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Co-extraction and selective stripping of vanadium (IV) and molybdenum (VI) from sulphuric acid solution using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester

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ABSTRACT

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) diluted with kerosene was used to co-extraction and selective stripping vanadium (IV) and molybdenum (VI) from sulphuric acid solution. The influence of aqueous pH, extractant concentration, stripping agents on the co-extraction and selective stripping of both metals were investigated. The extraction of both metals is sensitive to aqueous pH; however, molybdenum (VI) is extracted preferably to vanadium (IV) at acidic pH values. Both metals were co-extracted by a three-stage counter current extraction with 15%(v/v) EHEHPA at initial aqueous pH 2.0 and O/A phase ratio 1.0. Vanadium (IV) in the loaded organic phase was selectively stripped by 1.0 mol/L sulphuric acid. Molybdenum (VI) in the vanadium-free organic phase was completely stripped by aqueous solution containing 10 wt.% NH_4OH and 15 wt.% NH_4Cl with excellent phase separation. The separation factor of vanadium (IV) to molybdenum (VI) was 345. A process flow sheet has been developed to recover and separate vanadium (IV) and molybdenum (VI) from sulphuric acid solution.

1. Introduction

Separation vanadium (IV) and molybdenum (VI) from aqueous solution has been a problem due to their similar aqueous chemical behaviour. Much effort has been made to separate vanadium and molybdenum from aqueous solution, such as precipitation [1], adsorption with activated carbon [2], ion exchange [3] and solvent extraction [4–6]. Among these methods, solvent extraction has been widely used as a process for separation, purification and recovery of metals, due to its simplicity of equipment and operation. It is also proposed as the most promising method for separation and recovery of high purity vanadium and molybdenum [7].

In the solvent extraction processing there are two basic process approaches for metal separation in multi-elemental system: selective extraction and selective stripping. In most cases, selective stripping was more attractive because it requires fewer stages than selective extraction process. Zhang et al. [8] studied the co-extraction of vanadium (IV) and molybdenum (VI) from a sulphuric acid leach solution of spent hydrodesulphurisation catalysts in the present of various other metals, such as aluminium (III), cobalt (II), nickel (II) and iron (III) using oxime-LIX 63. Vanadium (IV) in the loaded organic phase was selectively stripped by 2 mol/L H_2SO_4 at first and then stripped with 10% ammonia water for recovery of molybdenum (VI). While high concentration of free sulphuric acid (about 2 mol/L) in the vanadium (IV) stripped solution would consume lots of ammonium water during the subsequent precipitation of ammonium vanadate. Zeng and Cheng [9] also investigated the co-extraction of vanadium (V) and molybdenum (VI) from a synthetic sulphuric acid leach solution of spent hydrodesulphurisation catalysts by LIX 63 at pH 1.5, the two metals in the loaded organic solution was stripped by NaOH. After precipitation most of vanadium (V) from the strip liquor, a pure molybdenum (VI) solution was obtained by further removing the small amount of vanadium (V) using Aliquat 336 at pH 8.5. Both pure molybdenum and vanadium products can be obtained by this separation process.

Besides the chelating extractants, both the cationic species of vanadium (IV) and molybdenum (VI) can be also extracted by acidic organophosphorus compound extractants, such as D2EHPA [10–12] and Cyanex 272 [13]. However, the disadvantage of D2EHPA is poor selectivity, while the problem for Cyanex 272 is the ready formation of emulsion or third phase in stripping of molybdenum (VI) from the loaded organic with aqueous ammonia solution [8]. 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (abbreviated as EHEHPA, commercially as PC-88A or P507) is one of the commonly used acidic organophosphorus extractant which has been used extensively for extraction and separation of rare earth metals [14,15], and non-ferrous metals such as Ni, Co, V, Zn from acidic solutions [16,17]. EHEHPA has the advantage of excellent selectivity extraction of vanadium (IV) and molybdenum (VI) over aluminium (III), cobalt (II) and iron (II). Also, it is being free from the formation of third phase in the stripping of vanadium

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(IV) and molybdenum (VI) from the loaded organic phase. EHEHPA is a promising extractant for recovery and separation of vanadium (IV) and molybdenum (VI) from acidic solutions. However, there is little information available on the use of this extractant for co-extraction of vanadium (IV) and molybdenum (VI) coupling with the selective stripping approach. Thus the present work attempts to study co-extraction both metals using EHEHPA from sulphuric acid solution and selective stripping for their separation. The parameters including aqueous pH, extractant concentration, kinds of stripping agent, additive for prevent formation of emulsion in the stripping, have been studied in detail to obtain the optimum condition for separation of vanadium (IV) and molybdenum (VI). Based on the present study, a process flow sheet has been proposed.

2. Experimental

2.1. Reagents and solutions

The commercial EHEHPA supplied by Luoyang Zhongda Chemical Co., Ltd., China, was used as such without further purification. Distilled kerosene (b.p: 433–473 K) mostly aliphatic (97.5%) was used as diluent. The stock solutions of vanadium (IV) and molybdenum (VI) were prepared by dissolving the requisite quantity of the analytical pure, $VOSO_4$ and Na_2MoO_4, in distilled water. Required H_2SO_4 was added to suppress hydrolysis of the metal ions. The concentrations of the metals in the stock solution were standardised by AAS. Working solutions were prepared by suitable dilution of the stock solution. All other reagents used were analytical pure.

2.2. Solvent extraction procedure

The typical composition of synthetic feed solution used for the present study contains 1.50 g/L vanadium (IV) and 1.06 g/L molybdenum (VI). The aqueous was adjusted to desired pH values using 2.5 mol/L H_2SO_4 or 5 mol/L NaOH solution. The redox potential of the feed solution is 0.8 ± 0.1 V. Suitable volumes of aqueous and organic phases (30 mL each, except for O/A ratio experiments) were taken in a 125 mL separating funnel. Solvent extraction and stripping experiments were carried out by mechanically shaking the organic and aqueous phases in separating funnels at room temperature (293 ± 1 K) for 10 min (initial experiments showed that equilibrium was reached within 8 min). After phase disengagement, the aqueous phase was separated and its metal concentrations were determined after suitable dilutions by AAS. The content of the metals in the equilibrated organic phases was calculated by mass balance.

Counter current simulation experiments were performed in a box style mixer–settler unit which contained six mixer–settler stages. The active mixer volume was 0.5 L and the settler volume was 1.5 L. The stirring speed was 800 rpm.

The distribution ratio D, was calculated as concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. From the D values, the percentage extraction ($E(\%) = D \times 100/D + (V_{aq}/V_{org})$ where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively, and separation factor ($\beta = D_V/D_{Mo}$) were calculated.

3. Results and discussion

3.1. Effect of aqueous pH on the co-extraction of vanadium (IV) and molybdenum (VI) with EHEHPA

In order to study the effect of aqueous pH on the extraction of vanadium (IV) and molybdenum (VI) with EHEHPA, experiments were conducted in the initial aqueous pH range of 1.0–3.0. Keeping EHEHPA concentration at 15%(v/v) and O/A ratio of 1.0. The plot of extraction percentage of vanadium (IV) and molybdenum (VI) versus initial aqueous pH values is shown in Fig. 1. It was observed that there was an obviously increase in the extraction of vanadium (IV) from 3.2% to 86.1% up to an initial pH of 3.0. The extraction of molybdenum (VI) was about 83% in the initial pH region of 1–1.8 (corresponding equilibrium pH was in the range of 0.95–1.55) and then decrease with rise in pH value (60% at initial pH 2.5).

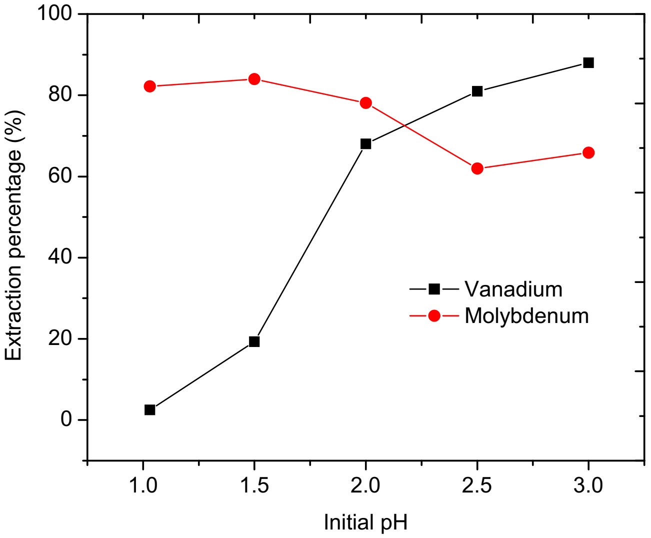

Fig. 1. Effect of initial aqueous pH on the extraction of vanadium (IV) and molybdenum (VI).

EHEHPA as an acid extractant is able to extract cationic of vanadium (IV) and molybdenum (VI) by an ion-exchange type extraction, according to the following equilibrium postulated in previous papers [18,19].

$$VO^{2+}_{(aq)} + 2(HA)_{2(org)} = VO \cdot A_2 \cdot 2HA_{(org)} + 2H^+_{(aq)} \tag{1}$$

$$MoO^{2+}_{2\,(aq)} + 2(HA)_{2(org)} = MoO_2 \cdot A_2 \cdot 2HA_{(org)} + 2H^+_{(aq)} \tag{2}$$

Where HA and $(HA)_2$ represent monomer and dimmer of EHEHPA, respectively, since this extractant exists as dimmer in aliphatic diluents.

Based on the solution chemistry of vanadium (IV) and molybdenum (VI) [20,21], cationic species of vanadium (IV) (exist as VO^{2+}) in aqueous solution prevailed only at pH value lower than 3.0. Over a pH value of 3.0, the predominant species of neutral and anionic species was presented and cannot be extracted by the alkylphosphonic acid extractant. This is consistent with the vanadium (IV) extraction results present in Fig. 1. Cationic species of molybdenum (VI) (exist as MoO_2^{2+}) in aqueous solution prevailed only at a low pH range (<1.8), the polynuclear anionic species of molybdenum (VI) including H_2MoO_4, $Mo_7O_{21}(OH)_3^{3-}$, $Mo_7O_{23}(OH)^{5-}$ and MoO_4^{2-} et al. are predominant in the pH range of exceed about 1.8, while those polynuclear anionic species and mononuclear anionic species cannot be extracted by the alkylphosphonic acid extractant. This explains why the molybdenum (VI) extraction efficiency remains constant when pH values are lower than 1.8 and decreased for pH values greater than 1.8 as presented in Fig. 1. Considering effectively co-extraction of both metals, the initial pH was kept at approximately 2.0 in the subsequent studies.