The Impact of Solvent Extraction on the Recovery of Molybdenum from Molybdenite Ore

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Summary: An investigation of the complex formed between molybdenum (VI) and hydrochloric acid has been carried out and its extractability by long chain high molecular weight amine (HMWA), Alamine 336 in organic solvent was examined. The chloro-complex formed is quantitatively extractable from an aqueous phase into the organic phase with tertiary amine. On the basis of this selective extractability a method has been developed for the extraction and recovery of Mo(VI). The effect of various diverse ions and certain other parameters was undertaken and discussed in order to explore the feasibility of the procedure for extracting molybdenum from various complex materials and ores.

The extractability of the complex by HWMA indicates that the chloro-complex is anionic in nature. The method was applied successfully for the recovery of molybdenum from molybdenite ore. The exhausted HMWA was regenerated and used over and over again. The results obtained were encouraging.

Introduction

A number of solvents and solvent extraction techniques have been used in the past for the extraction of Mo(VI) in different molar concentration of acids [1-4]. Tributyl phosphate [5] and few other solvents [6] were also used as extractants. Among the amines the high molecular weight amine (HMWA), particularly the highly branched alkylamines have been used as "liquid anion exchangers" and extractants for the separation of specific metal ion pairs [7-10], extraction of metals such as uranium, thorium and plutonium [11-14] and for the elucidation of structure of anionic species [15-18]. However, hydrometallurgical method for the extraction and recovery of molybdenum from its ores have received little attention. Therefore, in the present work the authors have investigated and developed a new method of hydrometallurgical nature for the extraction of molybdenum from molybdenite ores in chloride system, using high molecular weight amines, alamine 336 as extractant.

Experimental

Reagents

Molybdenum Standard Solution

Exactly 1.50 gram of MoO_3 was dissolved in few cm^3 of dilute sodium hydroxide solution, made slightly acidic with hydrochloric acid and then diluted to 1 dm^3. This solution was further diluted with 0.1M hydrochloric acid so that 1.0 cm^3 of the resulting solution corresponds to 10 μgs. of mlybdenum.

Ferrous Ammonium Sulphate Solution (0.025 M)

The solution (0.025 M) was prepared by dissolving 10 g of $FeSO_4$ $(NH_4)_2SO_4$. $6H_2O$. in 1 dm^3 of 0.2 M sulphuric acid.

Tin (II)-Chloride Solution (0.39M)

10.0g of Sn (II)-chloride dihydrate were dissolved in 100 cm^3 of 1M hydrochloric acid.

Potassium Thiocyanate Solution (1.03M)

Exactly 10.00g of KCNS were dissolved in 100 cm^3 of water. All the above reagents used were of Analar grade.

Organic Solvents

Benzene (thiophene free) and high molecular weight amine, alamine 336 (BDH), were used as extractant without further purification.

Procedure for the extraction of Mo(VI) as chlorocomplex in high molecular weight amine (HMWA)

To the solution containing Mo(VI), added 5.5 cm^3 of concentrated hydrochloric acid and diluted to 10 cm^3 with distilled water in a separating funnel. To the resulting solution was then added 10 cm^3 of 0.2M alamine 336 in benzene, the whole was then shaken for 2 minutes manually or on a mechanical shaker and allowed to stand for some time, so that the two phases should separate out. The aqueous phase was transfered to another separating funnel and added 1.0 cm^3 of ferrous ammonium sulphate, 3 cm^3 of potassium thiocynate and 3 cm^3 of stannous chloride solutions. The Mo (VI) - Sn (II) - CNS complex formed was then determined spectrophotometrically at 480 nm [19]. The amount of Mo (VI) in the aqueous phase was calculated from the calibration curve (Fig. 1) and then the amount of Mo(VI) extracted by alamine 336 was found out by differences.

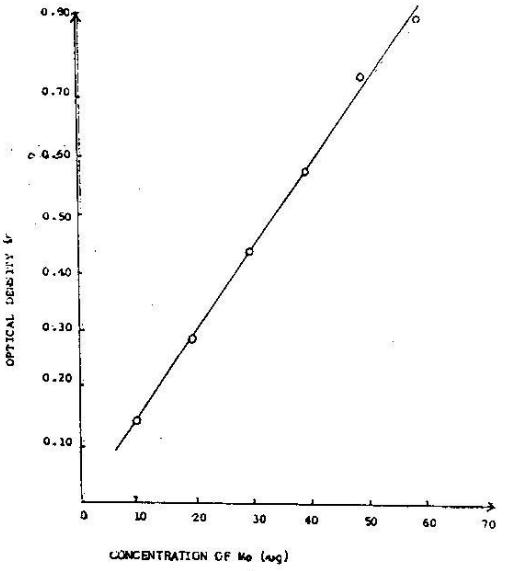

Fig.1: Calibration curve of Mo (VI) at 480 nm - Extraction by 0.2 M TBA in $CHCl_3$

Results and Discussion

Effect of Hydrochloric Acid Concentration

The effect of HCl concentration on the extraction of Mo(VI) by alamine 336 was carried out. The extent of extraction was studied using 0.5M - 8.8M HCl concentration. As indicated graphically in Fig. 2. 6.5N HCl was found to be the most

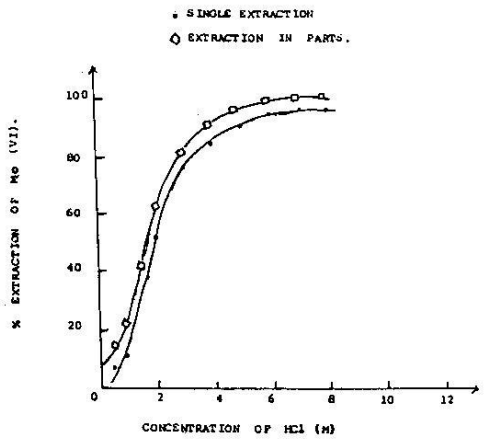

Fig.2: Extraction of Mo(VI) from HCl solutions by alamine 336.

Table-1: Determination of molybdenum in presence of diverse ions.

No.	Diverse ions	Amount (μg)	Molybdenum Taken (μg)	Stripped/recovered (μg)	Error (μg)
1.	Ca^{2+}	200	20	19.5	-0.5
2.	Mg^{2+}	200	20	19.5	-0.5
3.	Fe^{3+}	200	20	19.0	-1.0
4.	Al^{3+}	200	20	20.5	+0.5
5.	Pb^{2+}	100	20	19.0	-1.0
6.	Cu^{2+}	500	20	20.0	0.0
7.	Zn^{2+}	100	20	19.5	-0.5
8.	Cr^{6+}	500	20	20.0	0.0
9.	Co^{2+}	400	20	20.2	+0.2
10.	Ni^{2+}	100	20	18.5	-1.5
11.	Mn^{2+}	300	20	19.2	-0.8
12.	Ti4+	500	20	20.0	0.0
13.	Sn^{4+}	100	20	19.0	-1.0
14.	U^{3+}	100	20	18.0	-2.0
15.	V^{5+}	100	20	17.0	-3.0
16.	W^{6+}	100	20	19.0	-1.0

suitable concentration for achieving the maximum extraction of Mo (VI). However, using alamine 336 in portions instead of using the whole amount at once resulted in increasing of the extraction up to 98.80%.

Effect of the Organic Reagents

Two types of alkylamines, alamine 336 and tribenzylamine were used and their extraction efficiency was studied.When tribenzylamine was used as the extractant not more than 80% extraction of

molybdenum was possible, however when the same concentration of alamine 336 was applied, extraction and recovery of molybdenum achieved was above 99%. The results are shown in Fig. 3.

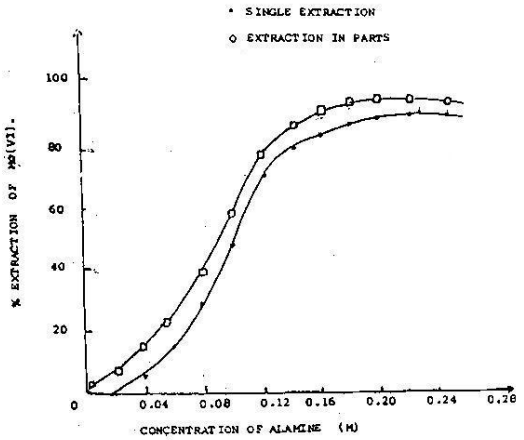

Fig.3: Effect of Extraction concentration on % extraction of Mo (VI).

Effect of Stripping Agents

To strip and recover the molybdenum (VI) from the loaded organic amine phase, various stripping agents with varying concentrations were examined. Soda ash 0.1M-0.14M was found suitable for quantitative stripping and recovery of molybdenum. The results are indicated in Fig. 4.

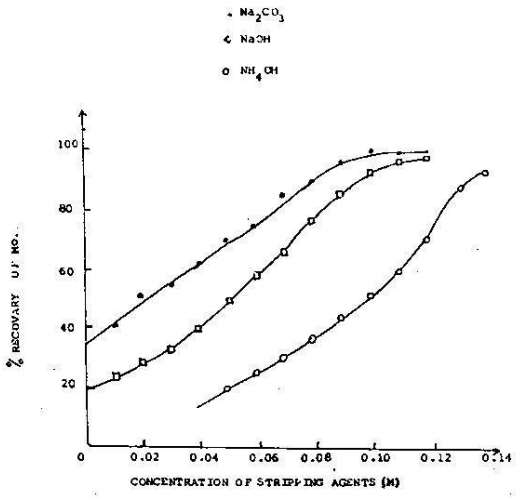

Fig.4: Effect of various stripping agents on recovery of Molybdenum from organic phase.

Table-2: Analysis of synthetic mixtures

No.	Molybdenum Present (μg)	Molybdenum Recovered (μg)	Error (μg)	Other elements (μg)
1.	0.0	0.00	0.00	Ca 100; Mg 100; Fe 100; Al 100; Na 100; K 100; Pb 100; Cu 100; Zn 100; Si 100.
2.	20.0	19.40	--0.60	Ca 100.
3.	20.0	19.40	-0.60	Ca 100; Mg 100.
4.	20.0	19.35	-0.65	Ca 100; Mg 100; Fe 100.
5.	20.0	19.20	-0.80	Ca 100; Mg 100; Fe 100; Al 100.
6.	20.0	19.25	-0.75	Ca 100; Mg 100; Fe 100; Al 100; Na 100.
7.	20.0	19.20	-0.80	Ca 100; Mg 100; Fe 100; Al 100; Na 100; K 100.
8.	20.0	19.20	-0.80	Ca 100; Mg 100; Fe 100; Al 100; Na 100; K 100; Si 100.
9.	20.0	19.30	-0.70	Ca 100; Mg 100; Fe 100; Al 100; Na 100; K 100; Si 100; Zn 100.
10.	20.0	19.00	-1.00	Ca Mg 100; Fe 100; Al 100; Na 100; K 100; Si 100; Zn 50; Pb 50.
11.	20.0	19.00	-1.00	Ca 100; Mg 100; Fe 100; Al 100; Na 100; K 100; Si 100; Zn 50; Pb 50; Cu 50.

Table-3: Chemical analysis of the samples (20).

Composition (%)	Lahore-1	Lahore-2	Pazang-1	Pazang-2
SiO2	42.60	43.50	45.00	44.98
Fe2O3	20.00	21.12	26.00	25.33
MgO	13.00	11.50	12.00	13.01
CaO	19.60	20.65	12.60	11.99
NaeO	0.67	0.73	1.00	1.03
KeO	1.55	1.43	1.24	1.39
Mo	0.50	0.75	0.30	0.45
Pb	0.25	0.33	0.46	0.25
Cu	0.19	0.15	0.17	0.16
Zn	0.01	Traces	0.07	0.06
Total	98.37	100.00	98.84	98.65

Stripping and Recovery of Molybdenum

Keeping the hydrochloric acid concentration constant (6.5M) which is the optimum concentration, equal volumes of the aqueous and the organic amine phase were transfered to a separating funnel. Shaken for 3 minutes and the two phases were then allowed to separate out. After the equilibrium was attained, the organic phase was separated and shaken with varying amount of different stripping agents. The amount of molybdenum stripped was determined spectrophotometrically [19]. It can be

Table-4: Recovery of molybdenum from molybenite ores (0.5 g sample), 25 cm^3 of aliquot in 6 M HCl + 5 cm^3 alamine 336 stripped with 0.1 M soda ash

No.	Method of Sample Preparation	Lahore Lahore-1 Mo Present (%) (21)	Lahore Lahore-1 Mo recovered (%)	Lahore Lahore--2 Mo present (%) (21)	Lahore Lahore--2 Mo recovered (%)	Pazang Pazang - 1 Mo present (%) (21)	Pazang Pazang - 1 Mo recovered (%)	Pazang Pazang - 2 Mo present (%) (21)	Pazang Pazang - 2 Mo recovered (%) (21)
1.	Leaching the agated sample with 6 M HCl for an hour.	0.50	0.10	0.75	0.25	0.30	0.13	0.45	0.15
2.	Fusion of the agated sample with soda ash and leaching the fused mass with 6 M HCl.	0.50	0.19	0.75	0.39	0.30	0.15	0.45	0.19
3.	Fusion with soda ash leaching and backing once with 6 M HCl.	0.50	0.22	0.75	0.48	0.30	0.20	0.45	0.24
4.	Fusion with soda ash and leaching, and then baking the fused mass twice with 6 M HCl.	0.50	0.30	0.75	0.55	0.30	0.22	0.45	0.30
5.	Fusion of agated sample with fusion mixture in the ratio 1: 4 and leaching with 6 M HCl.	0.50	0.34	0.75	0.60	0.30	0.25	0.45	0.35
6.	Fusion of the agated sample with fusion mixture (Na_2CO_3 + K_2CO_3 and KNO_3) in the ratio 1:4:0.4, baking with 6 M HCl and leaching with distilled water, removing the silica through filtration and making up the volume of filtrate with 6 M HCl.	0.50	0.45	0.75	0.70	0.30	0.28	0.45	0.40

seen from Fig. 4 that soda ash stripps off the molybdenum from the organic phase most effectively and 99% recovery is possible with a single stripping.

The same method was also applied for the recovery of molybdenum from molybdenite (Table-4) and the average recovery was 92%.

Effect of Diverse Ions

The effect of diverse ions which may cause the main interference during the extraction and recovery of molybdenum (VI), was examined up to the 100 fold concentration. It was found however, that the ions Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+} in the concentration 200 μg/20 μgs, Pb^{2+}, Ni^{2+}, Sn^{4+}, U^{6+}, Co^{2+} and Mn^{2+} up to a concentration of 100-400 μgs/20 μgs did not interfere to a significant extent. However, the interference of V^{5+} and W^{6+} even in the five fold concentration was significant which may be mainly due to co-extraction. As the ores of molybdenite did not contain V^{5+} and W^{6+} (confirmed by their X-ray diffraction studies and chemical analysis), the extraction of molybdenum

Table-5: Recovery of Mo (VI) with the regenerated solvent

No.	Regeneration of used solvent	Number of use	Mo (VI) Added (μg)	Mo (VI) Recovered (μg)	Recovered (%)
1.	Direct application of the used solvent without being washed.	1	20	19.00	95.0
2.	The used solvent was washed twice with distilled water before its reuse.	1	20	19.80	99.0
		II	20	19.80	99.0
		III	20	19.78	98.0
		IV	20	19.75	98.8

Table-6: Application of the regenerated solvent for the recovery of molybdenum from molybdentie ores

No.	Regeneration of used solvent	Number of uses	Pazang - 1 Mo present (%)	Pazang - 1 Mo reco-vered (%)	Pazang - 2 Mo present (%)	Pazang - 2 Mo reco-vered (%)	Lahor - 1 Mo present (%)	Lahor - 1 Mo reco-vered (%)	Lahor- 2 Mo present (%)	Lahor- 2 Mo reco-vered (%)
1.	Using directly the used solvent without being washed.	1	0.50	0.40	0.75	0.65	0.30	0.27	0.45	0.35
2.	Washing the used solvent twice with distilled water	1	0.50	0.40	0.75	0.65	0.30	0.29	0.45	0.44
		II	0.50	0.49	0.75	0.70	0.30	0.29	0.45	0.44
		III	0.50	0.49	0.75	0.70	0.30	0.29	0.45	0.44
		IV	0.50	0.48	0.75	0.69	0.30	0.28	0.45	0.43
		V	0.50	0.48	0.75	0.68	0.30	0.28	0.45	0.44

and its subsequent recovery was therefore, not seriously effected. The results are shown in Table-1.

Analysis of Synthetic Mixtures

As a final check on the method for the recovery of molybdenum from the molybdenite ores, various synthetic mixture were analysed. The results indicate that the maximum loss in the recovery of Mo(VI) did not exceed 5% though the mixtures contained five fold excess of each constituent other than Mo(VI). The results are shown in Table-2.

Recovery of Molybdenum from Molybdenite ores

General Procedure

An appropriate amount of molybdenite was taken, crushed and agated into a fine powder. Transfered 0.5 g of the fine powdered sample into a platinum crucible and mixed it with 20 g of flux of fusion mixture (Na_2CO_3 + K_2CO_3) and solid KNO_3 (0.2 grams) i.e., in the ratio of 1:4:0.4. The fused mass was leached with distilled water for an hour at 60-70°C at steam bath, filtered, and the solution was further diluted to 250 cm^3 in a volumetric flask using as much HCl and distilled water so that the final concentration is 6.0 M HCl. Transfered an aliquot (25 cm^3) of the sample to a 125 cm^3, separating funnel and shaked it with 10 cm^3 of 0.2M alamine 336/benzene for 3 minutes. The phases were allowed to separate and the organic phase was drawn up from the aqueous phase. Stripped the molybdenum loaded organic amine phase with 10 ml of 0.1M soda ash for 2-3 minutes and determined the amount of molybdenum in the aqueous phase spectrophotometrically [19]. The recovery of molybdenum from the molybdenite ore was also undertaken by direct acid leaching studies as well as fusion with alkali carbonate (Na_2CO_3 + K_2CO_3) only, but the results obtained were not encouraging. These results are shown in Table-4.

Regeneration of the used solvent (alamine 336)

The organic reagent (alamine 336/C_6H_6), loaded with molybdenum was backwashed/stripped with 0.1M soda ash in order to remove the molybdenum from the organic amine phase into the aqueous phase. The used solvent (alamine-benzene solution) was used as such and also after washing with distilled water. The results were reproduceable even using the exhausted solvent at least five times.

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