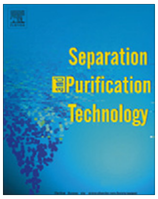
Separation and Purification Technology 99 (2012) 120–126

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Selective extraction of Mo using Cyanex-272 and tributyl phosphate from low grade Ni–Mo ore leach liquor

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ARTICLE INFO

Article history:
Received 15 May 2012
Received in revised form 1 August 2012
Accepted 4 August 2012
Available online 10 August 2012

Keywords:
Cyanex-272
Tributyl phosphate
Synergistic extraction
Selective extraction
Molybdenum

ABSTRACT

Selective extraction of Mo by Cyanex-272 and tributyl phosphate (TBP) was investigated from the leach liquor of a low grade Ni–Mo ore, which contains mainly Mo(VI), Fe(III), Ni(II) and a small quantity of other impurities. The elements in the leach liquor were divided into four groups based on the extraction mechanism of acid phosphorus extractants, and the behavior of four elements (Mo, Fe, As and V) was investigated. The separation factors of Mo to Fe, As and V were calculated separately using di-2-ethylhexylphosphoric acid, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester and bis(2,4,4-trimethylpentyl)phosphine acid (Cyanex-272) under the same conditions. Cyanex-272 was found to be the optimum extractant. The synergistic coefficients of Cyanex-272 and co-solvents (secondary caprylic alcohol and TBP) were calculated separately for the extraction of Mo, Fe, As and V and TBP was found to be the better choice. Several operational factors such as initial leach liquor pH, extractant concentration, co-solvent concentration and stripping reagent concentration were examined to establish suitable conditions for the effective extraction and stripping of Mo. The separation factors, $\beta_{Mo/Fe}$ = 1803.61, $\beta_{Mo/As}$ = 480.09 and $\beta_{Mo/V}$ = 103.22, were obtained under the optimum experimental conditions of 15%(v/v) Cyanex-272, 15%(v/v) TBP, initial leach liquor pH of 0.0 and organic/aqueous (O/A) phase ratio of 1.0. The theoretical number of stages required for extraction and stripping was determined from the McCabe–Thiele diagrams. Molybdenum (11.62 g/L) was extracted in five stages with an O/A ratio of 1.0, yielding a raffinate with only 0.30 g/L Mo. Three stripping stages yielded a 98.0% Mo stripping efficiency from 11.23 g/L Mo loaded organic phase, producing an enriched 55.05 g/L Mo solution that contained 0.058 g/L As and 0.023 g/L V. A high purity final MoO_3 product (99%) was obtained by re-crystallization from the stripped Mo solution.

1. Introduction

Molybdenum has strategic and industrial importance owing to its application in many technological fields [1]. However, primary high grade sources are being exhausted at a rapid rate with insufficient Mo available at present to supply demand. For this reason, low grade sources are being exploited increasingly. In southern China, a great amount of low grade black shale Ni–Mo ore that contains organic-rich rocks has been deposited over several kilometers [2,3]. With increased processing costs and requirements for environmental protection, many novel technologies have been attempted for processing Ni–Mo ore [4–10]. Recently, a process was proposed by our group, based on the oxidative pressure leaching of >90% Ni and 65–70% Mo from the Ni–Mo ore, with the remaining Mo being alkali leached from the residue. A high Mo and Ni leaching rate can be obtained using this technology. Recovery of the value metal from the multicomponent leach liquor is important. Therefore, the selective extraction of Mo from the leach liquor that contains reasonable amounts of acid and other elements from the Ni–Mo ore, such as Fe, Ni, V, As, Al, P, and Si, has been the focus of this study.

Many methods for Mo recovery from various solution have been adopted, including precipitation [4,9,11], adsorption with activated carbon [12–15], ion exchange [8,16,17] and solvent extraction. While the method of precipitation is most simple, it seldom yields high purity Mo products. Adsorption with activated carbon and ion exchange are limited by their small capacity, low selectivity and complexity process and are rarely applied in production practices. Comparatively speaking, solvent extraction has been used extensively in industrial practices owing to its low cost, simple process, recyclability of components, high separation coefficient of metal ions and high saturated loading capacity.

Researchers have developed solvent extraction processes for the recovery of Mo with various amine, phosphorus and chelate extractants from different solutions. Amine extractants, which include primary [18], secondary [19–21] and tertiary [6,7,22–25] amines and quaternary ammonium salts [26], have been applied widely in production practices owing to their large loading capacity. However, they co-extract P, As, Si and V species and require

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http://dx.doi.org/10.1016/j.seppur.2012.08.007

magnesium salt precipitation [27] to remove P, As and Si and ion exchange to remove V [28]. Some researchers have investigated the extraction of Mo with chelate extractants of LIX 622 [29], LIX 63 [30,31] and LIX 84-I [32,33], achieving some positive results. Of particular attention is the work by Mishra et al. [33] who have reported that Mo and V have been separated by LIX-84I in a leach liquor containing mainly Ni, V and Mo. Their results indicate that some chelate extractants can separate Mo from the liquor containing V, P, As and Si species to obtain high purity Mo products directly. Evidently the process shows more competitive advantages than the amine extractants.

The extraction mechanism of the acid phosphorus extractants is the same as the chelate extractant LIX-84I, being a type of cation exchange. The acid phosphorus extractants, such as di-2-ethylhexylphosphoric acid (D2EHPA or HDEHP, commercially available as PA-88A or P204), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA, commercially available as PC-88A or P507) and bis(2,4,4-trimethylpentyl)phosphine acid (commercially available as Cyanex-272) may be substituted for the LIX-84I to extract and obtain high purity Mo products directly. The extraction of Mo with acid phosphorus extractants has been investigated by a few researchers. Some have investigated the extraction of Mo from different acidic media with Cyanex-301 [1], di(octyl-phenyl) phosphoric acid (DOPPA) [34] and Cyanex-272 [35], to determine the optimum operating conditions for Mo extraction from pure Mo salt solutions. Some have investigated the separation of Mo from W with D2EHPA [36–38]. Valenzuela et al. [39] have recovered and separated Mo(VI) from the acid leach residual solution of a Chilean molybdenite concentrate with PC-88A. Brassier-Lecarme et al. [40] have proposed a process that recovers and purifys 99.7% of the Mo from the dissolution liquors of impure calcium molybdate, which contains P, V and Si with di-(2-ethylhexyl) phosphoric acid (HDEHP). Saily et al. [41] have separated Mo(VI) from V(V), Cr(III), Mn(II), Co(II) and Ni(II) over a wide range of aqueous phase acidities and partially from W(VI) and Fe(III) over a limited range with mono-(Cyanex 302) and di-(Cyanex 301). Fe(III) can also be separated from Mo(VI) by selective stripping. The purpose of this work is to study the selective extraction and separation of Mo using the acid phosphorus extractants D2EHPA, EHEHPA and Cyanex-272 from the leach liquor of a low grade black shale Ni–Mo ore and to try to obtain directly a high pure Mo product by the solvent extraction process.

2. Experimental

2.1. Apparatus and reagents

The commercial extractants D2EHPA, EHEHPA (both Luoyang Zhongda Chemical Co., Ltd., China) and Cyanex-272 (Shanghai Phosland Chemie Co., Ltd., China) were used without further purification. Distilled kerosene (b.p.: 160–200 °C) mostly aliphatic (97.1%) was used as diluent. The low grade black shale Ni–Mo ore was collected from southern China. The composition of the leach liquor is shown in Table 1, the valency of the Mo in the leach liquor was +6 and the pH of the leach liquor was 0.8. Molybdenum in the aqueous phase was analyzed by thiocyanate spectrometry and As, Fe and V were assayed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). All other reagents used were of analytical purity.

2.2. Experimental procedure

The leach liquor was adjusted to the desired pH using 2.5 mol/L H_2SO_4 or 5 mol/L NaOH solution. Suitable volumes of leach liquor and organic phase (50 mL each, except for the isotherm experiments) were placed in a 150 mL beaker. Mixtures for the solvent extraction and stripping experiments were agitated using a motor at the same stirring rate for 10 min (initial experiments showed that equilibrium was reached within 8 min) at room temperature (293 ± 1 K). The phases were allowed to separate using a separating funnel and the metal concentration in the aqueous phase determined after suitable dilution. The metal content in the equilibrated organic phase was calculated by mass balance.

The distribution ratio, D, was calculated as a concentration of metal present in the organic phase to that in the aqueous phase at equilibrium. From the D values, the percentage extraction (E (%) $= D/(D + V_{aq}/V_{org}) \times 100$, where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively), separation factor ($\beta_{Mo/b} = D_{Mo}/D_b$, where b is the impurity) and synergistic coefficient ($R = D_{A+B}/(D_A + D_B)$, where A and B are two different extractants) were calculated.

2.3. Principle of solvent extraction

Being a transition metal, Mo exhibits multiple valences of +3, +4, +5 and +6. The stable valency of +6 is important for solvent extraction. Species of Mo(VI) are complicated in the aqueous solution and form various isopolyanions [10,42] such as $MoO_4^{2-}, Mo_7O_{24}^{6-}, Mo_8O_{26}^{4-}$ and MoO_2^{2+}. In addition, Mo(VI) also can form heteropolymolybdic complexes of $PMo_{12}O_{40}^{3-}, AsMo_{12}O_{40}^{3-}$ and $SiMo_{12}O_{40}^{4-}$ in the presence of P, As and Si [40]. The predominant species formed depends on pH, oxidation state and concentration of metal and ligand in solution. However, the main species of Mo(VI) is MoO_2^{2+} in low pH solution (pH < 1) and MoO_4^{2-} in high pH solution (pH > 6) [42].

In the solvent extraction process, acid phosphorus extractants are able to extract cations by an ion-exchange type extraction, according to the following equilibrium:

$$M^{2+}_{(aq)} + 2(HX)_{2(org)} = M \cdot X_2 \cdot 2HX_{(org)} + 2H^{+}_{(aq)} \tag{1}$$

where HX and $(HX)_2$ represent the monomer and dimer of acid phosphorus extractants, respectively, since these extractants exist as dimers in aliphatic diluents and M represents the element ions.

Based on the extraction mechanism of the acid phosphorus extractants, the elements in the leach liquor were divided into four groups. The first group was Mo, which must be extracted. The second group was V, which can form various heteropolyvanadyl in leach liquor such as $VO_2^{+}, VO_2SO_4^{-}, H_2V_{10}O_{28}^{4-}, HV_{10}O_{28}^{5-}$ and $V_4O_{12}^{4-}$ [43]. Some cationic heteropolyvanadyl may be extracted by an ion-exchange type extraction. The third group consisted of As, P and Si, which can form heteropolymolybdic complexes and therefore may be extracted. The fourth group contained Fe^{3+}, Ti^{3+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}, which are cations in the leach liquor, may also be extracted by an ion-exchange type

Table 1
Leach liquor composition.

Composition	Mo	Ni	V	Fe	SiO_2	Al_2O_3	Zn	P
Concentration (g/L)	11.62	11.42	0.46	31.65	0.28	3.20	1.59	0.73
Composition	K	Na	As	Pb	CaO	Ti	Cu	MgO
Concentration (g/L)	0.75	0.22	2.61	0.1	0.27	0.14	0.72	4.71