

# Separation of Molybdenum, Vanadium and Nickel by Liquid-Liquid Extraction

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Elements in the ash of asphaltites that is used in thermal central for power generation units are Mo, V, U, Ti and Ni. The main goal of this study was to separate molybdenum, vanadium and nickel from the aqueous solution. The quantities of the above elements in solution were in the range of 50-80 ppm.

The separate these elements from solution, the liquid-liquid extraction method was applied to samples. Alamine 336 was used as extractant. During the reduction-oxidation processes, single and multiple extraction methods were applied to the solution in combination. The quantities of molybdenum, vanadium and nickel in the solution were determined by a Shimadzu AA-670 model Atomic Absorbtion Spectrometer. 100 % of the molybdenum was isolated from the solution, and during the fourth and fifth stages of extraction, approximately 100 % of the vanadium was isolated from the solution. In this extraction process 12.5 % of the Alamine 336 in kerosene was used. However, this extractant is not suitable for the isolation of nickel, so nickel was recovered by precipitation as NiS in 96 % yield. Although in the literature vanadium can be extracted in V<sup>5+</sup> state with Alamine 336, in our studies it was obtained also in V<sup>4+</sup> state.

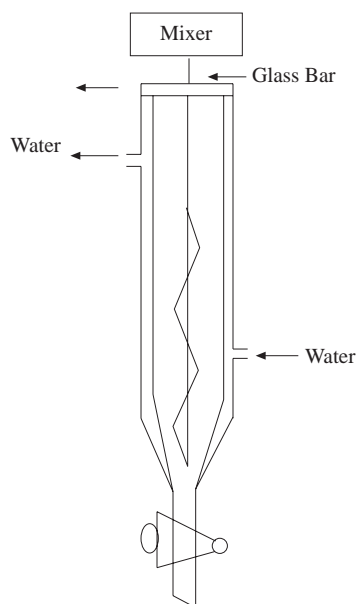
## Introduction

The solvent extraction method is widely used to separate the elements from a solution. The equations of amines, used as extractant, with metal ions have been given by other researchers (1). Furthermore, Atamer et al. tried to separate molybdenum, vanadium and nickel from acidic solutions by using solvents such as LIX 64N, Alamine 336 and Aliquat 336. They determined that vanadium was extracted only in 5+ oxidation state and between the pH values of 1.0 and 2.0, while approximately 95 % of molybdenum was extracted easily between the pH values of 1.0 and 10.00. However, vanadium was extracted only in 5+ oxidation state at pH 2.0 with Aliquat 336, but nickel was not extracted by these two solvents. Although molybdenum and vanadium were isolated by LIX 64N at lower percentages at pH 2.0, nickel was isolated easily between the pH values of 4.5 and 5.0 (2). Dorfler and Laferty performed the extraction of molybdenum from concentrated MoS<sub>2</sub> with Alamine 336 and they also performed stripping with NH<sub>4</sub>OH (3). Another group of researchers

also isolated molybdenum after vanadium with multiple extractions from acidic leach solutions by using amines (4). In addition, the influences of amines on vanadium and nickel have been studied by Burrieslo and Agers et al. (5,6). Giavarini tried to extract vanadium from the leach solution with various amine-kerosene mixtures (10-60 % of amine) and observed that the best extraction percentages were achieved by amine solutions in the range of 10-20 % (7). Gupta and Hayashi indicated that  $V^{4+}$  was not extracted by amine-type solvents because anionic complexes were not formed. (8,9). The raw material used in this study was acidic solution prepared by the roasting of the ash of southeastern Anatolian asphaltites with  $H_2SO_4$  (10). In addition, 10 % and 12.5 % solutions of Alamine 336 in kerosene were used as organic solutions. The complete separation of molybdenum, vanadium and nickel from aqueous solution was attempted. Also investigated was the suitability of the extraction conditions for the states of vanadium ( $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$ ). Transitions among these forms of vanadium were achieved with oxidizing agents ( $Cl_2$ ,  $H_2O_2$  and  $O_2$ ) and reducing agents ( $FeSO_4 \cdot 7H_2O$  and iron, elemental). The recovery of nickel from aqueous solution was achieved by analytical treatments.

## Experimental

The aqueous solution used in extraction studies was prepared by the roasting of the ash of asphaltites with 15m  $H_2SO_4$  for 1 hour and 40 minutes at  $175^\circ C$ . The following chemicals and solvents were used: n-Nonanol (fluka),  $NaClO_3$  (BDH),  $FeSO_4 \cdot 7H_2O$  (BDH),  $H_2O_2$ , 30 % (BDH); Iron, metal wire, 0.2 mm (BDH), nickel standard solution (BDH); vanadium standard solution (BDH); molybdenum standard solution (BDH) Alamine 336 (Merck); and Kerosene (b.p.175-250°C) (Merck). Extraction treatments were carried out in a glass apparatus with 100-ml volume (Figure 1). All tests were performed at constant temperature, time and stirring speed.

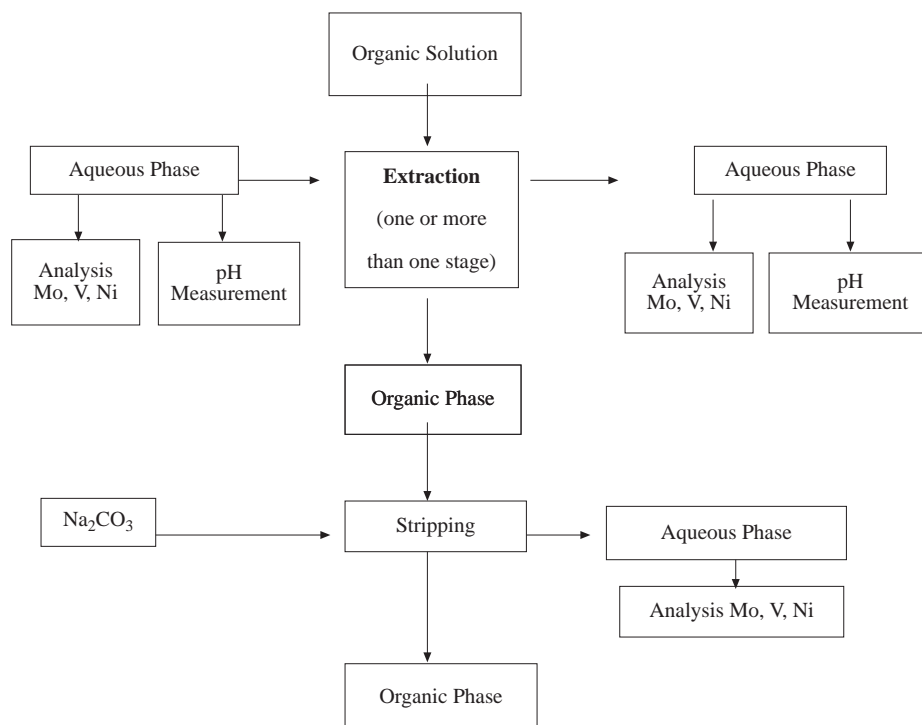


**Figure 1.** The glass extractor system used in extraction and stripping

Alamine solutions of 10 % and 12.5 % in kerosene were prepared. In addition, a quantity of n-nonanol was added to both of the above solutions so as to be 10 % in solution to prevent the third phase. Furthermore, 75 g/L  $Na_2CO_3$  solution is used as stripping solution.

Organic Phase : 20 ml      Extraction Time : 5 min  
 Aqueous Phase : 20 ml      Extraction Temperature : 30°C  
 Stirring speed : 1500 rpm

The analysis of vanadium, molybdenum and nickel were carried out by Shimadzu AA-670 model Atomic Absorbance Spectrometer. Extraction percentages were determined by the comparison of the amounts of these elements present in aqueous solution before and after extraction treatment. The pH measurements were also performed with a Teknom pHM13 model pHmeter. The flow diagram of the separation process is as follows:



**Figure 2.** The Flow Diagram of the Separation Procedure of molybdenum, vanadium and nickel with Alamine 336

## Results and Discussion

The main purpose of this study was to separate molybdenum, vanadium and nickel from solution individually. Vanadium exists in various forms, depending on the oxidation state of the element and the acidity of the solution. Molybdenum is easily isolated with alamine 336. However, nickel remains in aqueous solution as unreacted.

The extractions can be classified into two groups:

- 1) Extractions with 10 % Alamine 336
- 2) Extractions with 12.5 % Alamine 336

### 1) Extractions with 10 % Alamine 336

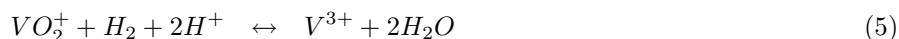
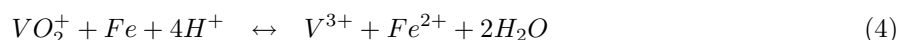
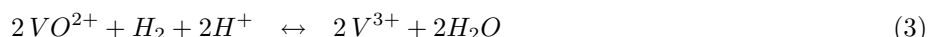
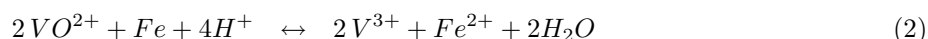
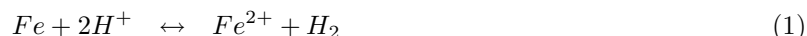
#### a) Two stage-extractions

An aqueous solution having a pH value of 1.17 was extracted using 10 % Alamine 336 in two successive steps. During the first and second extraction stages, vanadium and molybdenum was extracted as 52 % and 98 % respectively (Table 1, row 1a<sub>1</sub>). In the literature (8), the extraction process for vanadium has not

been performed at pH values lower than 1. In order to prevent the transition of molybdenum and vanadium together, the following extraction procedure, the second stage, was performed by the addition of one drop of concentrated  $H_2SO_4$ . It was observed that the passing of vanadium into organic solution decreased to 3.4% (Table 1, row 1a<sub>2</sub>).

*b) The reaction of acidic solution with elemental iron*

When elemental iron reacted with the aqueous solution, vanadium ions ( $V^{4+}$ ,  $V^{5+}$ ) were reduced to unextractable cationic ( $V^{3+}$ ) form with the following reactions (1, 2, 3, 4, 5):



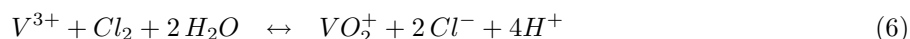
The aqueous solution thus reacted with elemental iron was extracted by 10 % Alamine 336 by two-stage extraction (Table 1, row 1b). It is obvious that < 1 % vanadium passed to the organic phase at second stage.

*c) The oxidation procedure of vanadium by  $H_2O_2$ ,  $Cl_2$  and air*

An aqueous solution which reacted with elemental iron by two-stage extraction. In the first stage, the solution was extracted with Alamine 336, and then  $Cl_2$  was passed through the aqueous solution before the second stage (Table 1, row 1c<sub>1</sub>). The same extraction was also performed using  $H_2O_2$  instead of  $Cl_2$  (Table 1, row 1c<sub>2</sub>).

In addition to these, an extraction was performed by passing dry air through the solution in first step for 1 hour, 3 hours and 6 hours, following which two-stage extraction was performed (Table 1, row 1c<sub>3</sub>).

In each extraction, the  $V^{3+}$  cations were oxidized to  $V^{5+}$  state. Reaction steps are given below.



*d) Four-stage extractions of the aqueous solution with 10 % Alamine 336*

In previous extraction studies, the best results have been obtained with  $Cl_2$  and it is accepted as fixed parameter for following extraction. The acidic solution was reacted with 10 % Alamine 336 in two-stage extraction. Then  $Cl_2$  passed through the solution for 1 hour before the third stage. The third and fourth stages were then carried out with 10 % Alamine 336 in the same way. Organic phases were also treated with  $Na_2CO_3$  solution (75 g/L) for stripping. Results are given in Table 2.

**Table 1.** The two Stage-extraction results with 10 % Alamine 336

APPLICATIONS	% EXTRACTION							
	Mo		V		Ni		pH	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd
1a <sub>1</sub>	86	97-98	-	52	-	-	1.48	2.4
1a <sub>2</sub>	88	98	-	3.4	-	-	1.48	1.4
1b	88	98	-	0.14	-	-	1.16	1.4
1c <sub>1</sub>	87	95	-	48	-	-	-	-
1c <sub>1</sub>	88	99	-	36	-	-	-	-
1c <sub>3</sub> (1 hour)	85	94.1	20	44	-	-	-	-
1c <sub>3</sub> (3 hours)	83.6	95	7.4	39.5	-	-	-	-
1c <sub>3</sub> (6 hours)	83.5	96	18	45.7	-	-	-	-

**Table 2.** The percentages of four Stage-Extraction with 10 % Alamine 336 and The Percentages of Strippings of Aqueous Solution

	% EXTRACTION				% STRIPPING			
	1st	2nd	3rd	4th	1st	2nd	3rd	4th
Mo	89	98.9	99.5	>99.9	98	98.1	95.8	-
V	-	-	68.2	89.7	-	-	70	69.5
Ni	-	-	-	-	-	-	-	-

**2) Extractions with 12.5 % Alamine 336**

In this study, complete separation of molybdenum and vanadium was achieved. Furthermore, vanadium was successfully extracted in  $V^{4+}$  state. In this extraction, three phases were observed between the aqueous and organic phases because of high pH value. In order to prevent the occurrence of these three phases, the organic solution was washed with  $H_2SO_4$  solution.

**a) Two-stage extraction**

The aqueous solution was extracted with 12.5 % Alamine 336 in the same way as with 10 % alamine (Table 3, row 2a).

**b) The reaction of aqueous solution with elemental iron**

In this stage, the acidic solution was first reacted with elemental iron to prevent the transition of vanadium to the organic phase, and then two-stage extraction was performed (Table 3, row 2b<sub>1</sub>). When the results are examined, it can be seen that molybdenum and vanadium were passed together at the second stage of extraction. Therefore, this extraction procedure was repeated by the addition of elemental iron to aqueous solution after the first stage of extraction. It was observed that the percentage of vanadium could be decreased to < 1% during the last stage (Table 3, row 2b<sub>2</sub>).

**c) Four-stage extraction of aqueous solution with 12.5 % Alamine 336**

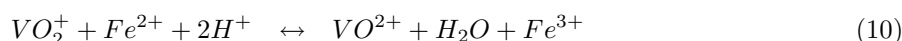
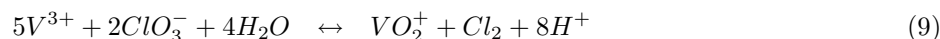
Aqueous solution was reacted with elemental iron before the first and second extraction steps, and then dry air was passed from aqueous solution for 1 hour before the third stage. After this, the third and fourth stages were performed. At the first and second stages, vanadium was  $V^{3+}$ . However, at the third and fourth stages, it was oxidized to  $V^{5+}$  (Table 3, row 2c).

**d) Extraction of  $V^{4+}$  by 12.5 % Alamine 336**

The aqueous solution was treated with 12.5 % Alamine 336 in two stages. The solution was reacted with elemental iron before every stage. In this way, most of the molybdenum was isolated from the solution.

Crystal  $\text{NaClO}_3$  was then added to the solution which was heated to  $60^\circ\text{C}$ . When the escape of gas was detected, crystal  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added to the solution. The third and fourth extraction stages were then performed (Table 3, row 2d).

According to the reactions given below, vanadium is  $\text{V}^{4+}$  state in solution.



**Table 1.** The Extraction Results with 12.5 % Alamine 336

Applications	% EXTRACTION															
	Mo				V				Ni				pH			
	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
2a	81	97	X	X	8.1	92	X	X	-	-	X	X	1.7	2.5	X	X
2b <sub>1</sub>	81	97	X	X	-	84	X	X	-	-	X	X	1.8	2.4	X	X
2b <sub>2</sub>	83	97	X	X	-	<1	X	X	-	-	X	X	1.7	2.6	X	X
2c	80	97	> 99	> 99	-	-	96	99	-	-	-	-	1.7	2.3	3.8	4.6
2d	82	96	97	99	-	-	90	98	-	-	-	-	1.7	2.4	3.7	4.3

(X: No extraction was not performed)

#### e) The procedure of washing the 12.5 % Alamine 336 with $\text{H}_2\text{SO}_4$ use in extraction

When previous studies are considered, it is seen that not all molybdenum ions were extracted after the second stage, so a small part of the molybdenum passed to the organic phase from the aqueous phase with vanadium ions at the third and fourth stages. In addition, after the 3rd and 4th stages, a cloudy condition occurred in the aqueous solution, and the phases were separated with difficulty by increasing the pH. Thus, the organic phase (12.5 % Alamine 336) was washed with  $\text{H}_2\text{SO}_4$  solution was increased to 2.48 from 1.48.

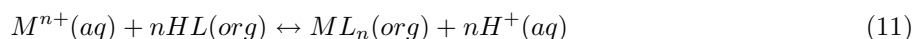
In this study the aqueous solution reacted with elemental iron was extracted in five stages with 12.5 % Alamine 336 (treated with  $\text{H}_2\text{SO}_4$ ). The aqueous solution was reacted with elemental iron at the beginning of each step of the 1st, 2nd and 3rd stages. Dry air was passed through the solution before the 4th stage. After this stage, the 4th and 5th stages were performed. After five-stage extraction, the pH of the aqueous solution was increased to 5 with  $\text{Na}_2\text{CO}_3$ . Then,  $\text{H}_2\text{S}$  was passed through the solution to precipitate the nickel as NiS. After this operation, about 96 % of the NiS recovered. Organic phases were stripped with  $\text{Na}_2\text{CO}_3$  (75 g/L). Results are given in Table 4.

**Table 4.** Four-Stage Extraction with 12.5 % Alamine 336 treated with  $\text{H}_2\text{SO}_4$  and Stripped with  $\text{Na}_2\text{CO}_3$  (75 g/L).

	% EXTRACTION					% EXTRACTION				
	1.st	2nd	3rd	4th	5th	1.st	2nd	3rd	4th	5th
Mo	81.7	99.7	>99.9	-	-	92	95	99	-	-
V	-	-	-	93	>99.9	-	-	-	80.3	82
Ni	-	-	-	-	-	-	-	-	-	-

It is seen that molybdenum was extracted easily with Alamine 336. The basic form of molybdenum is  $\text{MoO}_4^{2-}$  ( $\text{Mo}^{6+}$ ) in acidic solution, but vanadium is in the forms 3+, 4+ and 5+ according to the pH of the solution. Nickel cannot be extracted with Alamine 336.

A solvent extraction procedure is given in reaction 11.

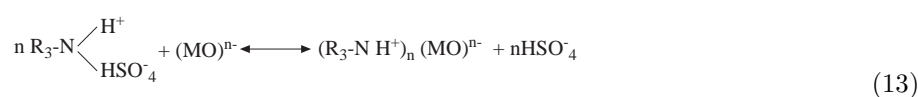


$M^{n+}(aq)$  : Metal ion in aqueous solution

$ML_n$  : Metal-extractant compound which dissolved in organic phase rather than aqueous solution

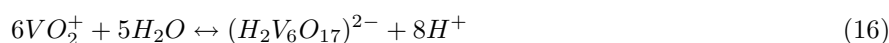
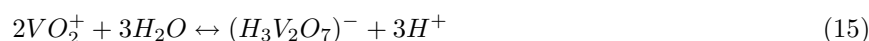
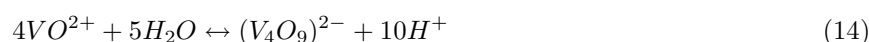
$HL(org)$  : Extractant

The equations of the extractions done with tertiary amines into  $H_2SO_4$  solution media are given below.



(R:  $C_8H_{17}$  for Alamine 336)

As seen from the reactions, molybdenum and vanadium can be extracted with Alamine 336 in  $H_2SO_4$  solution only in anionic form. Vanadium in  $VO_2^+$  and  $VO^{2+}$  forms is in anionic form, as seen in reactions 14, 15 and 16, but nickel is  $Ni^{2+}$  in this solution.



$(V_4O_9)^{2-}$ ,  $(H_3V_2O_7)^-$  and  $(H_2V_6O_{17})^{2-}$  ions, which occurred according to the equilibrium reactions in aqueous solution, give the compounds  $(R_3NH)_2V_4O_7$ ,  $(R_3NH)H_3V_2O_7$  and  $(R_3NH)_2H_2V_6O_{17}$ . Consequently, they pass to organic phase from aqueous phase.

Initially, the extraction treatments were achieved by 10% Alamine 336. Owing to the separation difficulties between molybdenum and vanadium in extraction stages, another alamine-kerosene solution (12.5 %) was prepared and used in the following extraction procedures. It is seen from Table 2 that a small amount of molybdenum was extracted with vanadium in the 3rd extraction stage and all the vanadium was not extracted in the 4th extraction stage using 10% Alamine 336. On the other hand, molybdenum and vanadium were entirely separated by 12.5 % Alamine 336 in the 3rd extraction stage and all the vanadium was extracted in the 4th extraction stage (Table 3, row 2c)

## Conclusions

Molybdenum was separated completely from vanadium and nickel in the third stage of five-stage extraction of aqueous solution with 12.5 % Alamine 336 (treated with  $H_2SO_4$ ).

Furthermore, vanadium was oxidized to 5+ from 3+. It was then extracted at about >99 % in the fourth and fifth stages while nickel remained in the aqueous solution. After the extraction stages about 96% of the nickel was precipitated as NiS. In addition, it was proved that vanadium could be extracted as  $V^{4+}$ .

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