



Recovery of molybdenum from spent catalyst leach solutions by solvent extraction with LIX 84-I

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ABSTRACT

The leach liquor (10 g/L Mo, 27 g/L Al, 2.0 g/L Ni) obtained from the baking and leaching process of spent catalyst was treated using solvent extraction to recover Mo(VI) by LIX 84-I. The influence of various basic variables such as pH, concentration of LIX 84-I, different stripping reagents, phase ratio and diluents, was examined. Using 40% LIX 84-I with the aqueous solution of pH 0.5 and a phase ratio O:A = 1:1, a two-stage McCabe–Thiele plot was constructed which showed 99.9% of Mo extraction with no co-extraction of Ni and Al. This was confirmed by a 6-cycle counter current simulation (CCS) study. The stripping of Mo(VI) was quantitative using a mixture of 1 M NH₄OH + 1 M (NH₄)₂CO₃. The counter current simulation condition (three stages, phase ratio O:A = 5:1) obtained from the stripping isotherm study further attributes to the enrichment (5 times) of Mo(VI) concentration in the strip solution. The stable complex MoO₂R₂ formed during extraction which supports the cation exchange mechanism, was confirmed by IR spectral analysis.

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1. Introduction

Molybdenum is a strategic metal which in general has an extensive demand for its use in radios, thermocouples, anticathode of X-ray tubes and in the production of alloys of special steels [1]. Various secondary molybdenum sources contain high values of metals such as U, V, W, Re, Al, Ni, Cu, Co, etc. [2–5]. During the refining of pure petroleum from crude oils, Mo is used as a catalyst/promoter with other base metals such as Co and Ni embedded on porous Al₂O₃ (which acts as a support material). After a number of cycles of use the activity of these catalysts gradually decreases with time, hence it is necessary to regenerate and reuse these catalysts. The spent catalyst source, obtained from a petroleum company (PVT LTD), contains valuable base metals including 11.6% Mo, 27.1% Al and 2.5% Ni as reported in the previous paper [6]. After the leaching of the spent catalyst with 4% sulphuric acid, the metal values were concentrated to a solution which was analyzed as 10 g/L Mo, 27 g/L Al and 2.0 g/L Ni, was subjected for the solvent extraction of Mo(VI) by LIX 84-I.

Hydrometallurgical techniques such as solvent extraction [7], adsorption [8], ion exchange [9], supported liquid membrane [10], precipitation [11], etc., have been used extensively for the recovery

of Mo from various solutions. Amongst these, solvent extraction is one of the most effective methods, and extensively used in separation science, (including recovery and preconcentration of Mo) which leads to wider ranges of application. The extraction of molybdenum and other valuable metal such as Re, V and W from the leach solutions, using alamine based extractants is quite common, in which metals are extracted as the anionic form [12]. Even though there is an abundant literature available on solvent extraction of Mo using various cation and anion based extractants, such as tri-*n*-octylamine, primary/tertiary/quaternary amine [7,13–15], D2EHPA [16], TBP [17], PC88A [2], Cyanex 301 [18], LIX 63 [19], etc., However the study on the solvent extraction of Mo(VI) using LIX 84-I has not been reported yet.

Treatment of a spent catalyst leach residue containing 2.05% Mo, 0.42% V, 65.6% Al₂O₃ and 10.7% SiO₂ by solvent extraction for separating Mo and V using a mixture of 20 vol.% trialkylamine (as extractant) and 10 vol.% secondary octyl alcohol (as the modifier) has been reported [8]. In another study a wash liquor containing 10 g/L of Mo was treated for the extraction and the selective recovery of Mo in a two-stage extraction using 10% (v/v) alamine diluted in Anisole 150 diluent [20] was observed. An acidic solution containing the molybdenum was significantly recovered using Cyanex 301, dissolved in kerosene [21]. Cosor has investigated the separation of Mo, Ni, V in the presence of Ti and U which consists of the solvent extraction of molybdenum and vanadium using 12.5% Alamine 336 and followed by precipitation of Ni [22]. The molybdenum extraction was completed in the third stage of a five-stage

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extraction from the aqueous solution using 12.5% Alamine 336 and the extracted species Mo was reported to exist as anionic MoO_4^{2-} (Mo^{6+}), suggesting anion based extraction mechanism by Alamine 336. Sastre et al. [25] demonstrated the extraction of Mo(VI) from the sulphate solution using oxime extractant like LIX 622, in which the extraction was carried out as the function of pH, different stripping reagents, time, temperature and extractant concentration. Amongst the three solutions (H_2SO_4 , HNO_3 and NH_4OH) used for stripping Mo from metal loaded LIX 622, NH_4OH was reported to be the best, while the stripping efficiency of other two acids (H_2SO_4 and HNO_3) was quite low.

Other extractants such as phosphoric acid derivatives, thio-phosphoric acids and amines have also been used [13–18], but the work on extraction of Mo using oxime-based extractants is limited in the literature. LIX 84-I is one of the many commonly used extractants which has been used extensively for the extraction of non-ferrous metal such as Cu, Ni, Co, etc., from acidic solutions [23,24]. Thus the present investigation attempts to study the selective extraction of Mo(VI) by LIX 84-I from the spent catalyst leach liquor. The process parameters studied include pH, LIX 84-I concentration, mixture of NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ concentration as the strip solution, phase ratio (O:A), effect of different diluents, extraction isotherm and stripping isotherm, have been studied in detail to obtain the optimum condition for quantitative extraction of Mo(VI). Extraction and stripping isotherms were also developed from equilibrium data selected in this study.

2. Experiment

2.1. Chemicals and apparatus

The leach liquor used for the solvent extraction of Mo(VI), was obtained after baking of the spent catalyst followed by leaching with H_2SO_4 [6]. The resulting leach liquor contains 10.0 g/L Mo(VI), 27.0 g/L Al and 2.0 g/L Ni. All the reagents were analytical grade (Merck, German). The pH of the aqueous phase was adjusted to the desired value by adding H_2SO_4 or NaOH. All the experiments were carried out at room temperature ($25 \pm 5^\circ\text{C}$) using separating funnels. The organic reagents were used as received from the suppliers without further purification. Distilled kerosene ($180\text{--}220^\circ\text{C}$) was used as the diluent to prepare the extracting solvents. LIX 84-I was used for the extraction of Mo(VI). LIX 84-I (2-hydroxy-5-nonylaceto-phenone oxime) is a chelating organic extractant and it was obtained from Cognis Corporation, USA. The concentration of metal ions in the aqueous phase was determined by ICP-AES (JOBIN-YVON JY 38). The pH of the aqueous solutions was measured by a pH meter (Orion, USA). The IR spectrum of the LIX 84-I and Mo-loaded-LIX 84-I were recorded using FTIR-Nicolet (USA)-3800-spectrophotometer.

2.2. Experimental procedure

The extraction of Mo(VI) from spent catalyst leached liquor was carried out with LIX 84-I dissolved in kerosene at an O:A phase ratio of 1:1 with initial pH range of 0.5–3.0. Equal volumes of aqueous and organic solutions were equilibrated using a separating funnel for 5 min. After phase disengagement both phases were separated and the trace content of the organic phases present in the collected aqueous samples was separated using a phase separator (IPS) and equilibrium pH of the raffinate was also measured. An aliquot of the raffinate was diluted to a suitable concentration with dilute 1% HNO_3 . The generated loaded organic samples were also stripped with 1 M NH_4OH and finally both the raffinate and strip solutions were analyzed.

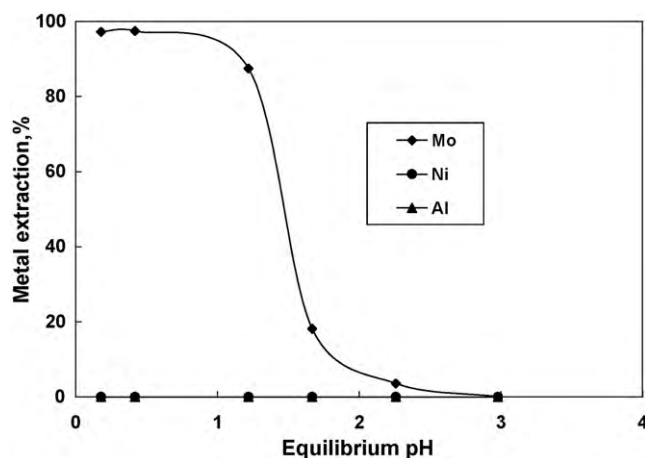
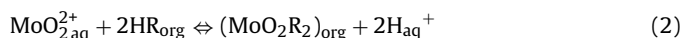
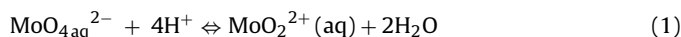


Fig. 1. Effect of equilibrium pH on the percentage of Mo(VI) extraction. Conditions: 40% LIX 84-I, O:A = 1:1.

2.3. Theory of solvent extraction

Mo(VI) is present in the aqueous solution as anions (MoO_4^{2-}) but in an acidic medium it converts to cations as shown by the reaction of Eq. (1) [25,26]. The extraction mechanism of Mo with the chelating extractant like LIX 84-I can be described in Eq. (2):



The equilibrium constant K_{ex} of the reaction is expressed as:

$$K_{\text{ex}} = \frac{[\text{MoO}_2\text{R}_2]_{\text{org}}[\text{H}^+]_{\text{aq}}^2}{[\text{MoO}_2^{2+}]_{\text{aq}}[\text{HR}]_{\text{org}}^2} \quad (3)$$

or

$$K_{\text{ex}} = \frac{D[\text{H}^+]_{\text{aq}}^2}{[\text{HR}]_{\text{org}}^2} \quad (4)$$

where D is the distribution coefficient and is expressed as $[\text{MoO}_2\text{R}_2]_{\text{org}}/[\text{MoO}_2^{2+}]_{\text{aq}}$ and on taking logarithm of Eq. (4) and rearranging, Eq. (5) can be obtained:

$$\log D = \log K_{\text{ex}} + 2 \log [\text{HR}]_{\text{org}} + 2\text{pH} \quad (5)$$

The percentage extraction of metal ion was calculated using Eq. (6):

$$\%E = \frac{(D \cdot (V_{\text{org}}/V_{\text{aq}}))}{1 + (D \cdot (V_{\text{org}}/V_{\text{aq}}))} \times 100 \quad (6)$$

where V_{aq} and V_{org} are the volume of the aqueous and organic phases, respectively. In this study volume of the aqueous phase was equal to the volume of the organic phase, so Eq. (6) is reduced to Eq. (7):

$$\%E = \frac{D}{1 + D} \times 100 \quad (7)$$

3. Results and discussion

3.1. Effect of pH

The initial pH was adjusted in the range 0.25–3.0 for which the corresponding equilibrium pH was varied from 0.18 to 2.2. The concentration of LIX 84-I (40%) and phase ratio (O:A) were kept constant during the extraction study. The plot of percentage of extraction of Mo(VI) vs. equilibrium pH is shown in Fig. 1. It was observed that the percentage of Mo extraction decreased from 97.2

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