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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mi	mile
g	gram	min	minute
g/L	gram per liter	mL	milliliter
h	hour	mV	millivolt
L	liter	pct	percent
lb	pound	vol pct	volume percent
lb/ton	pound per ton	wt pct	weight percent

VANADIUM-URANIUM EXTRACTION FROM WYOMING VANADIFEROUS SILICATES

By M. Hayashi,[1] I. L. Nichols,[2] and J. L. Huiatt[3]

ABSTRACT

The Bureau of Mines conducted laboratory studies on low-grade vanadiferous silicates from the Pumpkin Buttes and Nine Mile Lake deposits of Wyoming to examine techniques for extracting vanadium and uranium. Recovery from low-grade sources such as these could contribute to future vanadium production and reduce reliance on vanadium imports. The Pumpkin Buttes samples contained 0.03 to 0.04 pct V_2O_5 and 0.06 to 0.12 pct U_3O_8; the Nine Mile Lake samples contained 0.02 to 1.0 pct V_2O_5 and 0.06 to 0.19 pct U_3O_8. Leaching the Pumpkin Buttes samples for 18 h at 80° C with addition of 200 lb/ton H_2SO_4 resulted in recoverey of 80 pct of the vanadium contained in the samples. The Nine Mile Lake samples were readily leached, yielding 78 to 94 pct of the vanadium after 3 h at 80° C with addition of 100 lb/ton H_2SO_4.

A solvent extraction procedure was used to selectively recover uranium from Pumpkin Buttes and Nine Mile Lake leach solutions and to recover vanadium from the raffinates. In batch shakeout tests, Alamine 336 recovered over 95 pct of the uranium from leach solution adjusted to pH 1. Di-2-ethylhexyl phosphoric acid and Cyanex 272 recovered vanadium from the uranium raffinate after reduction and adjustment to pH 2; vanadium extractions of up to 96 pct and 92 pct, respectively, were achieved.

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INTRODUCTION

Vanadium is used primarily as an alloying agent in iron and steel. The addition of even small amounts of it can significantly increase the strength, toughness, ductility, and high-temperature abrasion resistance of steel. Vanadium-aluminum alloys of titanium are widely used in aircraft parts. Vanadium is also important, in the form of its pentoxide, V_2O_5, as a catalyst in the production of sulfuric acid.

In recent years U.S. import reliance for vanadium has ranged from 28 pct in 1979 to 42 pct in 1981. Vanadium availability is affected by factors that are not directly related to demand. For example, only a single domestic deposit is processed solely for its vanadium content--most vanadium is a coproduct of the production of another element, such as iron, phosphorus, or uranium (which alone accounts for as much as 50 pct of domestic vanadium production). Owing to stagnation of the nuclear power industry, with the attendant decrease in both the demand for and price of uranium, the future supply of vanadium from uranium production is uncertain. From a 1978 base, domestic demand for vanadium is expected to increase at an annual rate of about 4 pct through 1990,[4] which should make low-grade or byproduct resources more important in the future. For these reasons the Bureau of Mines has undertaken the evaluation of low-grade domestic vanadiferous resources as potential sources of vanadium. Although the principal objective of this research was to identify potential vanadium resources and techniques for their use, the minerals studied also contained uranium; therefore, analyses of the uranium and methods for separating it from coextracted vanadium are also reported.

A previous Bureau study of techniques for recovering vanadium from low-grade Colorado Plateau carnotite samples[5] showed that 91 pct of the vanadium could be extracted with 400 lb/ton H_2SO_4 and 10 lb/ton $NaClO_3$ in an 18-h leach at 80° C. However, depletion of the Colorado Plateau carnotite ores is expected to cause other low-grade vanadium resources, such as those found in Wyoming, to become important.

Many Wyoming ores now processed for uranium contain 0.01 pct or less V_2O_5. In view of this, the ores used in this study, which contain up to 1.0 pct V_2O_5, are of interest as future resource material. Possibilities for in situ leaching of uranium from Wyoming's Pumpkin Buttes and Nine Mile Lake deposits have been described in earlier publications,[6 7] but these publications presented little information on vanadium recovery.

The Pumpkin Buttes and Nine Mile Lake ores used in the present investigation contain 0.02 to 1.0 pct V_2O_5. By contrast, carnotite ores presently being processed from the Colorado Plateau contain 1.0 to 1.5 pct V_2O_5. Direct-leach studies on the low-grade vanadiferous Wyoming silicates were conducted to determine whether vanadium is recoverable along with uranium using methods similar to those used for processing the Colorado Plateau carnotite ores.

[4]Kuck, P. H. BuMines Mineral Commodity Summaries 1982, pp. 168-69.

[5]Nichols, I. L., G. R. Palmer. and J. L. Huiatt. Extracting Vanadium and Uranium From Low-Grade and Mill-Grade Ores From the Colorado Plateau. BuMines RI 8766, 1982, 16 pp.

[6]Engineering and Mining Journal. Cliffs Readies Uranium Solution Test in Pumpkin Buttes Area. V. 181, No. 1, Jan. 1980, pp. 43 and 47.

[7]Nigbor, M. T., W. H. Engelmann, and D. R. Tweeton. Case History of a Pilot-Scale Acidic In Situ Uranium Leaching Experiment. BuMines RI 8652, 1982, 81 pp.

DESCRIPTION OF ORE SAMPLES

Vanadiferous silicate samples were obtained from deposits in Pumpkin Buttes, which is located in Campbell County, WY, about 85 mi northeast of Casper, and from Nine Mile Lake, which is located about 10 mi north of Casper in Natrona County, WY. Chemical analyses of two samples from Pumpkin Buttes and three samples from Nine Mile Lake are presented in table 1.

Microscopic examinations of the samples from Pumpkin Buttes showed that quartz and feldspar were the most abundant minerals. Smaller amounts of muscovite, biotite, clay minerals, chert, and magnetite minerals were present, as were fragments of volcanic glass. A thin layer of carnotite was observed coating a few of the quartz grains.

Similar examinations of the Nine Mile Lake samples showed that they consisted mainly of quartz, chert, feldspar, clay minerals, and volcanic glass. Small amounts of carnotite coated some of the quartz grains. Minor amounts of hematite and magnetite were also present. Samples 4 and 5 contained less clay material, less black volcanic glass, and fewer carnotite-coated grains than sample 3.

EXPERIMENTAL STUDIES

Bench-scale experiments were performed to compare the extraction of vanadium and uranium from five low-grade vanadiferous silicate samples. Different amounts of H_2SO_4 were used with and without sodium chlorate ($NaClO_3$) oxidant. Batch shakeout tests were conducted on leach solutions to selectively extract uranium and vanadium using different extractants.

ACID AGITATION LEACHING

Comparative experiments were performed using H_2SO_4 in agitation leach tests with 100- and 200-g samples ground to minus 35-mesh. The samples were slurried with acid at a pulp density of 50 pct solids in a 1,000-mL beaker. Tests were conducted to determine the following parameters: (1) reagent addition, (2) duration of leaching, and (3) temperature. Most tests were conducted to approximate plant conditions of 80° C and lasted 18-h.

When $NaClO_3$ was used, it was added to the slurry mixture about 1 h after initiation of a test. This procedure prevented premature consumption of the oxidant by gangue minerals. After leaching, the pregnant leach liquor was filtered from the solid residue, and the pH and emf of the pregnant filtrates were measured to determine the acidity and degree of oxidation. The solid residue was given three displacement washes--two with a pH 1.5 sulfuric acid solution and one with distilled water. A sample of combined pregnant filtrate and wash solution was then collected for analysis. Emf values were determined, in millivolts, using a platinum-saturated calomel electrode couple. (In the tables that

TABLE 1. - Analyses of Wyoming vanadiferous silicate samples

Sample	Analyses, wt pct						
	V_2O_5	U_3O_8	CaO	Fe	Al_2O_3	Mo	SiO_2
Pumpkin Buttes:							
1.....	0.028	0.056	1.64	2.9	9.4	0.01	75.2
2.....	.038	.121	.83	2.2	7.7	.01	58.8
Nine-Mile Lake:							
3.....	1.000	.193	.09	.6	2.8	.01	78.5
4.....	.018	.061	.04	1.1	2.1	.01	78.6
5.....	.270	.099	.04	.7	3.0	.01	74.4

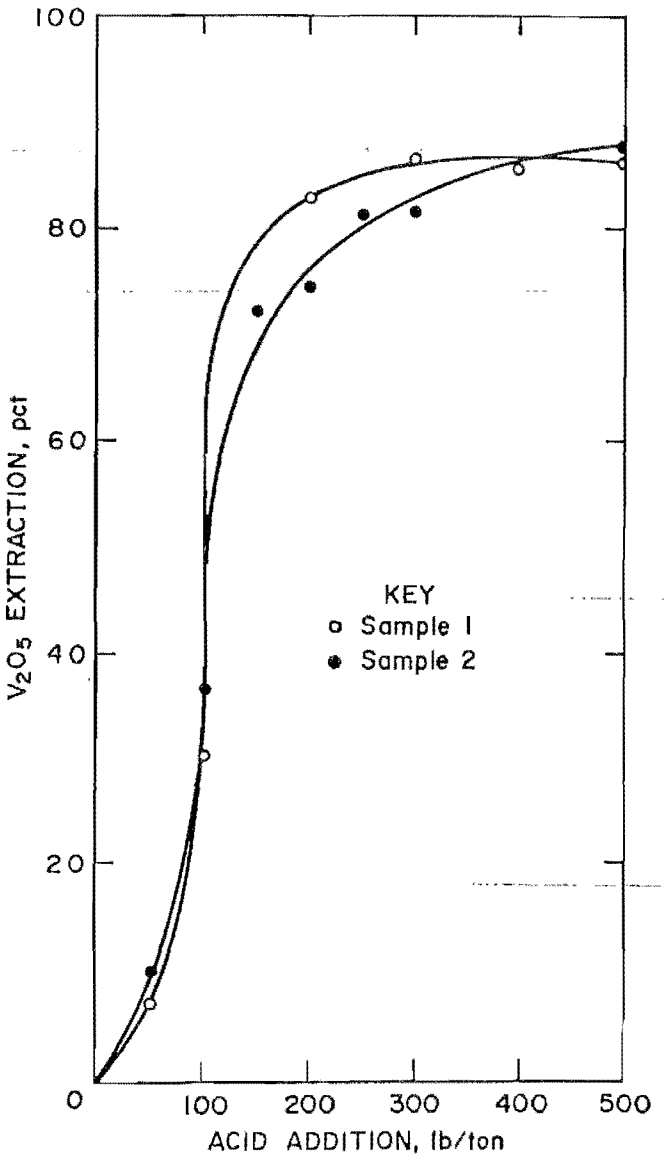

FIGURE 1. - Effect of acid addition on extraction of vanadium from Pumpkin Buttes ore.

follow, higher positive emf values indicate a more highly oxidized state.) Leached residues were dried at 110° C, pulverized, and then analyzed for vanadium and uranium.

Operating conditions and leaching results are presented in tables 2-6 for the five samples. Figures 1 and 2 show the effect of acid additions on the extraction of vanadium from the low-grade vanadium ores of Pumpkin Buttes and Nine Mile Lake.

The best vanadium extraction from sample 1 (Pumpkin Buttes) was 86 pct using 300 lb/ton H_2SO_4; however, extraction of over 80 pct of the vanadium was achieved with only 200 lb/ton acid. The best vanadium extraction from sample 2 was 88 pct, attained with 500 lb/ton acid. Extraction of over 80 pct of the vanadium was achieved from this sample with 250 lb/ton acid.

TABLE 2. - Results of acid agitation leaching of low-grade Pumpkin Buttes ore, sample 1[1]

Test duration, h	Addition, lb/ton		Filtrate		Extraction, pct	
	Acid	$NaClO_3$	pH	emf, mV	V_2O_5	U_3O_8
6.....	200	0	0.9	315	80	98
18.....	50	0	6.6	250	7	43
	100	0	2.7	250	31	90
	200	0	.9	335	83	97
	300	0	.4	345	86	99
	500	0	.0	335	86	96
	100	10	2.2	325	33	95
	200	10	.8	420	72	99
	300	10	.7	435	82	98
	400	10	.3	440	86	98
	500	10	.0	430	85	97

[1]Leach temperature 80° C.

TABLE 3. - Results of acid agitation leaching of low-grade Pumpkin Buttes ore, sample 2[1]

Test duration, h	Addition, lb/ton		Filtrate		Extraction, pct	
	Acid	$NaClO_3$	pH	emf, mV	V_2O_5	U_3O_8
6.....	250	0	0.6	345	80	99
18.....	150	0	1.3	315	72	98
	200	0	1.0	325	75	99
	250	0	.7	350	81	99
	300	0	.4	340	82	99
	500	0	.1	345	88	99
	50	10	2.5	320	10	88
	100	10	1.7	330	37	96
	200	10	1.2	400	69	98
	300	10	.7	420	80	98
	400	10	.7	430	82	98
	500	10	.0	420	88	99
	600	10	.0	430	85	99

[1]Leach temperature 80° C.

TABLE 4. - Results of acid agitation leaching of low-grade Nine Mile Lake ore, sample 3[1]

Test duration, h	Addition, lb/ton		Filtrate		Extraction, pct	
	Acid	$NaClO_3$	pH	emf, mV	V_2O_5	U_3O_8
[2]3.....	100	0	0.4	600	86	97
3.....	100	0	.5	370	94	97
6.....	200	10	.2	630	99	99
18.....	25	0	1.7	380	62	67
	50	0	1.3	335	89	97
	100	0	.9	340	97	98
	25	10	1.6	385	50	56
	100	10	.8	400	95	97
	200	10	.4	405	99	99
	300	10	.0	415	98	98

[1]Leach temperature, 80° C, except as otherwise indicated.
[2]Leach temperature, 22° C.

TABLE 5. - Results of acid agitation leaching of low-grade Nine Mile Lake ore, sample 4[1]

Test duration, h	Addition, lb/ton		Filtrate		Extraction, pct	
	Acid	$NaClO_3$	pH	emf, mV	V_2O_5	U_3O_8
3.....	100	0	0.2	350	78	99
6.....	100	0	.4	305	81	98
18.....	25	0	1.1	310	74	96
	50	0	.7	290	78	98
	200	0	.0	310	85	99
	300	0	.0	300	85	98
	500	0	.0	325	86	99
	50	10	.8	410	77	97
	100	10	.6	390	82	97
	200	10	.0	310	85	99
	300	10	.0	430	85	99

[1]Leach temperature, 80° C.

The Nine Mile Lake ores generally required less acid and leached more readily than the Pumpkin Buttes ores. When sample 3 was leached with 100 lb/ton acid for 3 h, 94 pct of the vanadium was extracted; leaching with 200 lb/ton acid for 6 h yielded 99 pct. Sample 4, containing only 0.02 pct V_2O_5, yielded 85 pct of the vanadium when leached with 200 lb/ton acid for 18 h. Extraction of 96 pct of the vanadium from sample 5 was achieved in 18 h by leaching with 100 lb/ton acid. When leached with 200 lb/ton acid for 6 h, 90 pct of the vanadium was extracted. Addition of $NaClO_3$ did not improve extraction for any of the ore samples.

TABLE 6. - Results of acid agitation leaching of low-grade Nine Mile Lake ore, sample 5[1]

Test duration, h	Addition, lb/ton		Filtrate		Extraction, pct	
	Acid	$NaClO_3$	pH	emf, mV	V_2O_5	U_3O_8
3.....	100	0	0.4	325	78	97
6.....	100	0	.5	300	87	98
	200	0	.3	330	90	99
18.....	25	0	1.2	320	74	97
	50	0	.9	305	84	97
	100	0	.6	320	96	97
	100	10	.6	355	96	98
	200	10	.4	410	97	99

[1]Leach temperature, 80° C.

Uranium extractions over 95 pct were achieved using 100 lb/ton acid on the Pumpkin Buttes ore samples and 50 lb/ton acid on the Nine Mile Lake ore samples. Acid requirements for these ores were lower than those determined for Colorado Plateau carnotite samples.

SOLVENT EXTRACTION

Leaching the low-grade vanadiferous silicate ores solubilized vanadium and other associated constituents such as uranium, aluminum, and iron. Vanadium can be separated from uranium by either ion exchange or solvent extraction; however, selectivity between them by either method depends upon the valence state of the vanadium. In the tetravalent form, vanadium does not form anionic complexes and therefore is not loaded by anion-exchange resins or amine-type solvents. The alkyl phosphoric acids are cation-exchange solvents, and will load both tetravalent vanadium and hexavalent uranium simultaneously.[8]

[8]Merritt, R. C. The Extractive Metallurgy of Uranium. U.S. Atomic Energy Commission, CSM Res. Inst., Golden, CO, 1971, pp. 342-344.

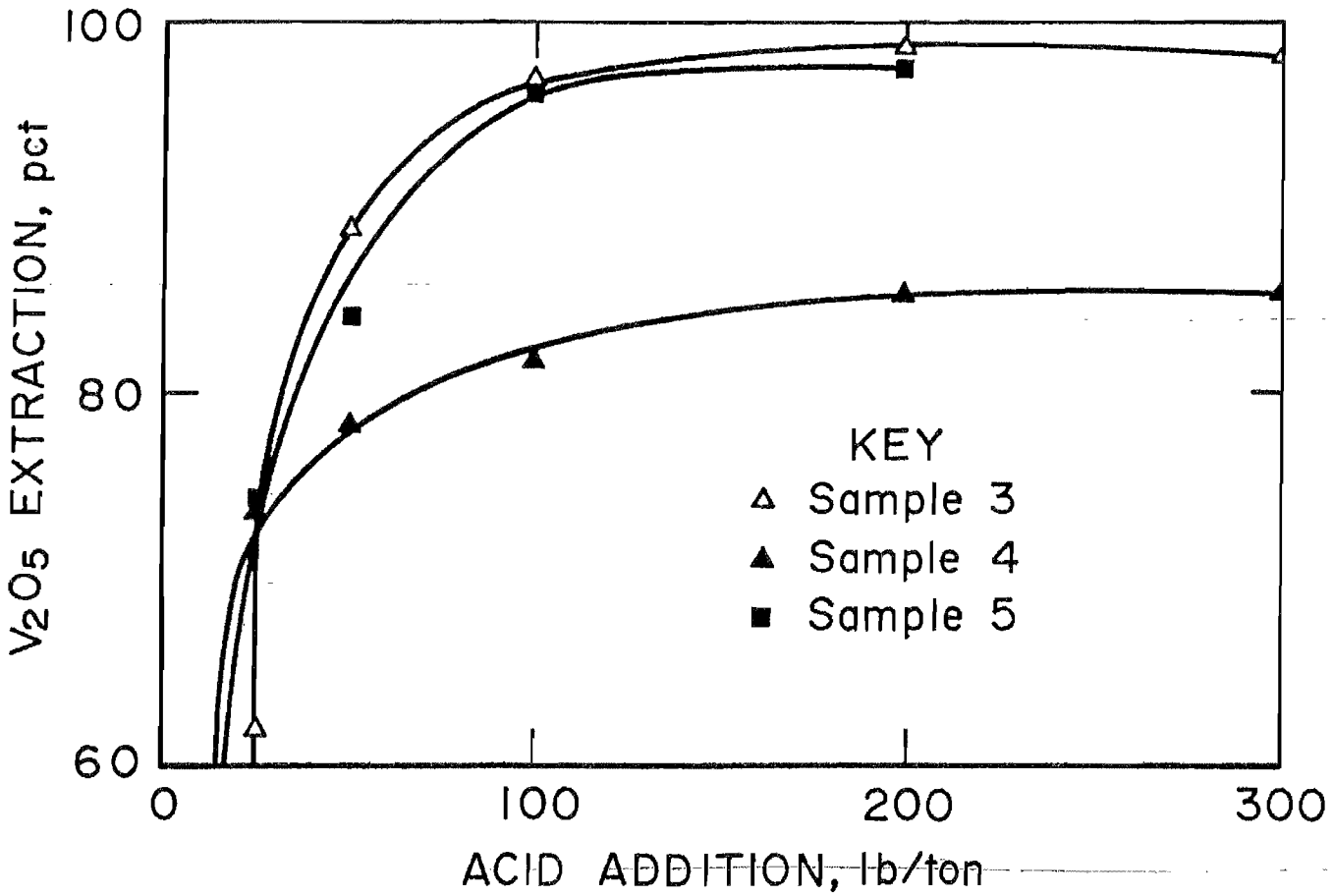

FIGURE 2. - Effect of acid addition on extraction of vanadium from Nine Mile Lake ore.

To determine the best procedure for treating leach solutions from each of the five ore samples, exploratory tests were conducted using several different ion-exchange resins and solvent extractants. Low-grade leach solutions from the acid agitation leach tests were used for these tests. A solvent extraction procedure for treating leach solution from each of the ore samples was selected after several exploratory tests.

To extract uranium, leach solutions were first adjusted to pH 1 with NH_4OH, then shaken for 10 min with 5 vol pct Alamine 336[9] (a tertiary amine) and 2-1/2 pct isodecanol in kerosine. Excellent selectivity and over 95 pct uranium extraction were achieved on leach solutions from both the Pumpkin Buttes and Nine Mile Lake samples.

The raffinate samples, barren of uranium, were adjusted to pH 2 with NH_4OH and either oxidized to greater than 610 mV with $NaClO_3$ or reduced to less than 115 mV with iron powder. The conditioned raffinate was contacted for 10 min with organic extractant. For shakeout tests performed at elevated temperatures, the solution in the separatory funnel was submerged in a water bath at the desired temperature and agitated for 10 min.

Vanadium extraction was more difficult from the Pumpkin Buttes leach solutions than from the Nine Mile Lake leach solutions. This is attributable to the lower vanadium content and higher aluminum and iron content of the Pumpkin Buttes ore. Aluminum crystallized as ammonium aluminum sulfate, hydrate [$NH_4\ Al(SO_4)_2 \cdot 12H_2O$], when NH_4OH was

[9]Reference to trade names or manufacturers is made for identification only and does not imply endorsement by the Bureau of Mines.

added to condition the solutions for extracting vanadium, and iron interfered in the oxidation of vanadium. Organic solvents used to extract vanadium were di-2-ethylhexyl phosphoric acid (D2EHPA) and Cyanex 272, an organophosphorus reagent. A summary of shakeout test results for vanadium extraction from both the Pumpkin Buttes and Nine Mile Lake leach solutions is shown in tables 7 and 8.

The best vanadium extraction, 96 pct, was obtained from the composited Pumpkin Buttes leach solution with 0.25*M* D2EHPA plus 0.125*M* tri-octyl phosphine oxide (TOPO), in a kerosine diluent. In addition, 6 pct D2EHPA plus 3 pct isodecanol (IDA) in kerosine, and 5 pct Cyanex 272 plus 2-1/2 pct IDA in kerosine extracted vanadium from the reduced leach solution at a pH of 2.0 to 2.5. Solvent extraction at 60° C did not improve vanadium recovery significantly compared with recoveries at ambient temperature; however, phase disengagement improved markedly.

Solvent extraction of vanadium from oxidized leach solutions from Nine Mile Lake samples 3 and 5 was effective with 5 pct Alamine 336 plus 5 pct IDA in kerosine. However, for the sample 4 solution, the V_2O_5 content was only 0.06 g/L, and interference by iron in the oxidation of vanadium precluded effective vanadium extractions with Alamine 336. Extraction of vanadium with D2EHPA from the reduced Nine Mile Lake solutions was excellent.

SUMMARY AND CONCLUSIONS

Vanadium and uranium can be leached from the low-grade vanadiferous silicate ores of Pumpkin Buttes and Nine Mile Lake, WY, using H_2SO_4, and can be

TABLE 7. - Summary of shakeout tests for solvent extraction of vanadium from Pumpkin Buttes leach solutions

Organic extractant in kerosine diluent	Aqueous feed V_2O_5, g/L	pH	emf, mV	Temp, °C	A:O	V_2O_5 extraction, pct
COMPOSITED LEACH SOLUTION FROM SAMPLES 1 AND 2						
0.25*M* D2EHPA, 0.125*M* TOPO.....	0.13	2.3	550	22	1:1	68
	.13	2.2	<115	22	1:1	96
LEACH SOLUTION FROM SAMPLE 1						
6 pct D2EHPA, 3 pct IDA.	0.13	2.5	630	22	1:1	28
	.12	2.0	<115	22	1:1	41
	.12	2.3	<115	22	1:1	61
	.12	2.4	<115	60	1:1	63
	.11	2.0	<115	60	1:1	57
	.10	2.0	<115	50	3:1	82
5 pct Cyanex 272, 2-1/2 pct IDA.....	.12	2.0	695	60	1:1	64
	.12	2.2	<115	60	1:1	66
	.11	2.0	570	60	1:1	74
	.11	2.0	<115	60	1:1	79
	.12	2.0	615	50	1:1	82
	.12	2.5	<115	22	1:2	88
	.12	2.5	<115	22	5:1	83
	.12	2.5	<115	22	10:1	68
LEACH SOLUTION FROM SAMPLE 2						
5 pct Cyanex 272.....	0.11	2.0	115	22	1:1	92
	.11	2.0	115	60	1:1	91

A:O Aqueous-to-organic ratio.

TABLE 8. - Summary of shakeout tests for solvent extraction of vanadium from Nine Mile Lake leach solutions

Organic extractant in kerosine diluent	Aqueous feed V_2O_5, g/L	pH	emf, mV	Temp, °C	A:O	V_2O_5 extraction, pct
LEACH SOLUTION FROM SAMPLE 3						
5 pct Alamine 336, 5 pct IDA.....	3.85	2.0	610	22	1:1	72
	3.81	2.0	655	22	1:1	78
	3.85	2.0	610	22	1:1	79
6 pct D2EHPA, 3 pct IDA.....	3.85	2.0	<115	22	3:1	57
	3.85	2.0	<115	22	1:1	89
	3.92	2.6	<115	22	1:1	75
	3.81	2.2	640	22	1:1	74
LEACH SOLUTION FROM SAMPLE 4						
5 pct Alamine 336, 5 pct IDA.....	0.06	2.0	550	50	1:1	31
	.06	2.0	615	50	3:1	7
6 pct D2EHPA, 3 pct IDA.....	.06	2.0	<115	22	4:1	72
	.06	2.0	<115	60	1:1	88
LEACH SOLUTION FROM SAMPLE 5						
5 pct Alamine 336, 5 pct IDA.....	0.79	2.0	600	22	1:1	80
	.95	2.2	600	22	2:1	63
	.95	2.2	600	22	4:1	67
	.95	2.2	600	22	8:1	65
6 pct D2EHPA, 3 pct IDA.....	.91	2.0	<115	22	4:1	74
	.91	2.4	<115	22	4:1	79
	.91	2.4	<115	22	4:1	80
	.91	2.7	<115	22	3:1	88
	.79	2.0	<115	22	1:1	84

A:O Aqueous-to-organic ratio.

recovered by solvent extraction. After adjusting the leach solution to pH 1, uranium was selectively extracted with Alamine 336. Vanadium was extracted from the uranium raffinate with either D2EHPA or Cyanex 272 after the raffinate had been conditioned to pH 2 and reduced with iron powder to less than 115 mV.

Acid agitation leach tests showed that ore samples from Pumpkin Buttes required 200 lb/ton H_2SO_4 to leach 80 pct of the vanadium and 300 lb/ton H_2SO_4 to obtain the best extraction, 86 pct. Ore samples from Nine Mile Lake generally required less acid and leached more readily than the samples from Pumpkin Buttes. Acid additions of 100 lb/ton extracted from 82 to 97 pct of the vanadium in 18 h of leaching at 80° C. Samples leached for only 3 h with 100 lb/ton acid extracted from 78 to 94 pct of the vanadium.

Vanadium is more easily leached from these Wyoming ores than from previously studied carnotite-bearing ores from the Colorado Plateau. For example, the acid requirement (100 to 300 lb/ton) was considerably less than the 400 lb/ton requirement for the Colorado Plateau ores.

Over 95 pct of the uranium was selectively extracted from the leach solutions with Alamine 336. Extraction of vanadium from uranium raffinate adjusted to pH 2 and oxidized with $NaClO_3$ was effective for two of the Nine Mile Lake ore samples. Interference by iron precluded effective vanadium extractions using Alamine 336 from leach solutions of the third Nine Mile Lake sample (sample 4) and the two Pumpkin Buttes ore samples that contained less than 0.13 g/L V_2O_5; however, D2EHPA and Cyanex 272 effectively extracted vanadium from these solutions. The best vanadium extraction, 96 pct, was from a Pumpkin Buttes reduced uranium raffinate solution and was obtained using 0.25*M* D2EHPA plus 0.125*M* TOPO, in kerosine.

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