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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 |
| g | gram |
| g/L | gram per liter |
| h | hour |
| L | liter |
| lb/ton | pound per ton |
| min | minute |
| mL | milliliter |
| mV | millivolt |
| pct | percent |
| psig | pound per square inch |
| vol pct | volume percent |
| wt pct | weight percent |

# VANADIUM EXTRACTION FROM IDAHO MUDSTONES

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

## ABSTRACT

The Bureau of Mines conducted laboratory studies on Idaho mudstones to examine techniques for extracting vanadium. Recovery of vanadium from low-grade sources could contribute to future vanadium production and reduce reliance on imports.

An Idaho mudstone surface sample containing 0.30 pct $V_2O_5$ and an underground sample containing 0.21 pct $V_2O_5$ were used in the extraction tests. Leaching of the surface sample for 18 h at 80° C with the addition of up to 1,000 lb/ton $H_2SO_4$ recovered 70 pct of the vanadium. However, leaching of the underground sample under the same conditions recovered only 47 pct. By adding 15 wt pct NaCl and roasting the samples at 750° C for 2 h, followed by leaching with 800 lb/ton $H_2SO_4$, vanadium extractions were increased to 78 pct from the surface sample and 83 pct from the underground sample. Water leaching of samples roasted at 750° C for 4 h with a 25-wt-pct NaCl addition yielded about 60 pct of the vanadium from both surface and underground samples. Autoclave leaching at 200° C for 3 h with 1,000 lb/ton $H_2SO_4$ extracted 97 pct of the vanadium from the surface sample and 86 pct from the underground sample.

An exploratory solvent extraction investigation to purify and concentrate vanadium in the leach solution using several organic reagents was also conducted.

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## INTRODUCTION

Vanadium is classified as a strategic and critical material because it is essential for use in equipment for defense, energy production, and transportation and because the United States relies on imports for much of its supply of vanadium (1).[4] Vanadium is primarily used as an alloying agent for iron and steel. Less than 0.1 pct V added to an ordinary carbon steel can significantly increase its strength and improve its toughness and ductility. Vanadium is also important in the production of titanium alloys and as a catalyst in the production of $H_2SO_4$ and key intermediate organic chemicals (1).

The United States produced 6,365 tons of vanadium from domestic sources in 1981, or about 66 pct of the U.S. demand. The remaining 34 pct of the U.S. demand was met largely by imports of ferrovanadium, vanadium pentoxide ($V_2O_5$), and vanadium-bearing feed materials such as slags, residues, and ashes. Vanadium produced in the United States is usually a byproduct or coproduct of uranium or phosphate mining; thus the vanadium supply depends partially on the mining of uranium or phosphate. Over half of the vanadium mined in the United States is recovered as a coproduct with uranium from carnotite in sandstone mined on the Colorado Plateau. Because of the depressed uranium market, domestic vanadium production has been significantly reduced. The recent decline in world steel production has depressed the market for vanadium; however, when the steel industry recovers, domestic vanadium producers may not be able to satisfy the demand, and a much greater dependence on imports could result (1).

To meet the Nation's demand for this critical material, other vanadium resources will have to be developed in the future, particularly as high-grade carnotite deposits become depleted. Additional domestic vanadium sources include phosphoritic shales in Idaho and Wyoming (2), dolomite shales in Nevada (3), metalliferous oil shales in central Montana and northeastern Nevada (4), and low-grade carnotite deposits in the Colorado Plateau (5).

Techniques for recovering vanadium from Colorado and Wyoming low-grade ore samples were examined in previous Bureau of Mines studies (5-6). Results showed that up to 91 pct of the vanadium was extracted from low-grade carnotite ores of the Colorado Plateau by leaching with 400 lb/ton $H_2SO_4$ and 10 lb/ton $NaClO_3$, and 80 pct of the vanadium was extracted from low-grade Pumpkin Buttes, WY, samples with 200 lb/ton $H_2SO_4$. Nine Mile Lake samples from Wyoming were readily leached to recover up to 94 pct of the vanadium.

This Bureau study was conducted to examine several techniques for extracting vanadium from Idaho mudstone samples. Idaho mudstone is an extensive potential vanadium-uranium resource that occurs in the McGowan Creek Formation of Idaho and Montana (7-8). The techniques examined were acid agitation, roast and autoclave leaching treatments, and purification of the leach solutions by solvent extraction.

## DESCRIPTION OF ORE SAMPLES

Two mudstone ore samples collected near Dubois, ID, were used in this investigation. Chemical analyses of the samples are presented in table 1. The surface ore sample (sample 1) contained 0.30 pct $V_2O_5$ and 0.03 pct $U_3O_8$, and the underground ore sample (sample 2) contained 0.21 pct $V_2O_5$ and 0.004 pct $U_3O_8$. Analyses of sized sample fractions (table 2) showed that vanadium was uniformly disseminated throughout the samples.

Microscopic examination showed that the two ore samples were shale or mudstone, consisting mostly of quartz and some

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

illite clay. Neither sample was very calcareous. Sample 1 was a brown oxidized surface sample; sample 2 was a black unoxidized underground sample. X-ray diffraction patterns showed that feldspar and limonite were also present. The samples contained traces of titanium, lead, nickel, and molybdenum. Because of the fine grain of the samples, isolation and identification of the vanadium mineral was not possible.

TABLE 1. - Analyses of Idaho mudstone samples, wt pct

| | Sample 1 (surface) | Sample 2 (underground) |
|---|---|---|
| $V_2O_5$...... | 0.30 | 0.21 |
| $U_3O_8$...... | .03 | .004 |
| C......... | .1 | 4 |
| $SiO_2$...... | 83.1 | 80.7 |
| $Al_2O_3$..... | 5.9 | 4.7 |
| Fe........ | 1.8 | 2.2 |

TABLE 2. - Wet-screen analyses of minus 35-mesh samples

| Particle size, mesh | wt pct | $V_2O_5$ analysis, pct | $V_2O_5$ distribution, pct |
|---|---|---|---|
| SAMPLE 1 | | | |
| Minus 35 plus 48.. | 32.3 | 0.27 | 28.8 |
| Minus 48 plus 65.. | 9.1 | .30 | 9 |
| Minus 65 plus 100. | 6.7 | .31 | 6.9 |
| Minus 100 plus 150 | 10.7 | .34 | 12 |
| Minus 150 plus 200 | 5 | .31 | 5.1 |
| Minus 200......... | 6.2 | .32 | 38.2 |
| Calculated head. | 100.0 | .30 | 100.0 |
| Assay head........ | NA | .30 | NA |
| SAMPLE 2 | | | |
| Minus 35 plus 48.. | 37.1 | 0.17 | 33.1 |
| Minus 48 plus 65.. | 13.3 | .18 | 12.5 |
| Minus 65 plus 100. | 10.6 | .20 | 11.1 |
| Minus 100 plus 150 | 6.2 | .18 | 5.8 |
| Minus 150 plus 200 | 6.7 | .21 | 7.4 |
| Minus 200......... | 26.1 | .22 | 30.1 |
| Calculated head. | 100.0 | .19 | 100.0 |
| Assay head........ | NA | .2 | NA |

NA Not applicable.

## EXPERIMENTAL PROCEDURES AND RESULTS

Bench-scale experiments were performed to compare methods of vanadium extraction from the two low-grade Idaho mudstone samples. These methods included the following: (1) acid agitation leaching, (2) roasting followed by acid or water agitation leaching, and (3) autoclave acid leaching. Batch solvent extraction shakeout tests using different organic reagents to selectively extract vanadium from leach liquors were compared. Uranium extraction is not reported because the samples contained less than 0.03 pct $U_3O_8$.

### ACID AGITATION LEACHING

Leaching experiments were conducted to determine the effect of acid and sodium chlorate ($NaClO_3$) additions. A 200-g charge of minus 35-mesh mudstone was slurried with 100 to 1,000 lb/ton $H_2SO_4$ at 50 pct solids in a 1,000-mL beaker. When the $NaClO_3$ oxidant was used, it was added to the slurry mixture about 1 h after the test was initiated. This procedure prevented premature consumption of the oxidant by gangue minerals. After leaching for 18 h at 80° C, the pregnant leach liquor was filtered from the residue, and the pH and emf of the pregnant filtrates were measured to determine acidity and degree of oxidation. Emf values in millivolts were determined using a platinum-saturated calomel electrode couple. The residue was given three 100 mL displacement washes--two with an $H_2SO_4$ solution of pH 1.5 and one with distilled water. A solution sample of combined pregnant filtrate and wash solution was then collected for analysis. Higher positive emf values indicated higher oxidation states. Leached residues were dried overnight at 110° C, pulverized, and analyzed for vanadium and uranium.

Operating conditions and leaching results for the two low-grade mudstone samples are presented in table 3; the effect of acid additions on the vanadium extraction from these samples is also shown in figure 1. These results show that vanadium extraction increased directly with acid addition. For sample 1, the vanadium extraction increased from 26 pct with 100 lb/ton acid to 70 pct with 1,000 lb/ton acid. For sample 2, the vanadium extraction increased from 11 pct with 100 lb/ton acid to 47 pct with 1,000 lb/ton acid. The addition of $NaClO_3$ was not beneficial to the extraction.

TABLE 3. - Acid agitation leaching results[1]

| $H_2SO_4$ addition, lb/ton | Filtrate | | | | | |
|---|---|---|---|---|---|---|
| | pH | emf, mV | Analyses, g/L | | | $V_2O_5$ extraction, pct |
| | | | $V_2O_5$ | Al | Fe | |
| SAMPLE 1 | | | | | | |
| 100..... | 1.0 | 410 | 0.34 | 0.9 | 3.6 | 26 |
| 200..... | .5 | 430 | .57 | 1.7 | 7.8 | 41 |
| 400..... | 0 | 430 | .67 | 2.8 | 8.2 | 47 |
| [2]400..... | 0 | 665 | .59 | 2.5 | 7.9 | 46 |
| 600..... | 0 | 425 | .81 | 3.6 | 8.4 | 58 |
| [3]600..... | 0 | 500 | .80 | 3.7 | 8.8 | 57 |
| 800..... | 0 | 450 | .82 | 3.9 | 8 | 60 |
| 1,000..... | 0 | 445 | .90 | 4.9 | 8.2 | 70 |
| SAMPLE 2 | | | | | | |
| 100..... | 0.7 | 370 | 0.10 | 0.5 | 4.2 | 11 |
| 200..... | .2 | 400 | .16 | .8 | 7.8 | 14 |
| 400..... | 0 | 380 | .22 | 1.3 | 6.9 | 22 |
| [2]400..... | 0 | 510 | .13 | .5 | 6.2 | 15 |
| 600..... | 0 | 380 | .31 | 1.6 | 7.1 | 32 |
| 800..... | 0 | 410 | .37 | 2.1 | 7.3 | 41 |
| 1,000..... | 0 | 435 | .42 | 2.2 | 7.5 | 47 |

[1] Leach temperature, 80° C; test duration, 18 h.

[2] $NaClO_3$ addition, 10 lb/ton.

[3] $NaClO_3$ addition, 5 lb/ton.

Leaching impurities such as aluminum and iron also directly increased with increased acid addition and affected solvent extraction as described in the "Solvent Extraction" section. For sample 1, aluminum concentration in the leach solution increased from 0.9 g/L with 100 lb/ton acid to 4.9 g/L with 1,000 lb/ton. For sample 2, aluminum concentration in the leach solution increased from 0.5 g/L with 100 lb/ton acid to 2.2 g/L with 1,000 lb/ton. With 100 lb/ton acid, 3.6 g/L Fe was leached from sample 1 and 4.2 g/L Fe was leached from sample 2. With additions greater than 200 lb/ton acid, 6.2 to 8.8 g/L Fe was leached from both samples.

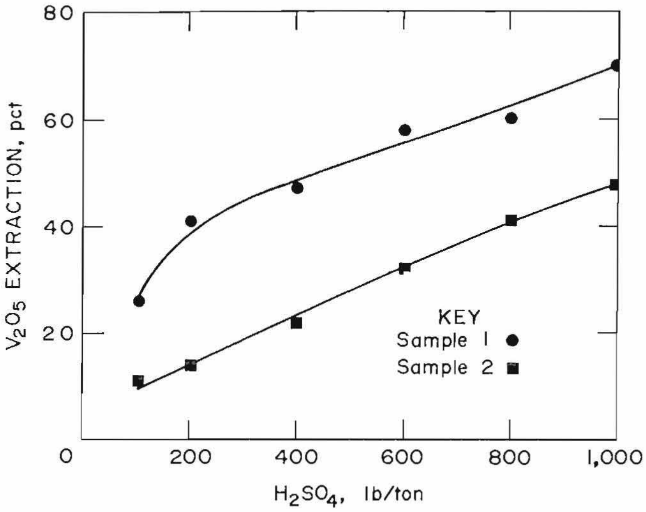

FIGURE 1. - Effect of acid addition on vanadium extraction (18-h leach at 80° C).

ROAST LEACHING

Roasting has been shown to be an effective pretreatment method for improving vanadium extraction from vanadium-uranium ores (5). The ore is roasted with common salt primarily to increase the solubility of the vanadium.

To improve the vanadium extraction from Idaho mudstone, a series of roast-leach tests was conducted. As in the acid agitation tests, a 200-g charge of minus 35-mesh size ore was used. Samples were placed in ceramic boats and heated in a muffle furnace at the desired temperature (as shown in tables 4 and 5) for 1 to 6 h. During roasting, the sample was rabbled every 30 min. After roasting, the calcines were air cooled to room temperature, and the material was leached by acid agitation for 18 h at 80° C and 50 pct solids. The residue was washed as described in the "Acid Agitation Leaching" section. Results of the roast-leach tests, showing the effects of roast temperature, NaCl addition, roast time, and

TABLE 4. - Roast leaching test conditions and results, sample 1[1]

| Roast conditions | | | $H_2SO_4$ addition, lb/ton | Filtrate | | | | | $V_2O_5$ extraction, pct |
|---|---|---|---|---|---|---|---|---|---|
| Temp, °C | Time, h | NaCl addition, wt pct | | pH | emf, mV | Analyses, g/L | | | |
| | | | | | | $V_2O_5$ | Al | Fe | |
| EFFECT OF ROAST TEMPERATURE | | | | | | | | | |
| 500 | 2 | 10 | 200 | 0.5 | 515 | 0.58 | 2.9 | 6.5 | 38 |
| 700 | 2 | 10 | 200 | .9 | 650 | .71 | 4.2 | .3 | 47 |
| 750 | 2 | 10 | 200 | .6 | 630 | 1.13 | 4.1 | .3 | 62 |
| 775 | 2 | 10 | 200 | .5 | 690 | 1.30 | 4.4 | .3 | 63 |
| 800 | 2 | 10 | 200 | .6 | 655 | 1.10 | NA | NA | 61 |
| 850 | 2 | 10 | 200 | .4 | 660 | .60 | 3.1 | .3 | 45 |
| 900 | 2 | 10 | 200 | .5 | 615 | .15 | NA | NA | 14 |
| EFFECT OF NaCl ADDITION IN ROAST | | | | | | | | | |
| 750 | 2 | 0 | 200 | 0.5 | 685 | 0.58 | 3.6 | 1.1 | 41 |
| | | 5 | 200 | 1 | 640 | .87 | 4.5 | .2 | 52 |
| | | 10 | 200 | .6 | 630 | 1.13 | 4.1 | .3 | 62 |
| | | 15 | 200 | .3 | 700 | 1.12 | 3.1 | .2 | 70 |
| | | 25 | 200 | .3 | 700 | 1.04 | 2.1 | .2 | 75 |
| EFFECT OF ROAST TIME | | | | | | | | | |
| 750 | 1 | 10 | 200 | 0.7 | 710 | 0.91 | 4.4 | 0.2 | 53 |
| | 2 | 10 | 200 | .6 | 630 | 1.13 | 4.1 | .3 | 62 |
| | 4 | 10 | 200 | .4 | 645 | .95 | 2.7 | .2 | 68 |
| | 6 | 10 | 200 | .6 | 705 | .98 | 1.2 | .2 | 63 |
| EFFECT OF $H_2SO_4$ ADDITION IN LEACH | | | | | | | | | |
| 750 | 2 | 15 | 0 | 7.5 | 100 | 0.59 | 0.002 | 0.001 | 45 |
| | | | 200 | .3 | 700 | 1.12 | 3.1 | .2 | 70 |
| | | | 500 | 0 | 700 | 1.16 | 3.9 | 2.2 | 76 |
| | | | 800 | 0 | 775 | 1 | 4.4 | 4.8 | 78 |
| WATER LEACH | | | | | | | | | |
| 750 | 4 | 15 | 0 | 8.6 | 200 | 0.63 | <0.01 | <0.01 | 51 |
| | | 25 | 0 | 8.2 | 175 | .78 | <.01 | <.01 | 61 |
| | | 35 | 0 | 8.2 | 135 | .75 | <.01 | <.01 | 63 |

NA Not available.

[1] Leach temperature, 80° C; test duration, 18 h.

$H_2SO_4$ addition on the vanadium extractions, are summarized in tables 4 and 5 and illustrated in figures 2 through 5.

Figure 2 shows that the best roasting temperature ranged from 750° to 800° C. The roast duration was 2 h, and the NaCl addition was 10 wt pct. Agitation leaching of the calcines roasted at 750° to 800° C, using 200 lb/ton $H_2SO_4$, extracted more than 60 pct of the vanadium. Figure 3 shows that a 4-h roast at 750° C with 10 wt pct NaCl yielded vanadium extractions of 68 pct for sample 1 and 70 pct for sample 2.

Vanadium extraction was increased by both NaCl addition in the roast and acid addition in the leach. Figure 4 shows that NaCl addition in a 750° C roast improved the extraction from 41 pct with no NaCl added to 75 pct with a 25-wt-pct-NaCl addition for sample 1 and from 32 pct with no NaCl added to 75 pct with a 25-wt-pct-NaCl addition for sample 2. Figure 5 shows the effect of acid addition on vanadium extraction from calcines produced in a 2-h 750° C roast with 15 wt pct NaCl. For sample 1, vanadium extraction with no acid (water leach) was 45 pct and increased to 78 pct with 800 lb/ton acid. For sample 2, the extraction was 48 pct with a water leach and increased to 83 pct with 800 lb/ton.

TABLE 5. - Roast leaching test conditions and results, sample 2[1]

| Roast conditions | | | $H_2SO_4$ addition, lb/ton | Filtrate | | | | | $V_2O_5$ extraction, pct |
|---|---|---|---|---|---|---|---|---|---|
| Temp, °C | Time, h | NaCl addition, wt pct | | pH | emf, mV | Analyses, g/L | | | |
| | | | | | | $V_2O_5$ | Al | Fe | |
| EFFECT OF ROAST TEMPERATURE | | | | | | | | | |
| 500 | 2 | 10 | 200 | 0.2 | 450 | 0.22 | 1.1 | 4.7 | 27 |
| 700 | 2 | 10 | 200 | .4 | 660 | .53 | 2 | .2 | 57 |
| 750 | 2 | 10 | 200 | .3 | 690 | .56 | 1.4 | .2 | 65 |
| 800 | 2 | 10 | 200 | .5 | 600 | .69 | 1.5 | .2 | 69 |
| 850 | 2 | 10 | 200 | .4 | 610 | .32 | 1.9 | .2 | 56 |
| 900 | 2 | 10 | 200 | .3 | 630 | .15 | 1 | .1 | 16 |
| EFFECT OF NaCl ADDITION IN ROAST | | | | | | | | | |
| 750 | 2 | 0 | 200 | 0.5 | 700 | 0.31 | 1.6 | 1.3 | 32 |
| | | 5 | 200 | .2 | 710 | .59 | 2 | 2.1 | 60 |
| | | 10 | 200 | .3 | 690 | .56 | 1.4 | .2 | 65 |
| | | 15 | 200 | .3 | 660 | .71 | 1.3 | .2 | 70 |
| | | 25 | 200 | 0 | 735 | .67 | 1 | .2 | 75 |
| EFFECT OF ROAST TIME | | | | | | | | | |
| 750 | 2 | 10 | 200 | 0.3 | 690 | 0.56 | 1.4 | 0.2 | 65 |
| | 4 | 10 | 200 | .2 | 635 | .67 | 1 | .2 | 70 |
| | 6 | 10 | 200 | .2 | 695 | .74 | 1.1 | .3 | 66 |
| EFFECT OF $H_2SO_4$ ADDITION IN LEACH | | | | | | | | | |
| 750 | 2 | 15 | 0 | 7.5 | 80 | 0.44 | <0.01 | <0.01 | 48 |
| | | | 200 | .3 | 660 | .71 | 1.3 | .1 | 70 |
| | | | 500 | 0 | 710 | .77 | 1.2 | 1.7 | 79 |
| | | | 800 | 0 | 750 | .87 | 1.9 | 6.3 | 83 |
| WATER LEACH | | | | | | | | | |
| 750 | 4 | 15 | 0 | 9 | 150 | 0.60 | <0.01 | <0.01 | 63 |
| | | 25 | 0 | 8.2 | 190 | .56 | <.01 | <.01 | 62 |
| | | 35 | 0 | 8 | 150 | .50 | <.01 | <.01 | 56 |

[1] Leach temperature, 80° C; test duration, 18 h.

Water leaching of the mudstone samples after a 4-h roast at 750° C with 25 wt pct NaCl yielded 61 pct of the vanadium from sample 1 and 62 pct of the vanadium from sample 2. Solutions derived from water leaching contained very low amounts of impurities; aluminum and iron concentrations were less than 0.01 g/L.

The best roasting conditions for the roast-leach procedure were determined to be a 4-h roast at 750° C with addition of 25 wt pct NaCl. No improvement in extraction occurred when the sample was roasted at temperatures higher than 800° C or when the roasting time exceeded 4 h. Vanadium extraction appeared to peak in the tests with 25-wt-pct-NaCl additions (fig. 4), although greater NaCl additions were not used, except in the water-leach tests. Although addition of 800 lb/ton $H_2SO_4$ during leaching yielded over 80 pct $V_2O_5$ extraction, a water leach, which in these tests extracted over 60 pct of the vanadium and leached low amounts of impurities, may be more economical and more viable than acid leaching for vanadium recovery from roasted ores when final vanadium separation and purification are to be accomplished by solvent extraction.

## AUTOCLAVE LEACHING

To determine the effect of pressure and elevated temperature on vanadium extraction, a series of autoclave-leach tests was conducted. Tests were carried

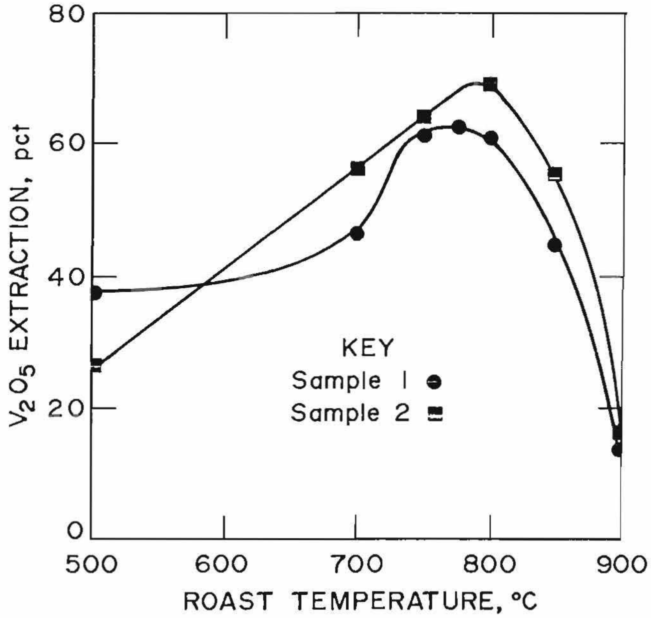

FIGURE 2. - Effect of roast temperature on vanadium extraction from salt-roasted samples (2-h roast with 10 wt pct NaCl followed by 18-h leach at 80° C with 200 lb/ton $H_2SO_4$).

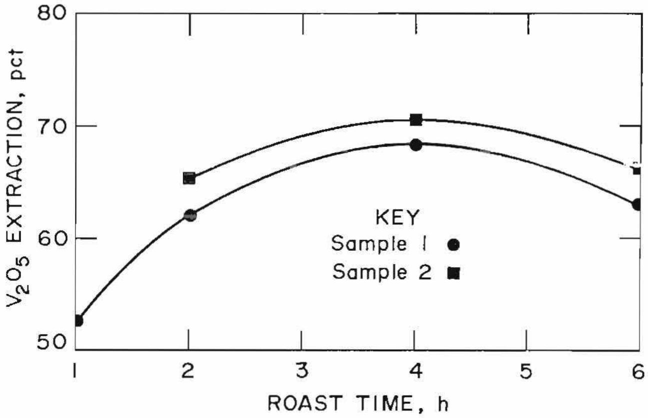

FIGURE 3. - Effect of roast time on vanadium extraction from salt-roasted samples (750° C roast with 10 wt pct NaCl followed by 18-h leach at 80° C with 200 lb/ton $H_2SO_4$).

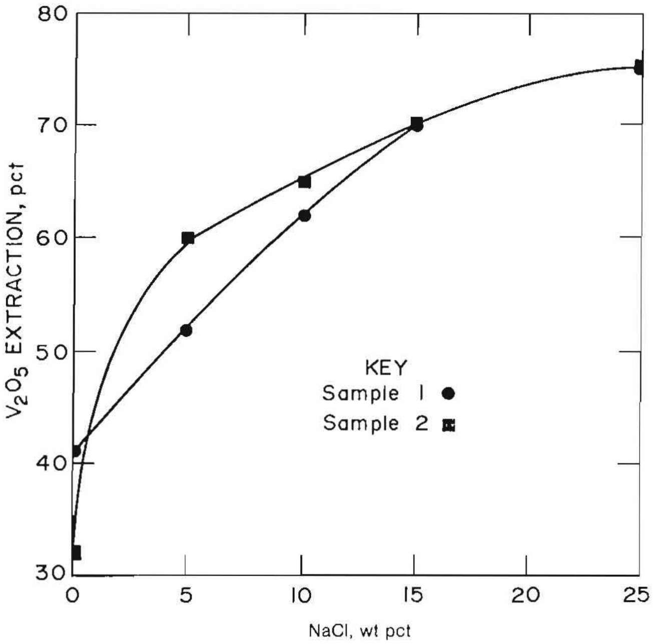

FIGURE 4. - Effect of NaCl addition on vanadium extraction from salt-roasted samples (2-h roast at 750° C followed by 18-h leach at 80° C with 200 lb/ton $H_2SO_4$).

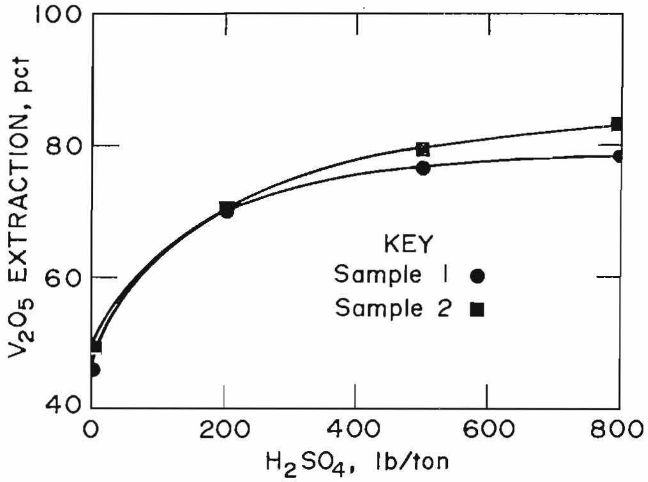

FIGURE 5. - Effect of acid addition on vanadium extraction from salt-roasted samples (2-h roast at 750° C with 15 wt pct NaCl followed by 18-h leach at 80° C).

out in a series 4500, 2-L Parr[5] autoclave. All tests were conducted at 20 pct solids to ensure good mixing. A 50-g charge of minus 35-mesh sample was combined with 200 mL of $H_2SO_4$ solution containing 200 to 1,000 lb/ton acid and heated to either 150° or 200° C (as shown in table 6). After autoclaving, the slurry was filtered, and the pH and emf of the pregnant filtrate were measured prior to addition of a wash solution. Combined filtrate and wash solutions and washed residue samples were then analyzed for vanadium and associated elements. Results of autoclave leaching for samples 1 and 2 are shown in table 6 and figures 6 and 7.

As with acid agitation leaching, autoclave leaching extracted more vanadium and impurities with increased acid addition. Table 6 and figure 6 show that vanadium extraction at 200° C increased from 22 to 97 pct for sample 1 and from 23 to 86 pct for sample 2 as acid addition increased from 200 to 1,000 lb/ton.

Autoclave leaching time and oxygen overpressure affected vanadium extraction from sample 2. Figure 7 shows that increasing the leaching time from 2 to 6 h increased vanadium extraction from 60 to 79 pct for sample 2 with the autoclave leaching temperature held constant at 200° C and using 600 lb/ton acid. Table 6 shows that vanadium extraction increased from 62 to 74 pct when the oxygen overpressure was increased to 50 psig above the steam pressure of 225 psig with temperature, time, and acid addition held

TABLE 6. - Autoclave leaching test conditions and results

(Test duration, 3 h, except as otherwise noted)

| Temp, °C | $H_2SO_4$ addition, lb/ton | Pressure,[1] psig | Filtrate | | Filtrate analyses, g/L | | | $V_2O_5$ extraction, pct |
|---|---|---|---|---|---|---|---|---|
| | | | pH | emf, mV | $V_2O_5$ | Al | Fe | |
| SAMPLE 1 | | | | | | | | |
| 150 | 200 | 70(S) | 1.2 | 380 | 0.13 | NA | NA | 23 |
| 200 | 200 | 225(S) | .9 | 385 | .30 | 0.7 | 0.5 | 22 |
| | 400 | 225(S) | .6 | 410 | .23 | 1.2 | .9 | 51 |
| | 600 | 225(S) | .5 | 410 | .30 | 1.7 | 1.1 | 72 |
| | 800 | 225(S) | .6 | 420 | .46 | 3.1 | 2.5 | 84 |
| | 1,000 | 225(S) | .3 | 405 | .69 | 5.1 | 4.2 | 97 |
| SAMPLE 2 | | | | | | | | |
| 150 | 200 | 70(S) | 1.2 | 360 | 0.06 | NA | NA | 15 |
| | | 70(S), 30(O) | 1 | 420 | .19 | NA | NA | 14 |
| | 600 | 70(S) | .4 | 395 | .18 | 1.4 | 2.4 | 45 |
| | 800 | 70(S) | .3 | 355 | .32 | 2.1 | 3.6 | 65 |
| 200 | 200 | 225(S) | .8 | 320 | .12 | .7 | 3.4 | 23 |
| | 400 | 225(S) | .7 | 265 | .19 | 1.3 | 3.1 | 49 |
| [2]200 | 600 | 225(S) | .7 | 355 | .19 | 1.2 | 3.3 | 60 |
| 200 | 600 | 225(S) | .5 | 335 | .26 | 1.9 | 2.9 | 62 |
| [3]200 | 600 | 225(S) | .8 | 290 | .32 | 2.3 | 3.7 | 67 |
| [4]200 | 600 | 225(S) | .6 | 315 | .45 | 3.1 | 4.5 | 79 |
| 200 | 600 | 225(S), 35(O) | .5 | 390 | .30 | 2 | 2.4 | 67 |
| | | 225(S), 50(O) | .3 | 440 | .35 | 2.2 | 3.1 | 74 |
| | 800 | 225(S) | .6 | 315 | .30 | 2.6 | 3.1 | 80 |
| | 1,000 | 225(S) | 0 | 270 | .40 | 3.3 | 4 | 86 |

NA Not available.

[1] (S) Steam pressure, (O) oxygen overpressure.

[2] Test duration, 2 h.

[3] Test duration, 4 h.

[4] Test duration, 6 h.

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[5] Reference to specific products does not imply endorsement by the Bureau of Mines.

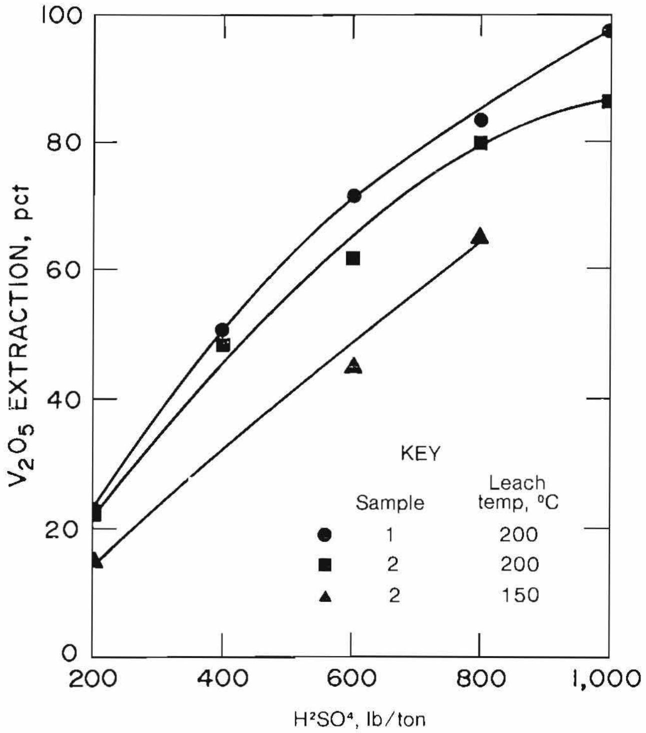

FIGURE 6. - Effect of acid addition on vanadium extraction by autoclave leaching for 3 h.

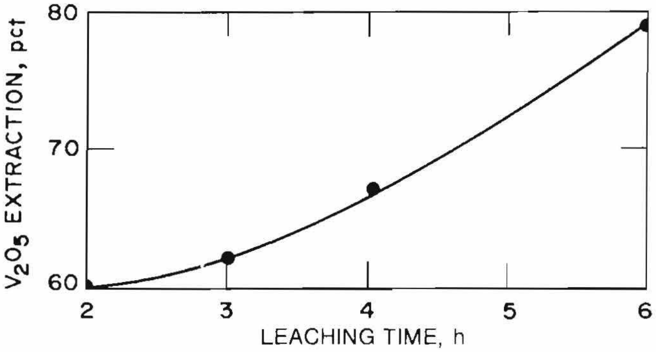

FIGURE 7. - Effect of leaching time on vanadium extraction by autoclave leaching, sample 2 (200° C leach with 600 lb/ton $H_2SO_4$).

constant at 200° C, 3 h, and 600 lb/ton, respectively.

In the autoclave-leach tests, increasing the temperature and steam pressure, leaching time, oxygen overpressure, and acid addition were all favorable to vanadium extraction. (However, for sample 1, increasing the temperature from 150° to 200° C did not improve vanadium extraction with the acid addition held constant. (See table 6.) The highest vanadium yields, 97 pct from sample 1 and 86 pct from sample 2, were attained using 1,000 lb/ton $H_2SO_4$ for 3 h at 200° C.

## SOLVENT EXTRACTION

Acid leaching of the Idaho mudstone samples solubilized vanadium and other associated constituents such as aluminum and iron; therefore, solvent extraction was used to selectively extract vanadium from the acid-leach solutions. Solvents most commonly used to extract vanadium are amines and alkylphosphates. Vanadium selectivity depends upon its valence state and the solution acidity. Tetravalent vanadium does not form anionic complexes and therefore is not loaded by anion-exchange resins or amine-type solvents. The alkylphosphates are cation-exchange solvents and will load tetravalent vanadium, while the amine-type solvents will extract pentavalent vanadium near pH 2.

Exploratory tests were conducted with several organic extractants to determine the selectivity of vanadium from the leach solutions. To facilitate vanadium extraction, the leach solutions required pH adjustment with either $NH_4OH$ or $H_2SO_4$ and emf adjustment with either iron powder (to reduce the solution) or $NaClO_3$ (to oxidize the solution). When $NH_4OH$ was added to the acid-leach solution prior to vanadium extraction, aluminum crystallized as hydrated ammonium aluminum sulfate $[(NH_4)Al(SO_4)_2 \cdot 12H_2O]$. The resultant precipitate occluded vanadium and prevented its complete oxidation and extraction. Ferrous iron in the acid-leach solution consumed excessive amounts of oxidant and prevented complete oxidation of the vanadium. The presence of these impurities also formed emulsions and caused poor phase separation. Solutions obtained from leaching roasted ore were sufficiently oxidized and did not require additional oxidation.

The organic extractant was contacted with the adjusted leach solution at a ratio of 1:1 and mixed on a shaker at room temperature for 10 min. The results of the shakeout tests for solvent extraction of vanadium from acid-leach solutions are shown in tables 7 and 8. These tables show that 6 vol pct di-2-ethyl hexyl phosphoric acid (D2EHPA) plus 3 vol pct isodecanol (IDA) in kerosene generally extracted over 80 pct of the vanadium in single contacts from reduced solutions. Other effective extractants were Azamine T-12 with IDA; triisooctylamine (TIOA); trinonylamine (TNA); tri-n-octylamine (TNOA); Alamine 336 with IDA; and octyl phenyl acid phosphate (OPAP) combined with tri-n-octyl phosphine oxide (TOPO), all used in kerosene diluents. These extractants recovered 34 to 96 pct of the vanadium in single contacts from oxidized leach solutions. Cyanex 272 under the conditions used in this study was generally ineffective.

Solvent extraction shakeout tests were also conducted using water-leach solutions (table 9). Table 9 shows that Alamine 336 was an excellent solvent; it extracted over 95 pct of the vanadium from solutions derived from water leaching of

TABLE 7. - Summary of shakeout tests for solvent extraction of vanadium from acid-leach solutions, sample 1

| Organic extractant in kerosene diluent | Aqueous feed,[1] g/L | | | Raffinate | | | | | $V_2O_5$ extraction, pct |
|---|---|---|---|---|---|---|---|---|---|
| | $V_2O_5$ | Al | Fe | pH | emf, mV | Analyses, g/L | | | |
| | | | | | | $V_2O_5$ | Al | Fe | |
| 5 vol pct Alamine 336, 5 vol pct IDA | 0.68 | 2.1 | 7.6 | 2.4 | 505 | 0.44 | NA | NA | 35 |
| | .68 | 2.1 | 7.6 | 2.7 | 465 | .35 | NA | NA | 49 |
| | .85 | 3.7 | .2 | 2.5 | 520 | .12 | 3.7 | 0.2 | 86 |
| | .68 | 4 | .06 | 3.2 | 450 | .03 | NA | NA | 96 |
| | .98 | 2.6 | .77 | 2.3 | 460 | .34 | 2.3 | .71 | 65 |
| 6 vol pct D2EHPA, 3 vol pct IDA | .50 | 4.3 | .3 | 1.8 | 300 | .10 | 4 | .8 | 80 |
| | .63 | 1.9 | 7.6 | 1.9 | 240 | .25 | 1.8 | 11.2 | 60 |
| | .70 | NA | NA | 2 | 220 | .13 | NA | NA | 81 |
| | .18 | 1 | 6.1 | 2 | 220 | .03 | 1 | 5.6 | 83 |
| | .95 | 2.6 | 3.1 | 2.1 | 260 | .08 | 2.4 | 2.9 | 92 |
| 0.25*M* TOPO, 0.125*M* OPAP | .94 | 4 | .4 | 1 | 610 | .25 | 3.9 | .4 | 73 |
| | .86 | 4 | .3 | 1.6 | 560 | .10 | 3.3 | .3 | 88 |
| | .80 | 4.1 | .1 | 1.8 | 510 | .05 | 3.3 | .01 | 93 |
| 0.2*M* OPAP, 0.1*M* TOPO | .94 | 4.1 | .4 | .8 | 550 | .11 | NA | NA | 88 |
| | .93 | 4.1 | .4 | .9 | 550 | .09 | 3.9 | .01 | 90 |
| | .90 | 4.2 | .3 | 1.4 | 550 | .15 | 3.3 | .01 | 83 |
| | .62 | 4.1 | .05 | 1.6 | 550 | .33 | 3.1 | .01 | 47 |
| 5 vol pct Cyanex 272, 2.5 vol pct IDA | .70 | NA | NA | 2.3 | 230 | .43 | NA | NA | 39 |
| | .18 | 1 | 6.1 | 2.2 | 230 | .09 | 1 | 5.7 | 50 |
| 5 vol pct TNOA | .91 | 2.9 | .8 | 2.6 | 470 | .11 | 2.9 | .8 | 88 |
| 5 vol pct TNA | .91 | 2.9 | .8 | 2.6 | 500 | .16 | 2.7 | 1.1 | 82 |
| 5 vol pct TIOA | .91 | 3.3 | .8 | 2.4 | 495 | .24 | 2.9 | .7 | 74 |
| 2.5 vol pct Azamine T-12, 2.5 vol pct IDA | .85 | 3.3 | .5 | 2.1 | 510 | .56 | 3.2 | .5 | 34 |

NA Not available. [1] 1:1 aqueous-to-organic ratio.

TABLE 8. - Summary of shakeout tests for solvent extraction of vanadium from acid-leach solutions, sample 2

| Organic extractant in kerosene diluent | Aqueous feed[1] g/L |  |  | Raffinate |  |  |  |  | $V_2O_5$ extraction, pct |
|---|---|---|---|---|---|---|---|---|---|
|  | $V_2O_5$ | Al | Fe | pH | emf, mV | Analyses, g/L $V_2O_5$ | Al | Fe |  |
| 5 vol pct Alamine 336, 5 vol pct IDA.................... | 0.48 | 2.1 | 0.1 | 2.5 | 450 | 0.20 | 2.1 | 0.1 | 58 |
|  | .49 | 2.1 | .3 | 2.4 | 420 | .29 | 2 | .2 | 41 |
|  | .56 | NA | NA | 2.2 | 420 | .23 | NA | NA | 59 |
| 6 vol pct D2EHPA, 3 vol pct IDA........................ | .14 | .7 | 5.9 | 2.2 | 240 | .03 | .6 | 7.8 | 79 |
|  | .23 | 1.2 | 7.1 | 2 | 180 | .02 | 1.2 | 12.1 | 90 |
|  | .22 | 1.2 | 7.1 | 2 | 190 | .02 | 1.1 | 14.2 | 91 |
|  | .23 | 1.1 | 10.3 | 2.1 | 200 | .03 | 1.1 | 10.1 | 88 |
|  | .48 | 2.2 | 2.4 | 2.2 | 190 | .23 | 2.1 | 2.3 | 52 |
| 5 vol pct Cyanex 272, 2.5 vol pct IDA.................... | .22 | 1.2 | 2.2 | 2.2 | 195 | .18 | 1.1 | 14.1 | 18 |
|  | .23 | 1.1 | 2.3 | 2.3 | 205 | .17 | 1.2 | 10.5 | 26 |
|  | .49 | 2.1 | 2 | 2 | 270 | .40 | 2.1 | 1.5 | 18 |

NA Not available. [1] 1:1 aqueous-to-organic ratio.

TABLE 9. - Summary of shakeout tests for solvent extraction of vanadium from water-leach solutions, sample 1

| Aqueous feed,[1] g/L |  | Raffinate |  |  |  | A:O | $V_2O_5$ extraction, pct |
|---|---|---|---|---|---|---|---|
| $V_2O_5$ | Al | pH | emf, mV | Analysis,[1] g/L $V_2O_5$ | Al |  |  |
| 5 VOL PCT ALAMINE 336, 5 VOL PCT IDA[2] |  |  |  |  |  |  |  |
| 0.60 | 0.003 | 3.7 | 380 | 0.02 | <0.001 | 1:1 | 97 |
| .60 | .003 | 3.2 | 450 | .03 | <.001 | 1:1 | 95 |
| .64 | .002 | 3.3 | 440 | .01 | <.001 | 1:1 | 98 |
| .64 | .002 | 2.9 | 460 | .02 | <.001 | 2:1 | 97 |
| .64 | .002 | 2.3 | 490 | .11 | <.001 | 5:1 | 83 |
| .64 | .002 | 2.2 | 490 | .18 | <.001 | 10:1 | 72 |
| .65 | .004 | 2 | 510 | .35 | <.001 | 25:1 | 62 |
| .67 | .004 | 2 | 525 | .40 | <.001 | 50:1 | 40 |
| .67 | .004 | 2.1 | 550 | .46 | <.001 | 75:1 | 31 |
| 6 VOL PCT D2EHPA, 3 VOL PCT IDA[2] |  |  |  |  |  |  |  |
| 0.60 | 0.003 | 3.6 | 410 | 0.37 | <0.002 | 1:1 | 57 |
| .60 | .003 | 2 | 565 | .26 | <.001 | 1:1 | 57 |
| .58 | .005 | 2 | 520 | .28 | <.003 | 1:1 | 52 |
| .58 | .005 | 2 | 540 | .34 | <.003 | 2:1 | 41 |
| .58 | .005 | 2.1 | 560 | .42 | <.002 | 5:1 | 28 |
| .58 | .005 | 2.1 | 570 | .50 | <.005 | 10:1 | 14 |
| 0.25*M* OPO, 0.125*M* OPAP[2] |  |  |  |  |  |  |  |
| 0.60 | 0.003 | 2.9 | 465 | 0.17 | 0.001 | 1:1 | 72 |
| .60 | .003 | 1.9 | 550 | .12 | .001 | 1:1 | 80 |

A:O Aqueous-to-organic ratio. [2] In kerosene diluent.

[1] <0.001 g/L Fe in all tests.

salt-roasted mudstone (sample 1). Because water leaching did not solubilize the impurities, as acid leaching did, solvent extraction was accomplished with good phase separation because emulsions or precipitates did not form. Aqueous-to-organic ratios as high as 75:1 were achieved with good phase disengagement.

## SUMMARY AND CONCLUSIONS

Vanadium was recovered from low-grade Idaho surface and underground mudstone samples by acid agitation leaching, roasting followed by acid agitation leaching, and autoclave acid leaching. Vanadium in the leach solutions was purified and concentrated by solvent extraction.

In the acid agitation leach tests, extractions of vanadium and impurities increased directly with increases in acid addition. Vanadium extraction from sample 1 (the surface sample) increased from 26 pct using 100 lb/ton $H_2SO_4$ to 70 pct using 1,000 lb/ton $H_2SO_4$. For sample 2, (the underground sample), the vanadium extraction increased from 11 to 47 pct using 100 and 1,000 lb/ton acid, respectively.

Salt roasting with 15 wt pct NaCl at 750° C for 2 h, followed by leaching with 800 lb/ton acid, extracted 78 pct of the vanadium from sample 1 and 83 pct from sample 2. Water leaching of mudstone that was salt roasted at 750° C for 4 h with 25 wt pct NaCl yielded more than 60 pct of the vanadium for both samples 1 and 2.

Autoclave acid leaching at 200° C for 3 h with 1,000 lb/ton acid extracted 97 pct of the vanadium from sample 1 and 86 pct from sample 2.

D2EHPA generally extracted over 80 pct of the vanadium in a single contact from acid-leach solutions reduced with iron powder. Azamine T-12, TIOA, TNA, TNOA, Alamine 336, and OPAP combined with TOPO were also effective extractants; they recovered from 34 to 96 pct of the vanadium in single contacts from oxidized solutions. Excellent phase separations were achieved in contacts with solutions obtained from water leaching of calcines. These solutions contained very low amounts of the impurities that cause emulsion and precipitate formation.

The results of this investigation of vanadium recovery from low-grade Idaho mudstone samples may technically favor the procedure comprised of salt roasting, leaching with water to minimize solubilization of impurities, and purifying and concentrating the vanadium in the leach solution by solvent extraction. However selection of the best method would depend on a more detailed study including a cost evaluation.

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