls to a level at which extraction is relatively inefficient.* Because of this pH effect and because the vanadium coefficient decreases as the system becomes more dilute, the extraction efficiency in the lower stages is sufficiently poor that high recoveries, >95%, are relatively difficult. This problem can be partially overcome (Sec. 9.1) by continuously feeding a base, e.g., ammonium hydroxide, to one or more extraction stages in order to maintain a higher overall pH in the system.

4.5 Effect of Diluent Modifiers

In previous development work on the Dapex process¹⁻³ for uranium recovery, it was shown that the addition of certain long-chain alcohols and neutral organophosphorus compounds to the D2EHPA-kerosene extractant was effective in rendering the sodium salt of D2EHPA miscible with kerosene during a sodium carbonate stripping cycle. The addition of alcohol decreased the uranium extraction coefficient, whereas the addition of the neutral organophosphorus compounds provided a synergistic reagent combination with considerably enhanced extraction power.

Since the processes proposed for vanadium recovery (Sec. 9.0 and 10.0) entail a carbonate stripping step, and,

*The effect of pH change is much less important with dilute vanadium liquors, e.g., 1 g of V_2O_5 per liter, since the magnitude of the pH change is much smaller.

consequently, use of a diluent modifier, two representative reagents of these types, capryl alcohol and tributyl phosphate (TBP), were tested to determine their effect on vanadium extraction with D2EHPA. As with uranium, vanadium extractions were appreciably depressed by the addition of alcohol to the solvent (Table 4.3). Unlike the uranium case, however, the vanadium extraction coefficient was also decreased by addition of TBP, although the effect was relatively small, and more pronounced at low than at higher vanadium loadings. The data were determined in the pH range 0.9-1.7 for 0.3 M D2EHPA in kerosene, in kerosene + 0.25 M capryl alcohol, and in kerosene + 0.16 M TBP.

Table 4.3 Effect of Diluent Modifiers on Vanadium(IV) Extraction

Head aqueous: 5.2 g of V₂O₅ per liter
 A: 0.47 M sulfate, pH 1.0
 B: 0.37 M sulfate, pH 1.5
 C: 0.37 M sulfate, pH 3.5
 Organic: 0.3 M D2EHPA in kerosene with indicated diluent modifier
 Phase ratio, a/o: 1/1
 Contact time: 10 min
 Temperature: 26°C

Modifier	Head Aqueous	Final pH	g V ₂ O ₅ /liter		Vanadium Extraction Coeff. (Eq)
			Organic	Aqueous	
None	A	0.90	2.3	2.8	0.82
None		0.90	2.3	2.9	0.79
0.15 M TBP		0.90	2.1	3.3	0.64
0.25 M capryl alcohol		0.93	1.2	4.0	0.30
None	B	1.30	4.0	1.2	3.3
None		1.30	3.9	1.0	3.9
0.15 M TBP		1.30	3.9	1.1	3.6
0.25 M capryl alcohol		1.33	3.3	1.9	1.7
None	C	1.70	4.9	0.38	13
None		1.70	4.9	0.38	13
0.15 M TBP		1.70	4.9	-	~13 ^a
0.25 M capryl alcohol		1.70	4.3	0.66	6.5

^aEstimated from analysis of organic phase.

To better define the effect of TBP on vanadium extraction, a second series of tests was made in which the TBP content of the organic phase was varied in the range 0-0.19 M (Table 4.4),

0.19 M being the approximate amount ordinarily used with 0.3 M D2EHPA. At a low vanadium level (~0.6 g of V₂O₅ per liter in the organic), the extraction coefficient decreased about 25% as the TBP concentration was increased from 0 to 0.19 M. With an organic vanadium loading of about 3.3 g of V₂O₅ per liter, the depressing effect of TBP was less pronounced, the coefficient with 0.19 M TBP being only about 10% lower than when no modifier was added to the kerosene.

Table 4.4 Effect of TBP Diluent Modifier on Vanadium(IV) Extraction

Head aqueous: pH 1.5

A: 0.9 g of V₂O₅ per liter, 0.73 M sulfate

B: 4.6 g of V₂O₅ per liter, 0.67 M sulfate

Organic: 0.3 M D2EHPA in kerosene with indicated concentration of TBP

Phase ratio, a/o: 1/1

Contact time: 15 min

Temperature: 27°C

TBP Present, <u>M</u>	Head Aqueous	Final pH	g V ₂ O ₅ /liter		Vanadium Extraction Coeff. (Eq)
			Organic	Aqueous	
0.0	A	1.47	0.66	0.25	2.6
0.04		1.47	0.66	0.29	2.3
0.11		1.47	0.64	0.29	2.2
0.19		1.47	0.61	0.32	1.9
0.0	B	1.34	3.3	1.38	2.4
0.04		1.34	3.3	1.41	2.3
0.11		1.34	3.3	1.43	2.3
0.19		1.34	3.3	1.54	2.1

4.6 Effect of Temperature on Extraction of Vanadium and Other Metals

Vanadium liquors obtained in direct treatment of an ore with sulfuric acid or in the "acid cure" process may be expected to be hot since elevated temperatures are used to achieve efficient dissolution of the vanadium minerals. If such a liquor is fed to the solvent extraction system while hot, the distribution of metal values and contaminants between the aqueous and organic phases might be different than if the liquor had been first cooled to ambient temperature. In studies on extraction of vanadium(IV) with 0.3 M D2EHPA in kerosene, the extraction coefficient increased 60-70% as the temperature was increased from 15 to 50°C (Fig. 4.4).

UNCLASSIFIED
ORNL-LR-DWG. 41658

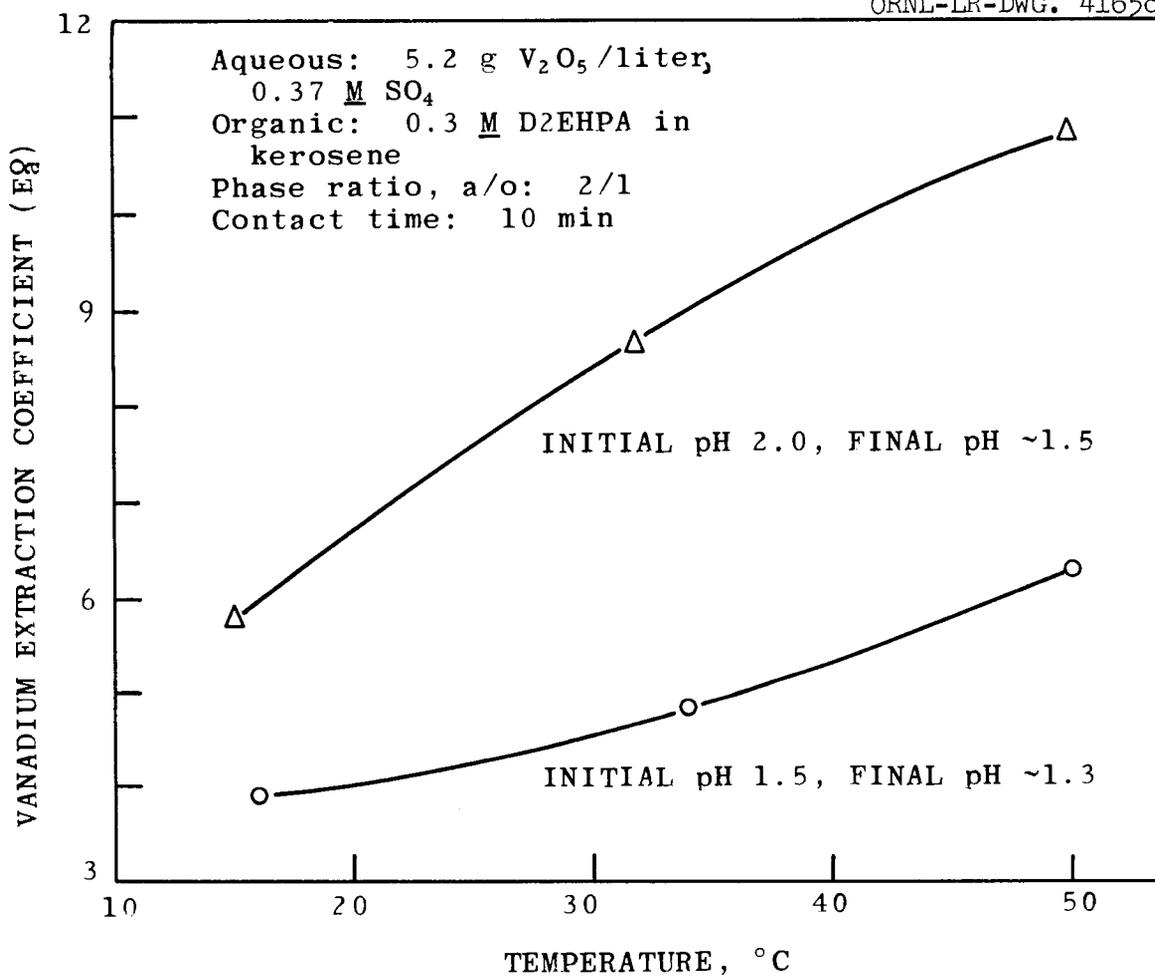


Fig. 4.4. Effect of temperature on vanadium(IV) extraction.

The effect of temperature in the range 20 to 50°C on extraction of vanadium(IV), uranium, iron(III), aluminum, and molybdenum was next investigated with 0.3 M D2EHPA in kerosene + 0.16 M TBP (Table 4.5). The extractant was in the form of its sodium salt and the extractions were therefore accompanied by an increase in pH. The effect of temperature on vanadium extraction was comparable to that observed above for unmodified solvent. Results were essentially the same after 60 min contact as after 10 min.

The extraction coefficient for uranium was adversely affected by an increase in temperature. However, the coefficients at this high reagent concentration and high pH were all of such great magnitude that the variation was of little practical importance. As with vanadium, the extraction after 60 min contact was essentially the same as after 10 min.

Data on the extraction of iron(III) and aluminum as a function of temperature do not allow positive conclusions since apparently the tests did not reach equilibrium. The extraction rates of these elements, particularly of aluminum, are exceptionally low^{1,2} and increase with increasing temperature. These data, although not showing the effect of temperature on metal distributions at equilibrium, suggest that, in process application where the time of contact would ordinarily not be sufficient for equilibrium to be reached, an increase in temperature would result in increased extraction of iron(III) and aluminum. Continuous countercurrent extraction runs (room temperature vs 45°C; see Sec. 9.1) verified this.

5.0 EXTRACTION OF VANADIUM FROM LEACH LIQUORS

5.1 Extractions from Sulfate-Chloride Liquors

Isotherms for extraction of vanadium with 0.4 M D2EHPA in kerosene + 0.3 M 2-ethylhexanol from two synthetic sulfate-chloride liquors, which, except for the absence of uranium were similar in composition to those obtained in the salt-roast acid-leach process⁹ for carnotite ores, showed effective extraction of vanadium when the initial pH was adjusted to 1.8 (Fig. 5.1). As expected, extractions were much weaker at initial pH 1.0 or 1.2. The first liquor contained 0.17 M and the second 0.5 M chloride. Most of the iron in the liquors was reduced to the ferrous state to minimize its extraction.

5.2 Simultaneous Vanadium-Uranium Extractions from Sulfate Liquors

Simultaneous extraction of vanadium and uranium from a synthetic leach liquor with 0.31 M D2EHPA in kerosene was effective at low metal loadings (Table 5.1). The organic was

Table 4.5 Effect of Temperature on Extraction of Several Metals with D2EHPA

Head aqueous: 0.5 M sulfate; pH 0.9; metal ions at concentrations shown

Organic: 0.3 M D2EHPA (Na⁺ salt) in kerosene + 0.16 M TBP

Phase ratio, a/o: 1/1

Metal	Contact Time, min	Temp., °C	Final pH	Metal Ion Conc., g/liter			Extraction Coeff. (E_a^0)	
				Head Aqueous	Final Aqueous	Organic		
V(IV) (as V ₂ O ₅)	10	20	1.45	5.3	1.50	4.2	2.8	
		35	1.45	5.3	1.22	4.5	3.7	
		50	1.45	5.3	1.04	4.7	4.5	
	60	20	1.45	5.3	5.3	1.47	4.2	2.9
		35	1.45	5.3	5.3	1.25	4.5	3.6
		50	1.45	5.3	5.3	0.95	4.8	5.1
U(VI)	10	20	1.66	1.02	4x10 ⁻⁵	1.04	26,000	
		35	1.66	1.02	7x10 ⁻⁵	1.04	15,000	
		50	1.66	1.02	12x10 ⁻⁵	1.04	8,000	
	60	20	1.67	1.02	1.02	5x10 ⁻⁵	0.99	20,000
		35	1.68	1.02	1.02	9x10 ⁻⁵	1.07	12,000
		50	1.69	1.02	1.02	13x10 ⁻⁵	1.05	8,000
Mo(VI)	10	20	1.60	0.27	0.0028	0.25	89	
		35	1.60	0.27	0.0032	0.27	84	
		50	1.60	0.27	0.0048	0.26	54	
	60	20	1.62	0.27	0.27	0.0027	0.26	96
		35	1.62	0.27	0.27	0.0028	0.27	96
		50	1.62	0.27	0.27	0.0045	0.25	56
Fe(III)	10	20	1.58	0.19	0.10	0.10	1.0	
		35	1.58	0.19	0.19	0.05	0.13	2.6
		50	1.58	0.19	0.19	0.01	0.17	17
	60	20	1.60	0.19	0.19	0.02	0.13	6.5
		35	1.60	0.19	0.19	0.0006	0.18	300
		50	1.60	0.19	0.19	0.0008	0.21	260
Al	10	20	1.70	5.4	4.6	0.61	0.13	
		35	1.67	5.4	5.4	4.4	0.74	0.17
		50	1.59	5.4	5.4	4.2	0.99	0.24
	60	20	1.67	5.4	5.4	4.0	0.74	0.19
		35	1.58	5.4	5.4	3.9	0.97	0.25
		50	1.46	5.4	5.4	3.7	1.57	0.42

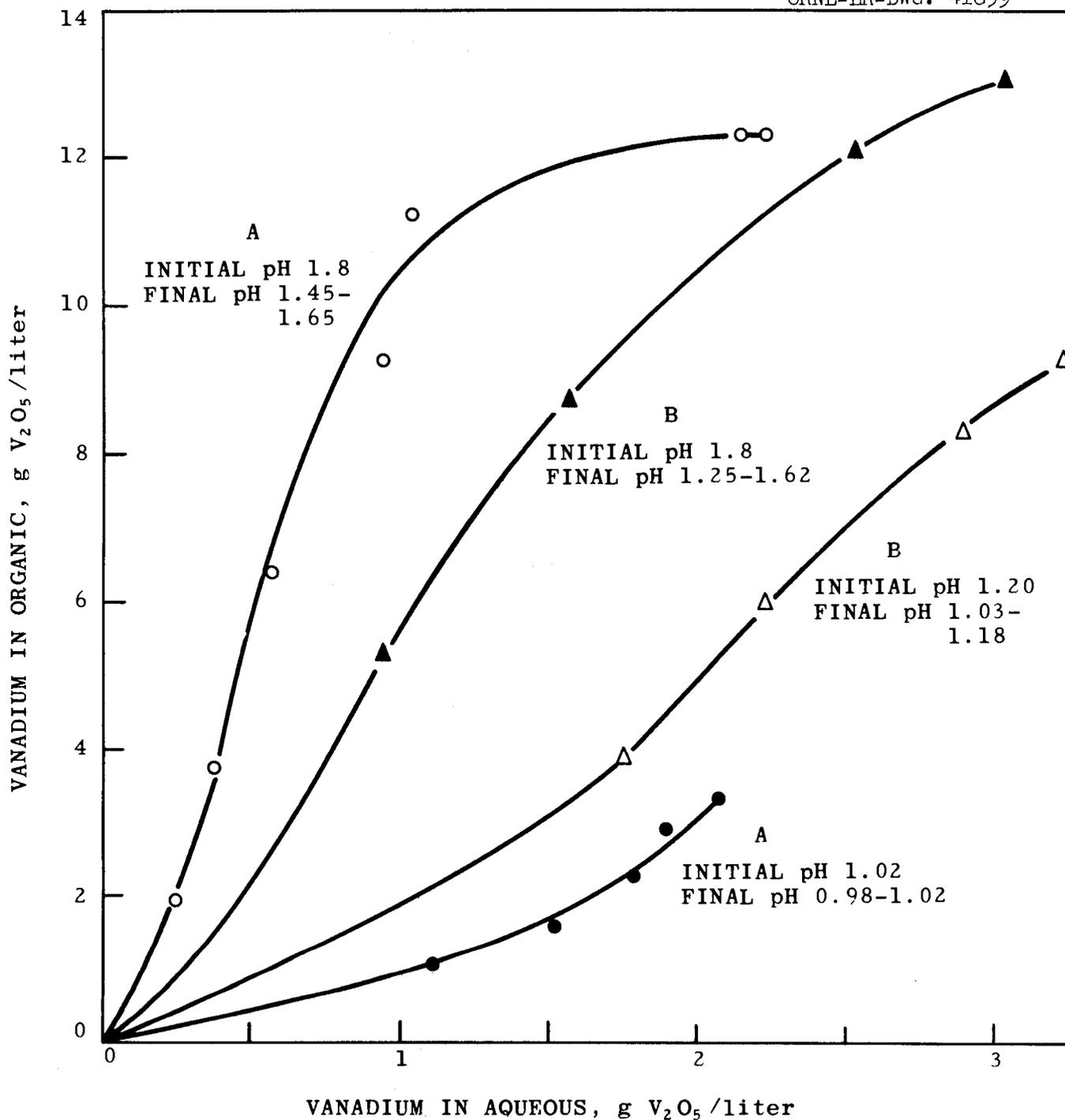


Fig. 5.1. Isotherms for Extraction of Vanadium from Sulfate-Chloride Liquors with 0.4 M D2EHPA in Kerosene + 0.3 M 2-ethylhexanol. Procedure: organic contacted with liquor at various phase ratios for 10 min at room temperature; synthetic leach liquors: A: 2.4 g of V₂O₅, 0.8 g of Fe(II), <0.1 g of Fe(III), and 0.38 g of Al per liter, 0.17 M Cl⁻, 0.2 M SO₄, indicated pH.

B: 3.9 g of V₂O₅, 0.94 g Fe(II), 0.03 g Fe(III), and 1.7 g of Al per liter, 0.5 M chloride, 0.1 M sulfate.

shaken with the liquor at various phase ratios for 5 min and the separated phases were analyzed. At higher loadings (high a/o phase ratios) the effect of competition of the various elements for the reagent became more evident. The amounts of uranium, iron, and molybdenum extracted increased with increase in phase ratio. In contrast, the concentrations of vanadium and aluminum in the solvent increased to a point and then dropped off as competition for the extractant became greater. These tests are not useful for showing the expected distribution of the various elements in treating a liquor of this composition since inordinately high phase ratios were used, but they do show the relative strength of extraction of contaminants in comparison to that of vanadium(IV) and uranium. In this respect, the large amounts of iron extracted (presumably, essentially all as ferric iron* since other tests^{1,5} have shown extractions of ferrous iron to be negligible), indicate the importance of thoroughly reducing the iron in the process liquor prior to the extraction step.

Table 5.1 Vanadium and Uranium Extraction from a Synthetic Leach Liquor

Head aqueous: 5.5 g of V₂O₅, 0.95 g of U, 4.8 g of Fe(II), 0.2 g of Fe(III), 5.0 g of Al, 0.16 g of Mo, and 53 g of sulfate per liter; pH 1.85
 Organic: 0.31 M D2EHPA in kerosene
 Contact time: 5 min

Phase Ratio, a/o	Final pH	Final Aqueous, g/liter		Final Organic, g/liter					Extraction Coeff., (E _a ^o)	
		V ₂ O ₅	U	V ₂ O ₅	U	Fe	Al	Mo	V	U
0.2	1.45	0.13	0.0005	1.1	-	0.32	0.06	0.04	8.5	-
0.5	1.49	0.37	0.0007	2.5	0.39	0.42	0.09	0.08	6.7	800
1	1.54	0.75	0.0018	4.5	0.75	0.74	0.13	0.15	6.0	400
2	1.60	2.0	0.0074	7.1	1.8	0.84	0.11	0.25	3.5	240
5	1.66	4.3	0.044	5.9	4.4	1.5	0.09	0.56	1.4	100
10	1.70	5.0	0.103	4.1	8.4	1.9	0.08	0.86	0.8	80

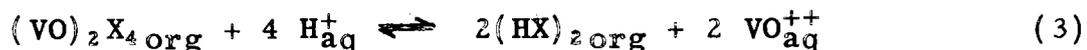
* In most of the tests, the amounts of iron extracted were larger than the amounts of Fe(III) supplied in the head aqueous solution. This can be accounted for by the fact that, in the presence of D2EHPA, Fe(II) can be oxidized by air.⁵ In a vanadium recovery process, the extraction mixers should be designed to minimize contact with air.

6.0 VANADIUM STRIPPING

Vanadium is stripped effectively from the extract with dilute solutions of mineral acids or bases.

6.1 Stripping with Sulfuric Acid

In acid stripping the reaction is the reverse of that occurring during the extraction operation (eq. 1):



Thus the stripping coefficient,

$$S_{\text{O}}^{\text{a}} = \frac{V_{\text{aq}}}{V_{\text{org}}} = K \frac{(\text{H}^+)^4}{[(\text{HX})_2]^2 (\text{VO}^{++})_{\text{aq}}} \quad (4)$$

would be expected to vary as the fourth power of the hydrogen ion concentration if other factors remained constant. In addition, again assuming constancy of the other factors, S_{O}^{a} should be inversely proportional to the aqueous vanadium concentration and to the square of the free reagent concentration. Since acid is consumed in stripping, the aqueous pH rises, the extent of the acidity change being dependent on the vanadium loading of the stripping solution.

a. Rate of Stripping of Vanadium(IV), Iron(III), and Aluminum

The rates of stripping with 1 M H_2SO_4 of vanadium(IV), iron(III), and aluminum from organic extracts consisting of 0.25 M D2EHPA in kerosene or kerosene + 0.2 M TBP diluent were studied at 25-30°C and 50°C in a small baffled mixer (stirring speed 600 rpm). Samples of the mixed phases were withdrawn at specific time intervals, allowed to separate over a period of approximately 1 min, and analyzed.

Stripping of Vanadium(IV). Vanadium stripping was relatively slow at 25°C (Fig. 6.1a). The stripping reached ~85% of its equilibrium value after 5 min and 95% after 10 min agitation. Vanadium transfer was much more rapid at 50°C, reaching ~85% of equilibrium after 1 min and >95% after 2.5 min. The equilibrium distribution, reached within 20 min, was essentially the same at both temperatures. With TBP in the diluent, slightly more vanadium was stripped at equilibrium but the extraction rate was essentially the same as in its absence. In all the tests the organic extract vanadium concentration was 6.2 g of V_2O_5 per liter and the o/a phase ratio was 10/1.

It should be noted that the rates indicated in Fig. 6.1a

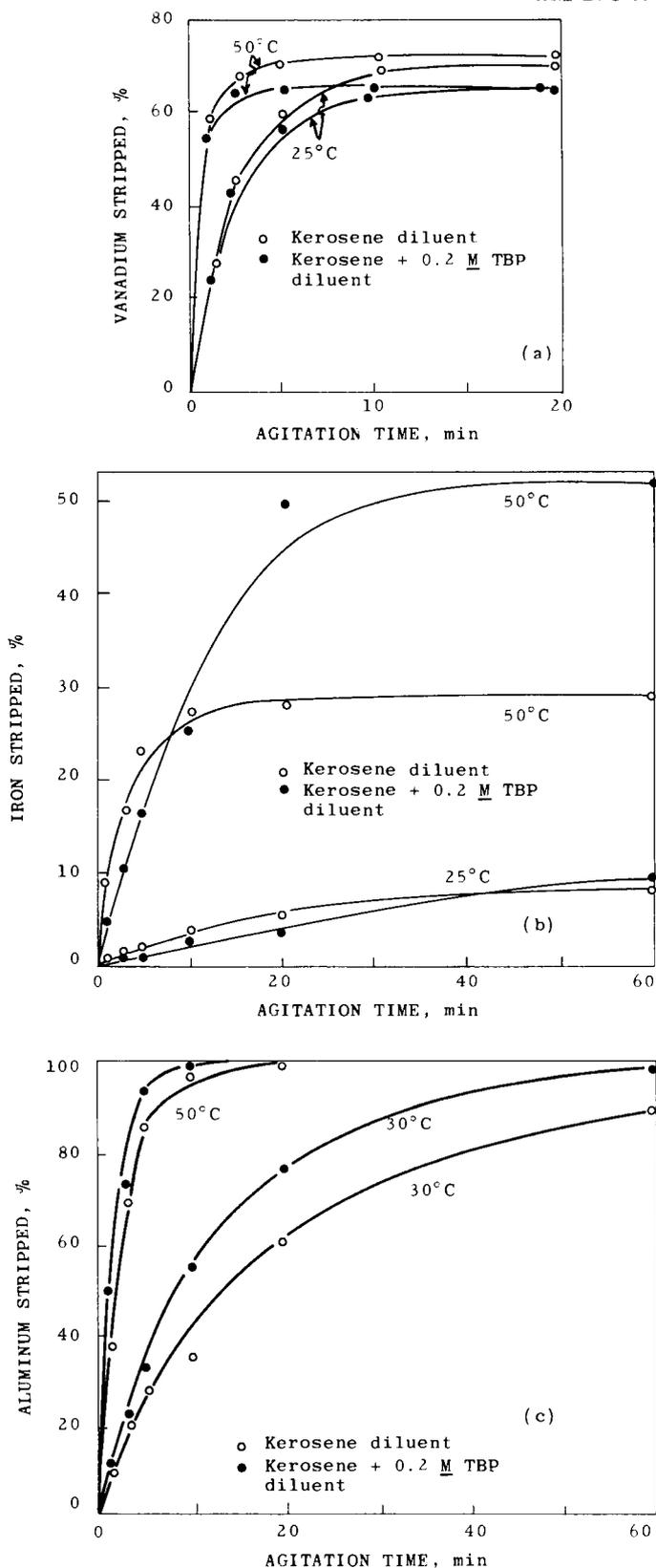


Fig. 6.1. Rate of stripping of (a) vanadium(IV), (b) iron(III), and (c) aluminum from 0.25 M D2EHPA with 1.0 M H₂SO₄. Organic continuous mixing in baffled beaker at ~600 rpm stirring speed. For 1 vol of acid stripping solution, 10 vol of vanadium extract (6.2 g V₂O₅ per liter), 1 vol of iron extract (~1.2 g Fe(III) per liter), or 1 vol of aluminum extract (~0.8 g Al per liter)

pertain only to the mixing conditions used. Much faster vanadium stripping at room temperature has been generally observed with more vigorous mixing and a phase ratio closer to unity. For example, in a test at a phase ratio of 1/1 and 900 rpm stirring speed, equilibrium was apparently reached after approximately 2.5 min of mixing:

Total Mixing Time, min	g V ₂ O ₅ /liter	
	Organic	Aqueous
1	0.47	5.8
2.5	0.086	6.5
5	0.086	6.4
10	0.086	6.2
20	0.084	6.4

Stripping was with 1 M H₂SO₄ from a solvent consisting of 0.25 M D2EHPA in kerosene loaded to 6.4 g of V₂O₅ per liter. Mixing was stopped after each time increment and then resumed after separation of the phases and sampling.

Stripping of Iron(III) and Aluminum. Both aluminum and iron(III), but particularly the latter, are stripped more slowly than vanadium. Iron stripping was extremely slow at 25°C, only about 5% of the iron being stripped after 20 min and 10% after 60 min (Fig. 6.1b). These tests apparently did not reach equilibrium. Increasing the temperature to 50°C* greatly increased the stripping rate, with approximately 25% of the iron being stripped in 10 min. Beyond 10 min the extent of stripping from the solvents with and without TBP diverged widely, with ~50% of the iron being removed at 60 min in the presence of TBP and ~30% in its absence. The curves suggest that, at 50°C, stripping was near equilibrium in 20-30 min.

Aluminum was stripped more rapidly and more completely than iron (Fig. 6.1c). However, at 30°C the rate was still relatively low, with ~25% stripped in 10 min, 60-75% in 20 min, and 85-95% in 60 min. At 50°C, >95% was stripped in less than 10 min. At 30°C the stripping rate was noticeably faster when TBP was in the solvent.

The above results are all from tests made at a phase ratio of 1/1 with the organic as the continuous phase. In tests with the aqueous phase continuous, results were essentially the same.

*Workers at Kerr-McGee Oil Industries, Inc. previously reported (private communication) that stripping at elevated temperatures removes the impurity metals more effectively.

In process practice the advantage or disadvantage of the higher iron and aluminum stripping rates at higher temperatures would depend primarily on the choice of method for subsequent recovery of vanadium from the pregnant strip solution (Sec. 7.1). If the vanadium is recovered as "red cake" by addition of sodium chlorate to the solution and heating, relatively high concentrations of metal contaminants in the strip solution can be tolerated since separation from vanadium is good in the precipitation. In this case hot stripping would appear advantageous both for improved vanadium stripping and for decreased need for solvent regeneration. In contrast, when vanadium is recovered by hydrolytic precipitation with ammonia, most of the iron and aluminum also precipitate, so that increased product contamination would probably outweigh the advantages of hot stripping when ammonia precipitation is used.

b. Effect of Acid Concentration

As suggested by eq. 4, the vanadium stripping efficiency is strongly dependent on the acid concentration, increasing with increase in acidity (Fig. 6.2). In tests in which 0.3 M D2EHPA in kerosene loaded to a vanadium concentration of 13 g of V_2O_5 per liter was stripped with sulfuric acid solutions, the stripping coefficient increased from ~1 to 52 as the H_2SO_4 was increased from 0.2 to 1 M at an o/a phase ratio of 1/1. At an o/a phase ratio of 3/1, the coefficients were lower for a given strip solution since the vanadium loading of the solution was higher and its final hydrogen ion concentration correspondingly lower.

Further stripping data showing the effect on vanadium stripping of sulfuric acid concentration variation in the range 0.75-1.5 M are presented in Fig. 6.3 in the form of stripping isotherms. In this case the organic phase contained 0.2 M TBP*. Assuming a loading of 6.2 g of V_2O_5 per liter in the organic phase in extraction, it is apparent from the isotherms that the maximum vanadium loading possible (i.e., with an infinite number of stages) with the 0.75, 1.0, and 1.5 M H_2SO_4 stripping solutions is approximately 39, 57, and 88 g of V_2O_5 per liter, respectively, corresponding to an acid usage of 1.88, 1.72, and 1.68 lb of H_2SO_4 per pound of V_2O_5 , respectively.

The gains in stripping efficiency with increase in acid concentration are amplified somewhat when the number of stripping stages is reduced to a practical level (Fig. 6.4). In Fig. 6.4 the acid requirements for a given stripping

*The presence of TBP slightly depresses the vanadium extraction coefficient (Sec. 4.5) and thus, conversely, should improve the stripping coefficient.

UNCLASSIFIED
ORNL-LR-DWG. 41662

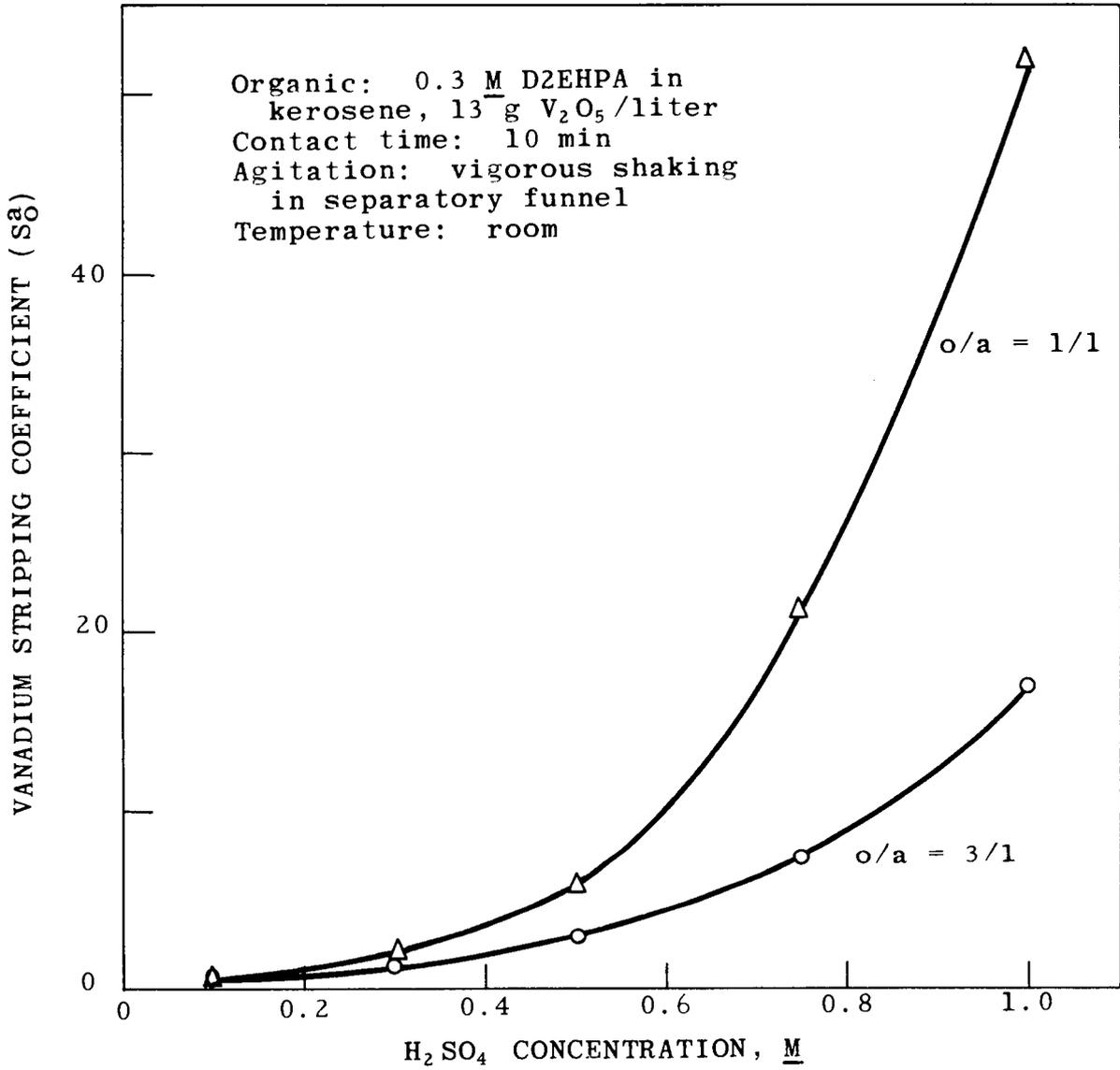
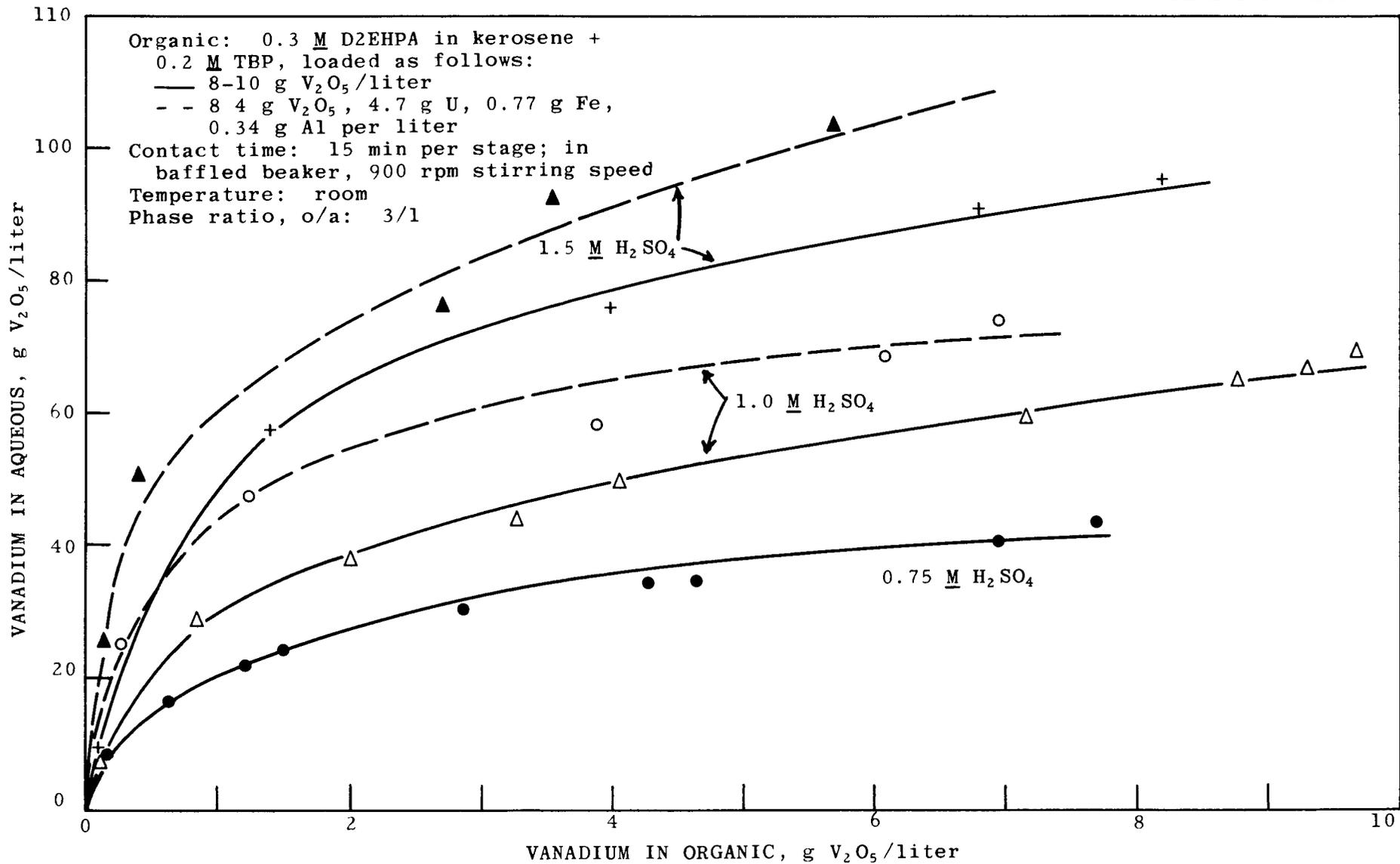


Fig. 6.2. Effect of acid concentration on vanadium(IV) stripping.



-26-

Fig. 6.3. Vanadium(IV) stripping isotherms; from batch simulated countercurrent contacts.

performance (reduction of the vanadium content of the organic phase from 6.2 to 0.09 g of V_2O_5 per liter) are plotted as a function of the number of ideal stripping stages (determined from McCabe-Thiel diagrams) required. The indicated acid requirements for 0.75, 1.0, and 1.5 M H_2SO_4 stripping solutions, when using two ideal stripping stages, are 3.9, 3.1, and 2.7 lb of H_2SO_4 per pound of V_2O_5 ; with three ideal stages, the requirements are 2.3, 2.1, and 2.0 lb of H_2SO_4 per pound of V_2O_5 , respectively.

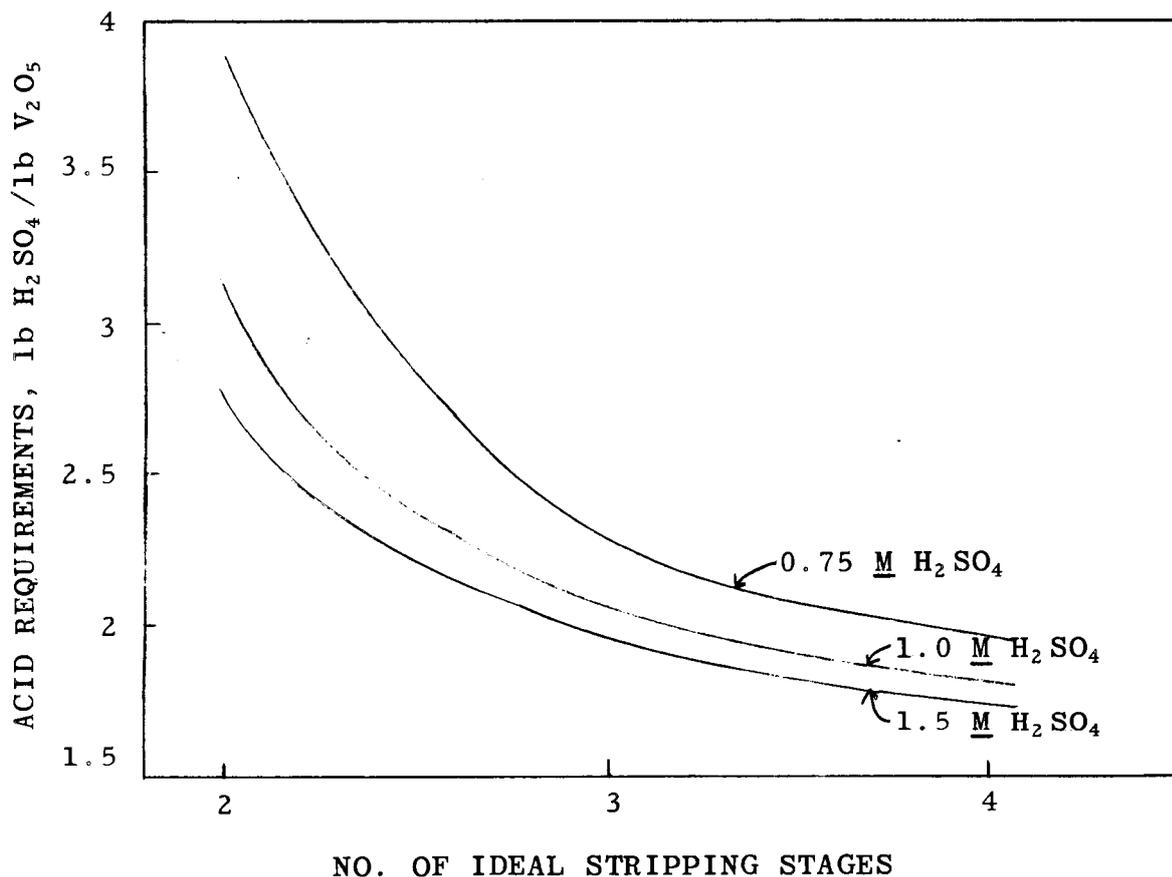


Fig. 6.4. Effect of Acid Concentration on Acid Requirements for Stripping Vanadium. Assumptions: organic extract, 0.3 M D2EHPA in kerosene-TBP diluent, loaded to 6.2 g V_2O_5 per liter and stripped to 0.09 g V_2O_5 per liter.

It should be emphasized that all the stripping tests previously described were performed on organic solutions that had been loaded with vanadium(IV) from "pure" solutions so that vanadium was the only extracted element. In process practice, the organic extract would also contain uranium (in a single-cycle process) and contaminants, e.g., iron, aluminum, and titanium. Hence, since some of the reagent would be complexed with these metals, the free reagent would be lower than in the tests described and the vanadium stripping efficiency correspondingly higher* (eq. 4). This is shown by the dotted curves in Fig. 6.3, which are isotherms for stripping an extract (0.3 M D2EHPA) containing 8.4 g of V_2O_5 , 4.7 g of U, 0.77 g of Fe, and 0.34 g of Al per liter with 1.0 and 1.5 M H_2SO_4 . It is apparent that the maximum possible loading (assuming the extract is loaded to 6.2 g of V_2O_5 per liter) is now approximately 71 and 107 g of V_2O_5 per liter, respectively, or about 25% higher than when uranium and contaminants were absent from the organic phase. Complete data for this experiment, showing the distribution of vanadium, uranium, iron, and aluminum between the aqueous and organic phases, are shown in Table 6.1. Although the analyses are not entirely consistent, it can be seen that the amounts of uranium, iron, and aluminum stripped with the vanadium were relatively small and did not vary greatly as the stripping acid concentration was changed from 1.0 to 1.5 M. With respect to iron and aluminum stripping, the effect of acid concentration presumably was strongly masked by the slow stripping rates of these elements at room temperature (Sec. 6.1a), i.e., the results do not represent equilibrium distributions.

6.2 Stripping with Solutions of a Base

On contact of the organic extract with a solution of a base,** e.g., Na_2CO_3 or NH_4OH , the vanadium is precipitated as black, or dark brown, hydrated vanadyl oxide; a small amount of vanadium may go into solution since it can be oxidized by air in basic solution to the soluble pentavalent state. The vanadium precipitate that forms is colloidal and usually cannot be filtered from the stripping solution. When mixing

* Similarly, an extractant concentration lower than 0.3 M would improve the stripping efficiency but at the expense of decreased efficiency in the extraction cycle. Choice of the optimum extractant concentration must necessarily be made after careful balancing of the advantages and disadvantages experienced in both the extraction and stripping systems for each concentration.

** Use of a diluent modifier, e.g., TBP, is recommended to avoid third-phase formation during alkaline stripping.

Table 6.1 Stripping of Vanadium with Sulfuric Acid

Organic: 0.3 M D2EHPA in kerosene + 0.2 M TBP loaded to 8.2 g of V₂O₅, 4.7 g of U, 0.77 g of Fe, and 0.34 g of Al per liter

Procedure: stripping solution cascaded against fresh volumes of extract with an o/a phase ratio of 3/1 per stage; 15 min contact per stage (mixed in a baffled beaker)

Temp.: room

H ₂ SO ₄ Conc., M	Con- tact No.	Analyses, g/liter								Aq pH	Vanadium Stripping Coeff. (S ₀ ^a)
		Aqueous				Organic					
		V ₂ O ₅	U	Fe	Al	V ₂ O ₅	U	Fe	Al		
1.0	1	24	0.06	-	0.33	0.25	4.7	0.73	0.25	--	96
	2	47	0.05	-	0.58	1.2	4.4	0.71	0.24	--	39
	3	58	0.07	-	-	3.9	4.7	0.77	0.26	--	15
	4	69	0.13	-	1.13	6.1	4.7	0.77	0.25	--	11
	5	75	0.26	-	1.51	7.0	4.8	0.60	0.23	0.8	11
	6 ^a	0.77	0.080	0.52	0.13	<0.09	4.7	0.70	0.20	--	--
1.5	1	26	0.09	0.17	-	0.12	4.5	0.80	0.22	--	220
	2	51	0.10	0.32	-	0.39	4.7	0.69	0.26	--	130
	3	77	0.09	0.47	-	2.7	4.5	0.77	0.28	--	29
	4	93	0.12	0.45	-	3.6	4.7	0.72	--	--	26
	5	104	0.16	0.52	1.87	5.7	4.6	0.71	0.26	0.45	18
	6 ^a	3.4	0.13	0.10	0.19	<0.09	4.6	0.74	0.18	--	--

^aPortion of organic phase from 1st contact contacted with a fresh volume of stripping solution (o/a = 1/1).

during stripping is with the organic as the continuous phase, the precipitate disperses in both phases, giving them a dark color and making visual finding of the interface almost impossible. However, the precipitate can be scrubbed from the organic phase by successive contacts with fresh stripping solution, indicating that, in a countercurrent stripping system, complete removal of the dispersed precipitate from the organic phase might be possible. When mixing is with the aqueous as the continuous phase, essentially all the precipitate distributes to the aqueous, leaving the organic clear. In either case, there is a strong tendency toward emulsion formation unless the stripping is performed at elevated temperatures, i.e., 35-45°C. In the limited number of tests performed, it was established that the vanadium could be quantitatively removed from the solvent, but no attempt was made to define the minimum base requirements.

After being stripped with sodium carbonate, the extractant is in the form of its sodium salt, which, on recycle to the extraction system, raises the pH in the last extraction stage. In many cases, addition of sulfuric acid to the last stage may be necessary to avoid a pH rise to the point of precipitation of hydrolyzable metals from the leach liquor.

7.0 RECOVERY OF VANADIUM FROM STRIP SOLUTIONS

7.1 Recovery from Acid Strip Solutions

The pregnant sulfuric acid strip solution contains vanadium(IV) sulfate and sulfuric acid, the vanadium sulfate/sulfuric acid ratio depending on the efficiency of the stripping, i.e., the number of stages, phase ratio, and acid concentration used. Concentrations of uranium* (in a single-cycle uranium-vanadium process) and contaminants such as iron and aluminum would be expected to be low, although the concentrations of contaminants may be appreciable if the stripping operation is conducted at elevated temperatures (Sec. 6.1a). Vanadium can be recovered from the solution by hydrolytic precipitation of vanadium(IV) or precipitation of vanadium "red cake."

* As described in Sec. 9.0, the small amount of uranium stripped can be easily re-extracted from the strip solution and recycled to the extraction operation.

a. Hydrolytic Precipitation of Vanadium(IV)

Vanadium was essentially quantitatively recovered by hydrolytic precipitation of vanadium(IV) with ammonium hydroxide. In precipitation with concentrated ammonium hydroxide from a synthetic strip solution (0.4 M VOSO_4 - 0.75 M H_2SO_4), precipitation began at a pH of ~3.5 and was essentially complete at pH 7:

Precipitation pH	Color of Filtrate	V_2O_5 in Filtrate, g/liter ^a	Vanadium Precipitated, %
3.8	Green-black	5.7	84
4.3	Green-black	1.7	95
5.5	Green-black	0.43	99
7.0	Colorless	0.02	99.9

^aBased on original solution volume.

The precipitate filtered reasonably rapidly, particularly when it was first digested for several hours at room temperature.

Hot digestion of the precipitate or excessive contact with air at room temperature prior to filtration resulted in poorer vanadium recoveries. When the vanadium was precipitated at pH 6 and heated to 90°C, dissolution of the precipitate was appreciable after 30 min:

Digestion Time at 90°C, min	Filtrate pH	V_2O_5 in Filtrate, g/liter ^a	V_2O_5 in Filtrate, %
0	6.0	0.05	0.14
10	5.4	0.13	0.36
30	4.7	1.2	3.3
60	4.5	2.9	8.1

^aBased on original solution volume.

The oxidation state of the vanadium in the filtrate was not determined, but the observed decrease in pH on heating suggests that some oxidation occurred. In a second test in which air was bubbled through the precipitate slurry at room temperature, vanadium dissolution was less than in the heated sample although appreciable:

Air Contact Time, min	Filtrate pH	V_2O_5 in Filtrate, g/liter ^a	V_2O_5 in Filtrate, %
0	6.0	0.05	0.14
10	5.9	0.08	0.22
30	5.5	0.23	0.64
60	5.6	0.93	2.6

^aBased on original solution volume.

Vanadium recoveries were about the same when sodium carbonate was used for pH adjustment. However, the precipitate settled and filtered more slowly than that obtained with ammonia. In addition, thorough washing of the precipitate to meet sulfur specifications (<0.15% S based on V_2O_5) is not required in the latter case since ammonium sulfate is volatile and can be removed by calcination. A product obtained by precipitating vanadium from a $VOSO_4-H_2SO_4$ solution with ammonia and calcining at $600^\circ C$ contained >99.5% V_2O_5 and only 0.07% S. The calcination product from a sodium carbonate precipitation test contained 50% V_2O_5 and 11.7% S. In these tests washing of the filter cakes was not thorough. Later experiments showed that the sulfate could be removed from the sodium carbonate-precipitated filter cake but only with extensive washing.

The quantity of base required for vanadium precipitation is approximately equivalent to the quantity of acid in the initial stripping solution; i.e., if 1 M H_2SO_4 is used for stripping, an equal volume of 2 M NH_4OH (or 1 M Na_2CO_3) is required for vanadium precipitation. Therefore for a given stripping solution the sulfuric acid and ammonia consumed per pound of V_2O_5 are inversely proportional to the vanadium concentration in the pregnant strip solution. The vanadium loading (lb V_2O_5 /lb H_2SO_4) in the stripping solution can be increased, for economy of reagents, by increasing the stripping acid concentration in the range 0.75-1.5 M (Sec. 6.1b).

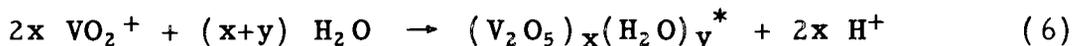
In this precipitation method, provision is usually required for removing inorganic phosphate from the pregnant stripping solution prior to vanadium precipitation in order to meet product phosphorus specifications. Methods of separating phosphate from the vanadium are described in Sec. 8.2.

Calcination of the precipitate at $600^\circ C$ produces a friable, dark gray product. Industry spokesmen claim that, unlike vanadium "red cake," the vanadium(IV) precipitate cannot be fused and therefore is not an acceptable product for domestic consumption, where dust-free products are required. However, it may be an acceptable product for the foreign market where specifications call for low-sodium (but not dust-free) products.

b. Precipitation of Vanadium "Red Cake"

The vanadium was partially precipitated from the pregnant strip solution by adding an oxidant ($NaClO_3$) and heating to near boiling. A coarse, granular precipitate, resembling in appearance and characteristics the precipitate formed in the usual "red cake" precipitations, formed readily and was easily filtered. The oxidation and precipitation reactions may be

expressed as



Since acid is generated in both the oxidation and precipitation reactions, the precipitation is accompanied by a large drop in pH.

The effects of variables on the precipitation efficiency were tested with synthetic strip solutions, using the following precipitation procedure. One liter of solution was heated to 60°C by a tantalum steam coil and sodium chlorate was added. The solution temperature was raised quickly (~2 min) to 90-95°C and held there for the desired digestion time. Water was added when necessary to compensate for changes in solution volume due to evaporation. Samples were removed and filtered at intervals to determine the amount of vanadium remaining in solution. The completeness of precipitation was calculated from the head solution and filtrate analyses. The completeness of the oxidation was judged from the color of the solution, which changes from deep blue to yellow as the vanadium is converted from the tetra- to the pentavalent state.

Oxidant Requirements. With an excess of sodium chlorate, the oxidation appeared complete in 15 min (Fig. 7.1). Approximately 58% of the vanadium precipitated when 5% excess sodium chlorate was used. Surprisingly, vanadium recoveries decreased to 52-55% with larger excesses. In all cases, a digestion time of approximately 1 hr appeared ample for maximum precipitation.

Effect of Vanadium Concentration. Recoveries increased with increased vanadium concentration in the head solution. With 105% of stoichiometric sodium chlorate to precipitate vanadium from two synthetic strip solutions with vanadium concentrations of 17 and 68 g V₂O₅ per liter (each at initial pH 0.5), recoveries were 52 and 74%, respectively (Table 7.1). In both tests the precipitation was near maximum after approximately 1 hr digestion.

* The precipitate is actually more complex than shown since it also contains a small amount of sodium.

UNCLASSIFIED
ORNL-LR-DWG. 41663

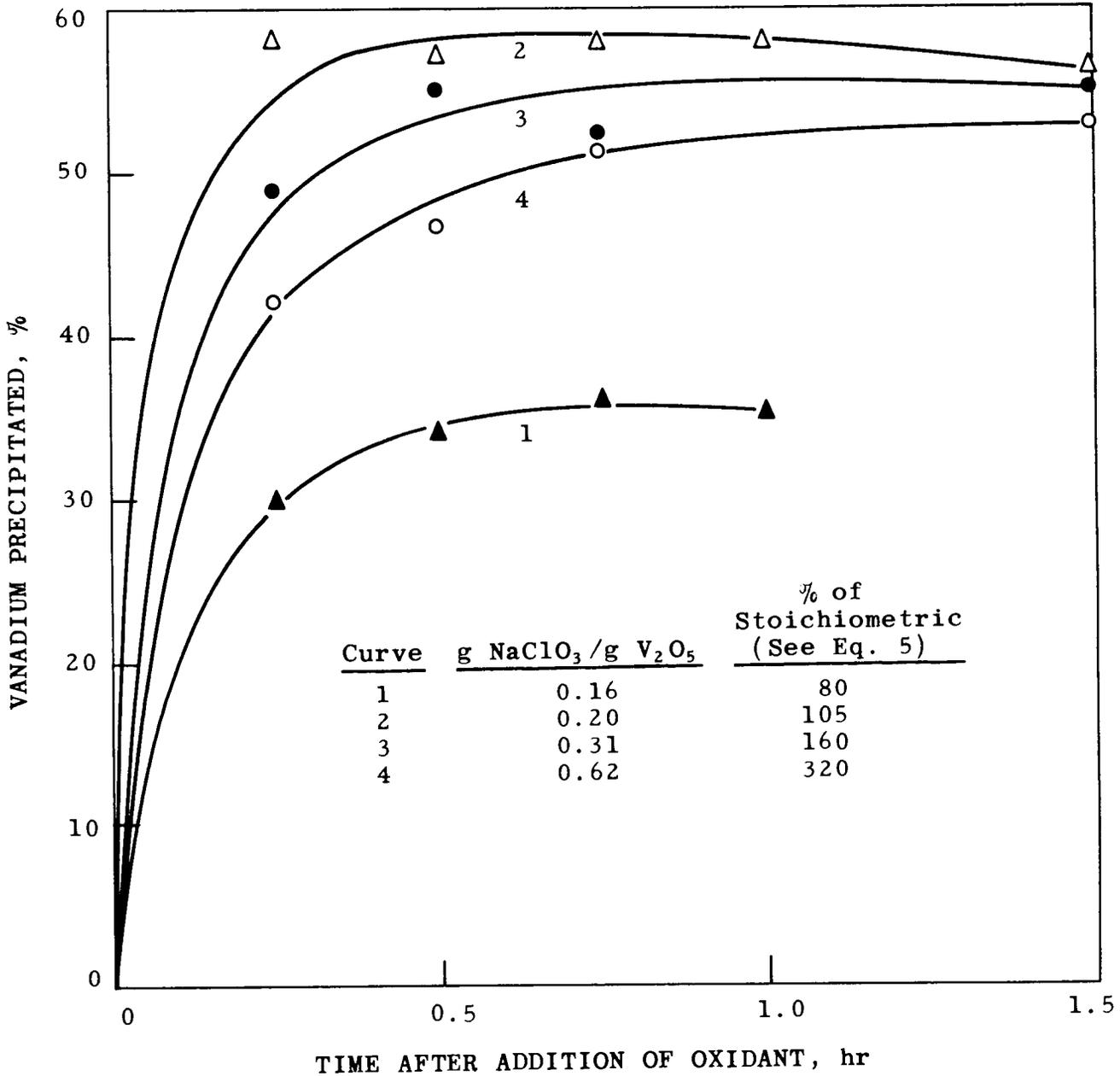


Fig. 7.1. Effect of Oxidation Time and NaClO_3 Supply on Vanadium Recovery. Head aqueous: $\text{VO}_2\text{SO}_4\text{-H}_2\text{SO}_4$ solution; 34 g V_2O_5 per liter, pH 0.5. Procedure: see p 33.

Table 7.1 Effect of Initial Vanadium Concentration on Vanadium Precipitation

V_2O_5 in Head Solution, g/liter	Digestion Time, hr	V_2O_5 in Supernatant, g/liter	Vanadium Precipitated, %
17	0.25	10.0	41
	0.5	9.1	47
	1	8.2	52
	3	8.4	51
	6	8.2	52
68	0.25	24	65
	0.5	19	72
	2	18	74
	6	18	74

Effect of pH on Vanadium Recovery and Product Phosphate Content. The precipitation efficiency was improved by increasing the precipitation pH. Although improvement was appreciable when the strip solution was adjusted to pH 1-2 prior to the addition of the oxidant, recoveries were considerably higher when the adjustment was made after the oxidation step. In the latter case, consumption of base was much greater since it was necessary to neutralize the acid produced by the oxidation-precipitation reactions (eqs. 5 and 6) in addition to the acid present in the pregnant stripping solution.

Results of tests in which the pH was adjusted with ammonia prior to oxidation are presented in Table 7.2. Precipitations were from two synthetic strip solutions (differing only in their phosphate content), with sodium chlorate 10-35% in excess of stoichiometric requirements. Vanadium recoveries were 67-83%, increasing with increase in pH. Adjustment of the strip solution pH with ammonia increased sodium chlorate requirements. Whereas 110% of stoichiometric sodium chlorate completely oxidized the vanadium in unadjusted solutions, oxidation was far from complete with this amount in tests with adjusted solutions. Vanadium recoveries in the latter tests were adversely affected by the failure to obtain complete oxidation. When the amount of sodium chlorate was increased to 135% of stoichiometric, a solution adjusted to pH 2 was completely oxidized and vanadium recovery was at the highest value obtained, 83%.

Table 7.2 Effect of Initial pH on Vanadium Precipitation

Synthetic strip solution: 55 g of V_2O_5 , 0.5 g of Fe(III), 0.5 g of Al, and 98 g of sulfate per liter, variable phosphate, at pH 0.4; pH adjusted with NH_3

Procedure: oxidant added and precipitate digested 1 hr at $90^\circ C$; precipitates then filtered, washed with water, and calcined at $600^\circ C$

PO ₄ in Strip Sol'n g/liter	Excess NaClO ₃ , %	Initial pH	Filtrate		Vanadium Pptd, %	Calcined Product, %		
			pH	V(IV)/V(V) Ratio		V ₂ O ₅	P	S
0.45	10	0.4	<0.0	<0.05	67	98	0.02	0.03
1.0	10	0.4	<0.0	<0.05	67	97	0.04	0.18
0.45	10	1.1	0.3	0.5	70	99	0.02	0.03
1.0	10	1.1	0.3	0.5	72	98	0.07	0.08
0.45	10	2.0	0.3	0.4	76	99	0.04	0.06
1.0	10	2.0	0.3	0.5	78	97	0.05	0.04
1.0	25	2.0	0.3	0.2	80	99	0.06	0.05
1.0	35	2.0	0.3	<0.05	83	99	0.06	0.09

The calcined products contained 97-99% V_2O_5 and 0.2-0.6% Na, and all except one met the sulfur specifications (0.15% S based on contained V_2O_5) for commercial vanadium. Separations from phosphate during precipitation were very favorable. Products from the strip solution containing 0.45 g of phosphate per liter (0.27 wt % P based on V_2O_5) contained 0.02-0.04 wt % phosphorus, the highest being obtained when the solution pH was adjusted to 2.0 prior to precipitation. Products from the solution containing 1.0 g of phosphate per liter (0.59 wt % P based on V_2O_5) barely met or slightly exceeded the phosphorus specification limit of 0.05% P based on V_2O_5 . The lowest result was obtained at the lowest pH. Since the efficiency of separation from sulfate (and to some extent from phosphate) depends on the effectiveness of the precipitate wash, product purity in these tests might have been improved by washing the precipitate more thoroughly.

When the solution pH was adjusted after vanadium oxidation with sodium chlorate (10% excess), vanadium recoveries increased to 94% at pH 1.2 and 97-99% at pH 2.1-2.2 (Table 7.3). After a 5-hr digestion the precipitate was filtered, washed with 0.2 M $(NH_4)_2SO_4$ solution, and dried.

Analyses showed:

Drying Temp., °C	Analysis, %			
	V ₂ O ₅	P	S	Na
110	87.5	0.17	0.40	0.01
600	97.2	0.20	0.32	0.02

Both the phosphorus and sulfur contents of the products were appreciably above the specification limit. Presumably more thorough washing of the precipitate would have decreased the sulfate content to an acceptable level. The phosphate concentration in the supernatant showed only a small drop as the pH was raised to 1.2 but a fairly large drop on further increase to 2.2, possibly because of precipitation of iron and/or aluminum phosphate. Phosphate specifications would apparently have been met if the pH had not been adjusted higher than 1.2.

Table 7.3 Effect of Adjusting pH of Strip Solution after Oxidation of Vanadium

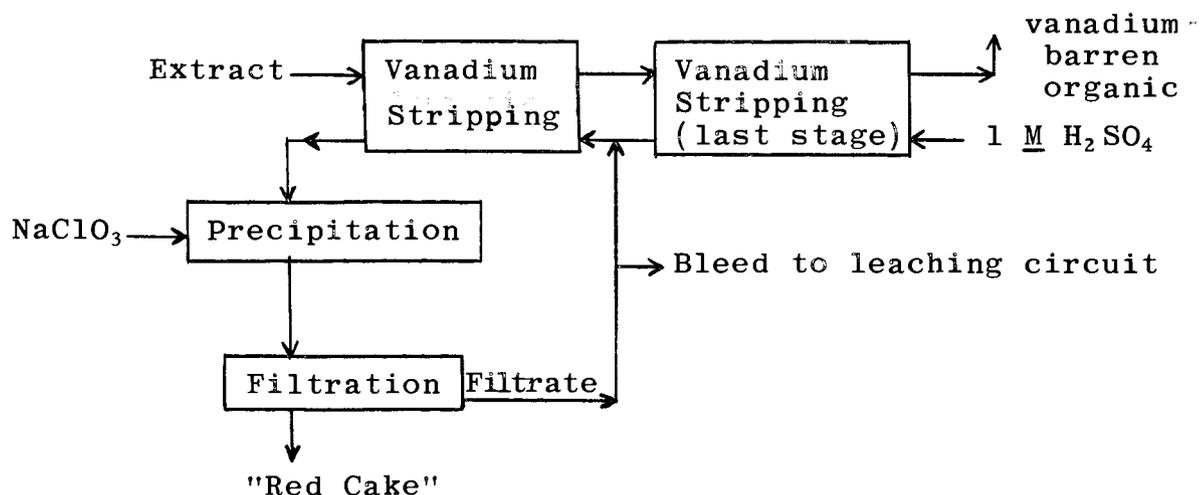
Synthetic strip solution: 55 g of V₂O₅, 1.0 g of PO₄, 0.5 g of Fe(III), 0.5 g of Al, 98 g of sulfate per liter at pH 0.4

Procedure: vanadium oxidized with 10% excess NaClO₃; precipitate digested 5 hr at 90°C; NH₄OH added during first hour to raise pH to 2.2

Time After Oxidant Addition, min	Supernatant			Vanadium Precipitated, %
	pH	V ₂ O ₅ , g/liter	PO ₄ , g/liter	
10	<0.0	22	1.01	60
20	0.1	15	0.99	73
30	0.3	9.5	0.97	83
40	0.7	4.3	0.95	92
50	1.2	3.4	0.92	94
60	2.2	-	0.50	-
120	2.2	1.4	0.51	97
180	2.1	0.57	0.40	99
240	2.1	0.46	0.46	99
300	2.1	0.48	0.40	99

Vanadium Recycle. As shown above, precipitation recoveries of ~90% can be obtained by adjusting the solution pH with ammonia to ~1 after oxidation with sodium chlorate. It is assumed that the vanadium remaining in solution would be recycled to the pregnant-liquor storage tank (preceding reduction). When no pH adjustment is made, or when the adjustment

is made prior to oxidation, a much larger fraction of the vanadium (20-35%) remains in solution and must be recycled. In both cases the recycle solution would contain relatively large amounts of sulfuric acid (most of the acid consumed during stripping is regenerated during oxidation-precipitation) and therefore would probably be recycled to the leaching step. Recycle of the solution to the stripping step appears more attractive, however, provided this proves to be operationally feasible. In batch stripping tests (results not presented), essentially complete stripping of an extract was obtained with a 1 M H_2SO_4 solution containing a fairly high concentration (~10 g of V_2O_5 per liter) of vanadium(V). To ensure complete stripping with such a system, the recycle stream should be fed to the next-to-the last stripping stage and a relatively small volume of fresh acid should be fed to the last stage:



Volume balance for the system would be maintained by bleeding a portion of the filtrate to the leaching circuit. This solution bleed would also prevent buildup of sodium chloride, metal contaminants, and phosphate to undesirable levels. The feasibility of this process scheme has not been established in continuous tests. One point of obvious concern is whether or not "red cake" would continually precipitate from the recycle stream, fouling the lines and the stripping system.

7.2 Recovery from Basic Strip Solutions

Attempts to recover the precipitated vanadium from a sodium carbonate strip solution by filtration were unsuccessful since the precipitate is colloidal and passes through even fine filter mediums. Originally this was considered a potential advantage since it was expected that it would allow effective separation from precipitated contaminants, e.g., iron and aluminum, in the pregnant strip solution. Subsequent tests, however, showed that, although separation was appreciable,

major portions of both the iron and aluminum tended to pass the filter along with the vanadium.

Direct recovery of a hydrated vanadyl oxide product from the strip solution would depend on finding a means of coagulating the vanadium precipitate sufficiently to allow filtration. Precipitate coagulation and settling after days of standing at room temperature have been observed, but methods for inducing rapid coagulation have not been studied, and it has not been determined whether the products would meet phosphorus specifications.

Oxidation of Vanadium with Air. A brief study was made of the possibility of oxidizing the vanadium precipitate (dispersed in the sodium carbonate strip solution) with air to soluble sodium metavanadate which could be recovered by the conventional "red cake" precipitation method. Initial tests, made by simply bubbling air through the pregnant strip slurry contained in a bubbling flask, showed the rate of oxidation to be strongly dependent on the basicity of the strip solution, increasing with increasing pH. The pH dropped during oxidation, as would be expected, since 1 mole of hydrogen ion is produced for each mole of vanadium oxidized. In one test, in which the initial pH of the precipitate slurry (34 g of V_2O_5 per liter) was 10.1, all the vanadium was oxidized after 16 hr air oxidation at room temperature. In tests with a precipitate slurry (34 g of V_2O_5 per liter) which had an initial pH of 9.0, only about 75% of the vanadium was oxidized after air oxidation for 21 hr at room temperature or 5 hr at 70°C. In these tests the pH of the slurry at the end of the oxidation period was 8.4. In a single test in which the strip slurry (24 g of V_2O_5 per liter, pH 9.5) was placed in a baffled mixing chamber to which air was introduced through a bottom inlet tube, approximately 83% of the vanadium was oxidized after 4 hr of violent agitation at room temperature. This recovery method shows some promise but needs more study, particularly of the oxidation step, to define reagent requirements and operational feasibility.

8.0 PHOSPHATE CONTENT OF VANADIUM PRODUCTS

As shown in Sec. 7.1b, vanadium separation from phosphate is favorable when the vanadium is recovered by precipitation as red cake.* The red cake products in most cases have met

* Other investigators have previously shown favorable separation of vanadium from phosphate by the red cake precipitation method in recovery of vanadium from ion exchange eluates.^{13,14} Results were also favorable for the ammonium precipitation method when phosphate had been precipitated from solution with zirconium prior to precipitation of vanadium.¹³

market specifications with regard to vanadium grade and impurity content provided the precipitate is washed sufficiently to remove sulfate. However, in the ammonium precipitation method, products containing more phosphate than the specified limit have been the rule rather than the exception. This has been found in tests by the Kerr-McGee Oil Industries* and the Climax Uranium Company,* and has been confirmed by more recent studies at this laboratory.⁴

Since the ammonium precipitation method, without the handicap of phosphate contamination, might have advantages in some process schemes from the standpoint of operation and product marketing, studies were made to determine the mechanism by which phosphate enters the product, and, if possible, to devise methods for controlling the phosphate content.

8.1 Sources of Phosphate Contamination

Both organic phosphate derived from the extraction reagents and inorganic phosphate in the leach liquor may contribute phosphate to the product.

Organic Phosphate. The strip solution may become contaminated with phosphate during stripping as a result of physical entrainment of the solvent in the aqueous phase or of solubility of the organophosphorus components from the solvent to the strip liquor. These organophosphorus components could be the D2EHPA extractant, the TBP additive, lower molecular weight organophosphorus components present as impurities in the original reagents,** or hydrolysis products of the D2EHPA and TBP.

Available information on the chemistry of these reagents and on the system in which they are used suggests that the most important source of organic phosphate contamination would

* personal communications.

** The various shipments of D2EHPA received from the vendor (Carbide) have contained 2-10% monoalkylphosphoric acid. The mono-compound has a relatively high distribution loss to acid solutions and can introduce phosphate into the vanadium strip solution far in excess of the allowable limit. In process use, it would be lost from the organic phase after a few cycles as a natural result of the extraction-stripping operations. For batch or limited-cycle laboratory tests, however, it is important that the solvent be thoroughly scrubbed prior to use. Sodium carbonate solution (5%) is an effective scrubbing agent.

be the low molecular weight impurities. On the other hand, only a small amount of phosphorus is required to exceed the specification limit and the sum of several small contributions could be important.

Products derived from a series of bench-scale continuous tests indicated the importance of organic phosphate as a contamination source. In these tests (described in detail in Sec. 9.1), the vanadium was extracted from several synthetic leach liquors with 0.3 M D2EHPA in kerosene + 0.2 M TBP, stripped with 0.75-1.0 M H₂SO₄, precipitated with ammonia at pH 7, washed with water, and calcined at 600°C. None of the synthetic liquors contained inorganic phosphate, and phosphate in the products therefore must have been of organic phosphate origin. The vanadium content of the products ranged from 93 to 99% V₂O₅. The products contained 0.02-0.05% phosphorus, with the lowest value in run 7 where loading of the strip solution was highest, 61 g of V₂O₅ per liter:

Run No.	Pregnant Strip Solution, g/liter		P in Calcined Product, %, based on V ₂ O ₅
	V ₂ O ₅	PO ₄	
Preliminary	17	-	0.05
1	22	-	0.03
2	19	-	0.03
3	21	-	0.03
5	25	-	0.03
7	61	0.036	0.02 ^a

^aCalculated on the basis of the strip solution analysis and assuming (probably incorrectly) that all the phosphate would report to the product.

A decrease in the P/V₂O₅ ratio would be expected with increase in loading of the strip solution since distributions of organic phosphates to the aqueous phase and entrainment of solvent in the aqueous phase should be virtually independent of vanadium loading. (Loading of a 1 M H₂SO₄ solution to approximately 60 g of V₂O₅ per liter is considered typical of the Dapex process.)

Although all the products met the specification of 0.05% P, it is evident that phosphate of organic origin is an important consideration. The solvent had been scrubbed with 10% Na₂CO₃ but not thoroughly. It is likely that mono(2-ethylhexyl)phosphate was an important phosphate contributor.

Inorganic Phosphate. Inorganic phosphate may be transferred to the stripping system by entrainment of the leach liquor in the extract or by actual extraction of the orthophosphate combined with extractable metals in the form of a

cationic metal complex. The possible importance of metal-phosphate complexing was studied by extracting vanadium(IV), iron(III), and aluminum from 0.5 M sulfate solutions containing 0-4 g of phosphate per liter. The extraction was made with 0.25 M D2EHPA in kerosene that had been thoroughly scrubbed with 10% Na₂CO₃ and 6 M HCl to eliminate readily soluble organophosphorus impurities. The amounts of extracted phosphate were determined by stripping the extracts (after filtering to remove entrained aqueous) with 6 M HCl and analyzing the strip solutions. Removal of the metals from the solvent was complete. To permit correction for any organic phosphate that might have been present despite the precautions taken, a sample of solvent that had not been contacted with one of the aqueous solutions was stripped with 6 M HCl, which was subsequently analyzed for phosphorus content. The test conditions were: aq/org phase ratio = 2/1; 10 min contact for V(IV) and Fe(III) tests, 30 min contact for aluminum tests; final pH 1.5-1.7. The results were:

Metal	PO ₄ in Head Aq, g/liter	Metal, g/liter			Extract. Coeff. (E _a ^o)	PO ₄ Ext'd by Organic, g/liter
		Head	Organic	Aqueous		
V(IV) (as V ₂ O ₅)	0	5.5	7.7	2.0	3.8	0.003
	1	5.5	7.5	2.0	3.8	0.003
	4	5.5	7.7	2.0	3.8	0.003
Fe(III)	0	0.41	0.6	0.13	5	<0.002
	1	0.41	0.8	0.008	100	<0.002
	4	0.41	0.8	0.001	800	<0.002
Al	0	5.3	0.6	4.9	0.12	<0.002
	1	5.3	1.0	4.8	0.21	0.015
	4	5.3	1.1	4.7	0.23	0.061

Extractions of phosphate with vanadium(IV) and iron(III) were negligible. Aluminum, on the other hand, carried appreciable amounts of phosphate into the solvent, i.e., 0.015 and 0.061 g of phosphate per liter, respectively, in extractions from head liquors containing 1 and 4 g of phosphate per liter. These amounts of phosphate are sizable in relation to the small amounts allowable. For example, assuming a loading of 5 g V₂O₅ in the solvent, 0.015 g PO₄/liter corresponds to 0.1% P based on V₂O₅ and 0.061 g PO₄/liter to 0.4% P.

Vanadium extractions were unaffected by the presence of phosphate. Both iron and aluminum extractions, however, were appreciably enhanced. The extractions of iron and aluminum are ordinarily slow in this system, and the 10-30 min contact time used is ordinarily not sufficient for equilibrium to be

reached. The enhancement of extraction may have been due, in these cases, to an increase in the extraction rate of the metals in the presence of phosphate.

Measurement of inorganic phosphate extraction with several common metal ions by radiotracer techniques⁵ gave results similar to the above, although the results for the two experiments were not quantitatively comparable owing to differences in extraction phase ratios and methods of contacting. Essentially no phosphate was extracted with vanadium(IV) or molybdenum(VI) but relatively large amounts were extracted with aluminum. With this more accurate technique, some extraction of phosphate with Fe(III) was detected but the amounts were not significantly large compared to the amounts extracted with aluminum.

8.2 Separation of Inorganic Phosphate from Vanadium

A number of methods were briefly examined for separating phosphate from vanadium including (1) scrubbing of the extract prior to stripping, (2) fractional precipitation of vanadium(IV), (3) precipitation of the phosphate with zirconium, (4) leaching of phosphate from the ammonium precipitate, and (5) adsorption of phosphate on activated zirconium oxide. Method 5 appeared to have the greatest merit, and methods 1 and 3 were partially successful.

Scrubbing the Extract Prior to Stripping. The extracted phosphate was partially removed by scrubbing a vanadium-loaded extract with ammonium sulfate solution or with dilute sulfuric acid. The loaded solvent was prepared for these tests by contacting 0.3 M D2EHPA in kerosene (thoroughly scrubbed with sodium carbonate and hydrochloric acid solutions prior to use to remove impurities) with a synthetic vanadium leach liquor containing 4 g of phosphate per liter. After being filtered to remove any entrained liquor, the solvent (4.1 g of V_2O_5 , 0.5 g of Fe, and 0.5 g of Al per liter) was divided into three portions. One portion was scrubbed twice (5 min per contact) at an o/a ratio of 5/1 with 1 M $(NH_4)_2SO_4$.* A second portion was scrubbed in the same way with dilute sulfuric acid (pH 2). The scrubbed and unscrubbed extracts were stripped twice with 6 M HCl at an o/a ratio of 1/1, and the phosphate contents of the strip solutions were compared:

* In a process plant ammonium sulfate would be available in the filtrate after precipitation of vanadium(IV) with ammonia.

Scrub Solution	P in 6 M HCl Strip Solution, ^a %, based on V ₂ O ₅	Amount	
		Removed by Scrubbing, V ₂ O ₅	% Extracted Phosphate
None	0.5-0.6	-	-
1 M (NH ₄) ₂ SO ₄ , pH 3	0.2	0.3	60-70
H ₂ SO ₄ , pH 2	0.3	0.7	40-50

^aDoes not include phosphate contributed by dissolved organic phosphate, which was estimated by carrying an organic blank, i.e., organic solution which had not been contacted with the liquor, through the test sequence.

The ammonium sulfate was the more effective of the two scrub solutions, removing approximately two-thirds of the extracted phosphate and only 0.3% of the vanadium. The remaining phosphate (0.2% P based on V₂O₅) was still considerably above the specification limit. However, the phosphate concentration of the liquor was higher than is usually encountered, and the amount of extracted phosphate was therefore probably extreme. For processing liquors more dilute in phosphate, the treatment may be sufficient. In addition to removing extracted phosphate, the scrub would also remove leach liquor that had been entrained in the solvent, thus minimizing phosphate transfer to the stripping system by this mechanism.

Fractional Precipitation of Vanadium. Attempts to separate phosphate from the bulk of the vanadium by stepwise precipitation of vanadium with ammonia were not successful.

Synthetic strip solutions (56 g of V₂O₅, 0.5 g of Fe(III), 0.5 g of Al, 98 g of sulfate, and 0.45-1.0 g of phosphate per liter) were used for the tests. The pH of the solution was raised with ammonia gas until initial precipitate formation was observed. After a 1-hr digestion, the slurry was filtered and the precipitate washed with water and analyzed. The rest of the vanadium was precipitated from the filtrate in two more steps, allowing a 1-hr digestion after each pH adjustment. In each case the phosphate content of the third fraction was approximately half that of the first two fractions but still considerably above the specification limit:

<u>PO₄ in the Strip Solution, g/liter</u>	<u>Precipitate</u>	<u>P in Ppt, %, based on V₂O₅</u>	<u>Vanadium Distribution, % of total</u>
0.45	1st fraction, pH 3.4	0.30	19
	2nd fraction, pH 3.7	0.32	44
	3rd fraction, pH 7.3	0.17	37
1.0	1st fraction, pH 3.4	0.77	17
	2nd fraction, pH 3.6	0.77	40
	3rd fraction, pH 7.6	0.39	43

In the hope that vanadic phosphate would precipitate at a lower pH than vanadyl phosphate, a similar test was made with a solution that had been spiked with vanadium(III). The V(III)/V(IV) ratio in the head solution was approximately 0.1. The precipitation was performed in two steps, again with no useful separation:

<u>PO₄ in the Strip Solution, g/liter</u>	<u>Precipitate</u>	<u>P in Ppt, %, based on V₂O₅</u>	<u>Vanadium Distribution, % of total</u>
0.45	1st fraction, pH 3.3	0.30	45
	2nd fraction, pH 7.0	0.20	55

Precipitation of Phosphate with Zirconium and Titanium.
Elimination of phosphate from the strip solution by precipitation with zirconium or titanium was studied briefly. The metal, in 1 M H₂SO₄, was added to the synthetic strip solution in quantities equivalent to 190 and 350% of the stoichiometric amount for precipitating the phosphate as M₃(PO₄)₄. After 15 min digestion, the solution was filtered and a portion of the filtrate was analyzed for vanadium and phosphate. The rest of the filtrate was adjusted to pH 2.1-2.3 (below the point of vanadium precipitation) with ammonia gas, digested 5 min, filtered, and analyzed. The results show precipitation of phosphate with both zirconium and titanium, but in only one test was the phosphate concentration reduced to the specification limit:

Metal Added	Amount, % of Stoichiometric	pH	P in Filtrate, % based on V_2O_5	Phosphate Precipitated, % of total
Zr	190	0.4	0.07	75
		2.3	0.05	80
	350	0.4	0.21	20
		2.2	0.11	60
Ti	190	0.4	0.26	<5
		2.1	0.15	40
	350	0.4	0.26	<5
		2.2	0.08	70

The synthetic strip solution contained 55 g of V_2O_5 , 0.45 g of phosphate, 0.5 g of Fe(III), 0.5 g of Al, and 98 g of sulfate per liter.

In all cases, precipitation was more complete at the higher pH. The first test (190% of stoichiometric zirconium) was different from the others in that the solution was filtered through No. 50 filter paper. Owing to the colloidal nature of the precipitate, filtration was very slow. In the last three tests, the solutions were filtered through relatively coarse, No. 42, paper and filtration was much more rapid. The poorer results achieved with the larger amounts of zirconium suggest that a considerable portion of the precipitate passed the coarse filter. Although these tests show some promise, further study of the system is needed to determine whether suitably effective separations could be obtained routinely if precipitation conditions were optimized.

Leaching of Phosphate from the Ammonium Precipitate of Vanadium(IV). Treatment of a vanadium(IV) precipitate with dilute sodium or ammonium hydroxide removed only a fraction of the phosphate.

A vanadium precipitate was prepared for these tests by neutralizing a synthetic strip solution (55 g of V_2O_5 , 0.45 g of phosphate, 0.5 g of Fe(III), 0.5 g of Al, and 98 g of sulfate per liter at pH 0.4) with ammonia gas. Samples of the wet precipitate were digested with hydroxide solutions, filtered, washed, and analyzed. Of the solutions tried, only 3% NaOH reduced the phosphate content of the vanadium by more than 50%. However, owing to the tendency of the precipitate to peptize and also to oxidize during digestion, a considerable portion of the vanadium was removed with the phosphate:

Leach Solution	lb Leaching Agent/lb V ₂ O ₅	Digestion Time, hr	pH	Amount in Filtrate, %		P in Leached Precipitate, % based on V ₂ O ₅
				V ₂ O ₅	PO ₄	V ₂ O ₅
None	-	-	-	-	-	0.26
Water	-	4	7.5	3	2	0.26
1% NaOH	0.08	0.5	9.5	5	15	0.23
1% NaOH	0.08	4	9.6	6	19	0.23
3% NaOH	0.25	0.5	11.1	21	56	0.17
3% NaOH	0.25	4	11.2	26	62	0.13
4% NH ₃	0.34	4	10.1	5	24	0.21

Removal of Phosphate by Adsorption on Zirconium Oxide.
 Separation of phosphate from vanadium was very effective when the strip solution was passed through a column of activated zirconium oxide. The column was readily regenerated with dilute sodium hydroxide.

The possibility of using zirconium oxide as an adsorbent for phosphate was suggested by the work of Kraus and Phillips, who, in the course of their investigation of the ion exchange properties of various inorganic materials, found hydrous zirconium oxide to have unusual anion exchange properties in acidic solutions.¹⁵ According to Kraus and Phillips, the temperature at which the precipitate is dried determines its degree of activity as an exchanger. The adsorptive capacity decreases as the drying temperature is increased, but this effect does not become excessive below 300°C.

Samples of zirconium oxide were prepared for test by dissolving zirconyl chloride in water, precipitating with ammonia to pH 8.5, filtering, and washing. The wet cakes were dried to constant weight at either 200 or 300°C, ground, and screened. Typical analyses of the products were:

<u>Drying Temp., °C</u>	<u>ZrO₂, %</u>	<u>Loss on Ignition at 1000°C, %</u>
200	85.9	14.3
300	89.4	10.6

In preliminary batch tests⁶ with synthetic strip solutions at pH 0.4 and 1.5, phosphate adsorption was slightly higher at pH 1.5 than at pH 0.4. Adsorptions were improved slightly by increasing the contact time from 5 to 30 min. Phosphate adsorption was somewhat higher with the 200°C than with the 300°C oxide, but dissolution of zirconium also was higher. With both oxides, zirconium dissolution appeared appreciably greater at pH 0.4 than at pH 1.5.

Initial testing of the zirconium oxide in a column showed that most of the very fine oxide should be eliminated to avoid excessive resistance to solution flow. Subsequent column runs were made with only the -50 +80 mesh screened fraction,* although presumably successful operation could be obtained with oxide covering a much wider particle size range. Gas pockets formed in the column as the column was switched from the elution to the adsorption cycle. These gas pockets increased the resistance to solution flow and tended to impair the solution-solid contact efficiency. The presence of carbonate in the sodium hydroxide eluting solution was suspected and confirmed. This problem was eliminated when reasonable care was taken to avoid excessive contact of air with the eluting solution during makeup and use.

In a preliminary column test⁶ with a synthetic strip solution (57 g of V_2O_5 , 0.6 g of Fe(III), 0.4 g of Al, 0.55 g of phosphate, 98 g of sulfate per liter at pH 1.6) and oxide dried at $300^\circ C$, approximately 98% of the phosphate was removed on passage of 44 column volumes of solution through the column. Average phosphate loading of the column was approximately 16 g per 1000 g of adsorbent. Elution of the adsorbed phosphate with 0.5 M NaOH, passed at a flow rate of ~ 90 gal/ft²/hr, was only partially successful, suggesting that a more concentrated caustic solution and/or a lower elution flow rate would be required for effective removal.

A five-cycle adsorption-elution test was made to determine whether the zirconium oxide would maintain its sorption capacity in cyclic operation and to establish reagent costs for the phosphate removal step. Breakthrough curves were approximately equivalent in each of the five cycles, indicating that there was no appreciable change in adsorption capacity of the zirconium oxide with cycling (Fig. 8.1). The P/ V_2O_5 ratio in the first ~ 21 column volumes of effluent was, in each cycle, less than the specification limit of 0.05 wt %, but beyond this point the phosphate concentration in the effluent increased rapidly. In the 22-29 and the 30-36 column volume increments, the P/ V_2O_5 ranges were 0.07-0.09 and 0.12-0.16 wt %, respectively. After 43 column volumes (the end of the adsorption cycle), the phosphate content of the effluent was approximately half that of the feed solution. The average phosphate loading, based on the effluent and feed solution analysis, was approximately 20 g/1000 g of adsorbent (~ 28 g per liter of wet-settled adsorbent).

Elution with 2 M NaOH was effective (Fig. 8.2). With the exception of cycle 1, where elution was relatively slow, the

*With an 11-in. bed of zirconium oxide, the pressure drop over the column was approximately 3 ft H₂O at a flow rate of ~ 90 gal/ft²/hr. The pressure drop did not change appreciably as the column was cycled.

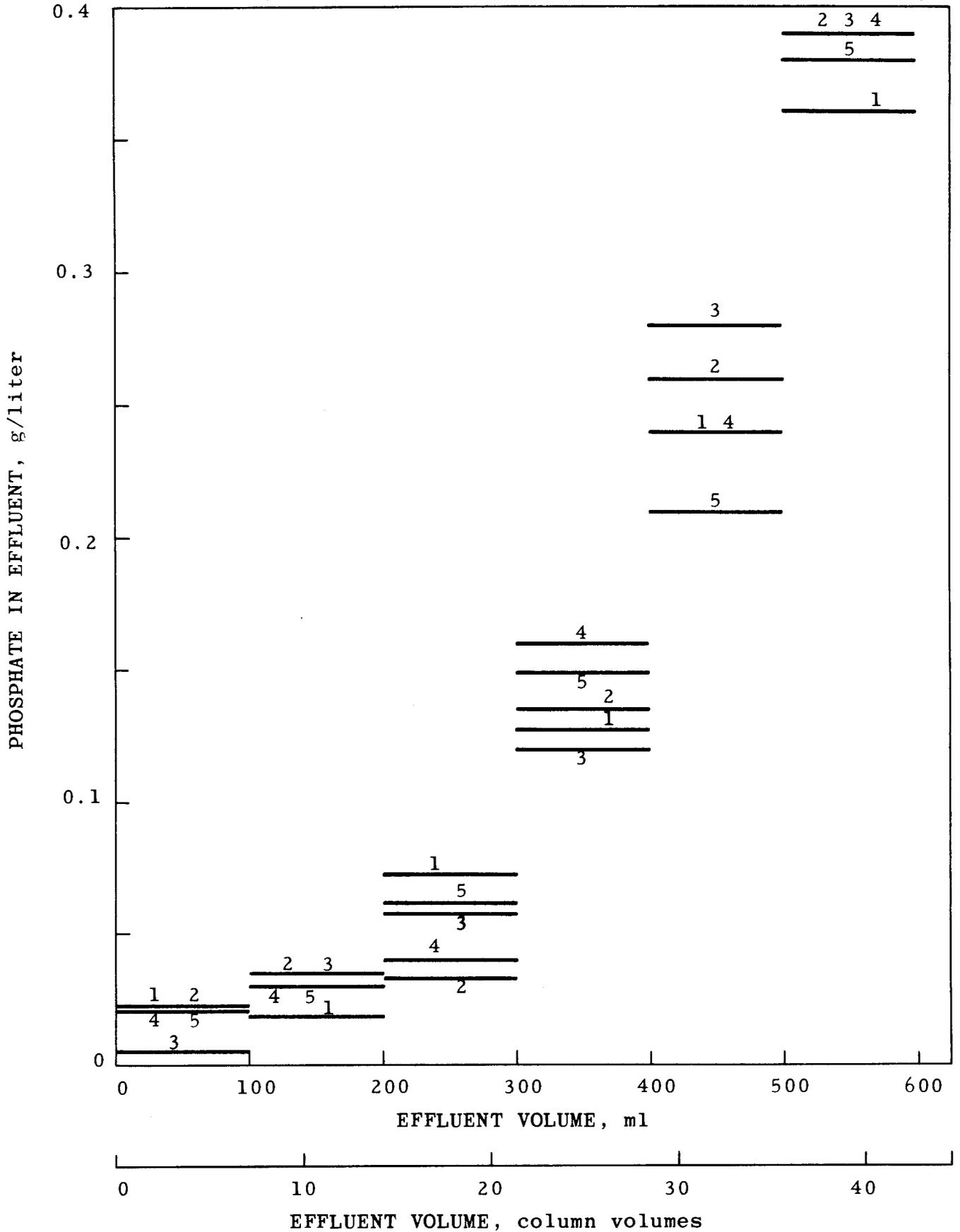


Fig. 8.1. Adsorption of Phosphate on a Zirconium Oxide Column. Aqueous feed to column: 0.8 g of phosphate per liter. Numbers indicate cycle.

UNCLASSIFIED
ORNL-LR-DWG. 41664

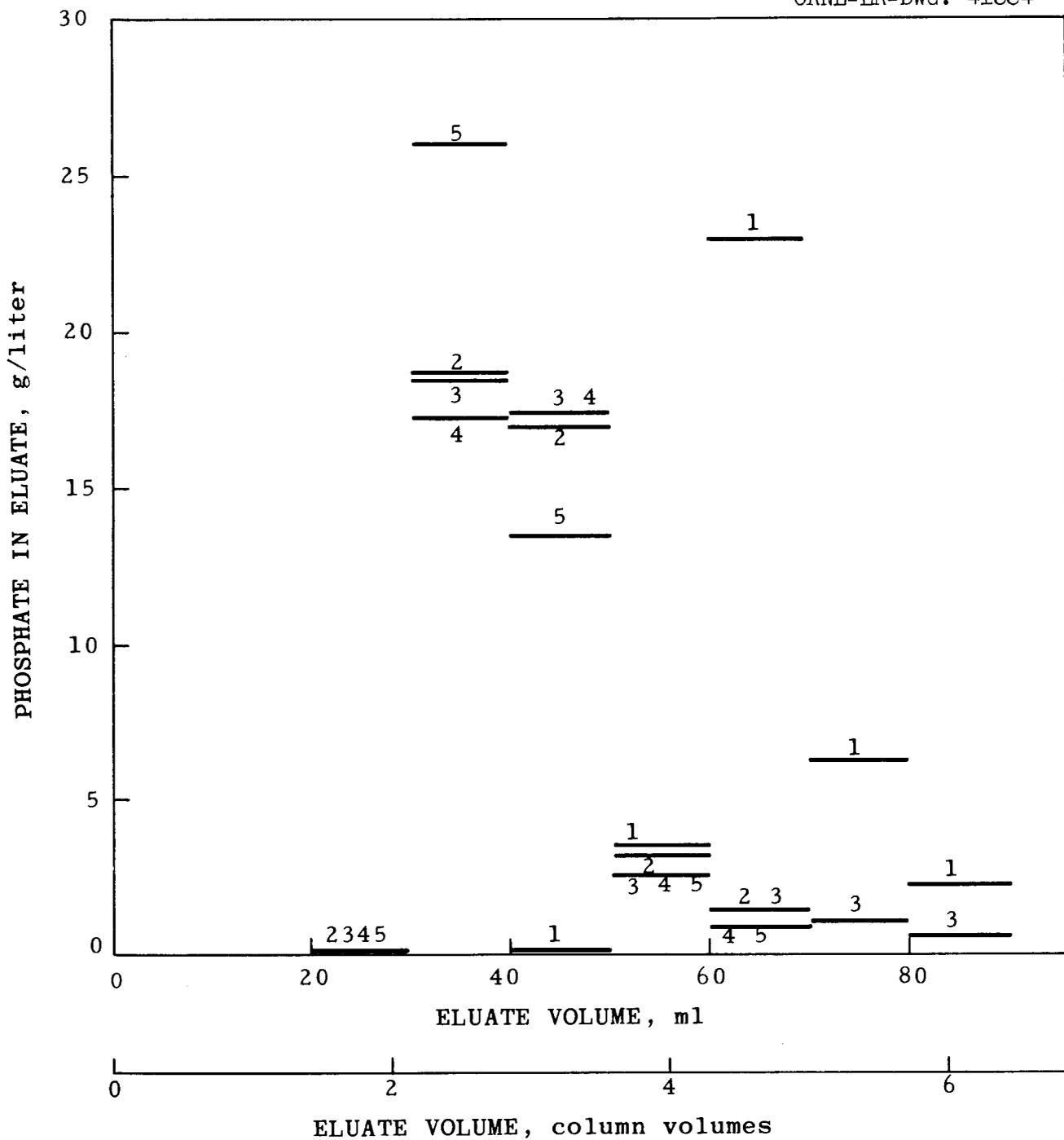


Fig. 8.2. Elution of Phosphate with 2 M NaOH. Numbers indicate cycle.

elution curves for each cycle were similar, showing essentially no phosphate in the first two column volumes but peaking in the third column volume in the phosphate range 17-25 g/liter. The phosphate concentration in the eluate at the conclusion of the elution cycles (5-6.5 column volumes) was 0.5-2 g/liter. In each cycle, a greenish elution band left the column shortly before the eluate pH changed from the acid to the basic side. Analysis of the eluate showed the presence of both iron and vanadium, the amounts of the latter being, however, only about 0.1% of the total vanadium passed through the column.

Phosphate was negligible in the C and D wash solutions and in the final 50 ml of the A and B wash solutions. The phosphate content of the first 50 ml of the A and B wash solutions was:

Wash Solution (First 50 ml)	Phosphate Concentration, g/liter				
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
A	0.15	0.15	0.18	0.18	0.19
B	0.34	0.04	0.15	0.28	0.08

A total of 1.96 g of phosphate was found in the eluates and wash solutions compared to a total of 1.98 g adsorbed (based on the head solution and effluent analyses) in the five cycles:

	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Total
g PO ₄ adsorbed	0.40	0.39	0.39	0.40	0.40	1.98
g PO ₄ in eluate and wash solutions	0.35	0.40	0.41	0.38	0.38	1.96

Small samples of the exit stream increments from the column were composited for zirconium analyses. The zirconium contents of the A, B, and D wash solutions and of the eluate were negligible. The highest zirconium losses were to the C wash solutions (0.5 M H₂SO₄), in which the zirconium concentration was 0.74-0.94 g/liter:

Solution	Loss of Zr, g					Total
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	
Effluent	0.07	0.07	0.03	0.04	0.03	0.24
C wash	0.08	0.09	0.08	0.09	0.07	0.41
						0.65

For the cyclic test, 300°C zirconium oxide (-15 +80 mesh) was loaded into a glass column (0.8 cm i.d.) to a depth of 28 cm. The total weight of the zirconium oxide was 20 g and the wet-settled volume was approximately 14 ml. Dilute sulfuric acid (pH 1.5) was passed through the column to convert the exchanger to the sulfate form in preparation for the

loading cycle. The procedure for a complete cycle was:

Operation	Solution	Vol, ml	Column Volumes	Flow Rate		Direction of Flow
				ml/min	gal/ft ² /hr	
Adsorption	Synthetic strip	600	42	2.0	60	Down
A wash	Water	100	7	3.0	90	Down
Elution	2 M NaOH	70-90 ^a	5-6.5	0.5	15	Up
B wash	Water	100	7	1.0	30	Up
C wash	0.5 M H ₂ SO ₄	100	7	3.0	90	Down
D wash	Water	100	7	3.0	90	Down

^a 90 ml in cycles 1 and 3, 70 ml in cycles 2, 4, and 5.

The synthetic strip solution analyzed 58 g of V₂O₅ (as V(IV)), 0.6 g of Fe(III), 0.5 g of Al, 0.8 g of phosphate, and 108 g of sulfate per liter at pH 0.4. The solution was adjusted to pH 1.5 with ammonia gas prior to feeding to the column. Adjustment of the solution pH prior to adsorption is considered desirable to minimize zirconium dissolution. In the adsorption, elution, and washing cycles the aqueous stream leaving the column was collected in increments, each of which was analyzed for phosphate.

On the basis of the results from the five-cycle run, reagent costs for the phosphate removal step are estimated at ~2¢ per pound of V₂O₅:

Chemical	Unit Cost, ¢/lb	Estimated Consumption, lb/lb V ₂ O ₅	Cost ¢/lb V ₂ O ₅
NaOH	4.5	0.25	1.1
Zr Oxide	200 ^a	0.004	0.8
			1.9

^a Rough guess of cost in place in column.

The above estimate assumes that the strip solution processed would contain 57 g of V₂O₅ and 0.8 g of phosphate per liter and that two columns in series would be used for the adsorption cycle to allow a phosphate loading on the column of 20 g/1000 g of zirconium oxide. No charge is made for the acid used to convert the column to the acid form* (C wash) since it is assumed that, in plant practice, this would be accomplished with a small portion of the pregnant strip solution which had not been adjusted in pH.

* Acid consumption for the adsorption pretreatment step (C wash) was in the range 0.1-0.15 lb H₂SO₄/lb adsorbent.

The reagent costs shown above are considered conservative since it is believed that the PO_4/V_2O_5 ratio in the pregnant strip solution would normally be much lower than in the above test.

Use of a zirconium oxide adsorption column thus appears, on the basis of very small-scale tests described above, to provide a feasible, low-cost method for separating phosphate from the strip solution. A larger scale evaluation, however, is needed.

9.0 PROCESS FOR SIMULTANEOUS RECOVERY OF URANIUM AND VANADIUM FROM LEACH LIQUORS

From the batch extraction and stripping data previously described, a process scheme (Fig. 9.1) for uranium-vanadium recovery with di(2-ethylhexyl)phosphoric acid as extraction agent was visualized using the following main steps:

1. Adjustment of the liquor pH to 1.8-2.2 and reduction of its ferric iron content to a low level.
2. Simultaneous extraction of the uranium and vanadium with 0.2-0.4 M D2EHPA in kerosene-TBP diluent.
3. Selective stripping of vanadium from the extract with dilute sulfuric acid.
4. Stripping of uranium with a solution of sodium carbonate (to decrease sodium carbonate consumption, only a fraction of the organic stream is stripped of its uranium content in each cycle); the alkaline stripping cycle also serves the important function of stripping extracted contaminants, preventing their buildup in the organic phase beyond a tolerable level.
5. Precipitation of uranium and vanadium from the pregnant strip solutions.

The organic stream leaving the vanadium stripping section is split into two fractions, the first fraction being recycled directly to the next to the last stage of the extraction system, while the other is passed through the uranium stripping section prior to recycle to the last extraction stage.

Preliminary shakedown runs in the countercurrent equipment indicated that the mixing power requirements in the extraction and vanadium stripping circuits were appreciably higher in this system than had been necessary in studies of the Dapex process for uranium recovery alone. It was also

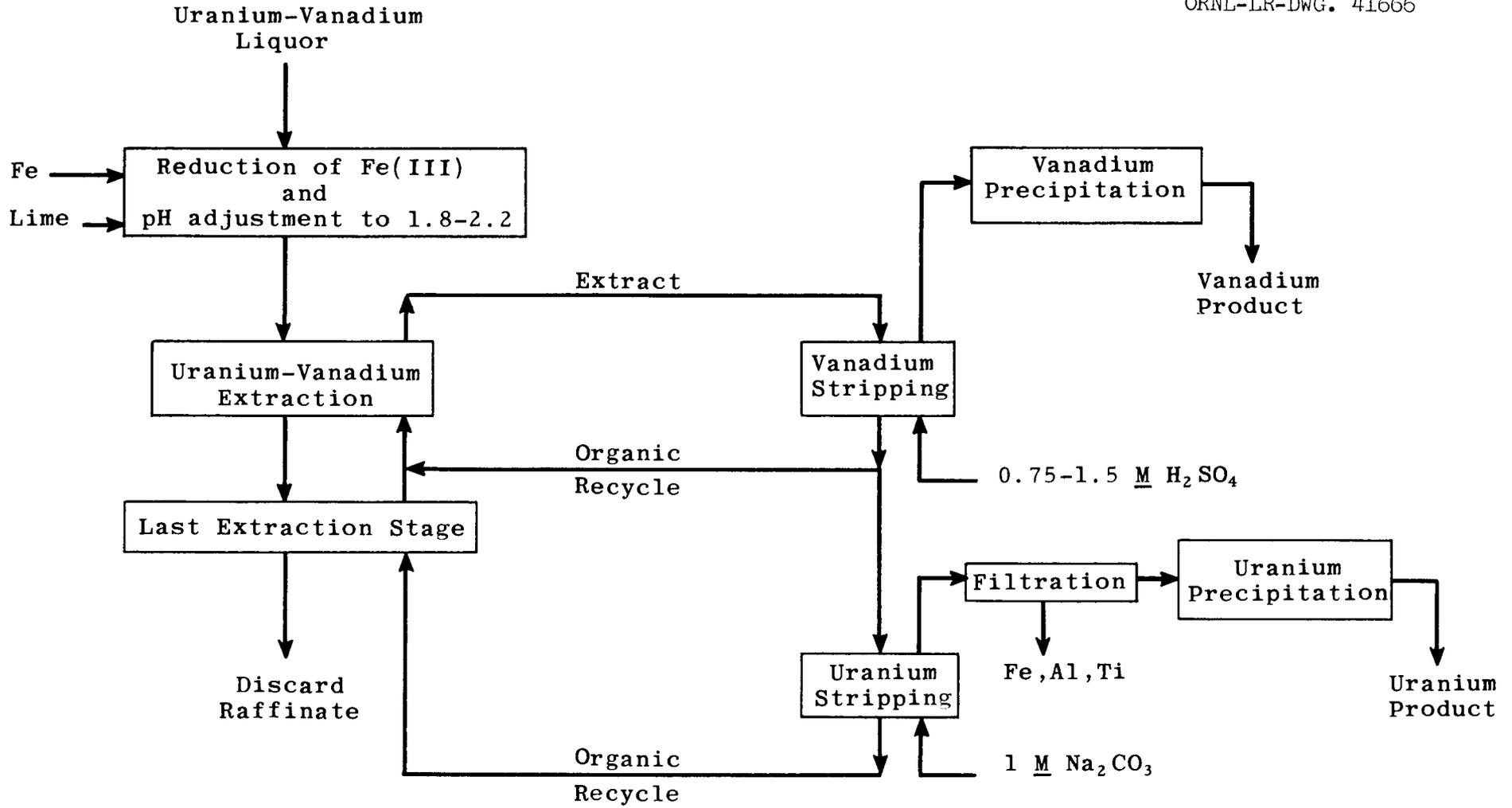


Fig. 9.1. Process for Simultaneous Recovery of Uranium and Vanadium from Leach Liquors. Organic phase: 0.2-0.4 M D2EHPA in kerosene + 0.2 M TBP.

apparent that the uranium stripping operation should be run at elevated temperatures to aid phase separation. Therefore in subsequent test runs the temperature in the uranium stripping circuit was maintained at 35-45°C. Since losses of uranium to the pregnant vanadium strip solution were higher than desirable, a uranium re-extraction stage was used in most test runs to recover most of this uranium with a small portion (~5%) of the organic recycle stream.

9.1 Continuous Runs

Seven continuous runs were made, with either adjusted "Plant D" liquor* (run 6) or synthetic liquors of similar composition, to study the chemical and operational feasibility of the suggested process and to evaluate the effect of such variables as temperature and liquor pH on extraction performance. In all tests, the D2EHPA concentration was in the range 0.30-0.34 M, and the fraction of the organic stream passing through the uranium stripping system in each cycle was regulated at approximately one-third the total organic flow.

A summary of the experimental conditions of continuous runs 1-7 is given in Table 9.1 and details of the operating conditions are given in Tables 9.2 and 9.3. Analyses of the "Plant D" liquor before and after adjustment are given in Table 9.4.

Three different variations of the extraction-stripping circuit were used (Fig. 9.2). In all cases, the organic stream that by-passed the uranium stripping circuit was, because of its high uranium content, recycled to the next to the last rather than to the last extraction stage. The organic stream that passed through the uranium stripping circuit comprised the organic feed to the last extraction stage. In runs 1-3, four extraction stages, three vanadium stripping stages, two uranium stripping stages, and one uranium re-extraction stage were included. The organic feed to the uranium re-extraction stage was split from the organic stream leaving the vanadium stripping system and was recombined with that stream after passing through the uranium re-extraction stage. In runs 4-6 the circuit was changed to include another extraction stage, and the organic feed to the uranium re-extraction stage was split from the organic stream leaving the uranium stripping section rather than from the stream leaving the vanadium stripping section. In run 7 six extraction stages, four vanadium stripping stages, and three uranium stripping stages were used and the organic and

* The "Plant D" liquor was produced by the "acid cure" process.

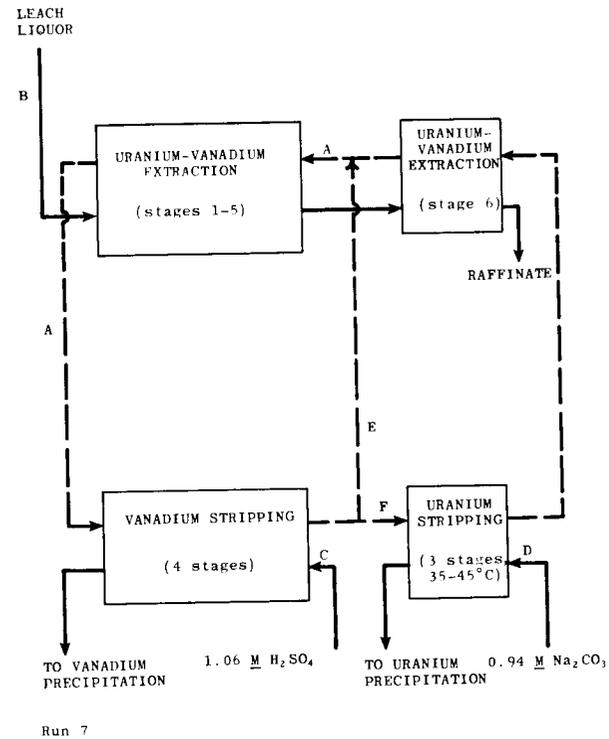
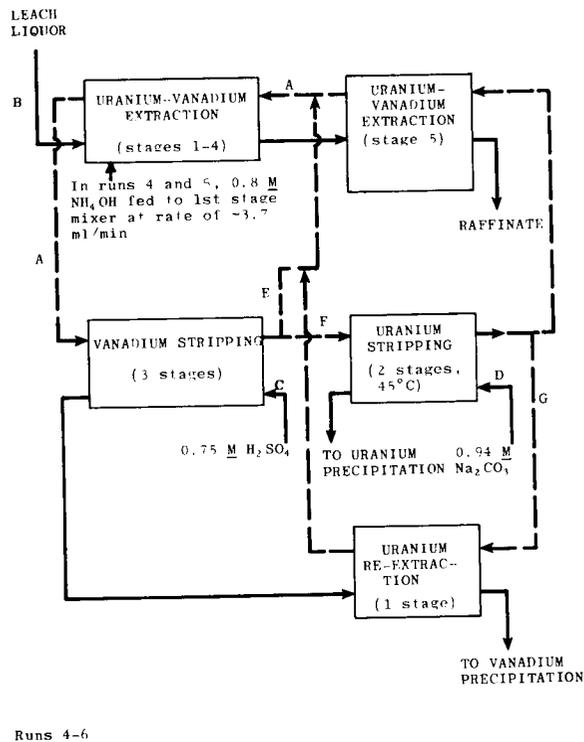
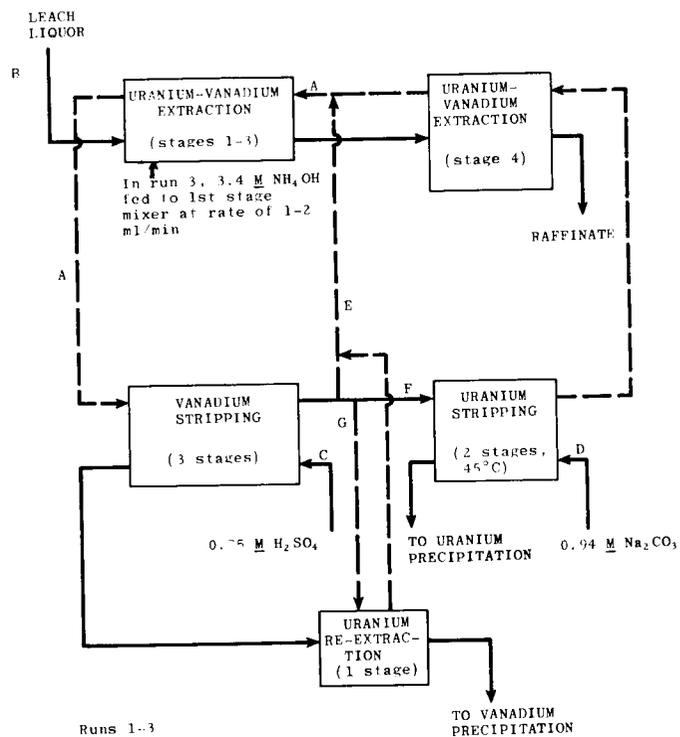


Fig. 9.2. Flow Diagrams for Runs 1-7. — Aqueous flow; --- Organic flow. Flow ratios A/B/C/D/E/F/G - 1/1/0.25/0.10/0.67/0.33/0.05 in runs 1-6 and 1/1.1/0.105/0.085/0.67/0.33/- in run 7.

Table 9.1 Summary of Experimental Conditions for Runs 1-7

Flow diagram: Fig. 9.2

Operating conditions: Tables 9.2 and 9.3

Liquor processed: runs 1-3, S-1; runs 4 and 5, S-2;

run 6, plant D (adjusted); run 7, S-3

NH₄OH fed to first extraction stage in runs 3-5

Run No.	Conc, <u>M</u>			Temp, °C		No. of Stages			
	D2EHPA	TBP	H ₂ SO ₄ for Vanadium Stripping	Extraction	Uranium Stripping	Extraction	Stripping		U Re-extraction
							V	U	
1	0.34	0.15	0.75	Room	40	4	3	2	1
2	0.30	0.15	0.75	45	45	4	3	2	1
3	0.32	0.15	0.75	45	45	4	3	2	1
4	0.30	0.2	0.75	45	45	5	3	2	1
5	0.30	0.2	0.75	Room	45	5	3	2	1
6	0.34	0.2	0.75	Room	45	5	3	2	1
7	0.30	0.2	1.06	Room	35-45	6	4	3	Not used

0.94 M Na₂CO₃ was used for uranium stripping in all tests. Vanadium stripping and uranium re-extraction sections operated at room temperature in all tests.

Table 9.2 Operating Conditions for Runs 1-6^a

Extraction System (stages 1-3 for runs 1-3; stages 1-4 for runs 4-6)

Mixers:	Aqueous feed rate, ml/min	60
	Organic feed rate, ml/min	60
	Residence time, min	2.5
	Turbine speed, rpm	800-1000
Settlers:	Aqueous residence time, min	~1.5
	Organic residence time, min	~1.5

Extraction System (stage 4 for runs 1-3; stage 5 for runs 4-6)

Mixers:	Aqueous feed rate, ml/min	60
	Organic feed rate, ml/min	20
	Residence time, min	3.7
	Turbine speed, rpm	800-1000
Settlers:	Aqueous residence time, min	~1.5
	Organic residence time, min	~4

Vanadium Stripping (3 stages)

Mixers:	0.75 M H ₂ SO ₄ feed rate, ml/min	15
	Organic feed rate, ml/min	60
	Residence time, min	4.0
	Turbine speed, rpm	800-1000
Settlers:	Aqueous residence time, min	~6
	Organic residence time, min	~1.5

Uranium Re-extraction (1 stage)

Mixer:	Aqueous feed rate, ml/min	15
	Organic feed rate, ml/min	3
	Residence time, min	5.5
	Turbine speed, rpm	800-1000
Settler:	Aqueous residence time	~6
	Organic residence time	~30

Uranium Stripping (2 stages)

Mixers:	0.94 M Na ₂ CO ₃ feed rate, ml/min	6
	Organic feed rate, ml/min	20
	Residence time, min	10.5
	Turbine speed, rpm	350
Settlers:	Aqueous residence time, min	~10
	Organic residence time, min	~6

^aUranium and vanadium material balances showed that, in runs 1-3, but particularly in runs 2 and 3, some of the flow rates differed appreciably from the values listed in the above table.

aqueous flow rates were decreased somewhat from those used in runs 1-6 to allow longer residence times in the mixers. The uranium re-extraction stage was not included in this run.

Table 9.3 Operating Conditions for Run 7

Extraction System (stages 1-5)

Mixers:	Aqueous feed rate, ml/min	35
	Organic feed rate, ml/min	32
	Residence time, min	4.5
	Turbine speed, rpm	800-1000
Settlers:	Aqueous residence time, min	~6
	Organic residence time, min	~6

Extraction System (stage 6)

Mixer:	Aqueous feed rate, ml/min	3.5
	Organic feed rate, ml/min	10.5
	Residence time, min	6.6
	Turbine speed, rpm	800-1000
Settlers:	Aqueous residence time, min	~6
	Organic residence time, min	~20

Vanadium Stripping (4 stages)

Mixers:	1.06 M H ₂ SO ₄ feed rate, ml/min	3.4
	Organic feed rate, ml/min	32
	Residence time, min	8.5
	Turbine speed, rpm	800-1000
Settlers:	Aqueous residence time, min	~40
	Organic residence time, min	~8

Uranium Stripping (3 stages)

Mixers:	0.94 M Na ₂ CO ₃ feed rate, ml/min	2.7
	Organic feed rate, ml/min	10.5
	Residence time, min	23
	Turbine speed, rpm	350
Settlers:	Aqueous residence time, min	~50
	Organic residence time, min	~25

Table 9.4 Analysis of Liquors Used in Continuous Tests

	Analysis, g/liter				
	Plant D		Synthetic Leach Liquor		
	Plant D Liquor (as received)	Liquor (adjusted) ^a	S-1	S-2	S-3
U	1.1	1.1	0.85	1.0	1.1
V ₂ O ₅	6.3	6.4	6.6	6.6	6.2
Σ Fe	4.8	5.5	4.6	4.6	6.0
Fe(III)	3.0	0.08	0.3	0.3	0.1
Al	7.3	6.2	6.8	6.8	6.0
Ti	0.24	0.04	-	-	-
Mo	0.012	0.009	-	-	-
SO ₄	110	68	55	55	66
PO ₄	0.4	-	-	-	-
pH	0.5	1.8	1.8	1.8	1.8
EMF, mv ^b	-	280	340	340	330

^aThe liquor was reduced with powdered iron and its pH raised with chemical lime. The precipitated calcium sulfate and excess powdered iron were removed by filtration.

^bPlatinum electrode referred to a saturated calomel electrode, a high positive potential indicating oxidation.

It should be noted that the residence times in the extraction and stripping mixers and settlers (Tables 9.2 and 9.3) are not meant to represent those that would be used in practice. The particular conditions used in these tests resulted from a choice of convenient flow rates as dictated by the size of the contacting equipment and pumps available. The runs were all of 6-10 hr duration, giving approximately six complete cycles of the organic phase through the extraction and vanadium stripping sections (two cycles through the uranium stripping section). Initial runs demonstrated that this was more than sufficient time for all circuits to reach steady-state conditions. Near the end of the run, aqueous and organic samples were removed from each settler to determine the distribution in the system of uranium, vanadium, and contaminants.

It should be pointed out that some data for the first three runs, particularly runs 2 and 3, are not consistent with good material balances. Owing to poor flow control, the o/a feed ratios in these runs differed appreciably from the planned values in Table 9.2. In runs 4-7 the flow rates were controlled much more accurately and the experimental results

are thus more easily interpreted. It should also be noted that runs 1-6 were made primarily to study operation of the extraction circuit and no attempt was made to optimize chemical reagent usage in either the vanadium or uranium stripping circuits. In run 7, however, both these circuits were operated reasonably efficiently, and thus the data for this run are suitable for calculations of chemical reagent requirements for the process.

In all runs phase separation in the extraction and stripping circuits was satisfactory. A brief description of the experimental results is given below. Table 9.5 shows the recoveries of vanadium and uranium in each test.

Run 1 (Table 9.6). The uranium and vanadium were extracted from synthetic leach liquor S-1 with an organic solution of 0.34 M D2EHPA in kerosene + 0.15 M TBP. As the liquor passed through the first three extraction stages, its pH decreased from an initial value of 1.8 to 1.2. In the final extraction stage, the pH rose to 1.6 since the extractant was fed to that stage as the sodium salt.

The raffinate contained 0.73 g of V_2O_5 per liter, corresponding to a vanadium recovery of 89% in the extraction circuit. Uranium recovery in the extraction circuit was >99.9%. The extract contained 0.91 g of iron and 0.16 g of aluminum per liter.

In the vanadium stripping section, 97% of the vanadium and only 0.2% of the uranium were removed from the solvent. About 43% of this uranium was recovered in the uranium re-extraction stage and recycled to the extraction system. Only minor amounts of iron and aluminum were stripped along with the vanadium.

In the carbonate stripping cycle, uranium, iron, and aluminum were essentially completely removed from the organic phase in two stripping stages.

Rough estimates showed stage efficiencies* (for vanadium) of 80-90% in the extraction system and 75-85% in the vanadium stripping system.

The overall vanadium recovery for the run was 88% and the overall uranium recovery, 99.6%.

* Stage efficiencies were estimated by recontacting (2-5 min in separatory funnels) portions of the aqueous and organic samples from the settlers at a phase ratio corresponding to the solution feed ratios and noting the change in vanadium distribution.

Table 9.5 Recovery of Vanadium and Uranium in Runs 1-7

Run No.	Extraction System		V Stripping System		U	U	Overall Recovery, %	
	V	U	V	U	Re-extr'n	Stripping	V ^f	U ^g
	Extr'd, ^a %	Extr'd, ^a %	Stripped, ^b %	Stripped, ^c %	Extr'd, ^d %	Stripped, ^e %		
1	89	>99.9	97	0.2	43	99.7	88	99.6
2	83	99.9	>98	0.4	46	99.8	82	99.0
3	91	99.9	>98	0.5	54	97.5	90	99.1
4	91	>99.9	>98	0.6	89	-	90	>99.7
5	91	>99.9	>98	0.4	88	99.8	91	>99.8
6	94	99.9	96	0.2	91	99.6	93	>99.8
7	92	>99.9	>98	0.3	not used	99.9	91	99.0

^aBased on analyses of feed liquor and raffinate.

^bBased on analyses of organic entering and leaving.

^cBased on analyses of entering organic and pregnant vanadium strip solution.

^dBased on analyses of aqueous entering and leaving.

^eBased on analyses of organic entering and leaving.

^fBased on analyses of feed liquor, raffinate, and organic entering the uranium stripping system

^gBased on analyses of feed liquor, raffinate, and aqueous leaving the uranium re-extraction stage for runs 1-6; based on analyses of the feed liquor, raffinate, and aqueous leaving the vanadium stripping system for run 7.

Table 9.6 Extraction and Stripping Data for Run 1

Test conditions: Tables 9.1 and 9.2 and Fig. 9.2

System	Analysis, g/liter								Vanadium Extr'n	
	Organic				Aqueous				Aq pH	Coefficient (E _a ⁰)
	U	V ₂ O ₅	Fe	Al	U	V ₂ O ₅	Fe	Al		
<u>Extraction</u>										
Stage 1	2.5	6.4	0.91	0.16	0.010	4.5	-	-	1.5	1.4
2	1.8	3.9	0.81	0.16	0.001	2.7	-	-	1.3	1.5
3	1.8	2.1	0.75	0.15	0.001	1.3	-	-	1.2	1.2
4	0.009	3.2	0.41	0.19	<0.0002	0.73	-	-	1.6	4.4
<u>Vanadium Stripping</u>										
Stage 1	2.6	2.0	-	-	0.021	23	0.16	0.089	0.4	-
2	2.5	0.34	-	-	0.018	7.0	0.048	-	0.2	-
3	2.6	0.18	0.82	-	0.016	1.1	0.015	-	0.2	-
<u>Uranium Re-extr'n</u>										
	2.4	0.50	-	-	0.012	23	0.16	-	0.4	-
<u>Uranium Stripping</u>										
Stage 1	a	a	a	a	8.8	0.11	-	-	-	-
2	0.008	<0.09	0.007	0.004	0.52	<0.09	-	-	-	-

^aThird phase formed on standing.

Run 2 (Table 9.7). This run was similar to run 1 with the exception that the extraction system was operated at 45°C rather than at room temperature. Comparison of the results with those of run 1, to determine the effect of increased temperature on extraction efficiency, is not possible since solvent loadings were appreciably different in the two runs. Material balances indicate that the rate of solvent flow through the system in run 2 was lower than planned, resulting in higher solvent loadings. Appreciably more aluminum was extracted than in run 1. This was probably the result of a higher rate of aluminum extraction in the former case owing to the higher extraction temperature (Sec. 6.1a). The iron content of the extract in run 2 was also higher than in run 1 but most of this difference may be attributed to the difference in extraction feed ratios for the two runs. The results in both runs suggest that most of the ferric iron in the liquor was extracted. Owing to the higher loading of the solvent with vanadium, iron, and aluminum, recovery of vanadium in the extraction section in run 2 was only 83%.

More than 98% of the vanadium and 0.4% of the uranium were stripped in the vanadium stripping section. About 46% of this uranium was recovered in the uranium re-extraction stage and recycled to the extraction system.

Overall vanadium and uranium recoveries for run 2 were 82 and 99.0%, respectively.

Run 3 (Table 9.8). Since vanadium extractions are so strongly dependent on pH (Sec. 4.2), the large drop in pH that occurs during extraction severely limits the extraction efficiency. To counteract this effect in run 3, ammonium hydroxide was fed continuously to the mixer of the first extraction stage at a rate sufficient to maintain the raffinate pH at approximately the same value (~1.8) as that of the feed liquor. Under these conditions the pH in the first extraction stage was 2.4. As in run 2, the temperature in the extraction system was maintained at 45°C.

Maintenance of a high pH in the extraction system appreciably improved the vanadium distribution coefficients over those in runs 1 and 2. However, vanadium recovery in the extraction section was improved only slightly, to 91%. Failure to achieve better recovery was due primarily to poor flow rate control since the a/o feed ratio to the extraction system was apparently about 1.45/1 instead of the desired 1/1, the resultant high loading of the solvent limiting the extraction efficiency. Increased extraction of aluminum at the higher pH also tended to lower the vanadium extraction efficiency.

Table 9.7 Extraction and Stripping Data for Run 2

Test conditions: Tables 9.1 and 9.2 and Fig. 9.2

System	Analysis, g/liter								Vanadium Extr'n Aq Coefficient pH (E_a^0)	
	Organic				Aqueous					
	U	V ₂ O ₅	Fe	Al	U	V ₂ O ₅	Fe	Al		
<u>Extraction</u>										
Stage 1	3.4	7.5	1.3	0.55	0.036	5.7	-	-	1.6	1.3
2	2.3	6.4	1.1	0.52	0.010	3.7	-	-	1.4	1.7
3	2.1	3.7	0.88	0.51	0.004	3.4	-	-	1.3	1.1
4	0.019	5.4	0.24	0.61	0.001	1.1	4.1	6.7	1.6	4.9
<u>Vanadium Stripping</u>										
Stage 1	3.4	1.1	1.3	0.36	0.056	19	0.21	0.42	0.3	-
2	3.6	<0.09	1.3	0.35	0.043	2.6	0.09	0.25	0.2	-
3	3.5	<0.09	1.3	0.35	0.045	0.23	0.03	0.10	0.2	-
<u>Uranium Re-extr'n</u>										
	3.4	0.18	1.2	0.34	0.030	19	0.21	0.33	0.4	-
<u>Uranium Stripping</u>										
Stage 1	a	a	a	a	9.4	<0.1	-	-	-	-
2	0.008	<0.05	0.003	0.002	0.58	<0.1	-	-	-	-

^aThird phase formed on standing.

Table 9.8 Extraction and Stripping Data for Run 3

Test conditions: Tables 9.1 and 9.2 and Fig. 9.2

System	Analysis, g/liter								Vanadium Extr'n	
	Organic				Aqueous				Aq pH	Coefficient (E _a ⁰)
	U	V ₂ O ₅	Fe	Al	U	V ₂ O ₅	Fe	Al		
<u>Extraction</u>										
Stage 1	3.1	8.9	1.2	0.82	0.075	6.1	-	-	2.4	1.5
2	2.1	7.8	0.80	0.81	0.015	3.7	-	-	1.8	2.1
3	1.5	5.2	0.90	0.64	0.004	2.0	-	-	1.5	2.6
4	0.06	5.2	0.18	1.1	0.001	0.61	-	-	1.8	8.5
<u>Vanadium Stripping</u>										
Stage 1	2.8	1.5	1.2	0.56	0.061	21	0.25	0.98	0.4	-
2	2.9	<0.09	1.2	0.50	0.050	3.4	0.10	0.27	0.2	-
3	3.1	<0.09	1.1	0.45	0.045	0.34	0.04	0.18	0.2	-
<u>Uranium Re-extr'n</u>										
	3.0	0.40	1.1	0.44	0.028	21	0.25	0.86	0.4	-
<u>Uranium Stripping</u>										
Stage 1	a	a	a	a	13.5	0.09	-	-	-	-
2	0.078	<0.05	0.007	0.006	3.1	<0.09	-	-	-	-

^aThird phase formed on standing.

Stripping of vanadium was >98% complete. Approximately 0.5% of the uranium reported to the vanadium strip solution, but 54% of this uranium was recovered in the uranium re-extraction stage.

After completion of run 3, a third liquid phase was noted in the first uranium stripping stage, indicating that the TBP concentration (0.15 M) in the solvent was not sufficiently high* to maintain the sodium salt of D2EHPA miscible with kerosene. The presence of a third phase had not been noticed during operation of the two previous runs, but organic samples from those runs showed that a third phase had formed on standing. To ensure miscibility, the TBP concentration was increased to 0.2 M in subsequent runs.

Overall recoveries of uranium and vanadium were 99.1 and 90%, respectively.

Run 4 (Table 9.9). In this and subsequent runs micro-bellows pumps rather than rotameters were used to regulate liquid flows and control of the system was much better.

Operating conditions for run 4 were the same as for run 3 except that an extra extraction stage was added, and the amount of ammonium hydroxide fed to the system was considerably decreased. The aqueous pH was 1.7 in the first and 1.6 in the last extraction stage. Vanadium recovery in the extraction system was 91%, the same as in run 3.

More than 98% of the vanadium and 0.6% of the uranium were stripped in the vanadium stripping system. Approximately 89% of this uranium was recovered in the uranium re-extraction stage and recycled to the extraction system. The improved uranium recovery (in the re-extraction stage) in this run was the result of feeding uranium-barren organic (organic leaving the carbonate stripping system) rather than organic containing 2-3 g of uranium per liter (organic leaving the vanadium stripping system) to the uranium re-extraction stage.

Overall recoveries were 90% for vanadium and >99.7% for uranium.

Run 5 (Table 9.10): Operating conditions for run 5 were essentially the same as for run 4 except that the extraction system was operated at room temperature rather than at 45°C. The aqueous pH was 1.8 in the first and 1.7 in the last extraction stage. Extraction of iron and aluminum was 30-40% lower

* The minimum TBP concentration required to maintain miscibility is higher when the carbonate strip system is operated at elevated rather than at ambient temperature.

Table 9.9 Extraction and Stripping Data for Run 4

Test conditions: Tables 9.1 and 9.2 and Fig. 9.2

System	Analysis, g/liter								Vanadium	
	Organic				Aqueous				Aq pH	Extr'n Coefficient (E_a^0)
	U	V ₂ O ₅	Fe	Al	U	V ₂ O ₅	Fe	Al		
<u>Extraction</u>										
Stage 1	3.3	6.4	1.3	0.51	0.037	5.2	-	-	1.7	1.2
2	2.5	4.8	1.0	0.47	0.008	3.2	-	-	1.5	1.5
3	2.4	2.9	0.98	0.47	0.003	2.1	-	-	1.4	1.3
4	2.5	1.6	0.95	0.45	0.003	1.4	-	-	1.3	1.1
5	0.23	2.7	0.47	0.81	<0.0005	0.62	-	-	1.6	4.3
<u>Vanadium Stripping</u>										
Stage 1	3.1	2.3	1.2	0.43	0.084	25	0.23	0.43	0.4	-
2	3.0	0.43	1.0	0.40	0.063	8.8	0.14	0.25	0.3	-
3	3.0	<0.09	1.2	0.38	0.054	1.5	0.17	0.07	0.2	-
<u>Uranium Re-extr'n</u>										
	0.55	2.5	0.13	0.14	0.009	25	0.23	0.30	0.5	-
<u>Uranium Stripping</u>										
Stage 1	0.084	<0.02	0.17	-	11.0	-	-	-	-	-
2	-	<0.02	-	-	0.14	-	-	-	-	-

Table 9.10 Extraction and Stripping Data for Run 5

Test conditions: Tables 9.1 and 9.2 and Fig. 9.2

System	Analysis, g/liter								Aq pH	Vanadium Extraction Coefficient (E_a^0)
	Organic				Aqueous					
	U	V ₂ O ₅	Fe	Al	U	V ₂ O ₅	Fe	Al		
Extraction										
Stage 1	3.0	6.6	0.90	0.31	0.018	4.6	-	-	1.8	1.4
2	2.1	4.5	0.82	0.29	0.002	2.9	-	-	1.5	1.6
3	2.0	2.7	0.75	0.29	0.001	2.0	-	-	1.4	1.4
4	1.8	1.6	0.69	0.28	0.001	1.3	-	-	1.4	1.2
5	0.008	2.5	0.29	0.34	<0.0005	0.59	-	-	1.7	4.2
Vanadium Stripping										
Stage 1	3.1	2.5	0.87	0.30	0.042	24	0.056	0.20	0.4	-
2	2.9	0.57	0.94	0.30	0.062	9.6	0.069	0.11	0.3	-
3	2.9	<0.09	0.85	0.21	0.026	2.1	0.034	0.05	0.2	-
Uranium Re-extr'n										
	0.22	2.1	0.015	0.017	0.005	24	0.068	0.25	0.5	-
Uranium Stripping										
Stage 1	0.11	<0.02	0.008	0.076	9.4	-	-	-	-	-
2	0.005	<0.02	0.007	0.026	0.52	-	-	-	-	-

than in run 4 but other extraction data were essentially the same. Ninety-one percent of the vanadium and >99.9% of the uranium were extracted.

In the vanadium stripping circuit, >98% of the vanadium and 0.4% of the uranium were stripped from the extract. About 88% of this uranium was recovered in the uranium re-extraction circuit.

Overall vanadium and uranium recoveries were 91 and >99.8%, respectively.

Run 6 (Table 9.11). Leach liquor from a western mill (Plant D) was processed in this run. Prior to extraction, the liquor was reduced with powdered iron and its pH was adjusted with lime, giving a feed liquor at pH 1.8 containing 0.08 g of Fe(III) per liter (Table 9.2). In this test ammonium hydroxide was not added to the extraction system for pH control.

Approximately 94% of the vanadium and 99.9% of the uranium were recovered in the extraction system. Iron extraction was considerably lower than in previous runs, reflecting the lower Fe(III) content of the feed liquor.

In the vanadium stripping system, 96% of the vanadium and 0.2% of the uranium were stripped from the solvent. Of this uranium, 91% was recovered in the uranium re-extraction stage.

Overall recoveries were 93% for vanadium and >99.8% for uranium.

Run 7 (Table 9.12). For this run an additional stage was added to the extraction, vanadium stripping, and uranium stripping systems, and the a/o feed ratios in the stripping systems were decreased to give effective loading of the strip solutions. The uranium re-extraction stage was not included in this run since a suitable pump was not available for controlling organic flow to that stage at the very low flow rate desired.

In spite of the additional extraction stage, vanadium recovery in the extraction section was slightly poorer than in run 6, i.e., 92%. More than 99.9% of the uranium was extracted. Apparently the difference in vanadium extraction efficiency for the two runs was due to the lower D2EHPA concentration in run 7 (0.30 M) compared to run 6 (0.34 M), resulting in higher saturation of the extractant in the former case.

Table 9.11 Extraction and Stripping Data for Run 6

Test conditions: Tables 9.1 and 9.2 and Fig. 9.2

System	Analysis, g/liter										Vanadium Extr'n	
	Organic					Aqueous					Aq pH	Coeff. (E _a ^O)
	U	V ₂ O ₅	Fe	Al	Ti ^a	U	V ₂ O ₅	Fe	Al	Ti ^a		
<u>Extraction</u>												
Stage 1	3.1	6.2	0.41	0.20	0.08	0.013	3.7	5.1	6.3	0.03	1.5	1.7
2	2.1	3.4	0.47	0.17	0.07	0.002	2.5	5.1	6.1	0.03	1.3	1.4
3	2.0	2.0	0.39	0.09	0.04	0.002	1.9	5.1	6.2	0.03	1.3	1.1
4	2.0	1.2	0.37	0.06	0.04	0.002	0.98	5.1	6.0	0.03	1.2	1.1
5	0.015	1.7	0.36	0.12	0.02	0.001	0.38	4.8	5.9	0.03	1.6	4.3
<u>Vanadium Stripping</u>												
Stage 1	3.1	3.4	0.36	0.24	0.08	0.023	23	0.19	0.08	0.01	0.5	-
2	3.2	1.2	0.34	0.20	0.08	0.016	13	0.09	0.04	0.01	0.4	-
3	2.7	0.27	0.30	0.20	0.08	0.016	3.6	0.05	0.03	0.01	0.3	-
<u>Uranium Re-extr'n</u>												
	0.18	3.6	-	0.04	0.02	0.002	22	0.18	0.05	0.013	0.5	-
<u>Uranium Stripping</u>												
Stage 1	0.24	<0.09	0.19	-	-	12.4	-	-	-	-	-	-
2	0.012	<0.09	0.02	0.01	-	0.82	-	-	-	-	-	-

^aTitanium material balances are poor.

Table 9.12 Extraction and Stripping Data for Run 7

Test conditions: Tables 9.1 and 9.3 and Fig. 9.2

System	Analysis, g/liter								Aq pH	Vanadium Extraction Coefficient (E _a)
	Organic				Aqueous					
	U	V ₂ O ₅	Fe	Al	U	V ₂ O ₅	Fe	Al		
Extraction										
Stage 1	3.4	6.2	0.69	0.17	0.036	4.8	6.0	6.0	1.6	1.3
2	2.2	4.8	0.67	0.17	0.003	3.2	5.9	6.1	1.5	1.5
3	2.2	3.0	0.66	0.17	0.001	2.1	5.8	6.1	1.4	1.4
4	2.2	1.8	0.59	0.18	0.001	1.5	5.8	6.1	1.4	1.2
5	2.2	1.1	0.58	0.15	0.001	1.2	5.8	6.1	1.3	1.0
6	0.006	2.0	0.32	0.20	0.0001	0.48	5.4	5.9	1.7	4.2
Vanadium Stripping										
Stage 1	3.3	3.9	0.69	0.16	0.10	61	0.12	0.38	0.7	-
2	3.3	1.6	-	0.15	0.073	37	0.10	0.35	0.4	-
3	3.2	0.27	0.72	0.13	0.067	14	0.09	0.23	0.3	-
4	3.2	<0.09	0.71	0.12	0.066	1.9	0.05	0.10	0.2	-
Uranium Stripping										
Stage 1	0.18	<0.09	0.19	0.018	19.0	-	-	-	-	-
2	0.031	<0.09	0.005	<0.002	2.5	-	-	-	-	-
3	0.003	<0.09	0.007	<0.002	0.19	-	-	-	-	-

In the vanadium stripping system, >98% of the vanadium and 0.3%* of the uranium were stripped from the solvent in four stages, giving a strip solution analyzing 61 g of V₂O₅, 0.10 g of uranium, 0.12 g of iron, and 0.48 g of aluminum per liter at pH 0.7.

In the uranium stripping system the 0.94 M Na₂CO₃ strip solution was loaded to 19 g of uranium per liter. Stripping of uranium and contaminants was essentially complete.

Overall recovery of vanadium was 91% and of uranium, 99.0%. The relatively poor recovery of uranium was due to omission of the uranium re-extraction stage from the circuit.

a. Recovery of Vanadium and Uranium from Strip Solutions

Vanadium and uranium were precipitated from the pregnant strip solutions obtained in several of the continuous tests.

Vanadium Recovery. The compositions of the pregnant vanadium strip solutions were approximately:

Run	pH	Sulfate	Amount, g/liter			
		Conc., M	V ₂ O ₅	U	Fe	Al
1	0.4	0.75	23	0.012	0.16	-
2	0.4	0.75	19	0.030	0.21	0.33
3	0.4	0.75	21	0.028	0.25	0.86
5	0.5	0.75	24	0.005	0.068	0.25
6	0.5	0.75	22	0.002	0.18	-
7	0.7	1.06	61	0.10	0.12	0.38

Vanadium was precipitated by adding concentrated ammonium hydroxide to pH 7-7.5, digesting for 2 hr, and filtering. Filtrate analyses showed vanadium recoveries in the precipitate of >99.5% in all tests.

The wet precipitates were calcined at 600°C, giving products containing 93-99% V₂O₅:

* This corresponds to 0.9% of the uranium in the feed liquor.

Run	Analysis of Calcined Product, %				
	V_2O_5	Fe	Al	U	P
1	99	0.75	0.25	0.05	0.03
2	97	0.87	1.4	0.08	0.03
3	93	1.1	3.1	0.12	0.03
5	99	0.27	0.53	<0.01	0.03
6	97	0.72	0.26	<0.01	-
7	95	0.16	0.06	0.10	0.02 ^a

^aCalculated on the basis of the strip solution analysis, assuming that all phosphate reported to the product.

All the products met the specifications for grade (>86% V_2O_5) and phosphorus content (<0.05% P). The products were not analyzed for sulfate to determine whether they met sulfur specifications.

Ammonia requirements for precipitation in run 7 were measured to be 0.61 lb/lb V_2O_5 .

For comparison, vanadium was recovered from a portion of the pregnant strip solution from run 7 by precipitation as "red cake" by the procedure described in Sec. 7.1b. Approximately 0.22 lb of $NaClO_3$ per pound of V_2O_5 (115% of stoichiometric) was used for oxidation. After a 1-hr digestion, the precipitate was filtered, washed with dilute ammonium sulfate solution, and calcined at 600°C. The product analyzed 94% V_2O_5 , 0.08% iron, 0.33% aluminum, and 0.01% uranium. Vanadium recovery in the precipitate was 67%.

Uranium Recovery. Uranium was recovered from the carbonate strip solutions (after filtering to remove precipitated iron and aluminum) by addition of sulfuric acid to pH 2 and then sodium hydroxide (except in runs 6 and 7, where ammonium hydroxide was used) to pH 8. The precipitates were filtered, washed, and dried at 110-120°C yielding products which analyzed 76-88% U_3O_8 :

Run	Analysis of Dried Product, %						
	U_3O_8	V_2O_5	Fe	Al	SO_4	PO_4	Na
1	81	1.4	0.17	0.05	<0.05	-	-
2	81	<0.1	0.39	0.05	-	<0.03	-
3	81	<0.05	0.04	0.05	-	<0.04	-
4	88	-	0.45	0.04	0.35	-	-
5	87	-	0.45	0.04	0.37	-	-
6	76	3.8	0.58	1.7	0.36	0.37	2.4
7	85	0.9	0.21	0.04	0.06	0.07	-

9.2 Estimated Process Reagent Costs

Reagent costs for the proposed process were estimated on the basis of the data accumulated in run 7. In arriving at this estimate, the following general assumptions were made:

1. The process flowsheet and operating conditions would be the same as in run 7 (Fig. 9.2 and Table 9.3) with the exception that the uranium re-extraction stage would be included to improve uranium recovery.

2. The leach liquor to be processed would contain 3 g of Fe(III) per liter (the same as in Plant D liquor) and would be adjusted to pH 1.8 and reduced with powdered iron to give a feed liquor containing <0.2 g of Fe(III) per liter. No charge is made against the extraction process for pH adjustment since it is assumed that neutralization of the waste liquor would be necessary prior to discard.

3. The organic solution would consist of 0.3 M D2EHPA in kerosene + 0.2 M TBP and the feed liquor would contain 6.2 g of V_2O_5 and 1.1 g of uranium per liter. Loadings of the extract and strip solutions and the recovery of vanadium would be the same as in run 7. Overall uranium recovery is assumed to be 99.7%.

4. The pregnant vanadium strip solution would be passed through a zirconium oxide column to remove inorganic phosphate. Vanadium would be precipitated from the column effluent by addition of ammonia to pH 7.

5. Uranium would be recovered from the carbonate strip solution (after filtration to remove precipitated contaminants) by addition of sulfuric acid to destroy the carbonate, and ammonia to precipitate the uranium.

6. Organic loss through entrainment and spillage would be 0.05% of the liquor raffinate volume. The cost of D2EHPA and TBP are taken as \$1.00 and 60¢ per pound, respectively. The cost of kerosene is taken at 14¢ per gallon.

7. Loss of D2EHPA through distribution to the raffinate and acid strip solution would be <5 ppm⁶ and thus of negligible cost significance. Loss of D2EHPA to the carbonate strip solution is estimated at 200 ppm.¹⁶ Loss of TBP² to the raffinate and strip solutions is estimated at 35 ppm.

Owing to the difficulty of apportioning costs between products of a two-product process, the chemical reagent

costs were calculated on the basis of 1000 gal of leach liquor. The reagent costs for recovery of 10.8 lb of U_3O_8 and 47 lb of V_2O_5 from 1000 gal of liquor are estimated at \$7.70 (Table 9.13). Allocating a charge against uranium as previously estimated¹ for uranium recovery alone, i.e., 14¢ per pound of U_3O_8 , reagent charges against vanadium are estimated at approximately 13¢ per pound of V_2O_5 recovered.

It should be noted that these estimated reagent costs are for one particular process arrangement and that alternative process paths, e.g., use of the "red cake" precipitation method, are possible which could give more favorable reagent costs.

Table 9.13 Estimated Chemical Reagent Costs for Uranium and Vanadium Recovery

Basis: 1000 gal of leach liquor containing 10.8 lb of U_3O_8 and 51.5 lb of V_2O_5 ; recovery of 10.8 lb of U_3O_8 (99.7% recovery) and 47 lb of V_2O_5 (91% recovery)

Chemical	Use	Unit Cost	Consumption per 1000 gal Liquor	Cost per 1000 gal Liquor
Powdered Fe	Liquor reduction	6¢/lb	14 lb	\$0.84
H_2SO_4	Vanadium stripping	1.5¢/lb	84 lb	1.26
NH_3	Vanadium precipitation	5.9¢/lb	30 lb	1.77
Na_2CO_3	Uranium stripping	2.3¢/lb	64 lb	1.47
H_2SO_4	Uranium precipitation	1.5¢/lb	24 lb	0.36
NH_3	Uranium precipitation	5.9¢/lb	3 lb	0.18
Organic	Loss by entrainment	\$1.20/gal	0.5 gal	0.60
D2EHPA	Loss through distribution	\$1/lb	0.1 lb	0.10
TBP	Loss through distribution	60¢/lb	0.3 lb	0.18
$ZrO_2, NaOH$	Phosphate removal ^a	-	-	0.94
				\$7.70

^aReagent costs for phosphate removal are estimated at ~2¢ per pound of V_2O_5 (see p 52).

10.0 PROCESSES FOR RECOVERY OF VANADIUM FROM URANIUM-BARREN LEACH LIQUORS

Several process paths have been considered for recovery of vanadium from liquors from which the uranium has already been removed by some method, e.g., solvent extraction or ion exchange. None of the suggested processes have yet been demonstrated in continuous equipment at ORNL,* although the data accumulated for the single-cycle uranium-vanadium process (Sec. 9.1) are useful for defining the expected operation of the acid stripping process (Sec. 10.1).

All the processes considered require a liquor feed of relatively high pH (1.6-2.0) and low ferric iron content. Operations of the extraction system are essentially the same; the processes differ in the way in which the vanadium is stripped and in how it is recovered from the pregnant strip solution.

10.1 Acid Stripping Process

The acid stripping process described above (Sec. 9.1) for single-cycle uranium-vanadium recovery is applicable to vanadium recovery alone. Since it is anticipated that some regeneration of the solvent with a base would be required to avoid buildup of contaminants in the organic recycle stream, the flow pattern visualized is essentially identical to that shown in Fig. 9.1 except that the total organic stream would be recycled to the last extraction stage. In this case the solvent regeneration step corresponds to the uranium stripping step of Fig. 9.1. It is expected that conditions that prove optimum for the single-cycle uranium-vanadium process (with respect to vanadium loading of the extract, concentration of stripping acid, and fraction of the organic phase regenerated in each cycle) will prove to be approximately optimum** for vanadium recovery alone.

* The acid stripping process has been operated on a production basis by Kerr-McGee Oil Industries at Shiprock, N. M., and Carbide Nuclear at Rifle, Colorado.

** It should be noted that this applies to treatment of liquors similar to those obtained in the "acid-cure" or direct leach processes, i.e., liquors that usually have a relatively high vanadium/uranium mole ratio, and would not apply in treatment of liquors in which the vanadium and uranium concentrations are more nearly equal, such as those usually obtained in acid leaching of a water-leached salt-roast calcine.

10.2 Sodium Carbonate Stripping Process

As described earlier (Secs. 6.2 and 7.2), vanadium is stripped readily with sodium carbonate solutions and probably can be recovered from the strip solution by air oxidation and "red cake" precipitation (Fig. 10.1). Examination of this

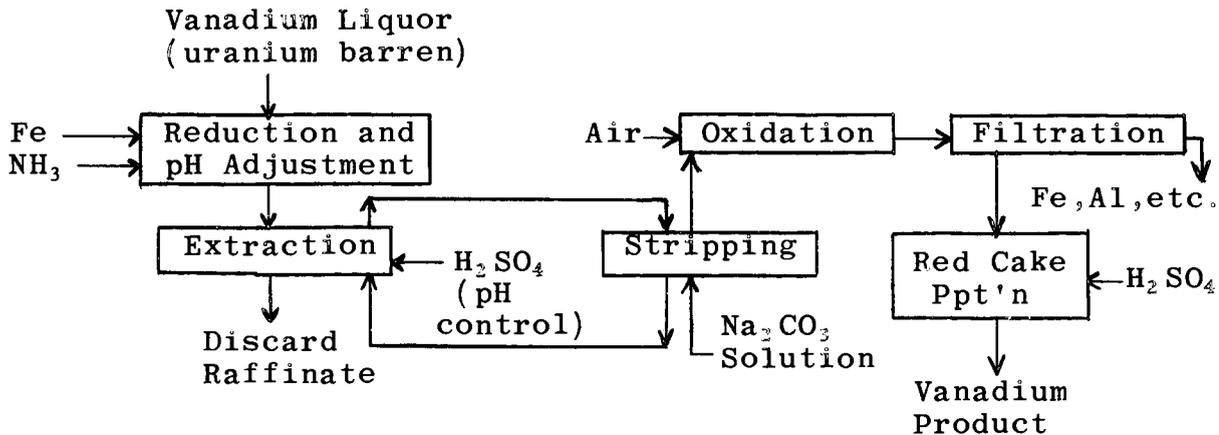


Fig. 10.1 Suggested Sodium Carbonate Stripping Process

approach has thus far been very limited and insufficient to define operational feasibility of the proposed process or to define reagent costs accurately. Oxidation of the vanadium with air appears to be the most difficult step in the process, although the oxidation rate may be sufficiently rapid if the solution is maintained at a high enough pH. Rough estimates suggest that reagent costs for vanadium recovery (assuming that the excess sodium carbonate needed for rapid oxidation would not be excessively high) would be only slightly higher (2-4¢ per pound of V₂O₅) than those anticipated for the acid stripping process. From the standpoint of product marketability, the carbonate stripping process should be attractive in that the vanadium product should be readily fusible.

10.3 Combination Acidic-Basic Stripping Process

Although it has not been checked experimentally, it appears, from the standpoint of reagent consumption, that some advantage could be gained by using the acidic and basic stripping processes in combination. In such a system the major portion of the extract would be stripped with sulfuric acid. A smaller but significant fraction of the extract would be stripped with sodium carbonate. The basic stripping would serve the dual function of stripping vanadium and of removing extracted contaminants from the solvent to ensure that the

contaminant concentration in the total organic recycle stream did not exceed a tolerable level. The carbonate strip solution, after filtration to remove precipitated contaminants, would be combined with the pregnant acid strip solution, and sufficient ammonia would be added to complete the vanadium(IV) precipitation. Use of the carbonate solution to partially neutralize the excess acid in the acid strip solution would decrease ammonia requirements for precipitation. The feasibility of the proposed flowsheet would, of course, depend to some extent on achieving a favorable separation of the colloidal vanadium precipitate from precipitated contaminants during filtration of the pregnant carbonate strip solution.

11.0 REFERENCES

1. C. A. Blake, K. B. Brown, C. F. Coleman, "The Extraction and Recovery of Uranium (and Vanadium) from Acid Liquors with Di(2-ethylhexyl)phosphoric Acid and Some Other Organophosphorus Acids," ORNL-1903 (May 13, 1955).
2. C. A. Blake, D. J. Crouse, C. F. Coleman, K. B. Brown, A. D. Kelmers, "Progress Report: Further Studies of Di-alkylphosphoric Acid Extraction (Dapex) Process for Uranium," ORNL-2172 (Sept. 6, 1956).
3. "Narrative Status Report, Raw Materials Chemistry Section," ORNL-2002 (Dec. 13, 1955).
4. K. B. Brown, C. F. Coleman, D. J. Crouse, A. D. Ryon, "Progress Report on Raw Materials for August, 1957," ORNL-2399.
5. K. B. Brown, C. F. Coleman, D. J. Crouse, A. D. Ryon, "Progress Report on Raw Materials for September, 1957," ORNL-2443.
6. K. B. Brown, C. F. Coleman, D. J. Crouse, A. D. Ryon, "Progress Report on Raw Materials for October, 1957," ORNL-2451.
7. D. C. McLean, "The Technique of Acid Pugging and Curing of Ores," AEC Rept. TID-5156 (June 30, 1953).
8. K. B. Brown, F. J. Hurst, J. M. Schmitt, "Studies of Recovery Processes for Western Uranium-Bearing Ores. XI. The Recovery of Uranium and Vanadium from High Lime Carnotite Ores," AEC Rept. Y-826 (Nov. 9, 1951).

9. V. L. Saine, K. B. Brown, "Studies of Recovery Processes for Western Uranium-bearing Ores. I. A Critical Examination of the Salt-roast, Acid-leach Process for Western Ores. II. Direct Acid-leaching of Western Ores," AEC Rept. AECD-3241 (October 1949).
10. R. E. Musgrove, E. E. Maurer, R. E. Fischer, "Climax Uranium Company's Approach to Vanadium Recovery by Solvent Extraction," AIME Meeting, New York (February 1958).
11. "Deco Trefoil Bulletin No. M4-B90," Denver Equipment Company, January-February, 1957.
12. C. F. Baes, Jr., R. A. Zingaro, C. F. Coleman, "The Extraction of Uranium(VI) from Acid Perchlorate Solutions by Di(2-ethylhexyl)phosphoric acid in n-Hexane," J. Phys. Chem., 62: 129 (1958).
13. Dow Progress Reports for 1950: Dow-23, January; Dow-25, February; Dow-26, March; Dow-31, June; Dow-34, August.
14. D. C. McLean, E. T. Hollis, R. A. Eisenhauer, "Development of an Ion Exchange Process for the Recovery of Vanadium," ACCO-63 (July 30, 1954).
15. K. A. Kraus, H. O. Phillips, "Anion Exchange Properties of Hydrated Zirconium Oxide," J. Am. Chem. Soc., 78: 249 (1956).
16. K. B. Brown, C. F. Coleman, D. J. Crouse, A. D. Ryon, "Progress Report on Raw Materials for November, 1957, ORNL-2466.

12.0 Appendix. COMPARISON OF VANADIUM EXTRACTION ABILITY OF SEVERAL DIALKYLPHOSPHORIC ACIDS

All the process studies on the use of dialkylphosphoric acids for vanadium recovery were made with di(2-ethylhexyl)phosphoric acid (D2EHPA) because it had shown performance characteristics favorable for process use and is readily available commercially. Other dialkylphosphoric acids, however, could have some advantages over D2EHPA with respect to process performance.

The extraction power of D2EHPA for vanadium was measured in comparison to that of two other representatives of this class of reagents. The results (Table 12.1) show bis(3,5,5-trimethylhexyl)phosphoric acid to have vanadium extraction coefficients about twice as high as D2EHPA under comparable test conditions, whereas the extraction performance of the

third compound, bis(di-isobutylmethyl)phosphoric acid, was decidedly inferior. The relative extraction power of these compounds for vanadium(IV) is similar to that shown previously for uranium (ORNL-1903, p 119) where the uranium extraction power of the dialkylphosphoric acids showed correlation with the relative acid strength of the compounds, and both extraction ability and acid strength could be correlated with the extent of branching of the organic side chains.

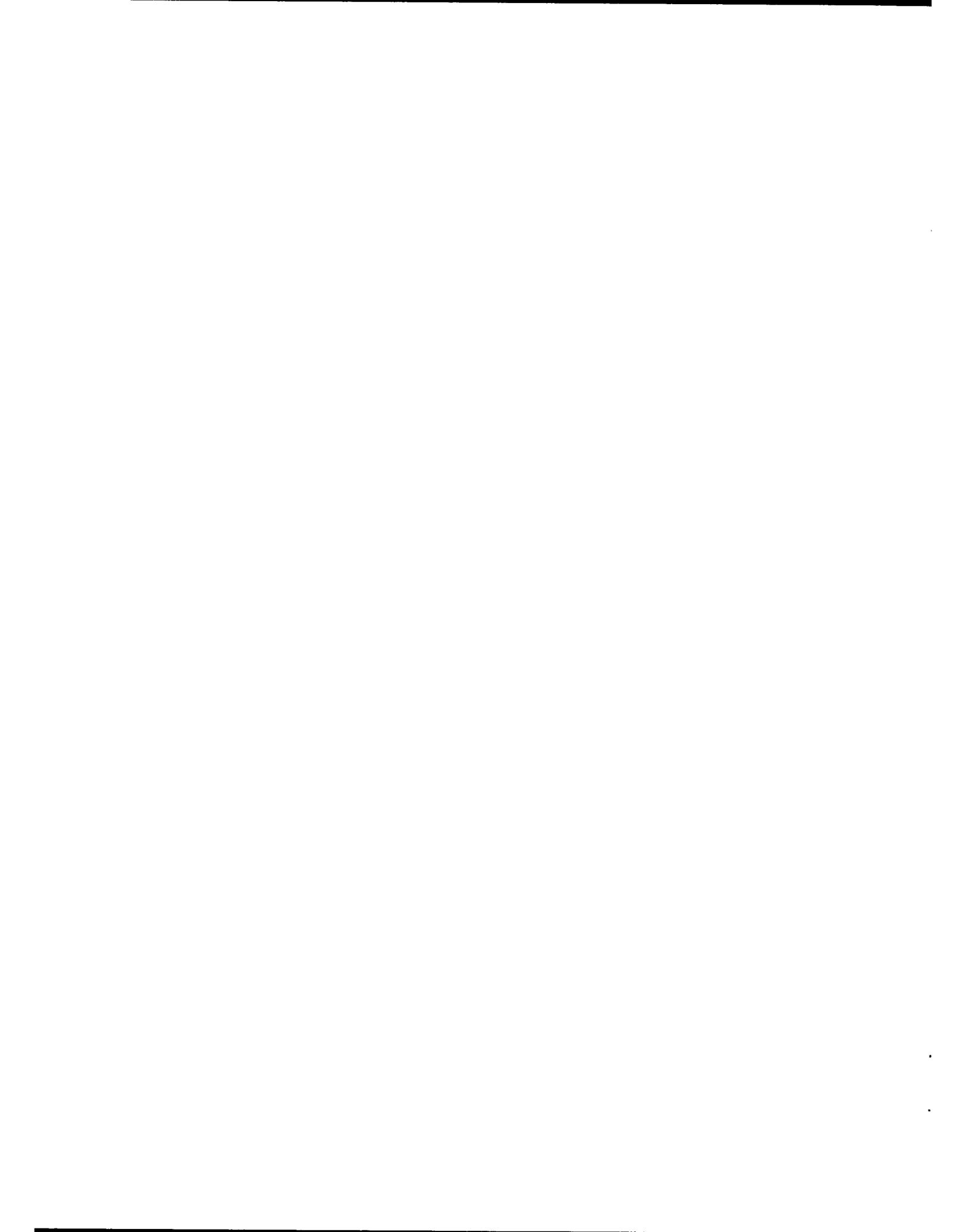
In spite of its relatively high extraction power, bis-(3,5,5-trimethylhexyl)phosphoric acid does not appear to be a suitable process extractant since it forms a kerosene-insoluble complex with ferric iron. Also, cursory tests showed its sodium salt to have limited miscibility with kerosene-TBP diluent. However, the large differences in vanadium extraction power shown for the different compounds suggests that certain other dialkylphosphoric acids might prove as good or better than D2EHPA for use in a vanadium recovery process. Further study would be required to define the most favorable extractant since the choice between compounds would, of course, have to be made, not only on the basis of vanadium extraction power, but also on the basis of other pertinent performance characteristics such as diluent compatibility, selectivity, losses to aqueous liquors, and ease of stripping,* as well as the potential availability of the compound at a reasonable price.

Table 12.1 Extractions of Vanadium(IV) With Dialkylphosphoric Acids

Organic: 0.3 M dialkylphosphoric acid in kerosene + 0.2 M TBP
 Aqueous: VOSO₄-Na₂SO₄ solutions; 0.62 M SO₄, pH 1.5
 Solution A, 0.93 g of V₂O₅ per liter
 Solution B, 4.6 g of V₂O₅ per liter
 Phase ratio, a/o: 1/1
 Contact time: 15 min
 Temperature: 27°C

Dialkylphosphoric Acid	Head Aqueous	Final pH	V ₂ O ₅ , g/liter		Vanadium Extraction Coefficient (E _a ^o)
			Aqueous	Organic	
Di(2-ethylhexyl)	A	1.45	0.28	0.66	2.4
	B	1.35	1.4	3.2	2.3
Bis(3,5,5-trimethylhexyl)	A	1.50	0.16	0.78	4.9
	B	1.35	0.75	4.1	5.5
Bis(di-isobutylmethyl)	A	1.50	0.66	0.31	0.47
	B	1.50	4.3	0.50	0.12

*Compounds with increased vanadium extraction power would be more difficult to strip by acid stripping methods.



INTERNAL DISTRIBUTION

- | | |
|--|---|
| 1. C. E. Center | 66. C. E. Guthrie |
| 2. Biology Library | 67. J. W. Ullmann |
| 3. Health Physics Library | 68. K. B. Brown |
| 4-5. Central Research | 69. K. O. Johnson |
| 6. Reactor Experimental
Engineering Library | 70. B. Weaver |
| 7-26. Laboratory Records Department | 71. J. C. Bresee |
| 27. Laboratory Records, ORNL R.C. | 72. C. A. Blake |
| 28. A. M. Weinberg | 73. J. G. Moore |
| 29. L. B. Emlet (K-25) | 74. K. A. Allen |
| 30. J. P. Murray (Y-12) | 75. C. F. Baes |
| 31. J. A. Swartout | 76. W. D. Arnold |
| 32. E. H. Taylor | 77. F. L. Daley |
| 33. E. D. Shipley | 78. D. E. Horner |
| 34. M. L. Nelson | 79. F. J. Hurst |
| 35-36. F. L. Culler | 80. B. B. Klima |
| 37. W. H. Jordan | 81. R. S. Lowrie |
| 38. J. B. Adams | 82. W. J. McDowell |
| 39. J. H. Frye, Jr. | 83. J. M. Schmitt |
| 40. S. C. Lind | 84. F. G. Seeley |
| 41. G. I. Cathers | 85. J. S. Drury |
| 42. A. Hollaender | 86. J. C. White |
| 43. F. F. Blankenship | 87. J. T. Long |
| 44. M. T. Kelley | 88. R. E. Leuze |
| 45. C. F. Coleman | 89. R. A. McNees |
| 46. R. S. Livingston | 90. J. T. Roberts |
| 47. C. P. Keim | 91. J. R. Flanary |
| 48. D. J. Crouse | 92. W. Davis |
| 49. C. E. Winters | 93. R. H. Rainey |
| 50. A. D. Ryon | 94. R. G. Mansfield |
| 51. D. Phillips | 95. F. A. Kappelmann |
| 52. W. K. Eister | 96. E. M. Shank |
| 53. F. R. Bruce | 97. J. O. Blomeke |
| 54. D. E. Ferguson | 98. C. D. Watson |
| 55. R. B. Lindauer | 99. W. H. Lewis |
| 56. H. E. Goeller | 100. E. Lamb |
| 57. R. A. Charpie | 101. W. R. Grimes |
| 58. M. E. Whatley | 102. P. M. Reyling |
| 59. M. J. Skinner | 103. M. Benedict (consultant) |
| 60. R. E. Blanco | 104. D. L. Katz (consultant) |
| 61. G. E. Boyd | 105. C. E. Larson (consultant) |
| 62. W. E. Unger | 106. J. H. Rushton (consultant) |
| 63. R. R. Dickison | 107. I. Perlman (consultant) |
| 64. A. T. Gresky | 108. H. Worthington (consultant) |
| 65. E. D. Arnold | 109. ORNL - Y-12 Technical Library,
Document Reference Section |

EXTERNAL DISTRIBUTION

- 110. Division of Research and Development, AEC, ORO
- 111. H. L. Hazen, Farmer's Union Bldg., Denver, Colo.
- 112. M. E. Wadsworth, University of Utah
- 113-121. E. C. Van Blarcom, Division of Raw Materials, Washington
- 122-600. Given distribution as shown in TID-4500 (15th ed.) under Technology-
Raw Materials category (75 copies - OTS)