Novel Method for Stripping of Molybdenum(VI) after Its Extraction with Cyanex 301

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Hydrofluoric acid has been used as a novel stripping agent for molybdenum(VI) after its extraction with Cyanex 301. In the extraction step, the effects of parameters such as type and initial concentration of acid, type of diluent, extractant concentration, metal concentration and temperature have been studied. In the stripping step, the effects of various stripping agents on stripping efficiency have been investigated. Hydrofluoric acid has been chosen as an effective stripping agent, and the effects of concentration of hydrofluoric acid, stripping time, volume of hydrofluoric acid and the number of stages of stripping have been studied. Molybdenum(VI) has been effectively separated from a large number of elements in binary mixtures, with a very high tolerance limit. Finally, the optimized method has been extended for the analysis of Mo(VI) in spent molybdenum catalysts.

Key Words : Stripping, Molybdenum(VI), Cyanex 301

Introduction

Molybdenum has extensive industrial applications and is regarded as one of the vital strategic metals in modern technology. An outstanding application of this element is in the manufacture of anticathode for X-ray tubes. Molybdenum wire is used extensively for the support of tungsten filament. [1] Due to molybdenum's widespread use this natural resource has become depleted, and, therefore, its extraction and purification from wastes and ores are important. Many investigations have been made on the solvent extraction of molybdenum(VI) from aqueous media containing sulfuric acid,[2-8] hydrochloric acid,[9-11] and nitric acid,[12-15] The use of different extractants, such as crown ethers,[16] α-benzoinoxime[17,18] organophosphate or organophosphoric acids,[3,11,19] especially di(2-ethylhexyl) phosphoric acid,[4,12] has been studied. Recently, some organophosphines and their sulfur analogues, known for their considerable resistance to decomposition by hydrolysis,[20] compared to their phosphoro analogues, have been used as extractants.

Radiolytical stability of Cyanex 301 (one of the organodithiophosphines) and of its purified form has been studied.[21] In the present paper, we present the extraction behavior of molybdenum(VI) in a wide range of concentrations (10^{-6}-10 M) of sulfuric, hydrochloric and nitric acids. To the best of our knowledge, there is no previous report on the stripping of molybdenum(VI) with HF. In this communication, we propose a simple method for extractive separation of molybdenum(VI), using Cyanex 301 and HF as extractant and stripping agent, respectively.

Experimental Section

Materials and reagents. Kerosene and the sample of Cyanex 301 containing 85% bis(2,4,4-trimethylpentyl) dithiophosphinic acid were purchased from Fluka (Switzerland). The Cyanex 301 concentrations mentioned throughout the text are actually those of bis(2,4,4-trimethylpentyl) dithiophosphinic acid. Kerosene was used as diluent throughout this work, except in diluent-effect experiments. All other chemicals, including solvents, were of analytical grade from Merck. Doubly distilled deionized water was used throughout.

Experimental procedure. The aqueous solutions were prepared by dissolving known amounts of metal salt (for example, Na_2MoO_4) in distilled water and then adding the proper acid to adjust the acid concentration. The organic solutions were prepared by dissolving known amounts of Cyanex 301 in organic solvents (for example, kerosene). Batch experiments were performed in a 10-mL flask containing equal volumes of aqueous and organic phases. The mixture was agitated at 25 °C, except in temperature effect experiments, by a temperature controlled mechanical shaker at 300 rpm, with ±1 °C accuracy in temperature measurement. Molybdenum was determined in the aqueous phase by ICP-AES (Varian, Liberty 150 AX Turbo). The concentration of the metal (for example, molybdenum) in the organic phase was calculated from the difference of the metal concentration in the aqueous phase before and after extraction. The distribution ratio (D) and percentage extraction (% E) were calculated accordingly. Shaking times for extraction and stripping were 20 minutes and one hour, respectively.

Results and Discussion

Effect of the type and initial concentration of acid. The extraction behavior of molybdenum(VI) from 10^{-6} to 10 M solutions of sulfuric, hydrochloric and nitric acids, using different concentrations of Cyanex 301 is shown in Figures 1, 2 and 3, respectively.

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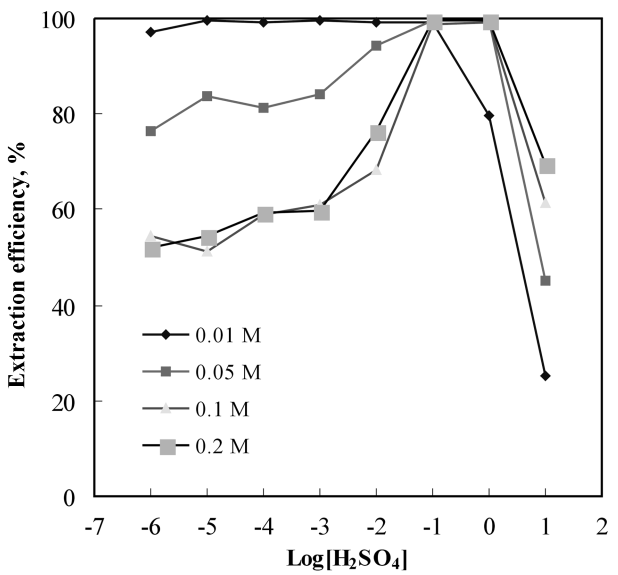

Figure 1. Effect of initial concentration of H_2SO_4 (molar) on extraction efficiency of molybdenum(VI). [Mo(VI)] = 10^{-4} M, [Cyanex 301] = 0.01 & 0.05 & 0.1 & 0.2 M.

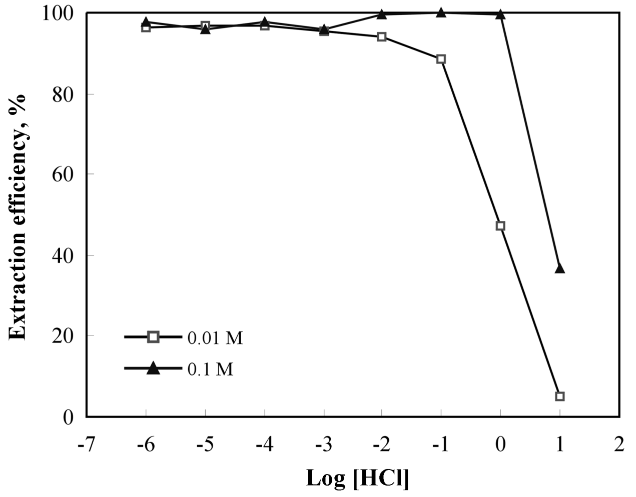

Figure 2. Effect of initial concentration of HCl (molar) on extraction efficiency of molybdenum(VI). [Mo(VI)] = 10^{-4} M, [Cyanex 301] = 0.01 & 0.1 M.

Effect of diluent type. The organic phase diluent can influence the extraction of metals because both physical and chemical interactions exist between diluent and extractant. The diluent can also affect the economics of a process, thus the suitability of the various diluents for the extraction of molybdenum(VI) by the proposed method was tested. We found that the extraction was quantitative with all diluents both aliphatic and aromatic. In light of this finding, selection of diluent is dependent on other parameters, such as availability and/or costs. The results obtained and the conditions of extraction are shown in Table 1.

Effect of extractant concentration. To study the effect of extractant concentration, molybdenum(VI) was extracted from 1 M HNO_3 with varying concentration of Cyanex 301. The Cyanex 301 concentrations were varied from 0.001 to 0.1 M. We found that the extraction was quantitative at 0.06 M Cyanex 301. The results are shown in Table 2. The log-log plot of distribution ratio versus Cyanex 301 concentrations at 1 M nitric acid gave a slope of 2.3, indicating that the metal to Cyanex 301 ratio in the extracted species is 1 : 2. Hence, the probable composition of the extracted species is MoO_2R_2.

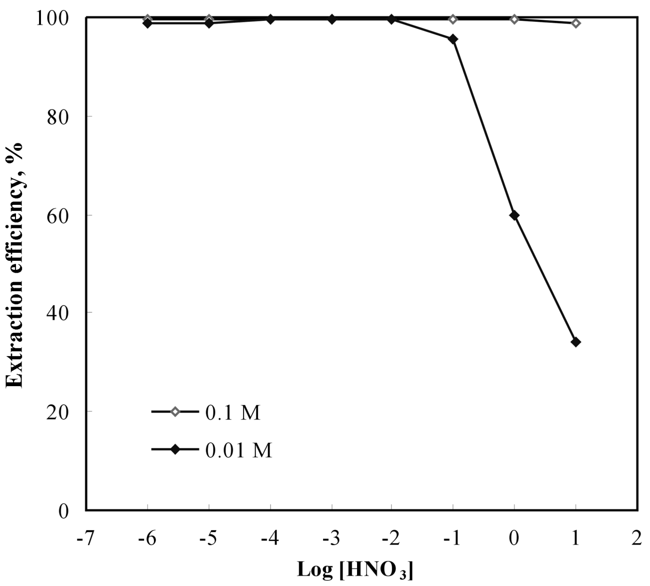

Figure 3. Effect of initial concentration of HNO_3 (molar) on extraction efficiency of molybdenum(VI). [Mo(VI)] = 10^{-4} M, [Cyanex 301] = 0.01 & 0.1 M.

Effect of varying metal ion concentration. The effect of metal ion concentration on the extraction of molybdenum (VI) was investigated for 1 M HNO_3 solution, employing 0.06 M Cyanex 301 in kerosene. The results of loading Cyanex 301 by molybdenum(VI) show that the extraction is quantitative up to 5×10^{-3} M molybdenum(VI). The results are shown in Table 3.

Effect of temperature. For obtaining optimum temperature, experiments were carried out on the extraction of molybdenum(VI) from 25 to 55 ºC at constant acid and

Table 1. Effect of Diluent Type on extraction efficiency

Diluent Type	Dielectric constant	D	E, %
Kerosene	1.8	53.0	98.1
Heptane	1.9	38.1	97.4
Dodecane	2	39.4	97.5
Benzene	2.28	70.3	98.6
Carbon Tetrachloride	2.34	64.7	98.5
Toluene	2.38	54.3	98.1
Chloroform	4.8	34.8	97.2
Dichloro methane	9.08	319.7	99.7
1,2 Dichloro ethane	10.5	508.6	99.8
Nitrobenzene	34.82	118.0	99.2

Extraction conditions: [Mo(VI)] = 10^{-4} M, [HNO_3] =1 M, [Cyanex 301] = 0.1 M.

Table 2. Effect of Cyanex 301 concentration on extraction efficiency

[Cyanex 301], M	D	E, %
0.100	343.2	99.7
0.080	141.5	99.3
0.060	139.2	99.3
0.050	16.4	94.3
0.040	15.2	93.8
0.020	1.3	55.7
0.010	0.5	33.8
0.008	0.4	27.7
0.006	0.3	21.4
0.004	0.2	14.6
0.002	0.1	11.2
0.001	0.1	0.1

[Mo] = 10^{-4} M, [HNO_3] = 1 M.

Table 3. Effect of metal ion concentration on extraction efficiency

[Mo] × 10^{-5}, M	D	E, %
10	75.1	98.7
25	47.9	98.0
50	43.4	97.8
75	33.5	97.1
100	37.5	97.4
250	18.3	94.8
500	12.3	92.5
750	5.4	84.3
1000	4.5	82.0

[HNO_3] = 1 M, [Cyanex 301] = 0.06 M.

Table 4. Effect of temperature on extraction efficiency

Temperature, ºC	D	E, %
25	87.6	98.9
35	147.4	99.3
45	232.2	99.6
55	232.2	99.6

[Mo(VI)] = 10^{-4} M, [Cyanex 301] = 0.06 M, [HNO_3] = 1 M.

Cyanex 301 concentrations. Table 4 shows that temperature has no significant effect on the extraction efficiency. Plotting log (D) versus 1/T over the range of temperatures (Figure 4) indicates that log (D) decreases with increasing temperature. The value of the slope is -0.2, so the extraction of molybdenum(VI) from nitric acid media with Cyanex 301 is an endothermic reaction. The standard enthalpy of the extraction reaction is 16.7 kJ/mol. On changing the aqueous phase from nitric acid to sulfuric acid, the reaction remains endothermic with higher standard enthalpy, 42 kJ/mol.

Effect of stripping reagents. Experiments were carried out for stripping molybdenum(VI) by washing the organic phase with an equal volume of aqueous solutions of reagents. The results of these experiments are shown in Tables 5, 6, and 7 and Figure 5. As can be seen, the results are not good. Further attempts resulted in a new and effective agent for stripping molybdenum(VI): HF. A concentrated HF solution (24.2 M) strips around eighty percent of molybdenum(VI) in a single contact. The results are shown in Table 8. Stripping with ammonia solution (1 to 10 M) and a mixture of ammonium nitrate and ammonia (1 to 10% NH_4NO_3 in 1 : 10 NH_4OH) resulted in an emulsion, or third-phase formation. For expelling HF from the stripping solution, 2 mL $HClO_4$ (71%) was added to the solution and heated at 90 ºC, with successive addition of distilled water. Then the solution was made up to 10 mL volume. The above procedure was followed in the experiments when necessary.

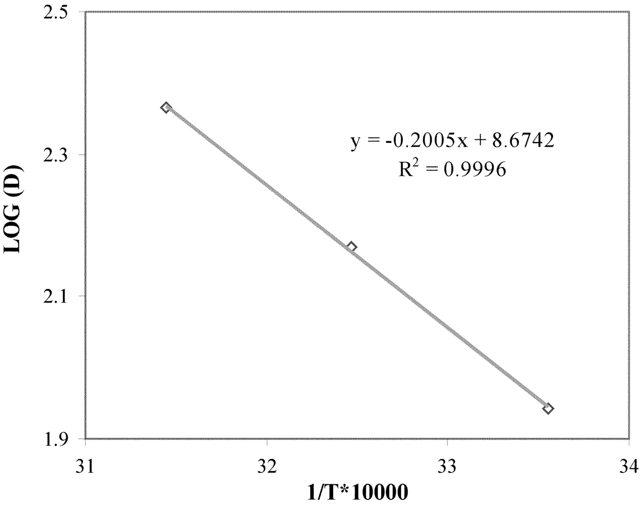

Figure 4. Effect of temperature on distribution ratio of molybdenum(VI). [Mo(VI)] = 10^{-4} M, [HNO_3] = 1 M, [Cyanex 301] = 0.06 M.

Effect of NaOH and rate of stripping on stripping

Table 5. Effect of concentration of HNO_3 and H_2O_2 on molybdenum(VI) stripping

H_2O_2, % HNO_3, M	0.5	1	2	3
0.05	0.0	2	0.5	1.0
0.1	0.0	0.0	0.0	0.5
0.5	0.0	0.0	4.0	6.0
1	19	0.0	0.0	1.0

Extraction conditions: [Mo(VI)] = 10^{-4} M, [HNO_3] = 1 M, [Cyanex 301] = 0.06 M.

Table 6. Effect of concentration of HCl and H_2O_2 on molybdenum(VI) stripping

H_2O_2, % HCl, M	0.6	6	12	18	27
0.001	0.0	0.0	2.0	2.0	1.0
0.01	0.0	0.0	1.0	0.0	1.0
0.1	0.0	0.0	4.0	4.0	16.0
1	0.0	0.0	0.0	1.0	4.0
3	–	0.0	1.0	1.0	–
5	–	–	0.0	–	–

Extraction conditions: [Mo(VI)] = 10^{-4} M, [HNO_3] = 1 M, [Cyanex 301] = 0.06 M.

Table 7. Effect of concentration of various stripping agents on molybdenum(VI) stripping

Stripping agent	Concentration of stripping agent, M	Stripping efficiency, %
$HClO_4$	2	0.0
	6	0.0
	10	0.0
Oxalic acid	0.1	1.2
	0.21	2.5
	0.42	2.5
Tartaric acid	0.1	1.8
	2.0	2.5
	0.4	3.0
$Cu(NO_3)_2 \cdot 2H_2O$	0.1	1.3
	0.2	4.0
	0.5	0.0
$FeCl_3$	0.1	0.0
	0.2	1.1
	0.5	0.0
$SnCl_2$	0.1	0.0
	0.2	0.0
	0.5	0.0
Sodium Thiosulfate	0.5	0.0
	1	0.0
	2	0.0
Thiourea	0.1	7.1
	0.2	4.4
Methionine	0.1	1.6
	0.2	12.8
Cysteine	0.1	0.6
	0.2	0.4
H_3PO_4	1	0.0
	5	0.0
	9	0.0

Extraction conditions: [Mo(VI)] = 10^{-4} M, [HNO_3] = 1 M, [Cyanex 301] = 0.06 M.

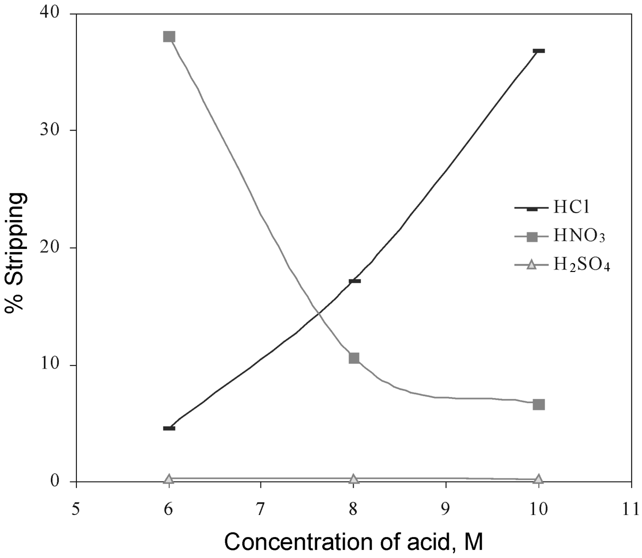

Figure 5. Effect of concentration of acids on stripping efficiency of Mo(VI). Extraction conditions: [Mo(VI)] = 10^{-4} M, [HNO_3] = 1 M, [Cyanex 301] = 0.06 M.

Table 8. Effect of concentration of HF on molybdenum(VI) stripping

HF, M	Stripping efficiency, %
2.7	16.9
14.5	28.5
16.9	37.5
19.3	48.8
21.7	59.9
24.2	82.6

Extraction conditions: [Mo(VI)] = 10^{-4} M, [HNO_3] = 1 M, [Cyanex 301] = 0.06 M.

Table 9. Effect of NaOH and stripping time on molybdenum(VI) stripping

Solution No.	Stripping reagent	Stripping time	Stripping efficiency, %
1	HNO_3, 6 M	4 days	1.6
2	HNO_3, 6 M	2 days	2.5
3	HNO_3, 6 M	1 hour	10.0
4	HNO_3, 6 M, without NaOH	1 hour	39.4
5	HCl, 6 M	4 days	8.3
6	HCl, 6 M	2 days	38.0
7	HCl, 6 M	1 hour	10.2
8	HCl, 6 M, without NaOH	1 hour	47.0

efficiency. Table 9 shows the effect of NaOH and rate of stripping on molybdenum stripping. In this experiment, before stripping molybdenum(VI), the organic phase was neutralized by 1 mL of 1 N NaOH (except solutions No. 4 and 8). Table 9 shows NaOH unexpectedly has an unfavorable effect on the stripping. It is assumed that free Cyanex 301 in organic phase was neutralized by NaOH and stripping was accomplished easier than before. Table 9 also shows that stripping efficiency decreases with increasing stripping time.

Effect of different volumes of HF on stripping efficiency. Stripping was carried out with different volumes (from 10 to 40 mL) of HF (24.2 M). Stripping efficiency decreases with increasing volume. The results are shown in Table 10.

Study of stage efficiency of molybdenum(VI) stripping. Single-stage to four-stage stripping was carried out with 24.2 M HF. The results show that increasing the stages, decreases stripping efficiency. The results are shown in Table 11.

Separation of molybdenum(VI) from binary mixtures. To an aliquot of the solution containing a fixed amount of molybdenum (10^{-4} M), varying amounts of foreign ions were added to study their interference in the recommended procedure. The tolerance limit was set at the amount of

Table 10. Effect of volume of HF on molybdenum(VI) stripping

Volume of 24.2 M HF, mL	Stripping efficiency, %
10	80.3
20	45.4
30	23.5
40	16.3

Table 11. Effect of stages of stripping on molybdenum(VI) stripping with 24.2 M HF

Stages of stripping	Stripping efficiency, %
1	82.2
2	78.6
3	72.4
4	62.7

Table 12. Separation of molybdenum(VI) from binary mixtures

Ion	Added as	Tolerance limit, mg
NH_4^+	$NH_4(NO_3)$	56.22
Na^+	$Na(NO_3)$	67.60
K^+	KCl	52.40
Rb^+	RbCl	70.70
Cs^+	$CsNO_3$	170.48
Mg^{2+}	$MgCl_2·6H_2O$	29.89
Ca^{2+}	$Ca(NO_3)_2·4H_2O$	42.43
Sr^{2+}	$Sr(NO_3)_2$	103.51
Ba^{2+}	$Ba(NO_3)_2$	131.40
Y (III)	$YCl_3·6H_2O$	73.27
ZrO^{2+}	$ZrOCl_2·8H_2O$	1.64
VO^{2+}	$VOSO_4·5H_2O$	15.36
Re (VII)	Re_2O_7	4.92
Fe^{3+}	$FeCl_3$	9.06
Os (VIII)	OsO_4	21.67
Ni^{2+}	$NiCl_2$	7.56
Cu^{2+}	$Cu(NO_3)_2·3H_2O$	3.69
Zn^{2+}	$ZnCl_2$	5.09
Cd^{2+}	$Cd(NO_3)_2·4H_2O$	5.66
Hg^{2+}	$HgCl_2$	8.06
Al^{3+}	$Al(NO_3)_3·9H_2O$	2.08
Sn^{2+}	$SnCl_2·2H_2O$	2.00
La (III)	$La(NO_3)_3·6H_2O$	4.31
Ce (III)	$Ce(NO_3)_2·6H_2O$	80.67
Nd (III)	Nd_2O_3	42.90
UO_2^{2+}	$UO_2(NO_3)·6H_2O$	2.25
PO_4^{3-}	H_3PO_4	72.49
ClO^{4-}	$HClO_4$	98.29
I^-	HI	90.99
Br^-	HBr	154.66
Cl^-	HCl	172.83
SO_4^{2-}	H_2SO_4	741.73
$C_2O_4^{2-}$	$H_2C_2O_4·2H_2O$	2.78
$C_4H_4O_6^{2-}$	$C_4H_6O_6$	13.78
$C_6H_5O_7^{3-}$	$C_6H_8O_7·H_2O$	50.31
CH_3COO^-	CH_3COOH	94.12

[Mo] = 10^{-4} M, [Cyanex 301] = 0.06 M, [HNO_3] = 1 M.

[Mo] = 10^{-4} M, [Cyanex] = 0.06 M, [HNO_3] = 1 M.

foreign ions required to cause a ± 5 percentage error in the recovery of molybdenum(VI). The results are reported in Table 12. Among the studied metals, transition metals compared to other metals show low tolerance limits. Tolerance limits for alkali and alkaline earth metals increase from top to bottom in each group. The organic acid anions were tolerated in lower concentrations compared to inorganic acid anions.

Table 13. Recovery of molybdenum(VI) from spent catalyst

Sample	Metal Ions	Concentration in A_1 & B_1 solutions (ppm)	Concentration in A_2 & B_2 solutions (ppm)	Concentration in A_3 & B_3 solutions (ppm)	Recovery, %	σ^a
A	Mo(VI)	10.6	0.0	10.3	97.1	± 2%
	Al(III)	90.6	18.9	0.0	0.0	
	B	1.0	0.7	0.3	30.0	
	Co(II)	2.7	0.7	0.0	0.0	
	In[b]	3.1	0.1	0.0	0.0	
	K	6.5	6.4	0.0	0.0	
	Si	48.6	3.1	0.0	0.0	
	Mg	5.1	0.0	0.0	0.0	
	Ca	7.2	0.0	0.0	0.0	
B	Mo(VI)	12.6	0.1	12.0	95.2	± 2%
	Al(III)	68.6	67.2	0.0	0.0	
	In[b]	2.4	0.1	0.0	0.0	
	K	3.4	3.3	0.0	0.0	
	Ni	4.4	4.3	0.0	0.0	
	Si	40.0	4.0	0.0	0.0	
	W[c]	5.5	1.2	0.0	0.0	
	Mg	7.3	6.9	0.0	0.0	

[a] Standard deviation based on 3 runs. [b] Interference was removed by selective stripping with 7 M HCl. [c] Masked by Citric acid

Recovery of molybdenum(VI) from spent Mo-Co (A) and Mo-Ni (B) catalysts. 0.2 g of the spent catalysts was digested and dissolved as described in the following section. Before subjecting the solutions to the solvent extraction step, the digested solutions of spent catalysts were diluted forty (A_1) and twenty (B_1) times, keeping the acid concentration to 1 M HNO_3. 10 mL aliquots of the solutions A_1 and B_1 were separately equilibrated with 10 mL of 0.1 M Cyanex 301. The raffinate of these solutions was marked as A_2 and B_2. Molybdenum(VI) was subsequently stripped by employing HF (24.2 M). The molybdenum(VI) solutions recovered from the organic phase were marked as A_3 and B_3. The results of the analysis are shown in Table 13.

Double acid digestion procedure. Each sample (0.2 g) was weighed into a 100 mL PTFE beaker. 10 mL of concentrated NHO_3 was added to the beaker and the sample was swirled until completely wetted. The beaker was covered with PTFE lids and gently heated at approximately 50 ºC for 48 hours. Then 5 mL of concentrated HF (38-40 %) was added and heating continued until the acid solution was clear. The PTFE lid was removed to accelerate the acid evaporation. The solution was quantitatively transferred to 100 mL plastic standard flasks and made up to volume with distilled/deionized water.

Conclusions

Finding of a new agent for stripping molybdenum(VI) from organic phase is the focus of this paper. The results reported here show that extraction efficiency of molybdenum(VI) is dependent on the type and concentration of aqueous phase acid, extractant concentration and metal ion concentration, but extraction efficiency is independent on the diluent type and temperature. Molybdenum(VI) can be extracted in the presence of a large number of ions with high tolerance limits. Cyanex 301 is an excellent extractant for molybdenum(VI).

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